THE SUBSTITUTION KINETICS AND ELECTRONIC ABSORPTION SPECTROSCOPY OF SOME MOLYBDENUM AND TUNGSTEN BIS-DINITROGEN COMPLEXES

Thesis by

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ABSTRACT

The electronic absorption spectra of trans-[$M(N_2)_2(dpe)_2$], trans-[$Mo(N_2)(RCN)(dpe)_2$], and cis-[$M(N_2)_2(PMe_2Ph)_4$] (M = Mo, W; dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; PMe_2Ph = $P(CH_3)_2C_6H_5$) were measured and assigned. All of the charge transfer (CT) transitions were metal-to-ligand CT transitions. The lowest energy CT transition in each spectrum was assigned as a $M \rightarrow Pd\pi$ CT transition, and the low energy shoulders on this transition were assigned as ligand field transitions. The highest energy CT transition was assigned as a $M \rightarrow N_2\pi^*$ CT transition in each case.

The kinetics and mechanisms for the substitution of nitriles for dinitrogen in trans-[$M(N_2)_2(dpe)_2$] and cis-[$M(N_2)_2(PMe_2Ph)_4$] were studied. In the reaction of trans-[$Mo(N_2)_2(dpe)_2$] with nitriles, one dinitrogen was replaced by a nitrile. All of the kinetic data support an S_N1 dissociative mechanism. The analogous reaction with trans-[$W(N_2)_2(dpe)_2$] was found to proceed only photochemically, with the loss of one dinitrogen induced by population of the ${}^{1,3}E_g$ state. In the reactions of cis-[$M(N_2)_2(PMe_2Ph)_4$] with nitriles, both dinitrogen ligands were replaced by nitriles. The reaction mechanism for both compounds consists of two consecutive S_N1 dissociative steps.

The reactions of cis-$[W(N_2)_2(C_6H_5CN)(PMe_2Ph)_4]$, cis-$[W(C_6H_5CN)_2(PMe_2Ph)_4]$, and trans-$[Mo(N_2)(C_6H_5CN)(dpe)_2]$ with anhydrous HCl were also studied. The reaction of the latter compound with HCl to yield $[Mo(Cl)(N_2H_2)(dpe)_2]$ was particularly noteworthy.

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INTRODUCTION

The field of transition metal dinitrogen chemistry began in 1965 with the discovery of $[Ru(N_2)(NH_3)_5]^{+2}$ by Allen and Senoff (1). A few years later, in 1967, it was found that this complex could be prepared from nitrogen gas under physiological conditions (2). Since the only other known reaction of dinitrogen (N_2) under physiological conditions was the enzymatic production of ammonia during N_2 assimilation by certain plants, it appeared that transition metal dinitrogen complexes could be considered as models for the assimilation and reduction of N_2 in nature. Thus, great effort was put forward to reduce the coordinated dinitrogen by both thermal (1) and photochemical means (3), but these attempts met with no success (4,5), as the dinitrogen ligand was always labilized. Still, many fundamental studies, crystal structures (6), substitution kinetics (7), and electronic absorption spectra (8) were carried out on this complex and similar complexes, to understand in more detail why this system would not activate coordinated dinitrogen towards reduction. With the help of these studies, many new compounds were synthesized and studied. It was not until several years later, however, that the goal of reducing coordinated dinitrogen was achieved (9,10,11).

In one of these successful systems, those of the VIB metals, $M(N_2)_2(P)_4$, much has been reported on both the thermal and photochemical reduction of the coordinated dinitrogen (11,12), but almost none of the fundamental studies have been performed. Thus, we initiated our studies into the electronic structure and substitution kinetics of these complexes, in the hopes of understanding why these compounds activate dinitrogen towards reduction, where others have failed.

To keep this thesis as short as possible, the absolute minimum of experimental data will be presented. Thus, the reader will not have to stumble through a forest of data to understand the arguments. The disadvantage of this is that most of the experimental failures, which were often more enlightening than the successes, will not be reported. The exception to this style of brevity will be Appendix I, which is where the initial experiments on the reactions of some relatively new Group VIB complexes, $M(N_2)(RCN)(P)_4$, with HCl are discussed. Here, most of the reproducible results will be presented as an aid to future researchers.

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CHAPTER 1

Interpretation of the Electronic Spectra of Low-Spin d^6 $M(N_2)_2(P)_4$ Complexes

INTRODUCTION

One has only to look at an inorganic chemistry text, such as that by Cotton and Wilkinson (1), to realize that the chemistry of transition metal carbonyl complexes is well understood, particularly when compared to the chemistry of isoelectronic transition metal dinitrogen complexes. Nowhere is this more evident than in electronic absorption spectroscopy and photochemistry. Although a good deal of photochemistry has been done on both Group VIB metal carbonyl (2,3) and dinitrogen complexes (4, 5,6), only in the carbonyl complexes has enough spectroscopy been reported to really understand the photochemistry. Thus, we initiated our studies on the electronic structure of trans-$[Re(Cl)(N_2)(dpe)_2]$ (dpe = 1,2-bis(diphenylphosphino)ethane), trans-$[M(N_2)_2(dpe)_2]$ (M = Mo,W), trans-$[Mo(N_2)C_6H_5CN)(dpe)_2]$, and cis-$[M(N_2)(P(CH_3)_2)C_6H_5)_4]$ (M = Mo, W), in the hopes of being able to better understand these d^6 dinitrogen complexes and their photochemistry. It should be noted that one report of the spectrum of 2 had already been reported in the literature (7), but little in the way of assignments had been proposed.

EXPERIMENTAL

Materials and Synthesis (8)

All solvents used were reagent grade, obtained from MCB. All solvents were freshly distilled *in vacuo* immediately before use. The liquid organonitriles were distilled from phosphorous (V) oxide, methanol was distilled from magnesium turnings, dichloromethane was distilled from Linde 4 Å molecular sieves, and THF was distilled from sodium/benzophenone. All other solvents were distilled from titanocene (9). Molybdenum (V) chloride and tungsten (VI) chloride were obtained from Roc/Ric and purified by refluxing in CCl_4, under a nitrogen atmosphere, for two days with visible irradiation (10, 11). 1,2-*Bis*(diphenylphosphino)ethane and dimethylphenylphosphine were obtained from Roc/Ric, triphenylphosphine was obtained from MCB, and all were used without further purification.

All reactions were carried out under an inert atmosphere, using vacuum line and dry box handling techniques which are standard for our group (9). *Trans*-$[M(N_2)_2(dpe)_2]$ and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) were prepared by published methods (12,13), with the following minor modifications. We used magnesium amalgum (14) for all reductions, and then the formation of *trans*-$[M(N_2)_2(dpe)_2]$ was over in 1 hr at room temperature, instead of 6 hrs, and the formation of *cis*$[M(N_2)_2(PMe_2Ph)_4]$ was over in 4 hrs at 0° C.

Also, it is much easier to isolate the compounds if only 80% of the stoichiometric amount of phosphine is used. Trans-[Mo(N_2)(PhCN)($dpe)_2$] (15) and trans-[ReCl(N_2)($dpe)_2$] (16) were also prepared by reported methods.

Analyses

The microanalyses were performed by the micro-analytical lab in our department. The results will be presented in the order: %C, %H, %N. The theoretical percentage of the element will be in parenthesis, following the experimental percentage.

trans-[Mo($N_2)_2$($dpe)_2$]: 65.31 (65.83), 5.15 (5.10), 5.93 (5.91). trans-[W($N_2)_2$($dpe)_2$]: 59.72 (60.24), 4.85 (4.67), 5.25 (5.40). cis-[Mo($N_2)_2$($PMe_2Ph)_4$]: 54.37 (54.55), 6.25 (6.29), 7.97 (7.95). cis-[W($N_2)_2$($PMe_2Ph)_4$]: 49.14 (48.50), 5.64 (5.59), 6.85 (7.07). trans-[Mo(N_2)(PhCN)($dpe)_2$] 69.74 (69.21), 5.25 (5.22), 4.10 (4.11). trans-[Re(Cl)(N_2)($dpe)_2$]: 58.79 (59.68), 4.89 (4.62), 2.62 (2.68).

Absorption Spectra

All ir spectra used to identify the products were measured on a Perkin-Elmer 457 or Beckman IR 12 using Nujol mulls. All electronic absorption spectra were measured using a Carry 17 uv-vis-nir absorption spectrophotometer. The room temperature spectra were obtained in a variety of solvents, using 1 mm quartz cells designed for handling air-sensitive solutions (17). Using 2-methyltetrahydrofuran as a solvent, low temperature glasses were obtained in the 1 mm quartz cell, which was sealed off with a torch from the rest of the apparatus. 20 K spectra were obtained by attaching the cell to the cooling head of a Model 20 Cryocooler by Cryogenic Technology, Inc.

Calculations

The non-linear least-squares fit of gaussians to the observed spectra was accomplished on an IBM 370 computer, using a slightly modified CURFIT program, described by Bevington (18). The plotting program was modified from one written by Duane Smith and Roy Mead, both from CIT (19).

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of trans-$[Re(Cl)(N_2)(dpe)_2]$, 1, trans-$[M(N_2)_2(dpe)_2]$ (M = Mo, 2; W, 3), trans-$[Mo(N_2)(PhCN)(dpe)_2]$, 4, and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, 5; W, 6) were measured. The absorption spectra of 3, Figure 1, 6, Figure 2, and 4, Figure 3, are representative of the spectra of the compounds which were studied. The data obtained

Figure 1

UV-VIS absorption spectrum of trans-$[W(N_2)_2(dpe)_2]$, 20 K.

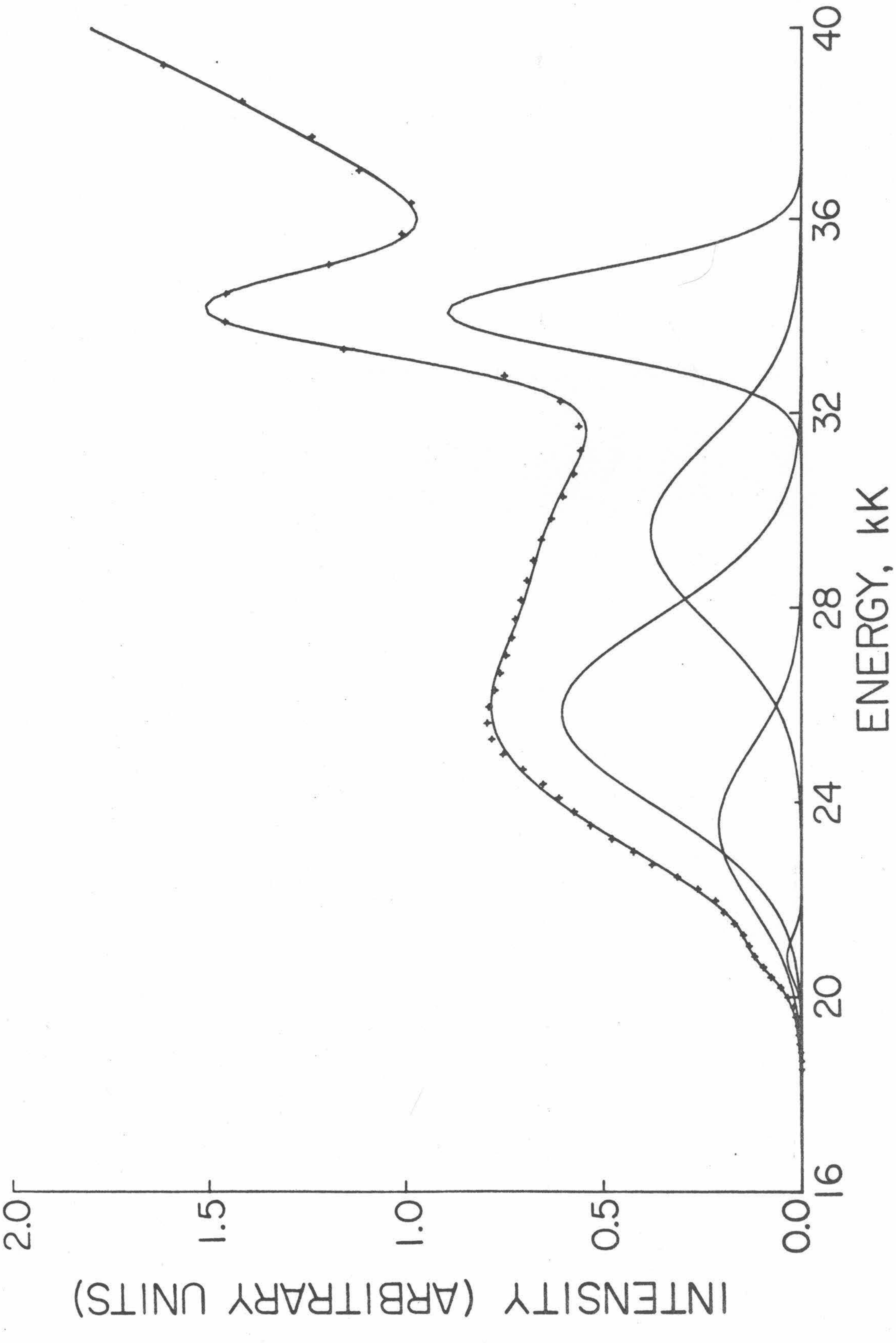
INTENSITY (ARBITRARY UNITS)
0.0
0.5
1.0
1.5
2.0
ENERGY, kK
16
20
24
28
32
36
40

Figure 1

Figure 2

UV-VIS absorption spectrum of cis-[$W(N_2)_2(PMe_2Ph)_4$], 20 K

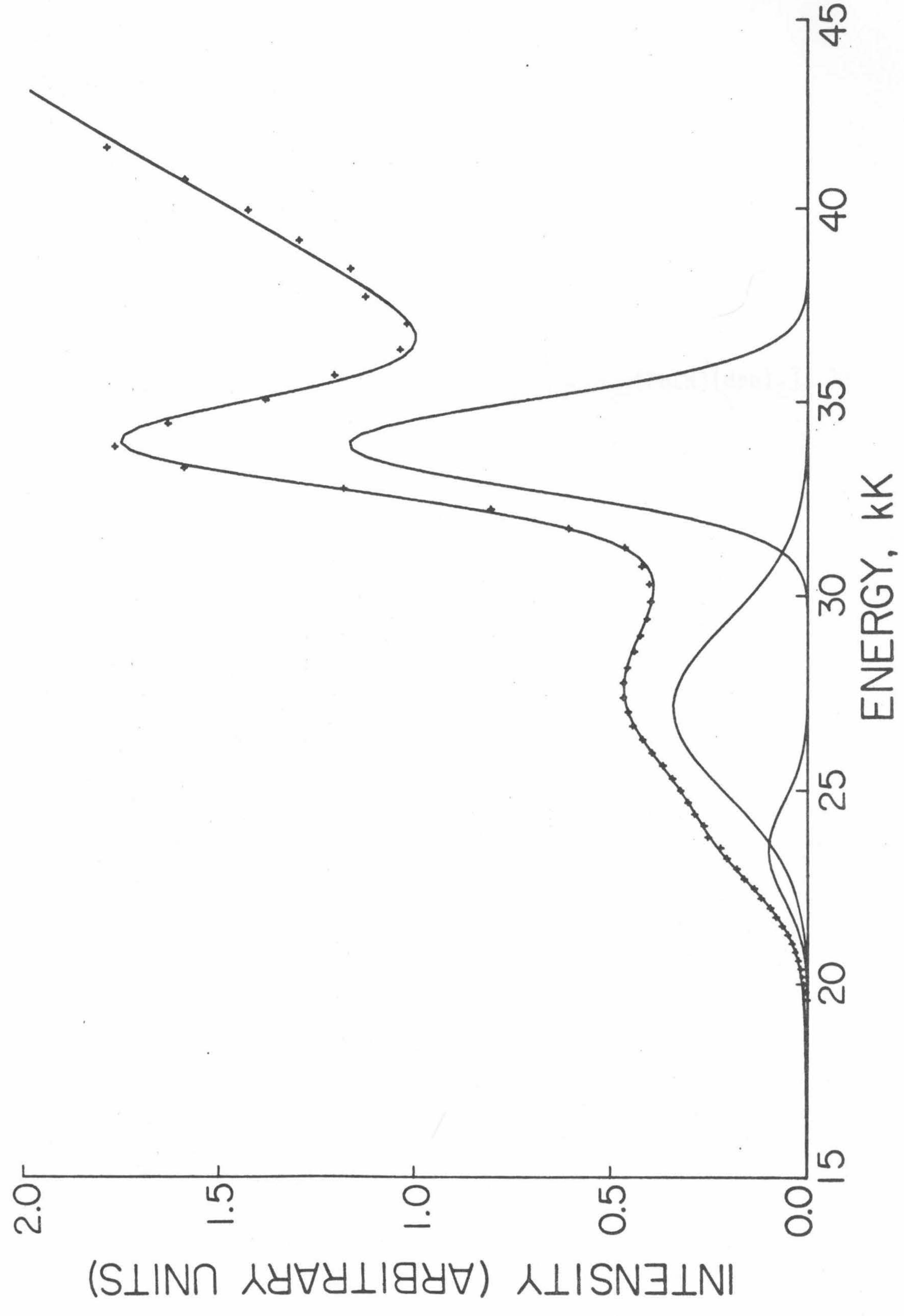
INTENSITY (ARBITRARY UNITS)
0.0
0.5
1.0
1.5
2.0
ENERGY, kK
15
20
25
30
35
40
45

Figure 2

Figure 3

UV-VIS absorption spectrum of trans-[Mo(N_2)(PhCN)(dpe)$_2$], 300 K.

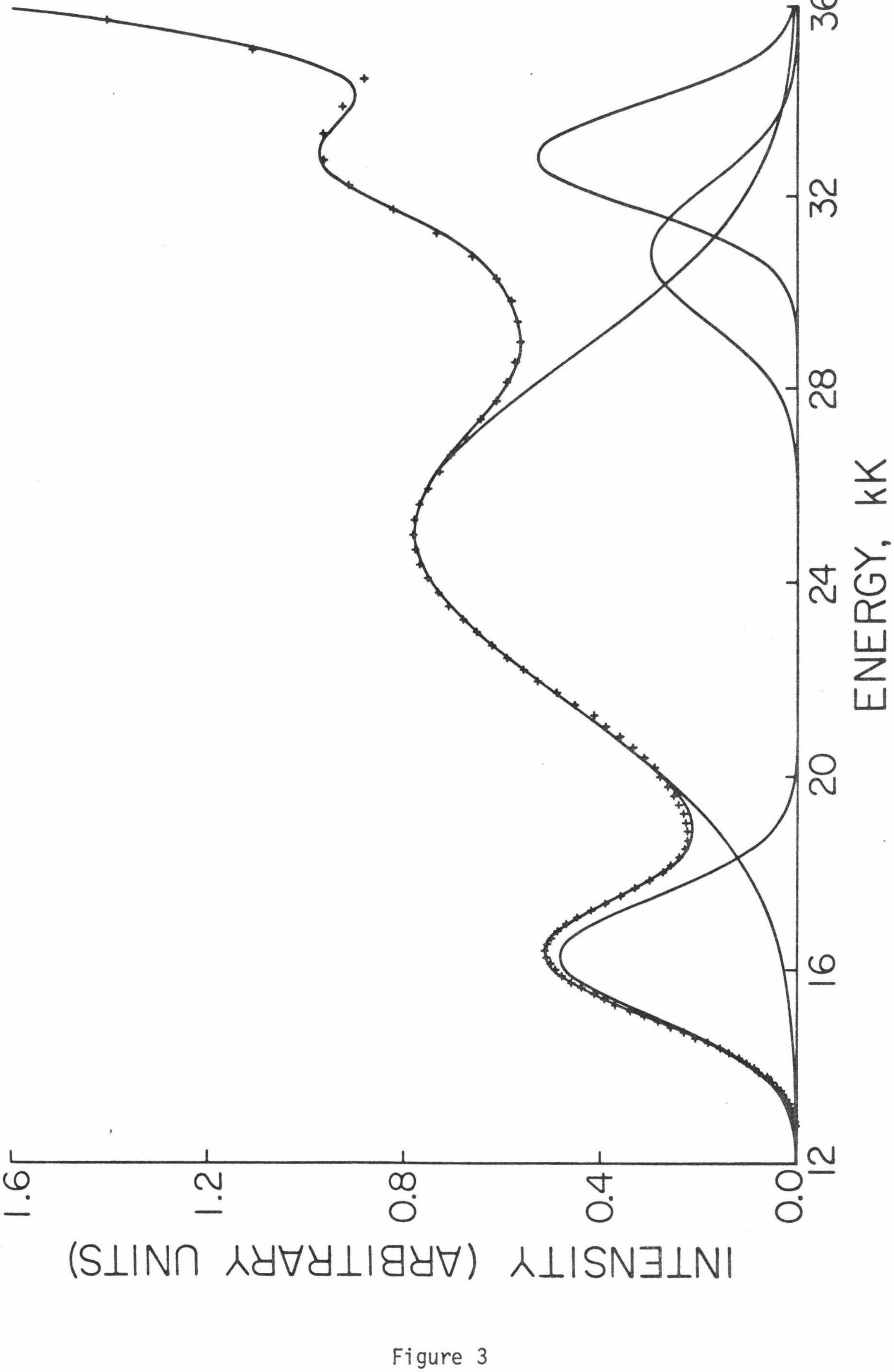
INTENSITY (ARBITRARY UNITS)
0.0
0.4
0.8
1.2
1.6
ENERGY, kK
12
16
20
24
28
32
36

Figure 3

from the least-squares fit of gaussians to the absorption spectra are summarized in Table I. There was some difficulty in fitting gaussians to bands I and II in 2, and thus, although the energies of these bands are well determined, the oscillator strengths are good to only ±30%. There was little difficulty in fitting gaussians to the spectra of the other complexes, and their oscillator strengths are good to approximately ±15%. It should be noted at this point that the improved resolution of the spectra in low temperature glasses is critical to the understanding of the electronic structure of the complexes under study.

Pseudo D_{4h} Complexes

For simplicity, we will treat 1, 2, and 3 as if they were of D_{4h} symmetry, although 2 and 3 are actually of D_{2h} (20) symmetry and 1 is at most C_{4v}. As can be seen from Figures 1 and 2 and Table I. There are two major absorptions below the onset of the ligand-to-ligand (LL) absorptions (*ca*. 300 nm), and there is at least one low energy shoulder on the lowest major band in each of the spectra. Because 2 and 3 have metals in the zero formal oxidation state, one would expect the fully allowed transitions, bands III and V (21), to be metal-to-ligand charge transfer (MLCT) transitions. Indeed, in the absorption spectrum of 1, band III has moved to considerably higher energy (*ca*. 3,000 cm^{-1}) and band V is not observed (22), which is the behavior one would

Table I. Electronic Absorption Bands in d^6 Metal Dinitrogen Complexes

A. Pseudo D_{4h} Complexes — Bands, kK (f)[a]

Compound	Band I	Band II	Band III	Band IV	Band V
trans-Re(Cl)(N_2)dpe)$_2$[b], 1	not observed	24.82 (1.5×10^{-2})	29.68 (1.7×10^{-1})	33.38 (6.5×10^{-2})	not observed
trans-Mo(N_2)$_2$(dpe)$_2$[b], 2	not observed	22.16 (1.4×10^{-2})	26.43 (3.3×10^{-1})	28.92 (1.2×10^{-2})	32.76 (3.4×10^{-1})
2[c]	18.62 (8.4×10^{-4})	22.13 (2.1×10^{-2})	25.60 (3.4×10^{-1})	29.61 (8.2×10^{-2})	33.09 (2.4×10^{-1})
trans-Mo(N_2)$_2$(depe)$_2$[d]	21.80, 20.61 (2.2×10^{-3}, 3.9×10^{-3})	?	---	---	--- (4.3×10^{-1})
trans-W(N_2)$_2$(dpe)$_2$[c], 3	20.84 (3.6×10^{-3})	24.00 (8.1×10^{-2})	26.25 (3.7×10^{-1})	30.08 (1.1×10^{-1})	34.10 (1.8×10^{-1})
trans-Mo(N_2)(PhCN)(dpe)$_2$[d], 4	not observed New band:	not observed 16.82 (1.3×10^{-1})	25.07 (5.9×10^{-1})	30.82 (9.4×10^{-2})	32.84 (1.3×10^{-1})

B. C_{2v} Complexes — Bands, kK (f)[a]

Compound	Band X	Band XI	Band XII
cis-Mo(N_2)$_2$(PMe_2Ph)$_4$[c], 5	23.55 (2.4×10^{-2})	27.57 (3.8×10^{-1})	33.24 (5.7×10^{-1})
cis-W(N_2)$_2$(PMe_2Ph)$_4$[c], 6	23.47 (3.5×10^{-2})	27.13 (2.1×10^{-1})	33.92 (3.8×10^{-1})

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[a] Values in parentheses are the oscillator strengths. [b] Spectrum recorded at room temperature. [c] Spectrum recorded at 20 K. [d] Reference 25. depe=$(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$.

expect for MLCT bands. It is noted that band IV also shows this MLCT behavior, and thus, although its oscillator strength is considerably lower, we assign it as a MLCT band as well. Since band II does not greatly increase in energy from 3 to 1, we assign it as a LF band. Because band I is not observed in the room temperature spectrum of 2, but is in 3, and its oscillator strength is larger in 3 than 2, we assign it as a spin forbidden LF band. Band I is probably observed in 2 and 3 because of 'intensity stealing' from the lowest CT band (21), and thus it is not observed in 1 because it is too far from the CT band to effectively 'steal' intensity.

Using the dπ orbitals of P, the π^* orbitals of N_2, and D_{4h} symmetry, one can construct the 'ligand' molecular orbitals, three of which yield possible fully allowed MLCT transitions. These molecular orbitals are shown in Figure 4, and the transitions are:

T1 $\quad {}^1A_{1g}(b_{2g}{}^2e_g{}^4) \rightarrow {}^1E_u(b_{2g}{}^2e_g{}^3a_{2u}{}^1)$

T2 $\quad {}^1A_{1g}(b_{2g}{}^2e_g{}^4) \rightarrow {}^1E_u(b_{2g}{}^1e_g{}^4 1e_u{}^1)$

T3 $\quad {}^1A_{1g}(b_{2g}{}^2e_g{}^4) \rightarrow {}^1A_{2u}(b_{2g}{}^2e_g{}^3 2e_u{}^1)$.

Thus, any M → Pdπ CT will have to be ${}^1A_{1g} \rightarrow {}^1E_u$, and M → $N_2\pi^*$ CT will have to be ${}^1A_{1g} \rightarrow {}^1A_{2u}$. By replacing one N_2 with PhCN, we

Figure 4

Ligand molecular orbitals for pseudo D_{4h} complexes and trans-[Mo(N_2)(PhCN)(dpe)$_2$], C_{2v}'.

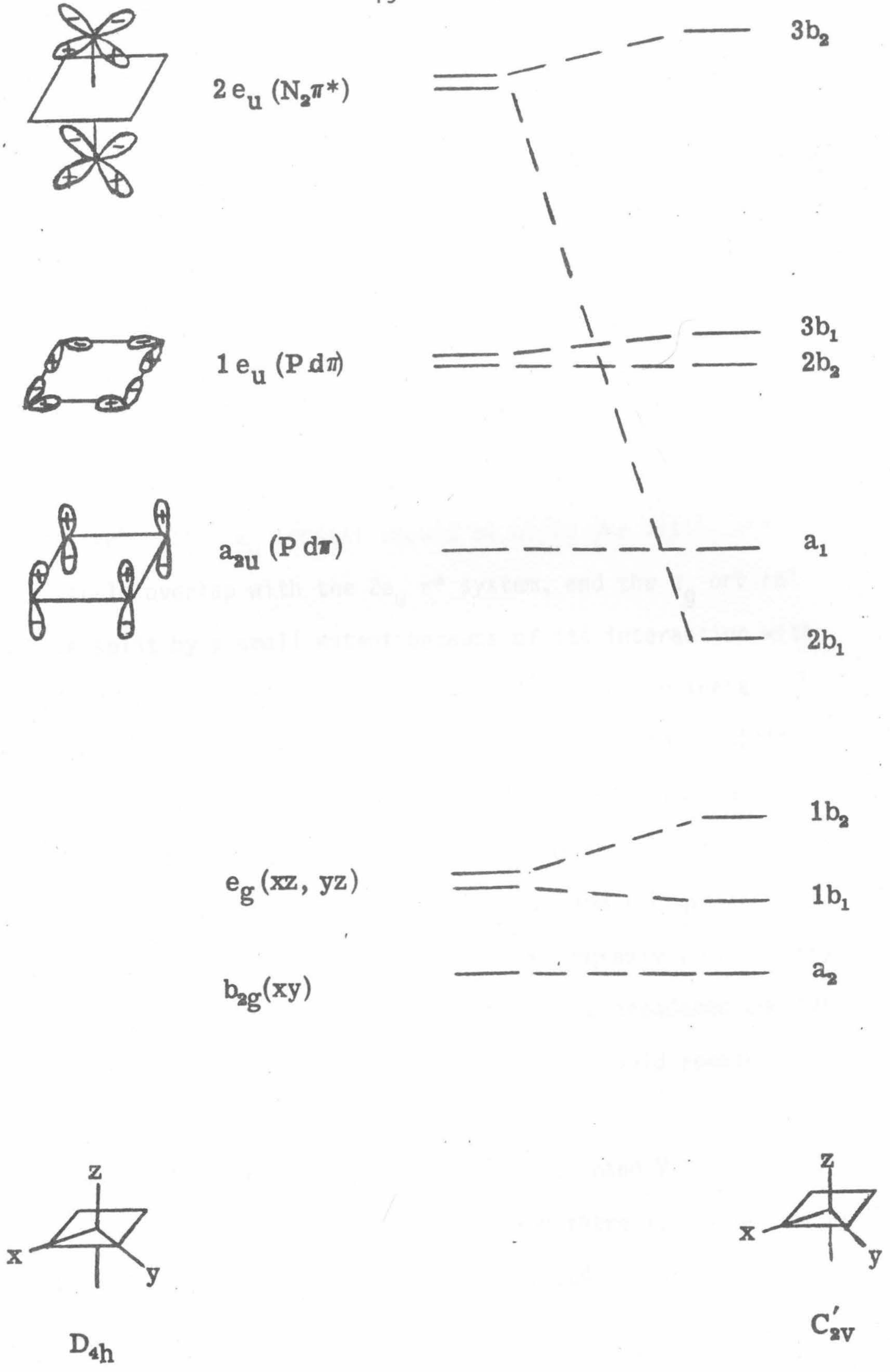
2 e_u ($N_2\pi^*$)
1 e_u (P dπ)
a_{2u} (P dπ)
e_g (xz, yz)
b_{2g}(xy)
$3b_2$
$3b_1$
$2b_2$
a_1
$2b_1$
$1b_2$
$1b_1$
a_2
+
−
z
x
y
D_{4h}
C_{2v}'

Figure 4

reduce the symmetry of the molecule to C_{2v}. Thus, in the spectrum of 4, transition T1 will be split by the amount e_g is split, transition T2 will be split by the amount $1e_u$ is split, and transition T3 will be split by the amount e_g and $2e_u$ are split. The $2e_u$ orbital should be split the most, since with PhCN, one of the CN π^* orbitals can effectively interact with the phenyl ring orbitals, greatly lowering its energy with respect to the other CN π^* orbital. The $1e_u$ orbital should be split the least, since it has little overlap with the $2e_u$ π^* system, and the e_g orbital should be split by a small extent because of its interaction with the 'e_g' π^* orbitals of [N_2,PhCN] (Figure 4). Based on these simple arguments, we predict that transition T3 should be split into two components in the spectrum of 4, each of approximately one-half the intensity of transition T3 in the spectrum of 2. One component should be at approximately the same energy as transition T3 of 2, and one should be of considerably lower energy (*ca.* 18 kK lower) (23). Transition T1 should be broadened considerably by the splitting of e_g in 4, and transition T2 should remain largely unchanged.

Examining the spectrum of 4, we find that band V is less than half as intense as in the spectrum of 2, and there is a new band at 16.28 kK which is of almost equal intensity (24). Band III is considerably wider in 4 as compared to 2, 8.20 kK as compared to 6.32 kK, and Band IV has hardly changed at all. Thus, we assign the spectrum of 4 as follows

New Band (16.28 kK) $^1A_1 \rightarrow {}^1A_1(1b_1^{\,1}2b_1^{\,1})$

Band III $^1A_1 \rightarrow {}^1B_1, {}^1B_2(1b_1^{\,1}a_1^{\,1}; 1b_2^{\,1}a_1^{\,1})$

Band IV $^1A_1 \rightarrow {}^1B_2, {}^1B_1(a_2^{\,1}3b_1^{\,1}; a_2^{\,1}2b_2^{\,1})$

Band V $^1A_1 \rightarrow {}^1A_1(1b_2^{\,1}3b_2^{\,1})$.

Band III might contain $^1A_1 \rightarrow {}^1B_2(a_2^{\,1}2b_1^{\,1})$ as one of its components, but from a simple look at the orbitals, we conclude that its intensity should be low. It is possible to assign band IV as the triplet of band V, but we prefer to assign this band as a fully allowed transition, somewhat more in line with its oscillator strength. Returning to the spectra of compounds 1, 2, and 3, we must assign their spectra as follows:

Band III $^1A_{1g} \rightarrow {}^1E_u(b_{2g}^{\,2}e_g^{\,3}a_{2u}^{\,1})$

Band IV $^1A_{1g} \rightarrow {}^1E_u(b_{2g}^{\,1}e_g^{\,4}1e_u^{\,1})$

Band V $^1A_{1g} \rightarrow {}^1E_u(b_{2g}^{\,2}e_g^{\,3}2e_u^{\,1})$,

to be consistent with the assignments proposed for the spectrum of 4.

These assignments are also in good agreement with the spectra of other transition metal dinitrogen complexes. The spectrum of trans-[Mo(N$_2$)$_2$(depe)$_2$] (depe = $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$) was provided by Dr. T. A. George (25). In this spectrum there is one major absorption, a band at 322 nm (31.06 kK) with ε = 28,800. Since depe should not be as good a π-acceptor as dpe, and depe should be a better σ-donor (26), it would be reasonable to expect a M → $N_2\pi^*$ CT band to move to lower energy in this complex as compared to 2, and for any M → Pdπ CT band to move to higher energy. Thus, we assign this band (31.06 kK) as MLCT, M → $N_2\pi^*$, and feel it is in good agreement with our ideas on the electronic structure of these Mo dinitrogen complexes. Also, there has been some work done on the electronic absorption spectrum of $Cr(N_2)_6$ (27), and in the spectrum, CT bands were observed at approximately 300 nm. Thus, we feel confident in the assignment of band V as the M → $N_2\pi^*$ CT band.

There is ample precedent in the literature to support the claim that N_2 is a weaker field ligand than dpe. From Lever's work on $Cr(N_2)_6$ (27), we have Dq(N_2) equal to 2,250 cm^{-1} (28), and from Sacconi's work on some Fe(II) phosphine compounds one obtains a Dq(P) of approximately 2470 cm^{-1} (29). From work on the spectra of the Group VIB hexacarbonyls (30), one would expect the value of Dq(N_2) to be approximately the same in $Cr(N_2)_6$, 2, and 3. Also, one would suspect that Dq(P) in 2 and 3 will be larger than 2,470 cm^{-1}, since in 2 and 3, the phosphine ligands can better act as π-acceptors, than in the Fe(II) complexes. And finally, assuming phosphines are better σ-donors than N_2, we can arrange the d orbitals in increasing energy: $d_{xy} < d_{xz}, d_{yz} \ll d_{z^2} \ll d_{x^2-y^2}$ (31,32). With this ordering, we assign the LF bands of 1, 2, and 3 as follows:

Band I	$^1A_{1g}(b_{2g}{}^2e_g{}^4) \rightarrow {}^3E_g(b_{2g}{}^2e_g{}^3a_{1g}{}^1)$
Band II	$^1A_{1g}(b_{2g}{}^2e_g{}^4) \rightarrow {}^1E_g(b_{2g}{}^2e_g{}^3a_{1g}{}^1)$

These assignments are in agreement with the literature of low-symmetry low-spin d^6 metals (2,33), where the E_g component is lower in energy than the A_{2g} component of the split $T_{1g}(O_h)$ [Dq(axial)<Dq(equitorial)], and in our system the $^1A_{2g}$ band is either of low oscillator strength and thus not observed, hidden by an intense CT band, or the splitting of the $^1T_{1g}(O_h)$ transition is not large enough to be observed.

In the spectrum of trans-$Mo(N_2)_2(depe)_2$, we assign the low energy doublet as follows:

20.61 kK	$^1A_{1g} \rightarrow {}^3E_g$
21.80 kK	$^1A_{1g} \rightarrow {}^3A_{2g}$,

where ^3E_g and $^3A_{2g}$ are components of the split $^3T_{1g}(O_h)$. Since we expect depe to be a stronger field ligand than dpe (26), it seems most reasonable to assign these bands as triplet LF bands, after comparing its spectrum with that of <u>2</u> and <u>3</u>. But because <u>trans</u>-$Mo(N_2)_2(depe)_2$ is probably of D_{2h} rather than D_{4h} symmetry (20), one might argue that these bands are just the components of the split $^3E_g(D_{4h})$ band. A splitting of 1.2 kK seems very large for such a splitting, and one would have expected the oscillator strengths of the two components to be almost equal in this case. Since the high energy component is approximately one-half the intensity of the other component, we feel our assignments are more reasonable. If we are correct in these assignments, then one calculates a value of Dt of 136 cm^{-1} in this system (34,35). With this value of Dt, one can return to the spectra of <u>2</u> and <u>3</u> and calculate Dq for each complex, along with an approximate Dq(P) and $Dq(N_2)$ (35). The necessary equations and the values obtained are found in Table II. Great significance cannot be placed on these calculated numbers, but as a guide to what should be expected in complexes like <u>2</u> and <u>3</u>, they are very interesting. $Dq(N_2)$ is considerably larger than anticipated based on the work on $Cr(N_2)_6$ (27), but the values are in better agreement with the 2,490 cm^{-1} obtained with my corrected assignments for the spectra of $Cr(N_2)_6$ (28). The values of Dq(P) are also larger than the 2,470 cm^{-1} reported

Table II. Calculations of Dq(P) and Dq(N_2) in pseudo D_{4h} bis-dinitrogen complexes

Compound	Dt[a]	Dq(complex)[b]	C[b]	Dq(P)[b]	Dq(N_2)[b]
2	136 cm^{-1}	2,510	1750	2,590	2,350
3	136 cm^{-1}	2,680	1580	2,760	2,520

[a] See text.

[b] Values are reported in cm^{-1}.

$$E(^3E_g) - E(^1A_{1g}) = 10\ Dq(complex) - 3C - \frac{35}{4}Dt$$

$$E(^1E_g) - E(^1A_{1g}) = 10\ Dq(complex) - C - \frac{35}{4}Dt$$

$$Dt = \frac{4}{7}[Dq(P) - Dq(N_2)]$$

$$Dq(complex) = \frac{1}{6}[rDq(P) + 2Dq(N_2)]$$

in Fe(II) complexes, but this was expected because Mo(0) and W(0) should be better π-bases than Fe(II).

C_{2v} Complexes

Not as much can be said about the spectra of complexes 5 and 6, since there were not as many factors which could be varied to elucidate the electronic structure of these complexes. By analogy with the spectra of the pseudo D_{4h} complexes, in particular the oscillator strengths of the bands, we expect bands XI and XII to be the result of two fully allowed MLCT transitions, and band X to be the result of a spin allowed LF transition.

It is a common practice, in the spectroscopy of cis, trans isomers of inorganic complexes, to treat each as if they were of D_{4h} symmetry. To do this for this cis isomer, which is of C_{2v} symmetry, one applies the 'rule of average environment.' Then there is one unique axis with a ligand field strength equal to the in-plane ligand field strength of the trans isomer, and there are two axes orthogonal to this unique axis, with ligand field strengths equal to average of the in-plane and out-of-plane ligand field strengths of the trans isomer. It is with this simple idea that we will attempt to explain the spectra of 5 and 6.

With the simple idea proposed above, it is easy to show, in a crystal field, that the splitting of the $T_{1g}(O_h)$ state in the lower symmetry of the cis isomer, will be half the splitting in the trans isomer, and in the opposite order (36). Thus, the A_{2g} state should be lower in energy than the E_g state in 5 and 6, and the two states may not be separated in energy enough to be observed as more than one band. Based on the information at hand, it is impossible to assign a symmetry designation to band X, and thus, we leave it assigned as a component of the LF transition, $^1A_{1g} \rightarrow {}^1T_{1g}$ in octahedral symmetry. It should be noted, however, that this transition is lower in energy than the singlet LF band in 2 and 3, and the transition is lower in energy in 6 than in 5. This is indeed strange behavior for a LF transition, one would have expected it to be higher in energy in 6 than in 5, and higher in energy than the LF transition in 2 or 3, because PMe_2Ph is a stronger field ligand than dpe.

To better understand the CT bands in the spectra of 5 and 6, we again used benzonitrile as a probe. In the case of 5 this proved to be exceedingly difficult, but in the case of 6 we had more success. With these C_{2v} complexes, addition of benzonitrile yields a mono-benzonitrile and bis-benzonitrile complex, both of cis configuration (37), and they are both more susceptible to thermal decomposition than the bis-dinitrogen complexes. Thus, an absolutely pure spectrum of the bis-benzonitrile complex was never obtained, but a spectrum of sufficient quality to understand the CT bands of 5 and 6 was obtained.

After addition of benzonitrile to a solution of 6, a new band grows in at 595 nm due to the mono-nitrile complex (37). This band then fades and a new band at 545 nm grows in, which is due to the bis-nitrile complex. During these changes, the intensity of band XII constantly decreases, to less than one-half its initial intensity. For band XI, it is difficult to report any accurate change without a good gaussian fit, but it appears to have changed very little (38). Thus, we assign band XII as primarily M → $N_2\pi^*$ CT, and band XI as primarily M → Pdπ CT, by analogy with our work on the spectra of 2, 3, and 4.

CONCLUSIONS

Our assignments of the lowest energy bands of 1, 2, and 3 as $^{1,3}E_g(e_g{}^3b_{2g}{}^2a_{1g}{}^1)$ are in good agreement with the photochemistry which has been observed in 3. In most of the work which has been done, broad band visible irradiation has been used (4,5), and loss of one dinitrogen has been observed, as in the reaction R1 (4)

$$\underline{\text{trans}}\text{-Mo}(N_2)_2(\text{dpe})_2 + CH_3I \xrightarrow{h\nu} \text{Mo(I)}(N_2CH_3)(\text{dpe})_2 + N_2 \qquad \text{R1}$$

and in flash experiments, both dinitrogens are reported loss (39). This is consistent with the photochemistry expected from a transition to an $E_g(e_g{}^3b_{2g}{}^2a_{1g}{}^1)$ state (40), where an electron has been excited from an orbital which is π-bonding with respect to the z-axis ligands, and placed in an orbital which is σ-antibonding with respect to the z-axis ligands; thus, the observed loss of dinitrogen in the photochemistry of 3. We feel this explanation of the observed photochemistry is better than the reported explanation in which it is assumed that the lowest energy CT band is M → $N_2\pi^*$ CT, and excitation into this band increases the electron density on the dinitrogen ligands, yielding the observed photochemistry (41).

Since labilization of one dinitrogen ligand is the fundamental photochemical reaction of 3, as with other transition metal dinitrogen complexes, one wonders why 3 is effective in photochemically activating dinitrogen towards reduction, where others have failed (42, 43). We propose that the reason is that 3 is a bis-dinitrogen complex, where the others, e.g. $[Ru(N_2)(NH_3)_5]^{2+}$, are mono-dinitrogen complexes. Thus when dinitrogen is lost from $[Ru(N_2)(NH_3)_5]^{2+}$, there is no dinitrogen left to be activated. However in 3, there is still one dinitrogen bound to the metal, which can be activated by the coordinatively unsaturated complex.

Our assignments of the CT bands are in very poor agreement with the extended Hückel calculations of Hoffmann (41), in which the lowest CT transition of the model compound, trans-$[Mo(N_2)_2(PH_3)_4]$, was calculated to be a M → $N_2\pi^*$ CT transition, at 3,200 cm^{-1}. It seems the reason for this large error is the fact that PH_3 was assumed to have no π-acidic character, and thus the d orbitals on P were not included in the calculations. This omission led to very serious errors in many of the calculations in the paper.

In summary, for the transition metal dinitrogen complexes 2, 3, 5, and 6, the highest energy CT band is assigned as a $M \rightarrow N_2\pi^*$ CT band, and the lowest energy CT band is assigned as a $M \rightarrow Pd\pi$ CT band. The shoulders on the lowest energy CT band are assigned as LF bands, and in the case of compound 3, they are probably responsible for the observed photochemistry.

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CHAPTER 2

Substitution Kinetics of Low-Spin d^6 $M(N_2)_2(P)_4$ Complexes

INTRODUCTION

There has been considerable interest in the study of transition metal dinitrogen complexes, in the hopes of understanding a system in which dinitrogen is reduced. Two such systems have been found. One system uses titanium or zirconium metals (1), and the other system uses molybdenum or tungsten metals (2).

In the molybdenum and tungsten system, the following reduction reactions have been observed (2).

$$\underline{\text{cis}}\text{-}[W(N_2)_2(PMe_2Ph)_4] + H_2SO_4 \longrightarrow 2NH_3 + N_2 + \text{other products}$$

$$\underline{\text{trans}}\text{-}[Mo(N_2)_2(dpe)_2] + RCOCl \longrightarrow [Mo(Cl)(N_2COR)(dpe)_2] + N_2$$

$$\underline{\text{trans}}\text{-}[Mo(N_2)_2(dpe)_2] + RX \longrightarrow [Mo(X)(N_2R)(dpe)_2] + N_2$$

$$PMePh = P(CH_3)_2(C_6H_5)$$

$$dpe = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$$

In each of the reduction reactions, one dinitrogen is lost as molecular nitrogen, and the other dinitrogen is reduced. Therefore, a study of the kinetics and mechanism of the loss of dinitrogen from these complexes should be of fundamental importance in understanding the mechansim by which coordinated dinitrogen is reduced. Thus, we initiated our study into the displacement of dinitrogen from trans-[M(N_2)$_2$(dpe)$_2$] and cis-[M(N_2)$_2$(PMe$_2$Ph)$_4$] (M = Mo, W).

EXPERIMENTAL

Materials and Syntheses

All solvents used were reagent grade, obtained from MCB. All solvents were freshly distilled *in vacuo* immediately before use. The liquid organonitriles were distilled from phosphorous (V) oxide, methanol was distilled from magnesium turnings, dichloromethane was distilled from Linde 4 Å molecular sieves, and THF was distilled from sodium/benzophenone. All other solvents were distilled from titanocene (3). Molybdenum (V) chloride and tungsten (VI) chloride were obtained from Roc/Ric and purified by refluxing in CCl_4, under a nitrogen atmosphere, for two days with visible irradiation (4,5). 1,2-bis(diphenylphosphino)ethane (dpe) and dimethylphenylphosphine were obtained from Roc/Ric, triphenylphosphine was obtained from MCB, and all were used without further purification.

All reactions were carried out under an inert atmosphere, using vacuum line and dry box handling techniques which are standard for our group (3). The syntheses and analyses of trans-[M(N_2)$_2$(dpe)$_2$] and cis-[M(N_2)$_2$(PMe$_2$Ph)$_4$] (M = Mo, W) were described in Chapter 1 of this thesis. Trans-[Mo(N_2)(L)(depe)$_2$] (L = C_6H_5CN, p - C_7H_7CN, CH_3CN) were prepared by published procedures (6). All compounds gave ir and elemental analyses in agreement with that expected.

Cis-[W(N_2)(PhCN)(PMe_2Ph)$_4$]: 13.5 μl (0.13 mmole) of PhCN was added to 100 mgs (0.13 mmole) of cis-[W(N_2)$_2$(PMe_2Ph)$_4$] in 10 ml of toluene. After 3.5 hrs at room temperature, the solution was reduced to 2 ml of volume, and 1 ml of pet ether was added. This solution was stirred at -78° C for 1/2 hr, and then it was filtered cold. The green solid was washed twice with cold pet ether, and then quickly dried in vacuo. Anal. Calcd. C, 53.99; H, 5.69; N, 4.84. Found: C, 55.75; H, 5.19; N, 5.19.

Cis-[W(PhCN)$_2$(PMe_2Ph)$_4$]: 35 μl (0.34 mmole) of PhCN was added to 100 mgs (0.13 mmole) of cis-[W(N_2)$_2$(PMe_2Ph)$_4$] in 10 ml of toluene. After 10 hrs at 30° C, the solution was reduced in volume to 1 ml and 1 ml of pet ether was added. This solution was stirred at -78° C for 1/2 hr and then it was filtered cold. The purple solid was washed twice with cold pet ether and quickly dried in vacuo. Anal. Calcd. C, 58.61; H, 5.77; N, 2.97. Found: C, 59.83; H, 5.96; N, 3.23.

Toepler Pump Reactions

Cis-[W(N_2)(PhCN)(dpe)$_2$]: 200 μl (1.89 mmole) of PhCN was added to 75 mgs (9.5×10^{-2} mmole) of cis-[W(Ni)$_2$(PMe_2Ph)$_4$] in

200 ml of toluene. The reaction was allowed to run at 30° C for 1 hr 40 min, at which point the solution was cooled to -78° C. The solution was toepler pumped through an LN_2 trap, and 8.1 x 10^{-2} mmole of N_2 was collected. The solution was then warmed to 30° C, and the reaction was allowed to continue another 6 1/2 hrs. The solution was then toepler pumped through an LN_2 trap and 1.04 x 10^{-1} mmole of N_2 was collected.

<u>Cis</u>-$[W(N_2)(PhCN)(PMe_2Ph)_4]$: 15.5 μl (0.15 mmole) of PhCN was added to 120 mgs (0.15 mmole) of <u>cis</u>-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After reacting for 4 hrs at 30° C, the solution was toepler pumped and 0.15 mmole of N_2 was collected.

<u>Cis</u>-$[W(N_2)(PhCN)(PMe_2Ph)_4]$: 35 μl (0.34 mmole) of PhCN was added to 120 mgs (0.15 mmole) of <u>cis</u>-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After reacting for 8 hrs at 30° C, the solution was toepler pumped and 0.29 mmole of N_2 was collected.

Physical Measurements

All ir spectra used to identify the products were measured on a Perkin-Elmer 457 or Beckman IR 12 using Nujol mulls. The proton nmr were run on a Varian EM-390, using C_6D_6 and nmr tubes which had been sealed with a torch. All elemental analyses were performed by the micro-analytical lab in our department.

Kinetic Measurements

The reactions of nitriles with trans-[Mo$(N_2)_2$(dpe)$_2$] were monitored by following the change in the visible spectrum of the reaction solutions, from 800 nm to 330 nm, for two reaction half-lives, and in most cases for over three half-lives. The spectral measurements were made using a Cary 15 spectrophotometer equipped with a Cary 1116100 Program Timer and the Cary 1115 Repetitive Scan accessories. The solutions were contained in anaerobic 1 mm pyrex cells similar to that described by Shriver (7). The cells were held in a thermostatable cell adapter, Cary #1444300, equipped with pyrex windows. The volume was filled with distilled water to improve thermal contact between the cell and the cell adapter. A Masterline 2095 bath and circulator by Forma Scientific was used to maintain the desired temperatures.

The reactions were initiated by injection of the nitrile using a calibrated Hamilton gas tight syringe; the data collections were begun after allowing 5 min for temperature equilibration.

Reaction rates were determined under pseudo-first-order conditions. Plots of $-\ln(A_\infty - A)$ vs. time were linear over the reaction times monitored, and the observed rate constants were obtained from the slopes of the weighted least-squares fit to these lines (8,9). The activation parameters were calculated using a simple least-squares program. In all cases, the calculated numbers are reported with their 95% confidence limits (8).

The reactions of nitriles with cis-[$W(N_2)_2(PMe_2Ph)_4$] were monitored by following the change in the visible spectrum of the reaction solutions, from 800 nm to 380 nm, for over two reaction half-lives of the slow reaction, and in most cases, for over three half-lives. All other experimental details are the same as before. Because the reaction was found to consist of two consecutive first-order reactions (8), the rate constants were obtained by a non-linear least-squares fit (9) of the spectrum to an expression of the form (10)

$$A(obs) = A_1 exp(-k_1 t) + A_2 exp(-k_2 t) + A_3 .$$

The activation parameters were calculated as before, and the calculated numbers are reported with their 95% confidence limits.

The reactions of nitriles with cis-[$Mo(N_2)_2(PMe_2Ph)_4$] were monitored by following the change in the visible spectrum of the reaction solution at 680 nm for over two reaction half-lives of the slow reaction. The spectral measurements were made using a Cary 14 spectrophotometer equipped with the thermostatable cell adapter described above. The solutions were contained in anaerobic 1 mm pyrex cells similar to those described above, except that they were modified so they could contain two separate solutions which could be quickly mixed. Then to initiate the reaction, the cell assembly was removed from the constant temperature bath, tipped, and then shaken vigorously. The cell was placed in the thermostated cell adapter and data collections were started. This entire procedure took less than 20 sec. All other experimental details and calculations are the same as for the reactions of cis-$[W(N_2)_2(PMe_2Ph)_4]$.

RESULTS AND DISCUSSION

The displacement of dinitrogen from trans-$[M(N_2)_2(dpe)_2]$ (M = Mo, 1; W, 2) and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, 3, W, 4) by nitriles was followed by the change in the visible spectrum of each solution with time. All reactions were run under pseudo-first-order conditions in toluene. For the slow reactions, the reactions of 1, 2, and 4 with nitriles, it was necessary to use a spectrophotometer with a repetitive scan accessory, in order to obtain reproducible results, since both the reactants and the products react photochemically. Representative spectra from the reactions of 1 with benzonitrile and acetonitrile are shown in Figures 1 and 2, respectively, and the plots of $-\ln(A_\infty-A)$ vs. time for these kinetic runs are shown in Figures 3 and 4, respectively. The observed rate constants are collected in Table I, and the average of the rate constants at high nitrile concentrations, k_1, along with the activation parameters can be found in Table II. A representative spectrum of

Figure 1

A visible spectrum of the reaction of trans-[Mo$(N_2)_2(dpe)_2$] with benzonitrile.

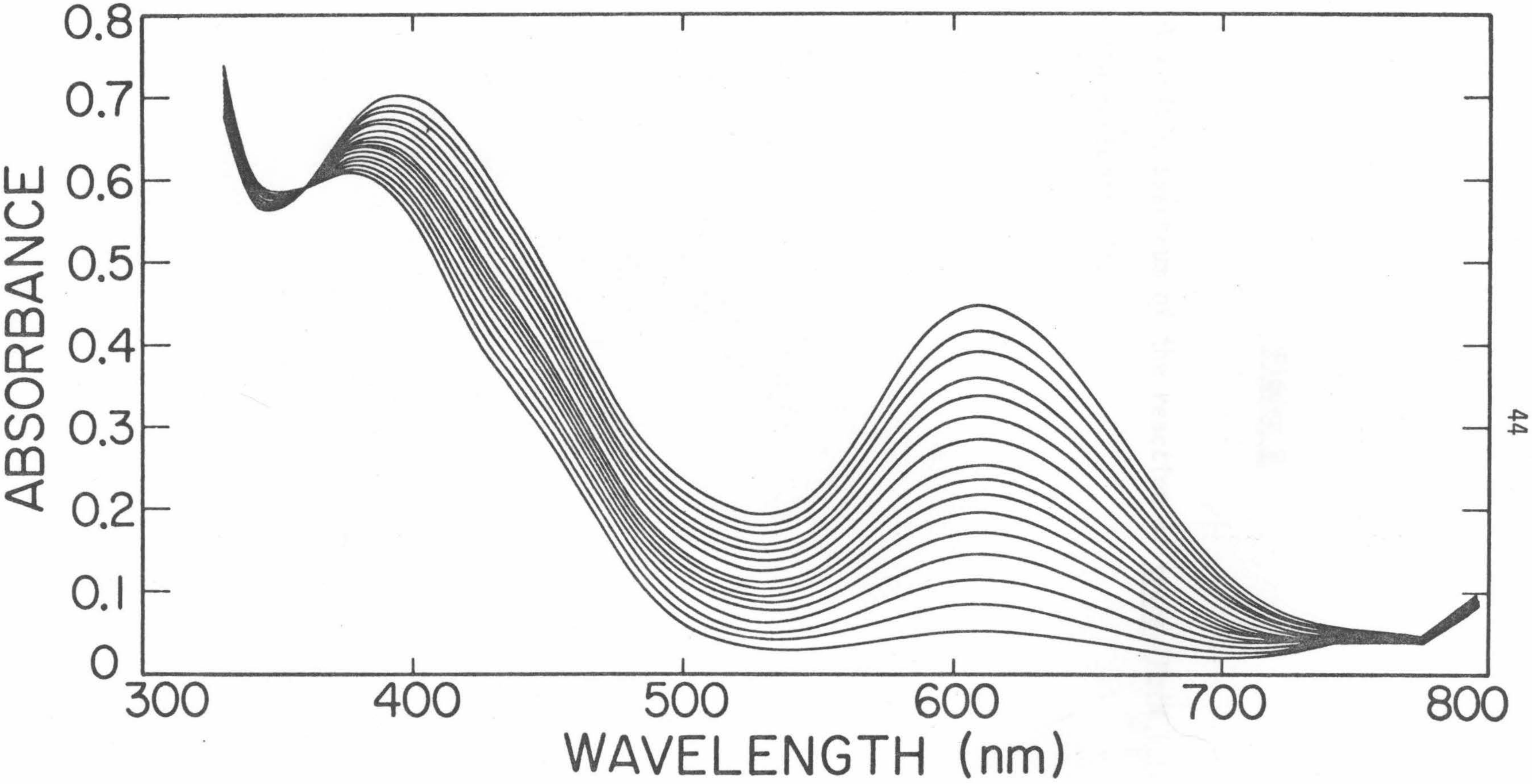
ABSORBANCE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
700
800
WAVELENGTH (nm)

Figure 1

Figure 2

A visible spectrum of the reaction of trans-[Mo$(N_2)_2$(dpe)$_2$] with acetonitrile.

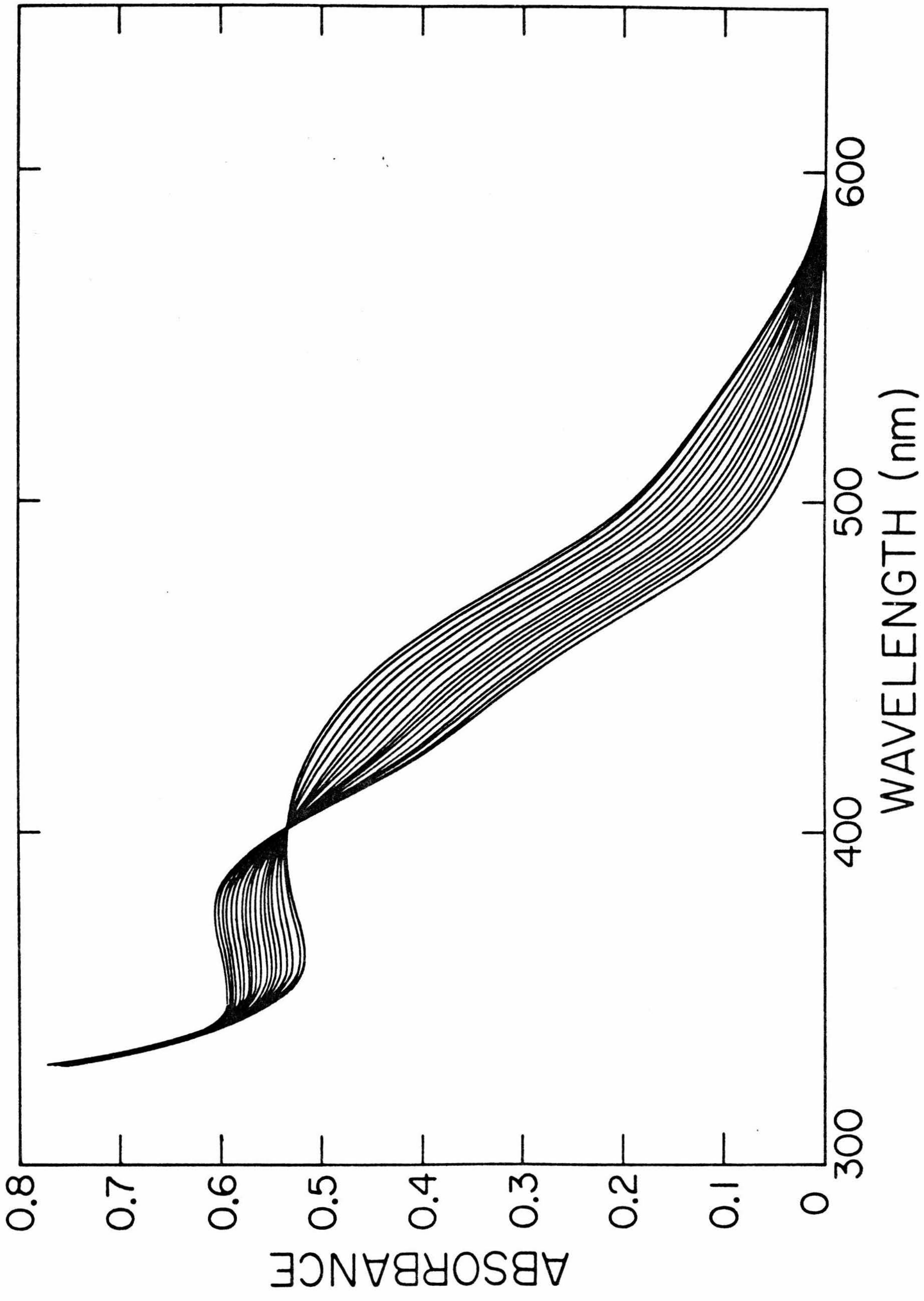
ABSORBANCE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
WAVELENGTH (nm)

Figure 2

Figure 3

The plot of $-\ln(A_\infty - A)$ vs. time for the reaction of Figure 1.

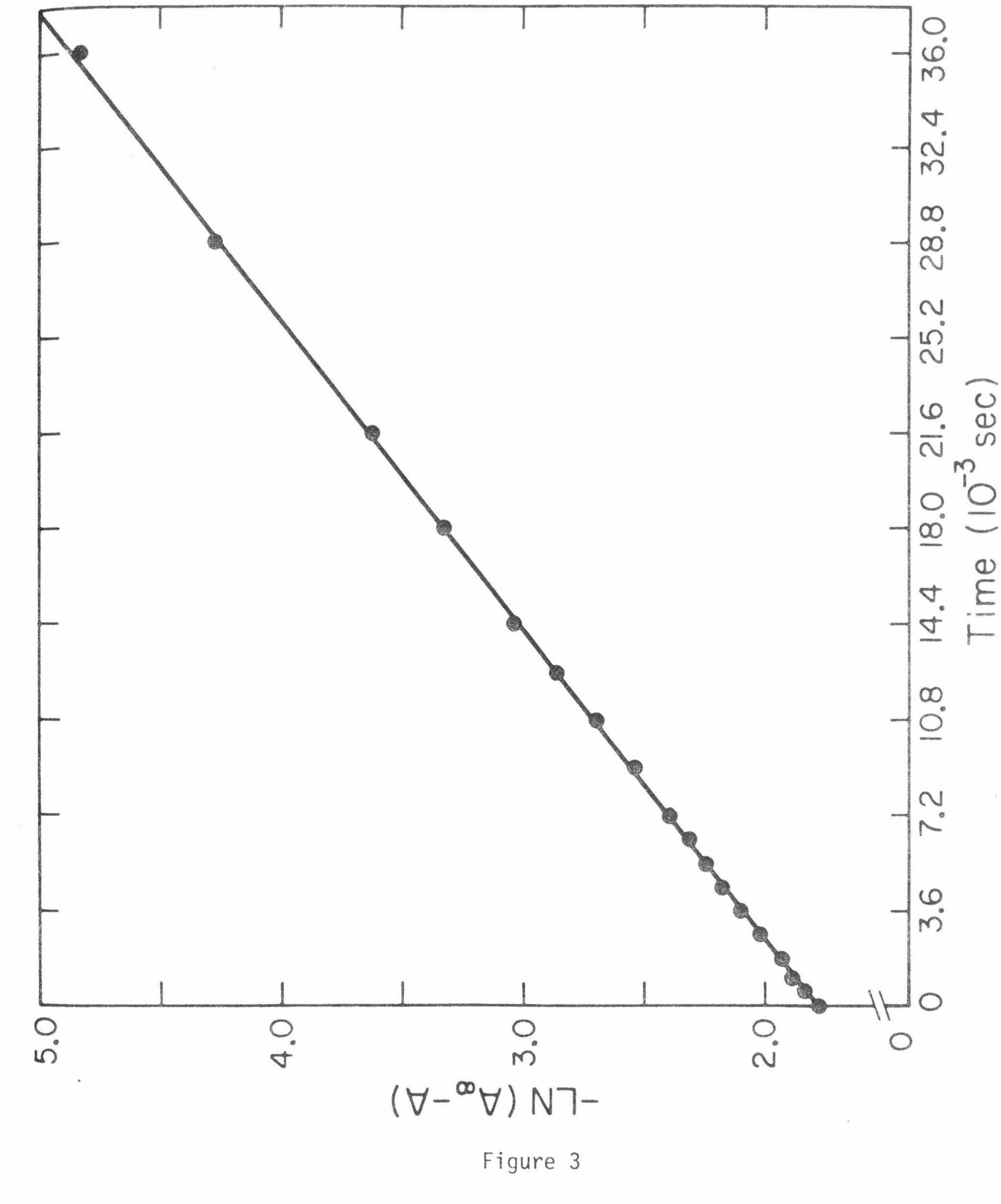
5.0
4.0
3.0
2.0
0
-LN (A_∞-A)
0
3.6
7.2
10.8
14.4
18.0
21.6
25.2
28.8
32.4
36.0
Time (10^{-3} sec)

Figure 3

Figure 4

The plot of $-\ln(A_\infty - A)$ *vs*. time for the reaction of Figure 2.

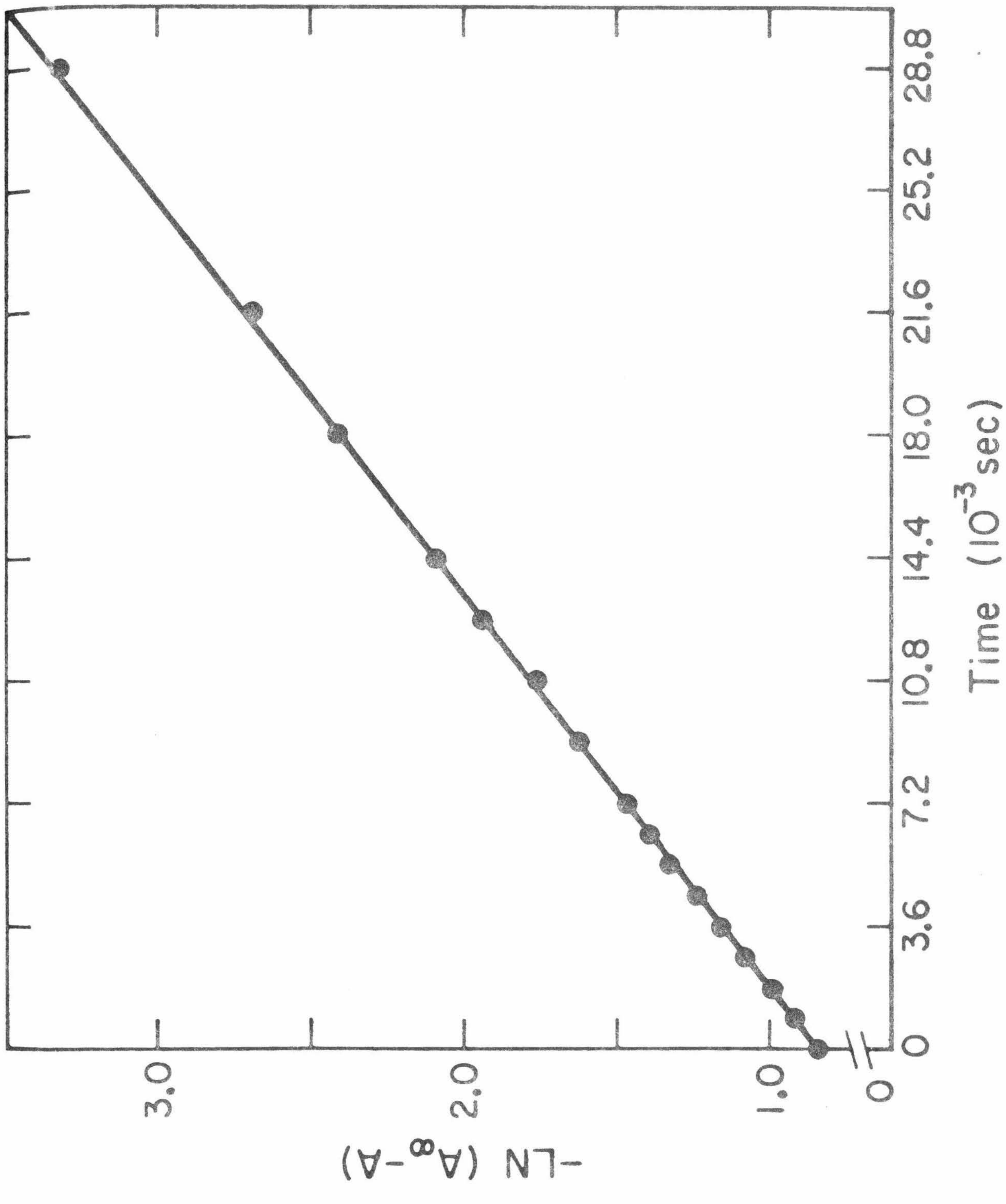

Figure 4

Table I. Observed Rate Constants for the Reaction of Trans-[$Mo(N_2)_2(dpe)_2$] with Nitriles.

Rx: $\underline{\text{trans}}\text{-}Mo(N_2)_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2 + RCN \longrightarrow \underline{\text{trans}}\text{-}Mo(N_2)_2(RCN)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2] + N_2$

RCN	Temp., K	10^4 [Mo], M	10^3 [RCN], M	10^4 k_{obs}, sec^{-1}[a]
C_6H_5CN	293.90	5.03	49.8	8.81 ± 0.07
		4.94	48.7	8.66 ± 0.11
		4.99	50.4	8.92 ± 0.06
C_6H_5CN	293.35	5.02	4.99	4.97 ± 0.05
	(under Argon)	4.98	4.90	7.50 ± 0.06
C_6H_5CN	303.35	5.00	4.94	2.54 ± 0.06
		5.10	12.8	3.06 ± 0.10
		4.96	26.4	3.61 ± 0.04
		4.95	37.5	3.50 ± 0.30
		4.96	52.4	3.53 ± 0.04

Table I (cont.).

RCN	Temp., K	10^4 [Mo], M	10^3 [RCN], M	10^4 k_{obs}, sec^{-1}[a]
p-C_7H_7CN	303.15	5.01	4.74	2.36 ± 0.04
		4.99	12.5	3.05 ± 0.02
		4.97	12.4	3.16 ± 0.29
		5.00	28.5	3.44 ± 0.05
		4.96	37.8	3.43 ± 0.04
		4.95	48.0	3.94 ± 0.03
CH_3CN	303.05	5.08	4.99	3.18 ± 0.25
		4.98	12.3	3.71 ± 0.17
		5.11	25.3	3.72 ± 0.07
		2.49	25.2	3.62 ± 0.23

[a] k_{obs} is given with 95% confidence limits.

Table II. Rate Constants and Activation Parameters for the Reaction of Trans-[$Mo(N_2)_2(dpe)_2$] with Nitriles.

RCN	Temp., K	k_1, sec^{-1} [a]	E_a, kcal/mol [b]	$\Delta H^{\ddagger}$, kcal/mol [b]	$\Delta S^{\ddagger}$, cal/mol deg [b]
PhCN	293.90	$8.80 \pm 0.24 \times 10^{-5}$	27.7 ± 0.9	27.1 ± 0.9	15.1 ± 2.1
	303.35	$3.55 \pm 0.10 \times 10^{-4}$	27.7 ± 0.9	27.1 ± 0.9	14.9 ± 2.0
	312.35	$1.471 \pm 0.041 \times 10^{-3}$	27.7 ± 0.9	27.1 ± 0.9	15.0 ± 2.0
p-TolCN	292.95	$7.17 \pm 0.26 \times 10^{-5}$	27.8 ± 0.8	27.2 ± 0.8	15.6 ± 1.9
	303.15	$3.60 \pm 0.54 \times 10^{-4}$	27.8 ± 0.8	27.2 ± 0.8	15.5 ± 2.1
	313.75	$1.704 \pm 0.097 \times 10^{-3}$	27.8 ± 0.8	27.2 ± 0.8	15.4 ± 1.8
CH_3CN	293.35	$9.34 \pm 0.90 \times 10^{-5}$	26.8 ± 0.9	26.2 ± 0.9	12.4 ± 2.1
	303.05	$3.68 \pm 0.10 \times 10^{-4}$	26.8 ± 0.9	26.2 ± 0.9	12.1 ± 2.0
	313.40	$1.675 \pm 0.051 \times 10^{-3}$	26.8 ± 0.9	26.2 ± 0.9	12.2 ± 1.9

[a] The mean value of k_1 is given with 95% confidence limits.

[b] All activation parameters are given with 95% confidence limits.

the reaction of 4 with benzonitrile is shown in Figure 5. The observed rate constants are collected in Table III, and Table IV contains the calculated rate constants and the activation parameters. Finally, the rate constants and activation parameters for the reaction of 3 with benzonitrile are collected in Table V.

The reaction of 1 with nitriles has the following stoichiometry (11)

$$\underline{\text{trans}}\text{-}[\mathrm{Mo(N_2)_2(dpe)_2}] + \mathrm{RCN} \longrightarrow \underline{\text{trans}}\text{-}[\mathrm{Mo(N_2)(RCN)(dpe)_2}] + \mathrm{N_2}\ .$$

Under pseudo-first-order conditions, the plots of $-\ln(A_\infty - A)$ vs. time were linear for over three half-lives of the reaction, and when the "metal" concentration was reduced by half, the reaction rate was reduced by one-half. Thus, the reaction is first-order in the concentration of 1. However, the reaction is not a simple order in nitrile concentration (Table I). At low nitrile concentrations, the reaction rate increases with increasing nitrile concentration, but at higher nitrile concentrations, the rate is constant with change in nitrile concentration. Also, at low nitrile concentrations, the reaction rate increases when the reaction is run under an atmosphere of argon rather than nitrogen.

These data are consistent with the S_N1 dissociative mechanism proposed in Scheme 1. The loss of dinitrogen from 1 is the rate determining step, and k_1 is the rate constant (Table II). The large positive entropies and enthalpies of activation, along

Figure 5

A visible spectrum of the reaction of cis-[$W(N_2)_2(PMe_2Ph)_4$] with benzonitrile.

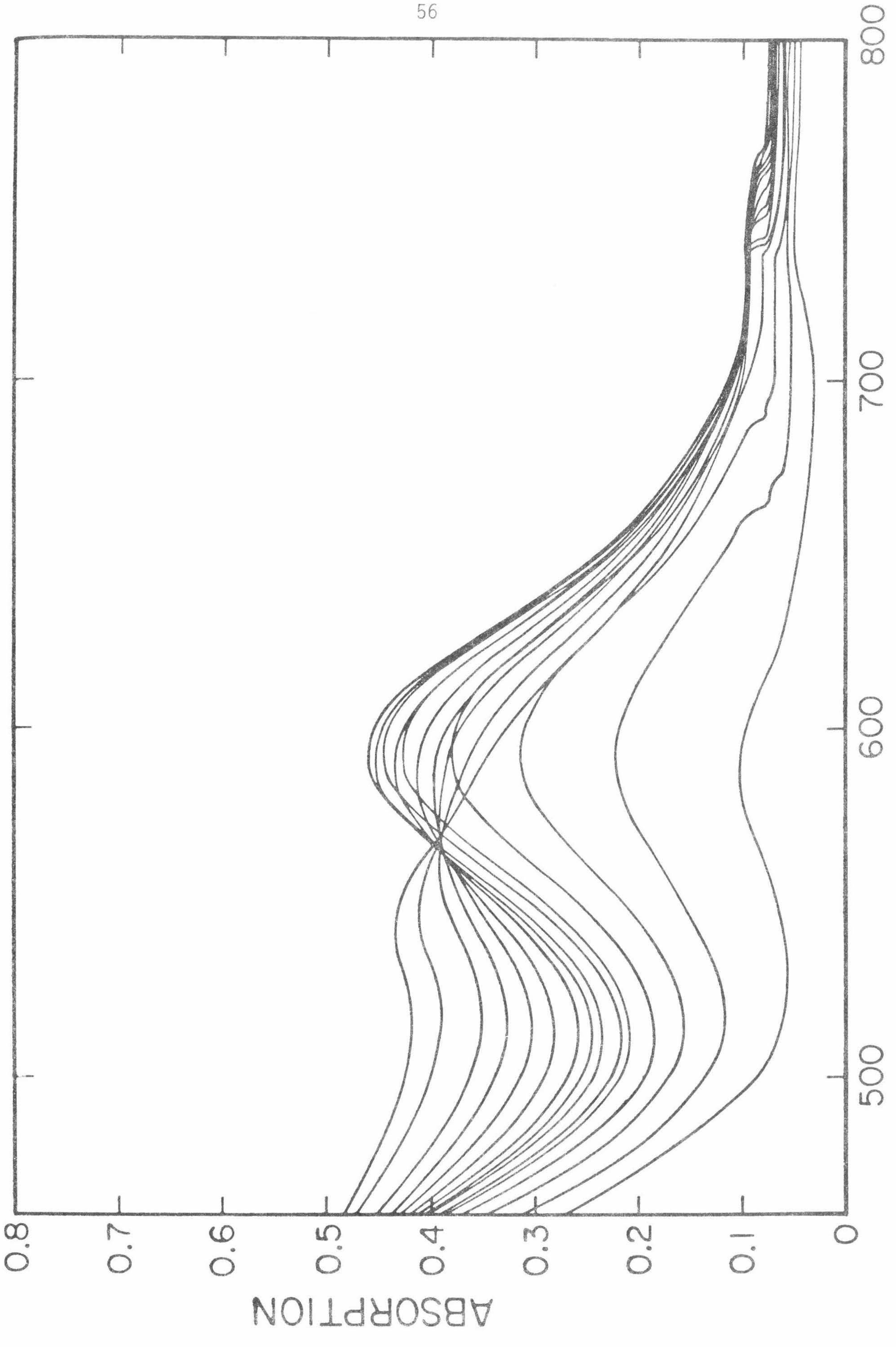
ABSORPTION
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
WAVELENGTH, mm
500
600
700
800

Figure 5

Table III. Observed Rate Constants for the Reaction of Cis-$[W(N_2)_2(PMe_2Ph)_4]$ with Benzonitrile.

Rx: cis-$[W(N_2)_2(PMe_2Ph)_4] + nC_6H_5CN \longrightarrow$ cis-$[W(N_2)_{2-n}(C_6H_5CN)_n(PMe_2Ph)_4] + nN_2$ n = 1,2

Temp., K	10^4 [W], m	10^2[RCN], m	$10^2[PMe_2Ph]$, m	10^4 $k1_{obs}$, sec^{-1} [a]	10^5 $k2_{obs}$, sec^{-1} [a]
303.30	9.87	6.60	7.72	2.56 ± 0.16	4.77 ± 0.54
	9.93	6.62	0.99	2.93 ± 0.15	6.35 ± 0.64
	9.97	7.37	0	2.86 ± 0.60	4.44 ± 1.63
	9.98	7.26	0	2.89 ± 0.38	5.22 ± 1.03
303.50	10.3	10.9	0	3.24 ± 0.30	8.79 ± 0.70
	9.87	9.51	0	3.66 ± 0.47	7.8 ± 2.6
	9.93	5.31	0	3.56 ± 0.15	7.73 ± 0.72
314.10	9.90	9.88	0	11.36 ± 2.83	32.5 ±11.8
	9.90	9.60	0	9.31 ± 1.53	31.9 ±12.3
	9.87	9.60	0	11.21 ± 3.53	31.6 ±18.7

[a] Observed rate constants are given with 95% confidence limits.

Table IV. Rate Constants and Activation Parameters for the Reaction of Cis-[W(N_2)$_2$(PMe_2Ph)$_4$] with Benzonitrile.

Temp., K	k1, sec^{-1} [a]	Ea, kcal/mole[b]	ΔH‡, kcal/mole[b]	ΔS‡, cal/mole·deg[b]
294.45	$(1.18 \pm 0.08) \times 10^{-4}$	20.7 ± 0.8	20.1 ± 0.8	-8.3 ± 1.7
303.50	$(3.37 \pm 0.20) \times 10^{-4}$	20.7 ± 0.8	20.1 ± 0.8	-8.3 ± 1.7
314.10	$(1.07 \pm 0.23) \times 10^{-3}$	20.7 ± 0.8	20.1 ± 0.8	-8.4 ± 2.1
Temp., K	k2, sec^{-1} [a]	Ea, kcal/mole[b]	ΔH‡, kcal/mole[b]	ΔS‡, cal/mole·deg[b]
294.45	$(2.50 \pm 0.40) \times 10^{-5}$	23.7 ± 1.2	23.1 ± 1.2	-1.1 ± 2.7
303.50	$(8.38 \pm 0.71) \times 10^{-5}$	23.7 ± 1.2	23.1 ± 1.2	-1.2 ± 2.6
314.10	$(3.15 \pm 1.20) \times 10^{-4}$	23.7 ± 1.2	23.1 ± 1.2	-1.2 ± 3.1

[a] Rate constants are given with 95% confidence limits.

[b] All activation parameters are given with 95% confidence limits.

Table V. Rate Constants and Activation Parameters for the Reaction of Cis-$[Mo(N_2)_2(PMe_2Ph)_4]$ with Benzonitrile.

Rx: cis-$[Mo(N_2)_2(P(CH_3)_2C_6H_5)_4] + nC_6H_5CN \longrightarrow$ cis-$[Mo(N_2)_{2-n}(C_6H_5CN)_n(P(CH_3)_2C_6H_5)_4] + nN_2$ n = 1,2

Temp., K	10^4 [Mo], m	10^2 [RCN], m	10^2 k1, sec^{-1}[a]	10^4 k2, sec^{-1}[a]
292.55	9.90	10.16	2.33 ± 0.30	7.5 ± 1.1
299.10	9.90	9.85	3.49 ± 0.42	25.9 ± 7.2
304.60	9.88	7.05	5.12 ± 0.28	46.7 ± 2.7

Temp., K	k1, sec^{-1}[a]	Ea, kcal/mole[b]	$\Delta H^{\ddagger}$, kcal/mole[b]	$\Delta S^{\ddagger}$, cal/mole·deg[b]
292.55	$(2.33 \pm 0.30) \times 10^{-2}$	11.4 ± 0.5	10.8 ± 0.5	-29 ± 4
299.10	$(3.49 \pm 0.42) \times 10^{-2}$	11.4 ± 0.5	10.8 ± 0.5	-29 ± 4
304.60	$(5.12 \pm 0.28) \times 10^{-2}$	11.4 ± 0.5	10.8 ± 0.5	-29 ± 2

Temp., K	k2, sec^{-1}[a]	Ea, kcal/mole[b]	$\Delta H^{\ddagger}$, kcal/mole[b]	$\Delta S^{\ddagger}$, cal/mole·deg[b]
292.55	$(7.5 \pm 1.1) \times 10^{-4}$	25.4 ± 1.4	24.8 ± 1.4	12.5 ± 3.5
299.10	$(2.59 \pm 0.72) \times 10^{-3}$	25.4 ± 1.4	24.8 ± 1.4	12.5 ± 5.5
304.60	$(4.67 \pm 0.27) \times 10^{-3}$	25.4 ± 1.4	24.8 ± 1.4	12.5 ± 2.3

[a] The mean value of k1(k2) is given with 95% confidence limits.

[b] All activation parameters are given with 95% confidence limits.

Mechanism:

$$Mo(N_2)_2(dpe)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo(N_2)(dpe)_2 + N_2$$

$$Mo(N_2)(dpe)_2 + RCN \xrightarrow{k_2} Mo(N_2)(RCN)(dpe)_2$$

$$\text{Rate} = \frac{d[Mo(N_2)(RCN)(dpe)_2]}{dt}$$

$$= k_{obs}[Mo(N_2)_2(dpe)_2]$$

where

$$k_{obs} = \frac{k_1 k_2[RCN]}{k_{-1}[N_2] + k_2[RCN]}$$

$$dpe = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$$

SCHEME 1

with the fact that k_1 does not depend on the incoming group, are strong evidence in support of the proposed rate determining step. In addition, this mechanism explains the dependence of the rate of the reaction on the nitrile concentration. At low nitrile concentrations, dinitrogen can compete for the coordinately unsaturated intermediate, and thus lower k_{obs}, but at high nitrile concentrations, every intermediate formed is quickly converted to product, and thus the observed leveling off of k_{obs} at high nitrile concentrations. It is clear, then, that this simple dissociative mechanism is capable of explaining all the experimental data.

Compound 2 reacts with nitriles to yield products analogous to those obtained from the reactions of 1 with nitriles, but the reactions only occurred in the presence of light. There was no detectable reaction of 2 with benzonitrile after 36 hrs at 70° C in the dark, but the reaction was found to proceed smoothly at 30° C in the visible spectrophotometer. However, the rate of reaction was slower if the reaction was constantly monitored at 605 nm rather than 380 nm. Therefore, with the aid of the spectral assignments of Chapter 1 of this thesis, it is proposed that the labilization of dinitrogen was accomplished by population of the $^{1,3}E_g$ excited states of 2.

In monitoring the visible spectrum of the reaction solution of 4 with benzonitrile (Figure 5), it was found that a band at 590 nm grew into the spectrum, at first, similar to the reaction of 1 with benzonitrile (Figure 1), but as the reaction proceeded, this band decreased in intensity and a new band at 540 nm grew into the spectrum. The reaction was scaled up, using the same concentrations, and the gases given off by the reaction were toepler pumped at times corresponding to the maximum absorption at 590 nm and 540 nm. Approximately 1 (0.85) equivalent of dinitrogen was evolved at the time of maximum absorption at 590 nm, and 2 (1.95) equivalents of dinitrogen were evolved at the time of maximum absorption at 540 nm. The two compounds were isolated, and elemental analyses and ir spectra confirmed the compounds to be $W(N_2)(PhCN)(PMe_2Ph)_4$ and $W(PhCN)_2(PMe_2Ph)_4$, respectively. It should be noted that the analysis for the intermediate was not a perfect match for the expected analysis of $W(N_2)(PhCN)(PMe_2Ph)_4$, but it was difficult to isolate the intermediate without some $W(PhCN)_2(PMe_2Ph)_4$ and <u>4</u> present, as exhibited by the ir spectra. However, it seems most reasonable to assign the intermediate as $W(N_2)(PhCN)(PMe_2Ph)$. The ir spectrum of $W(N_2)(PhCN)(PMe_2Ph)$ exhibited two bands at 1995 cm^{-1} and 1925 cm^{-1}, and the ir spectrum of $W(PhCN)_2(PMe_2Ph)_4$ contained two bands at 2030 cm^{-1} and 1990 cm^{-1}. The ^1H nmr in the methyl region of each compound consisted of a doublet and a triplet, at slightly higher field, each of equal integrated intensity (12). This same pattern was observed in the nmr spectrum of 4 (13), and the pattern is a fingerprint for a compound with two equivalent trans phosphines, and two equivalent phosphines cis to one another (14). Thus, it is reasonable to propose that both the mono-nitrile intermediate and bis-nitrile product are of cis geometry, and that the phosphines trans to the dinitrogen and the nitrile are almost equivalent in the nmr. Therefore, it is concluded that the reaction of 4 with nitriles is

$$\text{cis-}[\mathrm{W(N_2)_2(PMe_2Ph)_4}] + 2\mathrm{RCN} \longrightarrow$$

$$\text{cis-}[\mathrm{W(N_2)(PhCN)(PMe_2Ph)_4}] + \mathrm{N_2} + \mathrm{RCN} \longrightarrow$$

$$\text{cis-}[\mathrm{W(PhCN)_2(PMe_2Ph)_4}] + 2\mathrm{N_2}\ .$$

Under pseudo-first-order conditions initial rate experiments on the formation of the mono-nitrile intermediate showed that the reaction was first-order in 4, and initial rate experiments on the loss of the intermediate showed that this reaction was first-order in the intermediate's concentration. Finally, with the aid of computer fitting of the experimental data, it was confirmed that the reaction of 4 with nitriles consisted of two consecutive first-order reactions (8,10). Table III contains the observed rate constants for the formation of cis-$[\mathrm{W(N_2)(PhCN)(PMe_2Ph)_4}]$, $k1_{obs}$, and cis-$[\mathrm{W(PhCN)_2(PMe_2Ph)_4}]$, $k2_{obs}$, under pseudo-first-order conditions. Neither $k1_{obs}$ nor $k2_{obs}$ changed with change in nitrile concentration, which is consistent with the proposed rate law, and the rate did not depend on which nitrile was used (15). This data strongly suggests a mechanism which consists of two consecutive S_N1 dissociative steps (Scheme 2).

The averaged rate constants and activation parameters (Table IV) support this mechanism. The enthalpies of activation are reasonably large and positive, consistent with bond breaking in the rate determining step, but the entropies of activation are negative, implying an associative mechanism. Since the rate constants do not depend on the nitrile used, the possible dependence of the rate on free PMe_2Ph was investigated. The addition of PMe_2Ph had no effect on $k1_{obs}$ or $k2_{obs}$ (Table III) and thus it was concluded that both steps of the reaction proceed via a dissociative mechanism.

The visible absorption spectra of the reactions of 3 with nitriles were analogous to the spectra observed in the reactions of 4 with nitriles. When the gases given off by the reaction were toepler pumped, it was found that 1 (0.91) equivalent of dinitrogen was evolved at the time of maximum absorption of the intermediate (600 nm) and 2 (1.95) equivalents of dinitrogen were evolved at the time of maximum absorption of the final product (545 nm). The intermediate and final product were never obtained pure, and the characterization of the compounds remains inconclusive. The experimental data fit the same mechanism that was proposed for the reaction of 4 with nitriles, and thus it is proposed that the reactions of 3 and 4 with nitriles are analogous. The rate

Mechanism:

$$W(N_2)_2(P)_4 \xrightarrow{k_1} [W(N_2)(P)_4 + N_2] + RCN \xrightarrow{\text{fast}} W(N_2)(RCN)(P)_4 + N_2$$

$$W(N_2)(RCN)(P)_4 \xrightarrow{k_1} [W(RCN)(P)_4 + N_2] + RCN \xrightarrow{\text{fast}} W(RCN)_2(P)_4 + N_2$$

where

$P = PMe_2Ph$

SCHEME 2

constants for the formation of the intermediate, k1, and for loss of the intermediate, k2, are collected in Table V, along with the activation parameters. The enthalpy of activation for loss of the first dinitrogen is positive, but it is much smaller than the enthalpy of activation obtained in the other reactions under study. Also, the entropy of activation for loss of the first dinitrogen is large and negative. The enthalpy and entropy of activation for loss of the second dinitrogen from <u>3</u> are large and positive, and these parameters are similar to those obtained for the other reactions under study. Since neither k1 nor k2 were changed by adding free PMe_2Ph or using acetonitrile rather than benzonitrile (16), it is concluded that both steps of the reaction proceed via a dissociative mechanism. Thus, the negative entropy of activation for the loss of the first dinitrogen may be due to solvent reorganization, which should be greater in the <u>cis</u> rather than the <u>trans</u> complexes.

In all of the substitution reactions investigated in this chapter, the reactions of the molybdenum compounds were faster than the reactions of the analogous tungsten complexes. Based upon the proposed mechanisms, it can be concluded that the $M\text{-}N_2$ bond is stronger in the tungsten complexes. This is probably because tungsten is a better π-donor than molybdenum, and thus tungsten forms a stronger π-bond with a π-accepting ligand like dinitrogen (17). The energy of activation for the substitution reactions of <u>1</u>

should be a good estimate for the Mo-N_2 bond strength, since the entropies of activation for the reactions are so large and positive, and thus the W-N_2 bond strength can be estimated to be significantly larger than 28 kcal/mole. Because of the variation in the entropies of activation for the reactions of 3 and 4, an estimate of their M-N_2 bond strengths is difficult, but these compounds do provide an interesting comparison of the *trans* effect of dinitrogen, nitriles, and phosphines in d^6 octahedral complexes.

Only one dinitrogen is lost in the reactions of 1 with nitriles, and the product has a nitrile *trans* to the remaining dinitrogen. Thus, dinitrogen seems to have a greater *trans* labilizing effect than nitriles in this complex. Both dinitrogens are lost in the reaction of 3 and 4 with nitriles, and the intermediate, the mono-nitrile complex, is of *cis* geometry; there is a phosphine *trans* to the labilized dinitrogen in each step of the reaction. Thus it seems that phosphines also have a greater *trans* effect than nitriles in these octahedral complexes. Regrettably, a comparison of the *trans* effect of dinitrogen and phosphines is not possible.

In all of the reactions, except for the loss of the first dinitrogen in 3, the enthalpies and energies of activation are all in the twenties of kcal/mole, and they are remarkably close in energy. It is also remarkable that these parameters are so similar to those obtained in the kinetic studies of other transition metal dinitrogen complexes. In the decomposition of *trans*-

$[Mo(N_2)_2(dpe)_2]^+$ in methanol-tetrahydrofuran, the dissociation of dinitrogen is proposed as the rate determining step (18). The energy of activation was 24 kcal/mole and the entropy of activation was 19 eu. It is remarkable that this entropy of activation is so close to the value obtained in the reactions of 1 with nitriles, particularly because of the differences in the solvent systems. The energy of activation is smaller than that observed in the reactions of 1, which is consistent with Mo(I) being a weaker π-donor than Mo(0), and with dinitrogen being bonded like carbon monoxide (19). In the substitution reactions of $Os(N_2)(Br)_2[P(CH_3)_2C_6H_5]_2[P(OCH_3)_2C_6H_5]$ with free phosphines in toluene, the loss of dinitrogen is reported as the rate determining step, with an enthalpy and entropy of activation of 26.9 kcal/mole and 8.7 eu, respectively (21). The enthalpy of activation is remarkably similar to that found in our reactions, considering that ν(N≡N) for this complex is 2126 cm^{-1} and ν(N≡N) for the complexes under study range from 1930 cm^{-1} to 2000 cm^{-1} (22). From these ir data, one would expect the $Os-N_2$ bond to be stronger than the analogous bonds in 1, 2, 3, or 4, and thus the enthalpy of activation for loss of dinitrogen in the Os(II) complex was expected to be larger. But the experimental facts are not unreasonable, since the low entropy of activation (8.7 eu) implies there is less dissociation in the transition state of the Os(II) complex, and therefore there could be less bond breaking in the transition state. And finally, the enthalpy of activation for loss of dinitrogen from $[Ru(NH_3)_5(N_2)]^{2+}$ ion is 28 kcal/mole, which is similar to the enthalpies of activation previously discussed (23).

Many reactions of 1, 2, 3, and 4 are known in which coordinated dinitrogen is reduced, and one dinitrogen ligand is lost (2). For the reaction

$$[\mathrm{Mo}(\mathrm{N}_2)_2(\mathrm{dpe})_2] + \mathrm{RBr} \longrightarrow [\mathrm{Mo}(\mathrm{N}_2\mathrm{R})(\mathrm{Br})(\mathrm{dpe})_2] + \mathrm{N}_2 ,$$

preliminary kinetic data have been reported, in which the reaction was found to be first-order in the concentration of 1, with a rate constant of ca. 10^{-4} sec^{-1} at 20° C (24). This rate constant is in good agreement with that obtained in the reaction of 1 with nitriles, and thus it is proposed that the rate determining step in the reaction of 1 with alkyl halides is loss of dinitrogen. Thus, the coordinately unsaturated intermediate probably abstracts halide from the alkyl halide, and then the alkyl group adds to the coordinated dinitrogen, yielding the observed product. The loss of one dinitrogen is also observed in the reactions of 3 and 4 with H_2SO_4 to yield ammonia (2). In this reaction, 1.9 equivalents of ammonia are produced from 4, but only 0.7 equivalents of ammonia are produced from 3. Since the bulk of the remaining nitrogen is not accounted for in reduced nitrogen products, it could be lost as dinitrogen. Based on the values of k2 for 3 and 4, it is likely that the reduced yield of ammonia in the reaction of 3 is a result of the more rapid loss of the second dinitrogen in 3. Finally, the use of the rate constants reported in this chapter to explain the reactions in acidic solutions should be valid, since the rate constants for the reaction of 1 with nitriles did not change upon running the reaction in the presence of 0.1 equivalents of anhydrous HCl (25).

CONCLUSIONS

Dissociation of dinitrogen is a fundamental reaction of transition metal dinitrogen complexes, and thus the mechanism and kinetics of this process must be known to understand the mechanisms of the reactions of these complexes. The details for the displacement of dinitrogen from trans-$[M(N_2)_2(dpe)_2]$ and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) by nitriles have been presented. In each of the thermal reactions, an S_N1 dissociative mechanism was proposed to explain the kinetic data. With the aid of the kinetic data on the reaction of trans-$[Mo(N_2)_2(dpe)_2]$ with nitriles, it was possible to conclude that the rate determining step in the reaction of trans-$[Mo(N_2)_2(dpe)_2]$ with alkyl halides is the loss of dinitrogen, and thus it is the coordinately unsaturated intermediate which activates dinitrogen towards reduction.

Therefore, it is proposed that these molybdenum and tungsten bis-dinitrogen complexes activate dinitrogen towards reduction, where others have failed, primarily because there are two dinitrogens bonded to the metal. One can dissociate, leaving a coordinately unsaturated intermediate which activates the remaining dinitrogen towards reduction.

It is hoped that, with the aid of work presented in this chapter, future research will be able to explain in detail how coordinated dinitrogen is reduced in these complexes.

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(12) For both compounds, the peak locations were basically the same: doublet at δ 1.57 and 1.52; triplet at δ 1.46, 1.43, and 1.40.

(13) Doublet at δ 1.56 and 1.50; triplet at δ 1.43, 1.41, and 1.39.

(14) ^{31}P nmr spectra of $[W(N_2)(PhCN)(PMe_2Ph)_4]$ and $[W(PhCN)_2(PMe_2Ph)_4]$ were consistent with the assignment of <u>cis</u> geometry for these complexes.

(15) For the reaction of <u>4</u> with acetonitrile at 303.30 K, k1 was $(2.76 \pm 0.28) \times 10^{-4}$ sec^{-1} and k2 was $(5.5 \pm 0.8) \times 10^{-5}$ sec^{-1}.

(16) For the reaction of <u>3</u> with acetonitrile at 292.60 K, k1 was $(2.45 \pm 0.25) \times 10^{-2}$ sec^{-1} and k2 was $(7.8 \pm 1.0) \times 10^{-4}$ sec^{-1}. For the reaction of <u>3</u> with benzonitrile and ten molar equivalents of free PMe_2Ph, k1 was $(2.49 \pm 0.35) \times 10^{-2}$ sec^{-1} and k2 was $(7.7 \pm 1.1) \times 10^{-4}$ sec^{-1}.

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(19) By analogy to carbonyl complexes, $\nu(N\equiv N)$ should move to higher energy as the metal is oxidized. This is observed in <u>trans</u>-$[Mo(N_2)_2(dpe)_2]$ and <u>trans</u>-$[Mo(N_2)_2(dpe)_2]^+$, where $\nu(N\equiv N)$ is 1975 cm^{-1} and 2047 cm^{-1}, respectively (20).

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(25) For the reaction of *1* with benzonitrile and 0.1 molar equivalents of anhydrous HCl, k_{obs} was $(3.65 \pm 0.09) \times 10^{-4}$ sec^{-1} at 303.20 K.

APPENDIX I

Reactions of *cis*-$[W(N_2)(PhCN)(PMe_2Ph)_4]$ and *trans*-$[Mo(N_2)(PhCN)(Ph_2PCH_2CH_2PPh_2)_2]$ With Acids

INTRODUCTION

There has been considerable interest in the reactions of trans-$[M(N_2)_2(dpe)_2]$ and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W; dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; $PMe_2Ph = P(CH_3)_2(C_6H_5)$) with acids, since ammonia and other reduced nitrogen products are produced in these reactions (1,2).

$$\text{cis-}[W(N_2)_2(PMe_2Ph)_4] + H_2SO_4 \longrightarrow 2NH_3 + N_2 + \text{other products}$$

$$\text{trans-}[W(N_2)_2(dpe)_2] + HCl \longrightarrow [W(Cl)(N_2H_2)(dpe)_2](Cl) + N_2$$

However, little has been done along similar lines with trans-$[Mo(N_2)(RCN)(dpe)_2]$, 1, or cis-$[W(N_2)(RCN)(PMe_2Ph)_4]$, 2, even though the reactions of these compounds with acids would be particularly interesting, since either the dinitrogen could be reduced, or the nitrile could be reduced, possibly to amines.

Some reactions of 1 have been studied. The reaction of 1 with PhCOCl yielded trans-$[Mo(Cl)(N_2COPh)(dpe)_2]$, for which a crystal structure has been done (3), and this was the same product obtained by the reaction of trans-$[Mo(N_2)_2(dpe)_2]$ with PhCOCl (4). The electrochemistry of 1 has also been investigated (5), but the reactions of 1 or 2 with acids have not been reported. Thus, we initiated our study of these reactions.

EXPERIMENTAL

Materials and Syntheses

All solvents used were reagent grade, obtained from MCB. All solvents were freshly distilled in vacuo immediately before use. The liquid nitriles were distilled from phosphorous (V) oxide, methanol was distilled from magnesium turnings, dichloromethane was distilled from Linde 4 Å molecular sieves, and THF was distilled from sodium/benzophenone. All other solvents were distilled from titanocene (6). Molybdenum (V) chloride and tungsten (VI) chloride were obtained from Roc/Ric and purified by refluxing in CCl_4, under a nitrogen atmosphere, for two days with visible irradiation (7,8). 1,2-Bis(diphenylphosphino)ethane and dimethylphenylphosphine were obtained from Roc/Ric, triphenylphosphine was obtained from MCB, and all were used without further purification. HCl(g) was obtained from Matheson, and it was purified by freeze-pump-thawing.

All reactions were carried out using vacuum line and dry box handling techniques which are standard for our group (6). Trans-$[Mo(N_2)(PhCN)(dpe)_2]$ was prepared by published procedures (9), and the elemental analysis and ir spectrum were in agreement with the literature. The syntheses and analyses of cis-$[W(PhCN)(L)(PMe_2Ph)_4]$ ($L = N_2$, PhCN) were described in Chapter 2 of this thesis.

Toepler Pump Reactions

1.29 mmole of anhydrous HCl(g) was added to 65 mg (6.35 x 10^{-2} mmole) of trans-[Mo(N_2)(PhCN)(dpe)$_2$] in 10.5 ml of toluene. At -78° C, the solution changed from green to yellow in *ca*. 5 min, and no dinitrogen or hydrogen was evolved. The same reaction was also observed at room temperature. The product was formulated as [Mo(Cl)(N_2H_2)(dpe)$_2$][Cl]. *Anal*. Calcd. C, 62.58; H, 5.07; N, 2.82. Found: C, 63.31; H, 5.19; N, 2.42.

0.132 mmole of cis-[W(N_2)(PhCN)(PMe_2Ph)$_4$] was prepared *in situ*, in 11.0 ml of toluene. 2.64 mmole of anhydrous HCl(g) was added to this solution at -200° C. A rapid reaction occurred, in which no gases were evolved. The tar which remained was intractable.

0.149 mmole of cis-[W(N_2)(PhCN)(PMe_2Ph)$_4$] was prepared *in situ*, in 11.0 ml of toluene. 2.98 mmole of anhydrous HCl(g) was added to the solution at room temperature. A rapid reaction took place, in which 0.151 mmole of dinitrogen was evolved. Again, the tar which remained was intractable.

Physical Measurements

All ir spectra used to identify the products were measured on a Beckman IR 12 using Nujol mulls. All elemental analyses were performed by the micro-analytical lab in our department.

RESULTS AND DISCUSSION

In the reaction of 1 with anhydrous HCl, no dinitrogen is evolved, but in the reaction of trans-[Mo$(N_2)_2$(dpe)$_2$] with HCl, both dinitrogen ligands are lost and the metal hydride complex is formed (1). However, the reaction of trans-[W$(N_2)_2$(dpe)$_2$] with HCl yields trans-[W(NNH_2)(Cl)(dpe)$_2$][Cl] (1,10). Thus, by analogy with this latter reaction, it is proposed that the product of 1 with HCl is trans-[Mo(NNH_2)(Cl)(dpe)$_2$][Cl], 3. The elemental analysis for the product is in good agreement with that expected for 3, but the ir spectrum does not confirm this structure. No N-H stretching band is observed in the 3300 cm^{-1} region (11), but then this band should be broad and weak. There is a band at 1415 cm^{-1} which may be due to an NN stretch (4), but without the ^{15}N analogue it would be foolish to assign this band as the NN stretch. Finally, there are three bands at 740, 700, and 650 cm^{-1}, along with two bands at 530 and 480 cm^{-1}, which are observed in all the Group VIB metal complexes with two dpe ligands in a plane. Thus, the ir spectrum neither confirms nor disproves the proposal that the product is trans-[Mo(NNH_2)(Cl)(dpe)$_2$][Cl].

The reaction of 2 with anhydrous HCl yields different products at different temperatures. If the reaction is run at -200° C, then no gases are evolved. However, if the reaction is run at room temperature, then 1 molar equivalent of dinitrogen is evolved. The tar which remained after the solvent was removed from each reaction solution was intractable. These reactions were also observed when methanol was used as the solvent, and no HCl was added. Again, the 'products' were intractable.

It should be noted that the reactions of 1 and 2 with HCl are far faster than the reactions of the parent bis-dinitrogen complexes with HCl. For example, the reaction of 1 with HCl is complete after *ca*. 5 min at -78° C, but the reaction of *trans*-$[Mo(N_2)_2(dpe)_2]$ with HCl is only 16% complete after two days at 40° C. Furthermore, 2 reacts rapidly with methanol at -78° C, but the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with methanol at -78° C is negligible. Thus, it seems that the mono-nitrile complexes are much more reactive than their parent bis-dinitrogen complexes.

In the future, it would be useful to scale up the reactions of 1 and 2 so that any amines or reduced dinitrogen products could be more easily detected and analyzed (12). Also, it would be interesting to extend this study to the reaction of *cis*-$[W(PhCN)_2(PMe_2Ph)_4]$ with HCl, with particular attention paid to the possibility of 1° amine production.

CONCLUSIONS

It was found by Leigh and Pickett (5) that 1 could be attached to a tin oxide electrode, with the nitrile as the bridging ligand. It was proposed that this system may allow for the pseudo-catalytic electrochemical reduction of dinitrogen in the presence of acids. Based on the reaction of 1 with anhydrous HCl, it can be concluded that the proposed research of Leigh and Pickett should fail, since the metal-nitrile bond should be broken, and thus the complex should be lost from the electrode.

Finally, future research into the possible reduction of the nitriles of *cis*-$[W(RCN)(L)(PMe_2Ph)_4]$ ($L = N_2$, RCN) by simple acids under mild conditions could be fruitful.

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APPENDIX II

Programs

```
FORTRAN IV G LEVEL 20.7 VS             MAIN               DATE =    8/24/78      12:38:25           PAGE 0001
                 C      CURVE FITTING PROGRAM
                 C
  0001                  DOUBLE PRECISION ARRAY,WEIGHT,ALPHA
  0002                  DIMENSION X(30),Y(30),SIGMAY(30),A(10),SIGMAA(10),YFIT(30),DEV(30)
  0003                  DIMENSION WEIGHT(30),ALPHA(10,10),BETA(10),DERIV(10)
  0004                  DIMENSION ARRAY(10,10),B(10),TITLE(20)
  0005             25   READ(5,30) (TITLE(I),I=1,20)
  0006             30   FORMAT(20A4)
  0007             35   READ(5,40) (NPTS,NTERMS,MODE,FLAMDA)
  0008             40   FORMAT(3I5,F10.0)
  0009             45   READ(5,50) (Y(I),I=1,NPTS)
  0010             50   FORMAT(14F5.0)
  0011             55   READ(5,50) (SIGMAY(I),I=1,NPTS)
  0012             60   READ(5,50) (X(I),I=1,NPTS)
  0013             65   READ(5,70) (A(I),I=1,NTERMS)
  0014             70   FORMAT(7F10.0)
                 C
                 C      EVALUATE WEIGHTS
                 C
  0015             90   NFREE=NPTS-NTERMS
  0016             95   IF (NFREE) 100,100,110
  0017            100   CHISQ=0.0
  0018                  GO TO 450
  0019            110   DO 160 I=1,NPTS
  0020            115   IF (MODE) 120,145,155
  0021            120   IF (Y(I)) 135,145,125
  0022            125   WEIGHT(I)=1.0/Y(I)
  0023                  GO TO 160
  0024            135   WEIGHT(I)=1.0/(-Y(I))
  0025                  GO TO 160
  0026            145   WEIGHT(I)=1.0
  0027                  GO TO 160
  0028            155   WEIGHT(I)=1.0/(SIGMAY(I)**2)
  0029            160   CONTINUE
                 C
                 C      EVALUATE ALPHA AND BETA MATRICES
                 C
  0030            170   DO 445 N=1,100
  0031            175   DO 190 J=1,NTERMS
  0032            180   BETA(J)=0.0
  0033            185   DO 190 K=1,J
  0034            190   ALPHA(J,K)=0.0
  0035            195   DO 260 I=1,NPTS
  0036            200   DO 235 L=1,NTERMS
  0037            205   AL=A(L)
  0038            210   DELTA=1.0001*AL
  0039            215   A(L)=AL+DELTA
  0040            220   YFT=FUNCTN(X,I,A)
  0041            225   A(L)=AL-DELTA
  0042            230   DERIV(L)=(YFT-FUNCTN(X,I,A))/(2.0*DELTA)
  0043            234   A(L)=AL
  0044            235   CONTINUE
  0045            240   DO 265 J=1,NTERMS
  0046            245   BETA(J)=BETA(J)+WEIGHT(I)*(Y(I)-FUNCTN(X,I,A))*DERIV(J)
  0047            250   DO 255 K=1,J
  0048            255   ALPHA(J,K)=ALPHA(J,K)+WEIGHT(I)*DERIV(J)*DERIV(K)
FORTRAN IV G LEVEL 20.7 VS             MAIN               DATE =    8/24/78      12:38:25           PAGE 0002
  0049            260   CONTINUE
  0050            265   DO 275 J=1,NTERMS
  0051            270   DO 275 K=1,J
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                 C      EVALUATE CHI SQUARE AT STARTING POINT
                 C
 0053             280   DO 285 I=1,NPTS
 0054             285   YFIT(I)=FUNCTN(X,I,A)
 0055             290   CHISQ1=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
                 C
                 C      INVERT MODIFIED CURVATURE MATRIX, FIND NEW PARAMETERS
                 C
 0056             295   FLAM=FLAMDA*1000000.0
 0057             300   DO 315 J=1,NTERMS
 0058             305   DO 310 K=1,NTERMS
 0059             310   ARRAY(J,K)=ALPHA(J,K)/DSQRT(ALPHA(J,J)*ALPHA(K,K))
 0060             315   ARRAY(J,J)=1.0+FLAMDA
 0061             320   CALL MTINV(ARRAY,NTERMS,DET)
 0062             325   DO 340 J=1,NTERMS
 0063             330   B(J)=A(J)
 0064             335   DO 340 K=1,NTERMS
 0065             340   B(J)=B(J)+(BETA(K)*ARRAY(J,K))/DSQRT(ALPHA(J,J)*ALPHA(K,K))
                 C
                 C      CHECK CHI SQUARE , IF INCREASE, INCREASE FLAMDA
                 C
 0066             345   DO 350 I=1,NPTS
 0067             350   YFIT(I)=FUNCTN(X,I,B)
 0068             355   CHISQR=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
 0069             360   IF (CHISQ1-CHISQR) 365,380,380
 0070             365   IF (FLAMDA-FLAM) 370,525,525
 0071             370   FLAMDA=10.0*FLAMDA
 0072                   GO TO 300
                 C
                 C      EVALUATE PARAMETERS AND UNCERTAINTIES
                 C
 0073             380   DO 390 J=1,NTERMS
 0074             385   A(J)=B(J)
 0075             390   SIGMAA(J)=DSQRT(ARRAY(J,J)/ALPHA(J,J))
 0076             395   DV=0.0
 0077             400   DO 415 I=1,NPTS
 0078             405   DEV(I)=Y(I)-FUNCTN(X,I,A)
 0079             410   DV=DV+(DEV(I)*DEV(I))
 0080             415   CONTINUE
 0081             420   FLAMDA=FLAMDA/10.0
 0082             425   PTS=NPTS
 0083             435   DV=SQRT(DV)/PTS
 0084             440   IF (DV-.001) 450,450,445
 0085             445   CONTINUE
                 C
                 C      OUT PUT
                 C
 0086             450   WRITE(6,455) (TITLE(I),I=1,20)
 0087             455   FORMAT(1H1,20A4)
 0088             460   WRITE(6,465)
 0089             465   FORMAT(1H0)
FORTRAN IV G LEVEL 20.7 VS             MAIN                DATE =    8/24/78       12:38:25               PAGE 0003
 0090             470   WRITE(6,475)
 0091             475   FORMAT(63H0          T+             ABSB            K1              K2
                 1          N )
 0092             480   WRITE(6,485) A(4),A(3),A(1),A(2),N
 0093             485   FORMAT(1H0,2E15.5,2E15.4,I5)
 0094             489   WRITE(6,490)
 0095             490   FORMAT(58H0        SIGMA Y+       SIGMA ABSB       SIGMA K1        SIGMA K
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   0099          510  FORMAT(59H0          Y(EXP)          Y(CALC)            DIF
                     1 X )
   0100          515  WRITE(6,520) (Y(I),YFIT(I),DEV(I),X(I),I=1,NPTS)
   0101          520  FORMAT(1H04F15.4)
   0102               GO TO 535
   0103          525  WRITE(6,530)
   0104          530  FORMAT(18H0 DIVERGED AT 365 )
   0105          535  CONTINUE
   0106               GO TO 25
   0107               END
  FORTRAN IV G LEVEL 20.7 VS              MAIN             DATE =    8/24/78       12:38:25            PAGE 0004

                                   SUBPROGRAMS CALLED
 SYMBOL     LOCATION         SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
 IBCOM#        17C           FUNCTN        180          FCHISQ        184          MTINV         188          DSQRT         18C
 SQRT          190

                                   SCALAR MAP
 SYMBOL     LOCATION         SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
 I             228           NPTS          22C          NTERMS        230          MODE          234          FLAMDA        238
 NFREE         23C           CHISQ         240          N             244          J             248          K             24C
 L             250           AL            254          DELTA         258          YFT           25C          CHISQ1        260
 FLAM          264           DET           268          CHISQR        26C          DV            270          PTS           274

                                   ARRAY MAP
 SYMBOL     LOCATION         SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
 X             278           Y             2F0          SIGMAY        368          A             3E0          SIGMAA        408
 YFIT          430           DEV           4A8          WEIGHT        520          ALPHA         610          BETA          930
 DERIV         958           ARRAY         980          B             CA0          TITLE         CC8

                                   FORMAT STATEMENT MAP
 SYMBOL     LOCATION         SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
     30        D18               40        D1E              50        D27              70        D2E             455        D35
    465        D3E              475        D43             485        D86             490        D97             500        DD5
    510        DDF              520        E1E             530        E28

                                   STATEMENT NUMBER MAP
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      5        EF8                7        F38               9        F6C              11        FAC              12        FEC
     13        1C2C              15        106C             16        1078             17        1084             18        108C
     19        1092              20        10A2             21        10B4             22        10C6             23        10D6
     24        10DC              25        10EE             26        10F4             27        10FC             28        1102
     29        1116              30        1132             31        113A             32        114A             33        1152
     34        115C              35        1198             36        11B0             37        11BC             38        11C4
     39        11D0              40        11DC             41        11EE             42        11FA             43        121C
     44        1224              45        123C             46        124C             47        1284             48        1292
     49        12E8              50        1314             51        1324             52        1330             53        1370
     54        137C              55        13A6             56        13BE             57        13C4             58        13D4
     59        13E2              60        1422             61        144E             62        145C             63        1478
     64        1480              65        1494             66        1522             67        152E             68        1558
     69        156A              70        157A             71        158A             72        1596             73        159C
     74        15AC              75        15B4             76        15EE             77        15F6             78        1602
     79        161A              80        162A             81        1642             82        164E             83        166E
     84        1684              85        1694             86        16A8             88        16E8             90        16FC
     92        1710              94        174C             96        176C             98        1794            100        17A8
    102        1800             103        1806            105        181C            106        181C

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     *STATISTICS*  NO DIAGNOSTICS GENERATED
  FORTRAN IV G LEVEL
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      0002                DIMENSION X(30),A(10)
      0003          610   XI=X(I)+A(4)
      0004          615   Z1=(A(3)*A(1))/(A(2)-A(1))
      0005          620   FUNCTN=(Z1*EXP(-A(1)*XI))-(Z1*EXP(-A(2)*XI))
      0006          630   RETURN
      0007                END
    FORTRAN IV G LEVEL 20.7 VS              FUNCTN           DATE =    8/24/78      12:38:25             PAGE 0002

                                  SUBPROGRAMS CALLED
    SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
    EXP             90

                                  EQUIVALENCE DATA MAP
    SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
    FUNCTN          A0

                                  SCALAR MAP
    SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
    XI              A4        I               A8        Z1              AC

                                  ARRAY MAP
    SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
    X               B0        A               B4

                                  STATEMENT NUMBER MAP
    STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION
        1        158              3        158              4        178              5        18E              6        1DC

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       *STATISTICS*  NO DIAGNOSTICS GENERATED
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      0001          650   FUNCTION FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
      0002                DOUBLE PRECISION CHISQ,WEIGHT
      0003                DIMENSION Y(30),SIGMAY(30),YFIT(30)
      0004          665   CHISQ =0.0
      0005          670   IF (NFREE) 675,675,685
      0006          675   FCHISQ =0.0
      0007                GO TO 750
      0008          685   DO 735 I=1,NPTS
      0009          690   IF (MODE) 695,720,730
      0010          695   IF (Y(I)) 710,720,700
      0011          700   WEIGHT =1.0/Y(I)
      0012                GO TO 735
      0013          710   WEIGHT =1.0/(-Y(I))
      0014                GO TO 735
      0015          720   WEIGHT =1.0
      0016                GO TO 735
      0017          730   WEIGHT =1.0/SIGMAY(I)**2
      0018          735   CHISQ = CHISQ + WEIGHT*(Y(I)-YFIT(I))*(Y(I)-YFIT(I))
      0019          740   FREE=NFREE
      0020          745   FCHISQ=CHISQ/FREE
      0021          750   RETURN
      0022                END
    FORTRAN IV G LEVEL 20.7 VS              FCHISQ           DATE =    8/24/78      12:38:25             PAGE 0002

                                  EQUIVALENCE DATA MAP
    SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
    FCHISQ          E0
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  CHISQ        E8       WEIGHT       F0        NFREE        F8          I              FC         NPTS          100
  MODE        104       FREE        108

                                   ARRAY MAP
  SYMBOL    LOCATION    SYMBOL    LOCATION     SYMBOL    LOCATION      SYMBOL    LOCATION      SYMBOL    LOCATION
  Y            10C      SIGMAY       110       YFIT         114

                                   STATEMENT NUMBER MAP
  STATEMENT LOCATION    STATEMENT LOCATION     STATEMENT LOCATION      STATEMENT LOCATION      STATEMENT LOCATION
          1    1F0              4    1F0               5    1F8                6    204                7    20C
          8    212              9    232              10    244               11    256               12    266
         13    26C             14    27E              15    284               16    28C               17    292
         18    2A6             19    2EC              20    30C               21    31C

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    0001           800  SUBROUTINE MTINV(ARRAY,NTERMS,DET)
    0002                DOUBLE PRECISION ARRAY,AMAX,SAVE
    0003                DIMENSION ARRAY(10,10),IK(10),JK(10)
    0004           815  DET=1.0
    0005           820  DO 1015 K=1,NTERMS
                  C
                  C     FIND LARGEST ELEMENT IN ARRAY(I,J)
                  C
    0006           825  AMAX = 0.0
    0007           830  DO 860 I=K,NTERMS
    0008           835  DO 860 J=K,NTERMS
    0009           840  IF (DABS(AMAX)-DABS(ARRAY(I,J))) 845,845,860
    0010           845  AMAX =ARRAY(I,J)
    0011           850  IK(K)=I
    0012           855  JK(K)=J
    0013           860  CONTINUE
                  C
                  C     INTERCHANGE ROWS AND COLUMNS TO PUT AMAX IN ARRAY(K,K)
                  C
    0014           865  IF (AMAX) 880,870,880
    0015           870  DET =0.0
    0016                GO TO 1095
    0017           880  I=IK(K)
    0018           885  IF (I-K) 930,910,890
    0019           890  DO 905 J=1,NTERMS
    0020           895  SAVE=ARRAY(K,J)
    0021           900  ARRAY(K,J)=ARRAY(I,J)
    0022           905  ARRAY(I,J)=-SAVE
    0023           910  J=JK(K)
    0024           915  IF (J-K) 930,940,920
    0025           920  DO 935 I=1,NTERMS
    0026           925  SAVE =ARRAY(I,K)
    0027           930  ARRAY(I,K)=ARRAY(I,J)
    0028           935  ARRAY(I,J)=-SAVE
                  C
                  C     ACCUMULATE ELEMENTS OF INVERSE MATRIX
                  C
    0029           940  DO 955 I=1,NTERMS
    0030           945  IF (I-K) 950,955,950
    0031           950  ARRAY(I,K)=-ARRAY(I,K)/AMAX
    0032           955  CONTINUE
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      0036          975  IF (J-K) 980,985,980
      0037          980  ARRAY(I,J)=ARRAY(I,J)+ARRAY(I,K)*ARRAY(K,J)
      0038          985  CONTINUE
      0039          990  DO 1005 J=1,NTERMS
      0040          995  IF (J-K) 1000,1005,1000
      0041         1000  ARRAY(K,J)=ARRAY(K,J)/AMAX
      0042         1005  CONTINUE
      0043         1010  ARRAY(K,K)=1.0/AMAX
      0044         1015  DET=DET*AMAX
                   C
                   C     RESTORE ORDERING OF MATRIX
                   C
    FORTRAN IV G LEVEL 20.7 VS              MTINV              DATE =    8/24/78      12:38:25              PAGE 0002
      0045         1020  DO 1090 L=1,NTERMS
      0046         1025  K=NTERMS-L+1
      0047         1030  J=IK(K)
      0048         1035  IF (J-K) 1060,1060,1040
      0049         1040  DO 1055 I=1,NTERMS
      0050         1045  SAVE=ARRAY(I,K)
      0051         1050  ARRAY(I,K)=-ARRAY(I,J)
      0052         1055  ARRAY(I,J)=SAVE
      0053         1060  I=JK(K)
      0054         1065  IF (I-K) 1090,1090,1070
      0055         1070  DO 1085 J=1,NTERMS
      0056         1075  SAVE=ARRAY(K,J)
      0057         1080  ARRAY(K,J)=-ARRAY(I,J)
      0058         1085  ARRAY(I,J)=SAVE
      0059         1090  CONTINUE
      0060         1095  RETURN
      0061               END
    FORTRAN IV G LEVEL 20.7 VS              MTINV              DATE =    8/24/78      12:38:25              PAGE 0003

                                 SCALAR MAP
  SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
  AMAX         170         SAVE         178         DET          180         K            184         NTERMS       188
  I            18C         J            190         NTREMS       194         L            198

                                 ARRAY MAP
  SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
  ARRAY        19C         IK           1A0         JK           1C8

                                 STATEMENT NUMBER MAP
  STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION
        1      20E               4      2DE               5      2E6               6      32E               7      336
        8      350               9      364              10      37C              11      384              12      38C
       13      394              14      3C4              15      3D0              16      3D8              17      3DE
       18      3E6              19      3FC              20      40C              21      418              22      42C
       23      456              24      45E              25      474              26      484              27      490
       28      4AA              29      4DA              30      4E6              31      4F6              32      504
       33      51C              34      530              35      53A              36      54A              37      55A
       38      56E              39      5A2              40      5AE              41      5BE              42      5CA
       43      5E2              44      5F2              45      660              46      668              47      678
       48      688              49      698              50      6A8              51      6BE              52      6EC
       53      71A              54      72A              55      73A              56      74A              57      75A
       58      77C              59      7A4              60      788

       *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
       *OPTIONS IN EFFECT*  NAME = MTINV    , LINECNT =       58
       *STATISTICS*    SOURCE STATEMENTS =         61,PROGRAM SIZE =      1984
       *STATISTICS*  NO DIAGNOSTICS GENERATED
       *STATISTICS*  NO DIAGNOSTICS THIS STEP
```

```
   NAME  TYPE  ADDR       NAME  TYPE  ADDR       NAME  TYPE  ADDR       NAME  TYPE  ADDR       NAME  TYPE  ADDR
MAIN       SC  88010  FUNCTN      SD  89838  FCHISQ      SD  89A20  MTINV       SC  89D48  IHCSEXP *   SD  8A508
EXP     *  LR  8A508  IHCSSQRT*   SD  8A6A0  SQRT    *   LR  8A6A0  IHCLSQRT*   SD  8A7E8  DSQRT   *   LR  8A7E8
IHCECOMH*  SC  8A948  IBCOM#  *   LR  8A948  FDIOCS# *   LR  8AA04  INTSWTCH*   LR  8B88E  IHCCOMH2*   SD  8B8B0
SEQDASD *  LR  88C28  IHCERRM *   SD  8BF10  ERRMON  *   LR  8BF10  IHCERRE *   LR  8BF28  IHCUOPT *   SD  8C4E8
IHCEFNTH*  SD  8C7E8  ARITH#  *   LR  8C7E8  ADJSWTCH*   LR  8CB84  IHCEFIOS*   SD  8CD30  FIOCS#  *   LR  8CD30
FIOCSBEP*  LR  8CC36  IHCFIOS2*   SD  8DBF0  IHCFCVTH*   SD  8E120  ADCON#  *   LR  8E120  FCVAOUTP*   LR  8E1CA
FCVLOUTP*  LR  8E25A  FCVZOUTP*   LR  8E3AA  FCVIOUTP*   LR  8E758  FCVEOUTP*   LR  8EC5A  FCVCOUTP*   LR  8EE74
INT6SWCH*  LR  8F158  IHCUATBL*   SD  8F2C0  IHCETRCH*   SD  8F8F8  IHCTRCH *   LR  8F8F8  ERRTRA  *   LR  8F900
TOTAL LENGTH     7878 HEX     21608 DEC
ENTRY ADDRESS    88010
```

```
FORTRAN IV G LEVEL 20.7 VS             PEAKVA              DATE =    9/19/78      16:46:13           PAGE 0001
 0001                  FUNCTION PEAKVA(X,B,IDX)
 0002                  DIMENSION B(1)
 0003                  ID=(IDX/3) + 1
 0004                  GO TO(1,1,1,1,1,1),ID
 0005                1 PEAKVA=B(IDX+1)*EXP(-2.77259*((X-B(IDX)   )/B(IDX+2 ))**2)
 0006                  RETURN
 0007                  END
FORTRAN IV G LEVEL 20.7 VS             PEAKVA              DATE =    9/19/78      16:46:13           PAGE 0002

                                   SUBPROGRAMS CALLED
SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
EXP           98

                                   EQUIVALENCE DATA MAP
SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
PEAKVA        A0

                                   SCALAR MAP
SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
ID            A4         IDX           A8         X             AC

                                   ARRAY MAP
SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
B             B0

                                   STATEMENT NUMBER MAP
STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION
    1       162              3       162              4       176              5       1B4              6       1FA

  *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
  *OPTIONS IN EFFECT*  NAME = PEAKVA   , LINECNT =        58
  *STATISTICS*     SOURCE STATEMENTS =        7,PROGRAM SIZE =       514
  *STATISTICS*  NO DIAGNOSTICS GENERATED
FORTRAN IV G LEVEL 20.7 VS             GJR                 DATE =    9/19/78      16:46:13           PAGE 0001
 0001                  SUBROUTINE GJR(A,N,EPS,MSING)
             C GJR      OBJECT CECK DATE 9-18-73
             C         GAUSS-JORDAN-RUTISHAUSER MATRIX INVERSION WITH DOUBLE PIVOTING.          0030
 0002                  DIMENSION A(50,50),B(50),C(50),P(50),Q(50)                               0040
 0003                  INTEGER P,Q                                                              0050
 0004                  MSING=1                                                                  0060
 0005                  DO 39 K=1,N                                                              0070
             C         DETERMINATION OF THE PIVOT ELEMENT                                       0080
 0006                  PIVCT=0.                                                                 0090
 0007                  DO 13 I=K,N
 0008                  DO 13 J=K,N                                                              0110
 0009                  IF(ABS(A(I,J))-ABS(PIVOT))13,13,10                                       0120
 0010               10 PIVCT=A(I,J)                                                             0130
 0011                  P(K)=I                                                                   0140
 0012                  Q(K)=J                                                                   0150
 0013               13 CONTINUE                                                                 0160
 0014                  IF(ABS(PIVOT)-EPS)56,56,15                                               0170
             C         EXCHANGE OF THE PIVOTAL ROW WITH THE KTH ROW                             0180
 0015               15 IF(P(K)-K)16,21,16                                                       0190
 0016               16 DO 20 J=1,N                                                              0200
 0017                  L=P(K)                                                                   0210
 0018                  Z=A(L,J)                                                                 0220
 0019                  A(L,J)=A(K,J)                                                            0230
 0020               20 A(K,J)=Z                                                                 0240
             C         EXCHANGE OF THE PIVOTAL COLUMN WITH THE KTH COLUMN                       0250
 0021               21 IF(Q(K)-K)22,27,22                                                       0260
```

```
      0024                Z=A(I,L)                                                  0290
      0025                A(I,L)=A(I,K)                                             0300
      0026             26 A(I,K)=Z                                                  0310
      0027             27 CONTINUE                                                  0320
                C         JORDAN STEP                                               033
      0028                DO 36 J=1,N                                               0340
      0029                IF(J-K)33,30,33                                           0350
      0030             30 B(J)=1./PIVOT                                             0360
      0031                C(J)=1.                                                   0370
      0032                GO TO 35                                                  0380
      0033             33 B(J)=-A(K,J)/PIVOT                                        0390
      0034                C(J)=A(J,K)                                               0400
      0035             35 A(K,J)=0.                                                 0410
      0036             36 A(J,K)=0.                                                 0420
      0037                DO 39 I=1,N                                               0430
      0038                DO 39 J=1,N                                               0440
      0039             39 A(I,J)=A(I,J)+C(I)*B(J)                                   0450
                C         REORDERING THE MATRIX                                     0460
      0040                DO 54 M=1,N                                               0470
      0041                K=N-M+1                                                   0480
      0042                IF(P(K)-K)43,48,43                                        0490
      0043             43 DO 47 I=1,N                                               0500
      0044                L=P(K)                                                    0510
      0045                Z=A(I,L)                                                  0520
      0046                A(I,L)=A(I,K)                                             0530
      0047             47 A(I,K)=Z                                                  0540
      0048             48 IF(Q(K)-K)49,54,49                                        0550
      0049             49 DO 53 J=1,N                                               0560
    FORTRAN IV G LEVEL 20.7 VS          GJR            DATE =     9/19/78       16:46:13           PAGE 0002
      0050                L=Q(K)                                                    0570
      0051                Z=A(L,J)                                                  0580
      0052                A(L,J)=A(K,J)                                             0590
      0053             53 A(K,J)=Z                                                  0600
      0054             54 CONTINUE                                                  0610
      0055             55 RETURN                                                    0620
      0056             56 WRITE (6,57) P(K),Q(K),PIVOT
      0057             57 FORMAT(16HOSINGULAR MATRIX3H I=I3,3H J=I3,7H PIVOT=E16.8/)   0640
      0058                MSING=1
      0059                GO TO 55
      0060                END
    FORTRAN IV G LEVEL 20.7 VS          GJR            DATE =     9/19/78       16:46:13           PAGE 0003

                                  SUBPROGRAMS CALLED
    SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
    IBCOM#        13C

                                  SCALAR MAP
    SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
    MSING         14C          K             150          N             154          PIVOT         158          I             15C
    J             160          EPS           164          L             168          Z             16C          M             170

                                  ARRAY MAP
    SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
    A             174          B             178          C             240          P             308          Q             3D0

                                  FORMAT STATEMENT MAP
    SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
       57         498

                                  STATEMENT NUMBER MAP
    STATEMENT LOCATION         STATEMENT LOCATION         STATEMENT LOCATION         STATEMENT LOCATION         STATEMENT LOCATION
       1          584
```

```
      13       662          14       692          15       6A4          16       6B8          17       6C8
      18       6D4          19       6E4          20       6F8          21       71C          22       730
      23       740          24       74C          25       762          26       77C          27       7A0
      28       7A0          29       7B4          30       7C4          31       7D0          32       7D8
      33       7DE          34       7EC          35       7F4          36       7FC          37       824
      38       838          39       846          40       8DE          41       8E6          42       8F6
      43       90E          44       91E          45       92E          46       944          47       970
      48       99E          49       9B6          50       9C6          51       9D6          52       9E6
      53       A06          54       A2E          55       A42          56       A4A          58       A80
      59       A88

    *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
    *OPTIONS IN EFFECT*  NAME = CJR      , LINECNT =       58
    *STATISTICS*    SOURCE STATEMENTS =          60,PROGRAM SIZE =       2702
    *STATISTICS*  NO DIAGNOSTICS GENERATED
 FORTRAN IV G LEVEL 20.7 VS                  FCODE              DATE =    9/19/78       16:46:13            PAGE 0001
  0001                  SUBROUTINE FCODE(Y,X,B,F,I)
              C     THIS ROUTINE IS CALLED BY LSQENP.  IT FIGURES THE CONTRIBUTION OF THE
              C     BASELINE TO THE FUNCTION'S VALUE AND CALLS SUBROUTINE PEAKVA FOR THE PEAK'S
              C     CONTRIBUTION.
  0002                  DIMENSION Y(1),X(500,1),B(50)
  0003                  COMMON NPEAKS,M2
  0004                  F=B(M2+1)+B(M2+2)*X(I,1)
  0005                  DO 200 IDX=1,M2,3
  0006              200 F=PEAKVA(X(I,1),B,IDX)+F
  0007                  RETURN
  0008                  END
 FORTRAN IV G LEVEL 20.7 VS                  FCODE              DATE =    9/19/78       16:46:13            PAGE 0002

                                COMMON BLOCK /          / MAP SIZE       8
  SYMBOL    LOCATION         SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
  NPEAKS          0          M2               4

                                SUBPROGRAMS CALLED
  SYMBOL    LOCATION         SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
  PEAKVA         98

                                SCALAR MAP
  SYMBOL    LOCATION         SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
  F              A8          I               AC        IDX             B0

                                ARRAY MAP
  SYMBOL    LOCATION         SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION        SYMBOL    LOCATION
  Y              B4          X               B8        B               BC

                                STATEMENT NUMBER MAP
  STATEMENT LOCATION         STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION
       1        176               4        176              5        1A6              6        1B6              7        1FC

    *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
    *OPTIONS IN EFFECT*  NAME = FCODE    , LINECNT =       58
    *STATISTICS*    SOURCE STATEMENTS =           8,PROGRAM SIZE =        516
    *STATISTICS*  NO DIAGNOSTICS GENERATED
 FORTRAN IV G LEVEL 20.7 VS                  READI              DATE =    9/19/78       16:46:13            PAGE 0001
  0001                  SUBROUTINE READI (X,Y,N)
  0002                  DIMENSION X(500,1),Y(500)
  0003                  READ(5,99) N
  0004               99 FORMAT (I3)
  0005                  READ (5,101) (Y(I),I=1,N)
  0006              101 FORMAT (14F5.3)
  0007                  READ (5,100) XBG
  0008
```

```
    0010                  WRITE(6,2) DELTA
    0011          2       FORMAT(' THE SEPARATION BETWEEN TWO ADJACENT DATA POINTS IN NANOME
                         1TERS  IS', F10.5)
    0012                  WRITE (6,1) N
    0013                1 FORMAT (1H0,'NEW DATA SET USED',1X,I4,1X,'DATA POINTS')
    0014                  DO 103 I=1,N
    0015                  X(I,1)=XBG-((I-1)*DELTA)
    0016        103       X(I,1)=(1.0/X(I,1))*10000.0
    0017                  RETURN
    0018                  END
 FORTRAN IV G LEVEL 20.7 VS              READI              DATE =    9/19/78      16:46:13                PAGE 0002

                                 SUBPROGRAMS CALLED
   SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
   IBCOM#        98

                                 SCALAR MAP
   SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
   N             9C           I             A0           X33           A4         DELTA         A8

                                 ARRAY MAP
   SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
   X             AC           Y             B0

                                 FORMAT STATEMENT MAP
   SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION        SYMBOL     LOCATION
       99        B4             101         B8             100         BF               2         C4               1        100

                                 STATEMENT NUMBER MAP
   STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION        STATEMENT LOCATION
       1        1D8              3         1D8              5         1F4              7         23C              8         258
      10        274             12         290             14         2AC             15         2BC             16         2EA
      17        312

     *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
     *OPTIONS IN EFFECT*  NAME = READI     , LINECNT =        58
     *STATISTICS*    SOURCE STATEMENTS =         18,PROGRAM SIZE =        794
     *STATISTICS*  NO DIAGNOSTICS GENERATED
 FORTRAN IV G LEVEL 20.7 VS              PLOTPK             DATE =    9/19/78      16:46:13                PAGE 0001
    0001                  SUBROUTINE PLOTPK(TITLE,X,Y,N,E,M2)
                C    STORED ON DISK AS PLOTPK
                C    THIS ROUTINE HANDLES THE CALCOMP PLOTTING.
    0002                  DIMENSION TITLE(1),X(500,1),Y(1),B(1),DOC(3),PEAK(151),SUM(151)
    0003                  DIMENSION C(100)
    0004                  COMMON/PLOT/IFP,YMIN,YMAX
    0005                  COMMON/PLOT1/XMIN,XMAX
    0006                  DATA DOC/0.,0.,1./
                C    DRAW THE AXES.
    0007                  CALL VLABEL(0.,0.,XMIN,XMAX,15.,6,'  CM -1',7,0,'(F8.1)',8)
    0008                  CALL VLABEL(0.,0.,YMIN,YMAX,10.,4,'INTENSITY (ARBITRARY UNITS)',
                         1  27,1,'(F8.1)',8)
                C    WRITE THE TITLE AT THE TOP OF THE SHEET.
    0009                  CALL SYSSYM(0.,10.1,.20,TITLE,30,0.)
                C    REDUCE THE NUMBER OF DATA POINTS TO LESS THAN 120.
    0010                  DO 200 I=1,5
    0011                  NPLOT=N/I
    0012                  IF(NPLOT.GT.120)GOTO 200
    0013                  ISP=I
    0014                  GO TO 204
    0015              200 CONTINUE
                C    PLOT THE RAW DATA POINTS.
```

```
      0018              XINC1=XINC*10.
                 C    DRAW THE BASELINE.
      0019                DO 205 I=1,16
      0020              XVAL=XMIN+(I-1)*XINC1
      0021          205 PEAK(I)=B(M2+1)+B(M2+2)*XVAL
      0022                CALL CPLOT(PEAK,16,16,DOC,YMAX,YMIN,0)
                 C    DRAW EACH PEAK, THEN DRAW THEIR SUM.
      0023              DO 202 I=1,151
      0024              XVAL=XMIN+(I-1)*XINC
      0025          202 SUM(I)=B(M2+1)+B(M2+2)*XVAL
      0026              DO 203 IDX=1,M2,3
      0027              DO 201 I=1,151
      0028              XVAL=XMIN+(I-1)*XINC
      0029              PEAK(I)=PEAKVA(XVAL,B,IDX)
      0030          201 SUM(I)=PEAK(I)+SUM(I)
      0031          203 CALL CPLOT(PEAK,151,151,DOC,YMAX,YMIN,0)
      0032              CALL CPLOT(SUM,151,151,DOC,YMAX,YMIN,-1)
      0033              RETURN
      0034              END
    FORTRAN IV G LEVEL 20.7 VS            PLOTPK            DATE =    9/19/78      16:46:13            PAGE 0002

                                  COMMON BLOCK /PLOT    / MAP SIZE       C
     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION
     IFP              0     YMIN             4     YMAX             8

                                  COMMON BLOCK /PLOT1   / MAP SIZE       8
     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION
     XMIN             0     XMAX             4

                                  SUBPROGRAMS CALLED
     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION
     VLABEL          C0     SYSSYM          C4     PLOTXY          C8     CPLOT           CC     PEAKVA          D0

                                  SCALAR MAP
     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION
     I              1D4     NPLOT          1D8     N              1DC     ISP            1E0     XINC           1E4
     XINC1          1E8     XVAL           1EC     M2             1F0     IDX            1F4

                                  ARRAY MAP
     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION     SYMBOL    LOCATION
     TITLE          1F8     X              1FC     Y              200     B              204     DOC            208
     PEAK           214     SUM            470     C              6CC

                                  STATEMENT NUMBER MAP
     STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION
         1        996           6        996           7        996           8        9A4           9        9B2
        10        9C8          11        9D0          12        9E0          13        9EE          14        9F6
        15        9FC          16        A10          17        A2E          18        A42          19        A4E
        20        A5A          21        A8A          22        ABE          23        ACC          24        AD8
        25        B08          26        B3C          27        B44          28        B50          29        B80
        30        B9A          31        BBE          32        BE0          33        BEE

      *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
      *OPTIONS IN EFFECT*  NAME = PLOTPK   , LINECNT =       58
      *STATISTICS*    SOURCE STATEMENTS =        34,PROGRAM SIZE =      3062
      *STATISTICS*  NO DIAGNOSTICS GENERATED
    FORTRAN IV G LEVEL 20.7 VS            PCODE             DATE =    9/19/78      16:46:13            PAGE 0001
      0001              SUBROUTINE PCODE(P,X,B,F,I)
                 C    STORED ON DISK AS PCODEDUM
                 C    THIS IS A DUMMY ROUTINE REQUIRED BY LSQENP.  IF IT WERE ACTIVE, IT WOULD
                 C    CALCULATE THE PARTIAL DERIVATIVES.
      0002              DIMENSION
```

```
   0004              END
 FORTRAN IV G LEVEL 20.7 VS              PCODE              DATE =    9/19/78      16:46:13            PAGE 0002

                                     SCALAR MAP
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
 F               90       I               94

                                     ARRAY MAP
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
 P               98       X               9C       B               A0

                                     STATEMENT NUMBER MAP
 STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION
     1         152            3         152

    *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
    *OPTIONS IN EFFECT*  NAME = PCODE    , LINECNT =        58
    *STATISTICS*     SOURCE STATEMENTS =          4,PROGRAM SIZE =        346
    *STATISTICS*  NO DIAGNOSTICS GENERATED
 FORTRAN IV G LEVEL 20.7 VS              OUTPUT             DATE =    9/19/78      16:46:13            PAGE 0001
   0001                 SUBROUTINE OUTPUT(C,NPEAKS)
   0002                 DIMENSION C(1)
   0003                   WRITE(6,1)
   0004               1 FORMAT(5HOPEAK,T16,7HINITIAL,T32,5HFINAL,T48,7HINITIAL,T64,5HFINAL,
                       1      T80,7HINITIAL,T96,5HFINAL,T112,5HFINAL)
   0005                 WRITE(6,3)
   0006               3 FORMAT(1H ,T16,8HPOSITION,T32,8HPOSITION,T48,6HHEIGHT,T64,6HHEIGHT,
                       1T80,5HWIDTH,T96,5HWIDTH,T112,4HAREA)
   0007                 DO 10 I=1,NPEAKS
   0008                 IDX=6*(I-1)
   0009                 AREA=1.06447*C(IDX+4)*C(IDX+6)
   0010              10 WRITE(6,2) (I,(C(IDX+J),J=1,6),AREA)
   0011               2 FORMAT(1H ,I3,2X,7F16.3)
   0012                 WRITE(6,9)
   0013               9 FORMAT(1H0,19HBASELINE PARAMETERS)
   0014                 WRITE(6,4)
   0015               4 FORMAT(1H ,T16,7HINITIAL,T32,5HFINAL,T48,7HINITIAL,T64,5HFINAL)
   0016                 WRITE(6,5)
   0017               5 FORMAT(1H ,T16,6HOFFSET,T32,6HOFFSET,T48,5HSLOPE,T64,5HSLOPE)
   0018                 WRITE(6,6) C(6*NPEAKS+1),C(6*NPEAKS+2),C(6*NPEAKS+3),C(6*NPEAKS+4)
   0019               6 FORMAT(5X,4F16.3)
   0020                 WRITE(6,12)
   0021              12 FORMAT(26(5H*****))
   0022                   RETURN
   0023                   END
 FORTRAN IV G LEVEL 20.7 VS              OUTPUT             DATE =    9/19/78      16:46:13            PAGE 0002

                                     SUBPROGRAMS CALLED
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
 IBCOM#          98

                                     SCALAR MAP
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
 I               9C       NPEAKS          A0       IDX             A4       AREA            A8       J               AC

                                     ARRAY MAP
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
 C               80

                                     FORMAT STATEMENT MAP
 SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
                                                                              9          158          4          175
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                                   STATEMENT NUMBER MAP
    STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION     STATEMENT LOCATION
        1       284            3       284            5       298            7       2AC            8       284
        9       2C6           10       2E2           12       358           14       36C           16       380
       18       394           20       42C           22       440

  *OPTIONS IN EFFECT*  ID,EBCCIC,SOURCE,NOLIST,NOJECK,LOAD,MAP
  *CPTIONS IN EFFECT*  NAME = CUTPUT   , LINECNT =       58
  *STATISTICS*    SOURCE STATEMENTS =        23,PROGRAM SIZE =       1096
  *STATISTICS*  NO DIAGNOSTICS GENERATED
 FORTRAN IV G LEVEL 20.7 VS              MAIN              DATE =     9/19/78       16:46:13             PAGE 0001
                  C    MAIN PROGRAM FOR LINESHAPE ANALYSIS
                  C    STOREC ON CISK AS MAIN
 0001                    REAL*8 FITSLO,FITOFF,SLOPE,OFFSET
 0002                    DIMENSION TITLE(20),X(500,1),Y(500),B(50),BA(50),IB(50),IVARY(50)
 0003                    DIMENSICN C(100)
 0004                    COMMCN NPEAKS,M2
 0005                    COMMON/PLCT/IFP,YMIN,YMAX
 0006                    COMMON/PLCT1/XMIN,XMAX
 0007                    DATA BLANK,SLOPE,OFFSET/'    ','SLOPE','OFFSET'/
 0008                    WRITE (6,1)
 0009                  1 FORMAT(1H1,'LINESHAPE ANALYSIS PROGRAM, WRITTEN JUNE, 1977',
                       1 'BY ROY MEAD, MODIFIED BY DUANE SMITH')
 0010                209 REAC(5,100)(TITLE(I),I=1,20)
 0011                100 FORMAT(20A4)
 0012                    IF(TITLE(1).NE.BLANK)GOTO 200
 0013                    WRITE (6,2)
 0014                  2 FORMAT(1H-,'**** LAST RUN COMPLETED ****')
 0015                    STOP
 0016                200 WRITE(6,3)(TITLE(I),I=1,20)
 0017                  3 FORMAT(1H1,20A4)
 0018                    READ(5,101)NEWDAT,NEWPAR,IPRINT,IPUNCH,IFP,IPLOT,IDVT,IQUIT
 0019                101 FORMAT(7I1,I3)
 0020                    IPRNT=IPRINT-1
                  C    CHECK FOR NEW DATA.  JUMP TO PARAMETER READ ROUTINE IF OLD DATA IS USED.
 0021                    IF(NEWDAT.EQ.0) GO TO 201
 0022                    WRITE(6,4) N
 0023                  4 FORMAT(1H0,'PREVIOUS DATA SET USED,',I4,' DATA POINTS')
 0024                    GOTO 202
 0025                201 CALL READI (X,Y,N)
                  C    FIND THE EXTREME VALUES OF DATA AND DETERMINE SCALE FOR PLOTS.
 0026                    CALL MAXMIN(X,N,XMX,XMN)
 0027                    CALL MAXMIN(Y,N,YMX,YMN)
 0028                    CALL SCALE(XMX,XMN,XMAX,XMIN,6,K)
 0029                    CALL SCALE(YMX,YMN,YMAX,YMIN,4,K)
                  C    CHECK FOR NEW PARAMETERS.  JUMP TO PARAMETER COPY ROUTINE IF OLD VALUES USE4
 0030                202 IF(NEWPAR.NE.0)GOTO 208
 0031                    IP=0
 0032                204 REAC(5,103)NPEAKS
 0033                103 FORMAT(I3)
                  C    EACH PEAK HAS THREE PARAMETERS.
 0034                    M2=3*NPEAKS
 0035                    M=M2+2
 0036                    DO.205 I=1,NPEAKS
 0037                    IDX=3*(I-1)
 0038                    REAC(5,104)(B(IDX+J),J=1,3)
 0039                104 FORMAT(3F10.3)
 0040                    REAC(5,105)(IVARY(IDX+J),J=1,3)
 0041                105 FORMAT(3I1)
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   0043               IF(IVARY(IDX+J).EQ.1)GOTO 206
   0044               IP=IP+1
   0045               IB(IP)=IDX+J
   0046           206 CONTINUE
   0047           205 CONTINUE
  FORTRAN IV G LEVEL 20.7 VS          MAIN              DATE =    9/19/78      16:46:13                 PAGE 0002
                C       THE OFFSET IS THE Y DISPLACEMENT FOR THE FIRST DATA POINT IN THE
                C        DATA SET.
                C    PUNCHING 'OFFSET      ' IN THE OFFSET CARD FIXES THIS PARAMETER.
   0048               READ(5,102)FITOFF,B(M-1)
   0049           102 FORMAT(A8,2X,F10.3)
   0050               IF(FITOFF.NE.OFFSET)GOTO 203
   0051               IP=IP+1
   0052               IB(IP)=M-1
                C       THE SLOPE IS DETERMINED BY THE SLOPE FROM THE FIRST DATA POINT
                C        IN THE DATA SET, ENDING ON THE  LAST. THUS IF THE  THE BASELINE
                C        OFFSET DECREASES AS THE DATA SET IS READ, THE SLOPE IS NEGATIVE
                C    PUNCHING 'SLOPE       ' IN THE SLOPE CARD FIXES THIS PARAMETER.
   0053           203 READ(5,102)FITSLO,B(M)
   0054               IF(FITSLO.NE.SLOPE)GOTO 210
   0055               IP=IP+1
   0056               IB(IP)=M
                C    SAVE THE PARAMETERS, SINCE LSQENP CHANGES THEM.
   0057           210 DO 213 I=1,M
   0058           213 BA(I)=B(I)
   0059               GOTC 207
                C    GET THE CLD PARAMETERS, SINCE THEY WERE CHANGED BY LSQENP.
   0060           208 DO 214 I=1,M
   0061           214 B(I)=BA(I)
   0062           207 CALL LSQENP(N,M,1,Y,X,B,IP,IB,IDVT,0,IQUIT,IPRNT)
                C       CREATE THE ARRAY C WHICH CONTAINS THE INITIAL VALUE OF PARAMETER ONE
                C       IN C(1), FINAL VALUE OF PARAMETER ONE IN C(2), INITIAL VALUE OF PARAMETE9
                C       TWO IN C(3), FINAL VALLE OF PARAMETER TWO IN C(4), ETC., ETC.
                C       THE INITIAL VALUE OF A PARAMETER IS SUPPLIED BY THE USER. THE FINAL
                C       VALUE IS SUPPLIED BY LSQENP IF THE PARAMETER IS FLOATING OR THE FINAL
                C       VALUE IS THE USER'S INITIAL GUESS IF THE PARAMETER IS NOT FLOATING.
                C       THE ARRAY C IS CREATED SOLELY FOR MAKING DATA OUTPUT EASIER--SEE
                C       SUBROUTINE OUTPUT FOR DETAILS.  BA(I) CONTAINS THE INITIAL PARAMETERS
                C       AND B(I) CONTAINS THE FINAL PARAMETER VALUE.
   0063               DO 112 I=1,M
   0064               C(2*I-1)=BA(I)
   0065               C(2*I)=B(I)
   0066           112 CONTINUE
   0067               WRITE(6,11)
   0068            11 FORMAT(26(5H*****))
   0069               WRITE (6,3)(TITLE(I),I=1,20)
   0070               CALL OUTPUT(C,NPEAKS)
   0071               IF (IPUNCH.EQ.0)GOTO 211
   0072               WRITE (7,100)(TITLE(I),I=1,20)
   0073               WRITE(7,99)((B(I+3*(J-1)),I=1,3),TITLE(19),TITLE(20),J=1,NPEAKS)
   0074            99 FORMAT(3F10.3,42X,2A4)
   0075               WRITE(7,98)B(M-1),TITLE(19),TITLE(20),B(M),TITLE(19),TITLE(20)
   0076            98 FORMAT('OFFSET      ',F10.3,52X,2A4/'SLOPE       ',F10.3,52X,2A4)
   0077               WRITE(6,106)
   0078           106 FORMAT(1H-,'OUTPUT PARAMETERS PUNCHED')
   0079           211 IF(IPLOT.EQ.1)CALL PLOTPK(TITLE,X,Y,N,B,M2)
   0080               GOTO 209
   0081               END
  FORTRAN IV G LEVEL 20.7 VS          MAIN              DATE =    9/19/78      16:46:13                 PAGE 0003
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                              COMMON BLOCK /PLOT     / MAP SIZE        C
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
   IFP              0       YMIN             4       YMAX             8

                              COMMON BLOCK /PLOT1    / MAP SIZE        8
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
   XMIN             0       XMAX             4

                              SUBPROGRAMS CALLED
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
   IBCOM#         144       READI          148       MAXMIN         14C       SCALE          150       LSQENP         154
   CUTPUT         158       PLCTPK         15C

                              SCALAR MAP
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
   SLOPE          210       OFFSET         218       FITUPP         220       FITSLO         228       BLANK          230
   I              234       NEWDAT         238       NEWPAR         23C       IPRINT         240       IPUNCH         244
   IPLOT          248       IDVT           24C       IQUIT          250       IPRNT          254       N              258
   XMX            25C       XMN            260       YMX            264       YMN            268       K              26C
   IP             270       M              274       IDX            278       J              27C

                              ARRAY MAP
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
   TITLE          280       X              200       Y              AA0       B             1270       BA            1338
   IB            1400       IVARY         14C8       C             1590

                              FORMAT STATEMENT MAP
   SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION       SYMBOL    LOCATION
        1        1720          100        177B            2       1781            3       17A4          101       17AD
        4        1785          103        17E3          104       17E7          105       17EE          102       17F4
       11        17FD           99        1809           98       1816          106       1843

                              STATEMENT NUMBER MAP
   STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION       STATEMENT LOCATION
        7        18E4            8        18E4           10       18F8           12       193C           13       194A
       15        1960           16        196E           18       1984           20       1A0C           21       1A1C
       22        1A2A           24        1A48           25       1A4E           26       1A5C           27       1A6A
       28        1A78           29        1A86           30       1A94           31       1AA6           32       1AAE
       34        1AD0           35        1ADC           36       1AE8           37       1AF0           38       1B06
       40        1B58           42        1BA8           43       1BB8           44       1BD2           45       1BDE
       46        1BF2           47        1C0E           48       1C26           50       1C5C           51       1C6A
       52        1C76           53        1C8A           54       1CC0           55       1CCE           56       1CDA
       57        1CEA           58        1CFA           59       1D1E           60       1D24           61       1D34
       62        1D58           63        1D66           64       1D7A           65       1D82           66       1D8A
  FORTRAN IV G LEVEL 20.7 VS                MAIN                 DATE =      9/19/78       16:46:13              PAGE 0004
       67        1DAA           69        1DC0           70       1E04           71       1E12           72       1E24
       73        1E64           75        1EF4           77       1F48           79       1F5C           80       1F7C

    *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
    *OPTIONS IN EFFECT*  NAME = MAIN      , LINECNT =       58
    *STATISTICS*     SOURCE STATEMENTS =         81,PROGRAM SIZE =        8066
    *STATISTICS*  NO DIAGNOSTICS GENERATED
    *STATISTICS*  NO DIAGNOSTICS THIS STEP
                                                  OS/CIT LOADER
 OPTIONS USED - PRINT,MAP,NOLET,CALL,RES,NOTERM,SIZE=106496,NAME=**GO
      NAME   TYPE  ADDR         NAME  TYPE  ADDR          NAME  TYPE  ADDR          NAME  TYPE  ADDR          NAME  TYPE  ADDR
   PFAKVA      SD  88010     GJR        SD  88218      FCJDE      SD  88CA8      READI      SD  88EB0      PLOTPK     SD  89100
   PCODE       SD  89CC8     OUTPUT     SD  89F28      MAIN       SD  8A370      LSQENP  *  SD  8C2F8      PLOT    *  SD  8E5B8
   PARAM   *   SD  8E5C8     WEITS   *  SD  8E5E8      SCALE   *  SD  8EDB8      $PRIVATE   PC  8F3A0      MAXMIN  *  LR  8F3A0
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SEQDASD *  LR  93778   IHCSEXP *  SD  93A60   EXP      *  LR  93A60   IHCERRM *  SD  93BF8   ERRMON   *  LR  93BF8
IHCERRE *  LR  93C10   IHCUCPT *  SD  941D0   IHCEFNTH*  SD  944D0   ARITH#  *  LR  944D0   ADJSWTCH*  LR  9486C
IHCEFIOS*  SD  94A18   FIOCS#  *  LR  94A18   FIOCSBEP*  LR  94A1E   IHCFIOS2*  SD  958D8   IHCFCVTH*  SD  95E08
ADCON#  *  LR  95E08   FCVAOUTP*  LR  95EB2   FCVLOUTP*  LR  95F42   FCVZOUTP*  LR  96092   FCVIOUTP*  LR  96440
FCVEOUTP*  LR  96942   FCVCOUTP*  LR  96B3C   INT6SWCH*  LR  96E43   OUTCOR  *  SD  96FA8   CMP      *  SD  971F8
AFTER   *  LR  971F8   ALPHA   *  LR  97230   BEFORE   *  LR  972EC   CAT     *  LR  97322   DELEL    *  LR  97364
DELETE  *  LR  973A6   DELETS  *  LR  973D8   EC       *  LR  97410   ECS     *  LR  9743E   FROM     *  LR  9749A
INDEX   *  LR  974CE   INSERT  *  LR  974FA   KOUNT    *  LR  9758C   LENGTH  *  LR  975C2   NUMER    *  LR  975E6
PUTAFT  *  LR  97650   PUTBEF  *  LR  97686   REPLAC   *  LR  976BA   REPS    *  LR  97700   REVERS   *  LR  97742
SETDEL  *  LR  977E0   SPRAY   *  LR  97818   STRMAX   *  LR  9786C   SUBSTR  *  LR  978A6   UPTO     *  LR  978D2
CMPERR  *  SD  97E60   IHCSLOG *  SD  97E68   ALOG10   *  LR  97E68   ALOG    *  LR  97E80   IHCFRXPI*  SD  98020
FRXPI#  *  LR  98020   IHCSSCN *  SD  98168   COS      *  LR  98168   SIN     *  LR  98180   $PRIVATE    PC  98348
NARGS   *  LR  98348   SYSPIO  *  SD  983A0   SYSWHR   *  LR  983A8   SYSPSZ  *  LR  983D6   SYSPAT   *  LR  9842C
SYSXMX  *  LR  98468   SYSOFF  *  LR  98476   SYSPLT   *  LR  98480   SYSCLS  *  LR  9867C   SYSEND   *  SD  989C0
IHCFEXIT*  SD  98CB8   EXIT    *  LR  98CB8   CONLIM   *  SD  98CD8   IHCSSQRT*  SD  99E70   SQRT     *  LR  99E70
IHCLSQRT*  SD  99F88   DSQRT   *  LR  99F88   IHCUATBL*  SD  9A118   IHCETRCH*  SD  9A750   IHCTRCH  *  LR  9A750
ERRTRA  *  LR  9A758   APCLSQ     CM  9A9E0   PLOT1       CM  9D388   $BLANKCOM   CM  9D390
TOTAL LENGTH    15388 HEX     86920 DEC
ENTRY ADDRESS   8A370
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