"Senior Thesis"

PHOTOSENSITIZED ISOMERIZATION OF PIPERYLENES

(Research Report for Summer 1962- revised)

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I. Photostationary States of Piperylene. A) Abstract.

In the presence of many compounds capable of forming triplets of energy equal to and somewhat above its own first triplet, piperylene can be made to isomerize under UV light. Plotting the ratio of cis to trans isomers at the photostationary state against the triplet energy of the sensitizer gives a definite curve which may be interpreted theoretically.

B) Theory.

The cis-trans isomerization of olefins under the influence of excited sensitizers has been used to study the mechanisms for energy transfer and the configurations of the excited olefins. In this system the sensitizer used is usually a conjugated or aromatic carbonyl compound, for these have a high probability of intersystem crossing after absorption of of the appropriate light quantum, and hence readily give the long-lived triplets. Such a two component system allows a much more efficient production of olefin triplets than by direct absorption.

The data presented here are a part of the experimental evidence that now permits the formulation of a theory for the sensitized excitation and isomerization of cis-trans isomers. In the general model, the excited states of the cis and trans isomers are expected to be different. If the energy (E_t)

of the excited sensitizer (S^*) is considerably larger than the energies of either of the excited substrates (s^*), that is, if the reaction

$$S^* + s \longrightarrow S + s^* \qquad (1)$$

is substantially exothermic, then the transfer is expected to be non-selective toward either isomer. Whether the excited substrate triplet for the cis and trans is the same or different, the definite probabilities of decay to either cis or trans ground state thus give rise to a "natural decay ratio" when high energy sensitizers are used. As E_t of the sensitizer approaches that of the more energetic substrate triplet, certain selective phenomena, better defined in the 1,2 diphenyl propene system than in the piperylene system, are observed. In the diphenyl propene system, to which the following interpretation is directed, these include (a) an inflection point, followed by two maxima and a minimum in the plot of the ratio of cis to trans isomers at photostationary state, and (b) a surprising sensitization by compounds whose E_t is lower than the observed spectroscopic transitions of either of the substrate isomers. To explain this pattern, whose outline at least appears in all the systems investigated, it has been postulated that excitation may occur by non-Franck-Condon processes. In particular, it appears that there are three excited forms of the substrate, the "cis triplet," and "trans triplet", and a "phantom triplet" whose configuration is unlike either of the others. A direct promotion of either isomer from its ground state to the phantom, which has a lower energy than either of the other excited forms, would explain the fairly efficient endothermic transfer observed in the stilbenes and the diphenyl propenes.

The inflection point and the two maxima probably reflect first the disappearance of the reaction

$$S^* + c \longrightarrow S + c^* \quad , \qquad (c = \underline{cis} \text{ isomer}) \quad (2)$$

and then the maxima in the rates of energy transfer to the lower energy trans substrate while the reaction

$$S^* + c \longrightarrow S + p \qquad (p = \text{phantom triplet}) \quad (3)$$

is fairly constantly exothermic. That is, once the E_t of the sensitizer is insuffficient to effect reaction (2), isomerization will occur by formation of p from either isomer or by formation of t*, the excited trans triplet. This would reasonably be expected to lead to a higher plateau region ~~just~~ on the graph just below the spectroscopic transition of the cis isomer. And indeed this explanation is corroborated in the diphenyl propene system, where the transition is observed near the inflection point. That the subsequent maxima are due to selective factors in transfer to the trans isomer is also corroborated, for the energy difference between the two maxima fits approximately in the vibronic progression of a weak carbon-carbon bond.

The evidence for this theory is less complete in the piperylene system.

C) Experimental.

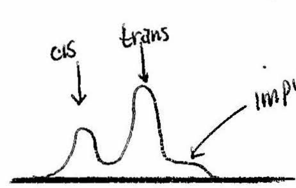
All solutions were in benzene and contained 0.2 M cis or trans piperylene and enough sensitizer to absorb all of the incident light at their absorption maxima. The solutions were degassed three times to less than 2×10^{-3} mm Hg, sealed in pyrex tubes, and photolyzed at 29-32 degrees C. with the 450 w. UV lamp in the "merry-go-round."

Both cis and trans piperylene were purified on the Beckman "Megachrome" by N. Turro. Benzene was reagent grade washed three times with sulfuric acid and distilled. Sensitizers were employed as available.

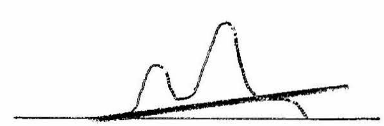
Analysis of the photolyzed solution proceeded on the Loenco VPC. A single 9' 60-40 silver nitrate-ββ'-oxydipropionitrile column at room temperature carried the burden of the separations except samples 1 to 20. These were run on varying columns before 23 July. Change in concentration of the sensitizer through decomposition and reaction was followed by "UV analysis" on the Beckman DU spectrophotometer. A rough tab could be kept on the piperylene by dividing total area under both peaks by microliters injected. However, the variables involved in these numbers permitted only a crude estimation of the change in piperylene concentration.

D) Errors and Uncertainties.

Under ideal invariant conditions calculations of percentage trans isomer is CONSISTENT to ± 0.5%. However, unsteady base lines, impurities just before the trans peak, and especially different columns increase this figure. The latter can make a difference of several percent. (see naphthyl phenyl ketone) The ACCURACY of the percentage value is uncertain and remains to be calibrated with known piperylene mixtures. Another source of error stems from the method of calculating areas. Impurities before the trans peak leave a choice in the way the base line is to be drawn. Method (a) was adopted consistently,



(a)


(b)

that is, the area was taken as the product of peak height times half-width.

It is to be noted especially that the scatter of high energy points on Graph I is in large measure due to the use of different VPC columns. New sensitizing products may also be involved.

E.) Results.

In the piperylene system, insufficient data were collected to document accurately the same phenomena as in the diphenyl propenes and the stilbenes. There are just not enough sensitizers available to define the curve exactly. However, there do seem to be 2 maxima and perhaps an inflection point (see Graph I). Thus the piperylene data do support the theory.

Table I and Graph I summarize all pertinent information on those sensitizers which gave good photostationary values and whose triplet energies are known. Only ethyl pyruvate and duroquinone have uncertain % trans coordinates. In the former the consumption of the substrate is very high. In the latter there is also consumption, presumably a Diels-Alder adduct is formed. Since such a product would probably be a sensitizer too, it is unclear whether the E_t coordinate of the duroquinone point reflects only duroquinone sensitization. Very short exposure experiments might clarify whether isomerization proceeds faster than addition.

Note that there is an indication of a shoulder on the curve near 59 kcal, and another dip near 61 kcal. These may or may not be artifacts. All endeavors to enrich the lower energy portion of the graph with a few more points failed. Benzanthrone, 3-acetopyrene, and 9-anthraldehyde, with known triplets in the 50 kcal range, failed to give photostationary states, although all were inefficient sensitizers. The figures available (see Table II) suggest that the photostationary states might be approximately: acetopyrene-55%, benzanthrone-65%, anthraldehyde-80%. In a separate experiment to determine the range of the photostationary values for anthraldehyde and dibenzal acetone, known mixtures of cis and trans piperylene were prepared; Photolysis for 2½ hours produced alteration in the cis-trans ratio just over the experimental error (see Table III). These figures must be regarded as inconclusive.

Another series of low energy ketones (Table II) contains compounds with direct conjugation of the carbonyl group with a double bond. These compounds are thought to have quite low triplet energies, hence the very poor sensitization properties. This explanation is in agreement with the fact that mesityl oxide quenches the triplets of Michler's ketone without sensitizing significantly the piperylene isomerization. But note that the conjugated ketone, benzal acetophenone gives a nice photostationary value of 55.4%. An explanation for the "inertness" of mesityl oxide and phorone might be rapid internal reaction of the triplet to give the enol form of either of these compounds. To test this idea it has been proposed to watch for such a process with deutero-ethanol.

The simple cyclic ketones, whose triplet energies are not certain but undoubtedly high, give values reasonably consistent with the straight part of the curve. They seem disconcertingly high, however.

Work on some interesting non-carbonyl compounds was begun near the end of the ten weeks' tenure. (Table II) The bromo- and iodo-naphthylenes, having absorption peaks near the cut off point of pyrex, were run in quartz tubes. All of these compounds showed decomposition; all of them sensitized the piperylene isomerication. Of the substituted naphthylenes, the 1-nitro-derivative gave a good photostationary value in 13 hours with no significant consumption of olefin. Since this and a number of other nitro- and amino-naphthylenes have E_t values in the critical and interesting range of 50 to 58 kcal, it will be worth while to investigate this series. The halo-naphthylenes decomposed significantly and caused disappearance of piperylene. With more carefully timed exposure, good photostationary states should be in reach, however.

Of the number of low energy sensitizers that seem to be capable of transferring energy to the olefin, not a single one is beyond some doubt. All show significant consumption of the olefin or formation of some new absorbing product. If any of these photostationary values could be trusted, there would be a fine documentation of transfer to the hypothetical "phantom" of lower energy than either cis or trans triplets. Duroquinone, benzal acetophenone, and especially dibromoanthracene are likely contenders which should be investigated further with short-exposure measurements.

In conclusion, the data presented here on the piperylene system, as far as they go, do corroborate the theory.

II. The Effect of Solvent of Photostationary States of Piperylene.

A) Introduction.

Non-quenching solvent is expected to have no influence on photostationary mixtures according to the scheme proposed. To test this expectation, a representative sensitizer was photolyzed with piperylene in polar, aromatic, viscous, and hydrocarbon solvents.

B) Experimental Results.

The stable sensitizer, 2-acetonaphthone was chosen as the representative sensitizer. Solutions 0.25 M or saturated (isopentane, ethylene glycol, mineral oil) were prepared and 5 ml of each was diluted with 5 ml 1.0 M piperylene in benzene to 25 ml. The samples were degassed three times, sealed, and then exposed for ½, 1, and 24 hours in the "merry-go-round." All the samples were analyzed on a 10' pure "ββ"column, except where noted otherwise (Table IV). Analysis proved extremely difficult because of evaporation of the low boiling solvents and the slow injection time of the viscous ones. On the column used, which separates olefins poorly, the cis and trans peaks were sharp and run together. In the cases where half-widths could not be calculated, peak heights were used. It is clear from the data that these are consistently several percent too high. The accuracy and consistency of the figures leaves much to be desired, due to the difficulty in obtaining good tracings. Yet some trends are very clear. Excepting ethylene glycol and mineral oil, the photostationary states appear to be unaffected by solvent. The rate, too, as shown roughly by the ½ and 1 hour figures, does not vary significantly, again excepting the two viscous solvents. Isopentane is anomalous in its rate probably because the original solution of sensitizer was saturated at a concentration considerably below 0.25 M. The two viscous solvents offer several riddles that should be investigated. First is the photostationary value for both, which is manifestly too low. Then, in ethylene glycol, both piperylene and sensitizer are consumed. Mineral oil not being soluble in methanol, a UV analysis was not attempted. The area under the piperylene peaks is roughly half that of the other solvents, though. One partial explanation of the low photostationary values and apparent piperylene consumption hinges on the viscous nature of these solvents. Since upon injection into the VPC these solvents are not vaporized, the volatile piperylene will be removed from them relatively slowly. Such a partially delayed release of olefin at the head of the column would tend to smear the peaks over a longer time and chart length. And indeed this effect is observed as an extended "tail" sweeping behind the <u>cis</u> peak. That such a phenomenon would effect an apparent increase in <u>cis</u> is palpable. It is clear from the data from the other column (see Table) that at least a large percentage of the observed anomaly is an artifact of the column.

C) Conclusions.

Although the data are mediocre at best, they do imply a lack of solvent dependency in the piperylene system as expected.

III. Decomposition of Pinacalone under Ultraviolet Light.

A) Abstract.

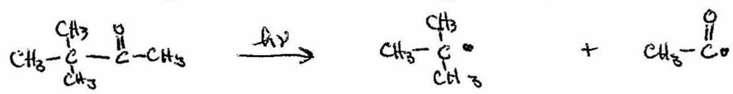
Under the same conditions as in other photostationary studies, a solution of pinacalone and piperylene in benzene is found to undergo drastic changes after several hours exposure. The piperylene is observed to disappear completely, and at least two new peaks corresponding to low boiling compounds appear on the VPC trace. Infra-red spectra in general show close similarities to, but also some differences from, isobutane and isobutene. Carbon monoxide is detectable in evolved gases and acetaldehyde is almost certainly also present. Distillation of reaction mixture shows considerable quantities of high boiling oils. A free radical reaction is definitely implicated.

B.) Experimental results.

The photolysis of simple ketones in vapor phase has been well documented since 1935. That decompositions involving free radicals as intermediates occur in solution is also known.[1,2,3] The surprising aspect of the case of pinacalone is the apparently high quantum yield. It is imperative that a careful study of quantum yields be made. The simplest of all possible estimates, of course, is to measure the disappearance of pinacalone itself. This was not tried for lack of time. On the VPC ($\beta\beta$-$AgNO_3$) the pinacalone peak comes out after about 45 minutes at room temperature. A slightly elevated temperature would sharpen the peak to make it quantitatively measurable. Although UV analysis of the original pinacalone-piperylene mixture proved impossible because of new highly-absorbing products, the same procedure applied to photolyzed pinacalone in benzene should yield some information. The knowledge gained so far stems from analyses of ampules of pinacalone-piperylene and pinacalone solutions, and from the analysis of a half liter pinacalone-piperylene pot photolyzed in a 250 w. quartz immersion reactor (no filter). The state of knowledge is summarized most conveniently by simply listing probable events and evidence.

(1) Pinacalone itself decomposes in benzene solution by free radical intermediates giving at least two major gaseous products. Evidence: Piperylene disappears at an accelerated rate (7 hours and 12 hours: no significant consumption; 22 hours: 100% consumption. Data from immersion reactor,) High boiling oils are formed. The piperylene in solution does not affect the appearance of the two new peaks.

(2) Pinacalone splits according to the following reaction:



The fairly long-lived t-butyl radicals undergo disproportionation as the major reaction, giving isobutane and isobutene. The acyl radicals can abstract a hydrogen from some methyl or methylene group to give acetaldehyde or can initiate polymerization. Since they are much shorter-lived than the t-butyl radicals, carbon monoxide may split out, leaving the methyl radical to increase the number of possible species.

Evidence: The IR spectra of the two peaks are similar to the vapor phase spectra of isobutane and isobutene given in the literature. Clearly there is one olefin and one saturated hydrocarbon. The first fraction of the distillation of products from the"pot" smells exactly like acetaldehyde. Both saturated and unsaturated carbonyl absorption peaks appear in the IR spectra of the oils from the distillation. Carbon monoxide is observed in the spectrum of evolved gas collected over silicone oil, as is an aldehyde, presumably acetaldehyde.

C.) Conclusion.

Collecting the evolved reaction products on a larger scale on the "Megachrome" would give enough material for nmr spectra, which should corroborate the IR spectra. Isobutane and isobutene knowns would help greatly in the positive identification of the reaction products. (Unfortunately these were not available) A sure-fire say to determine quantum yields for the photolysis would throw the problem into high relief.

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I would like to express my appreciation to those who have offered me needed help and who have studiously glossed over the many stupidities of one form or another that an ignorant person,loathe to show his ignorance, has committed. I am especially indebted to N. Turro for his guidance.

TABLE I

Information on the sensitizers plottedon Graph.

Note the following abbreviations:
sens. = sensitizer; # = number of sample; hrs. photo. = hours photolyzed; area = total area under both <u>cis</u> and <u>trans</u> peaks; % t = percent <u>trans</u>; BAV % t = Best average value of percent <u>trans</u>; E_t = triplet energy of sensitizer; cons. of sens. = consumption of sensitizer; abs. prod = absorbing products

sitizer	# [a]	hrs. photo.	filter	area	% t	BAV % t	E_t [b]	cons. of sens.	Comments
to-enone	9A	24	(c)	148	54.6	54.0	73.9	4%	
	9B	"	"	148	53.4				
zo-enone	1A	"	"	108	57.0	56.7	68.7	5%	
	1B	"	"	91	56.4				
aldehyde	6A	"	"	109	53.2	54.1	72.0	20%	
	6B	"	"	63					sens. reacts with <u>cis</u>.
yl ruvate	16A	36	"	24	58.4	54.2	64.8	decomposes rapidly; piperylene cons.	
	16B	"	"	52	50.1 ±3			x <u>cis</u> value approximate	
ra-uinone	33A	24	"	~~[illegible]~~	57.0	57.2	62.4	ca. 40%	
	33B	"	"		57.4				
ler's tone	5A	"	"	124	58.4	56.1	61.0	26%	resin formed on inside of ampule
	5B	"	"	127	56.2				
	10A	36	"	124	56.1				slightly more yellowish
	10B	"	"	136	56.1				
phth-lehyde	38A	24	3200		72.2	71.6	ca. (d) 59.5	33%	
	38B	"	"		71.0				
eto-hthone	2A	"	(c)	113	71.9	72.0	59.3	0.5%	
	2B	"	"	94	72.1				
	2A	48			71.7				
phthil	30A	24	3600	~~[illegible]~~	75.8	75.8	58.2	significant cons., new abs. prod.	
	30B	"	"		60.2			(8)	impure <u>cis</u>, reject
	35A	"	"	100	71.8				
	35B	"	"	118	72.2				
	35A	"	blue sol.	127	75.2			Improved stability with blue filter	
	35B	"	ca.4200?	154	76.4				
phth-lehyde	3A	"	(c)	102	78.8	78.8	57.0 (d)		
	3B	"	"	103	78.8				
eto-hthone	39A	2	3200	160	80.4	79.7	~~[illegible]~~ (A) 56.9	4%	

(continued)

TABLE I - continued

itizer	#	hrs. photo.	filter	area	% t	BAV % t	E_t	cons. of sens.	comments
etonaphthone									
	39A	[illegible]	3200	160	80.4	79.7	[illegible] (h) 56.9	[illegible]	
	39B	2	"	168	78.7				
	39A	24	"		78.0				
	39B	"	"		78.2				
	39A	"	"	231	80.3			4%	
	39B	"	"	124	79.2				
etyl	7A	"	(c)	103	7718	7716	54.9	little	
	7B	"	"	115	77.4				
pentane one	29A	2	3600		78.0	76.3	54.7	(f)	
	29B	"	"		44.0				impurity in *cis*:reject
	36A	24	"	58	80				
	36B	"	"	37	80				
	36A	"	blue sol.	120	76.7				
	36B	"	"		76.0				
lourenone&	4A	"	(c)	138	69.0	67.6	53.0	5%	
	4B	"	"	75	66.2				orig. *cis* less concent.
	4B	48			67.3				
il	8A	24	"	124	57.8	56.7	53.7	ca. 50%	yellow sample turns colorless
	8B	"	"	81	55.6				

(a) A denotes starting with *trans* piperylene, B starting with *cis*.
(b) determined here by Herkstroeter, et.al. unless otherwise noted.
(c) uncertain: N. Turro ran the merry-go-round and I took down no values.
(d) Lewis and Kasha value: in e.p.a.
(f) see notebook
(g) photolyzed in quartz tubes.
(h) these E_t values from "Mechanisms of photochemical reactions in solution", XXI. (1964)

TABLE II

Information on compounds which did not sensitize, did not give photostationary states, or whose E_t were kot known.

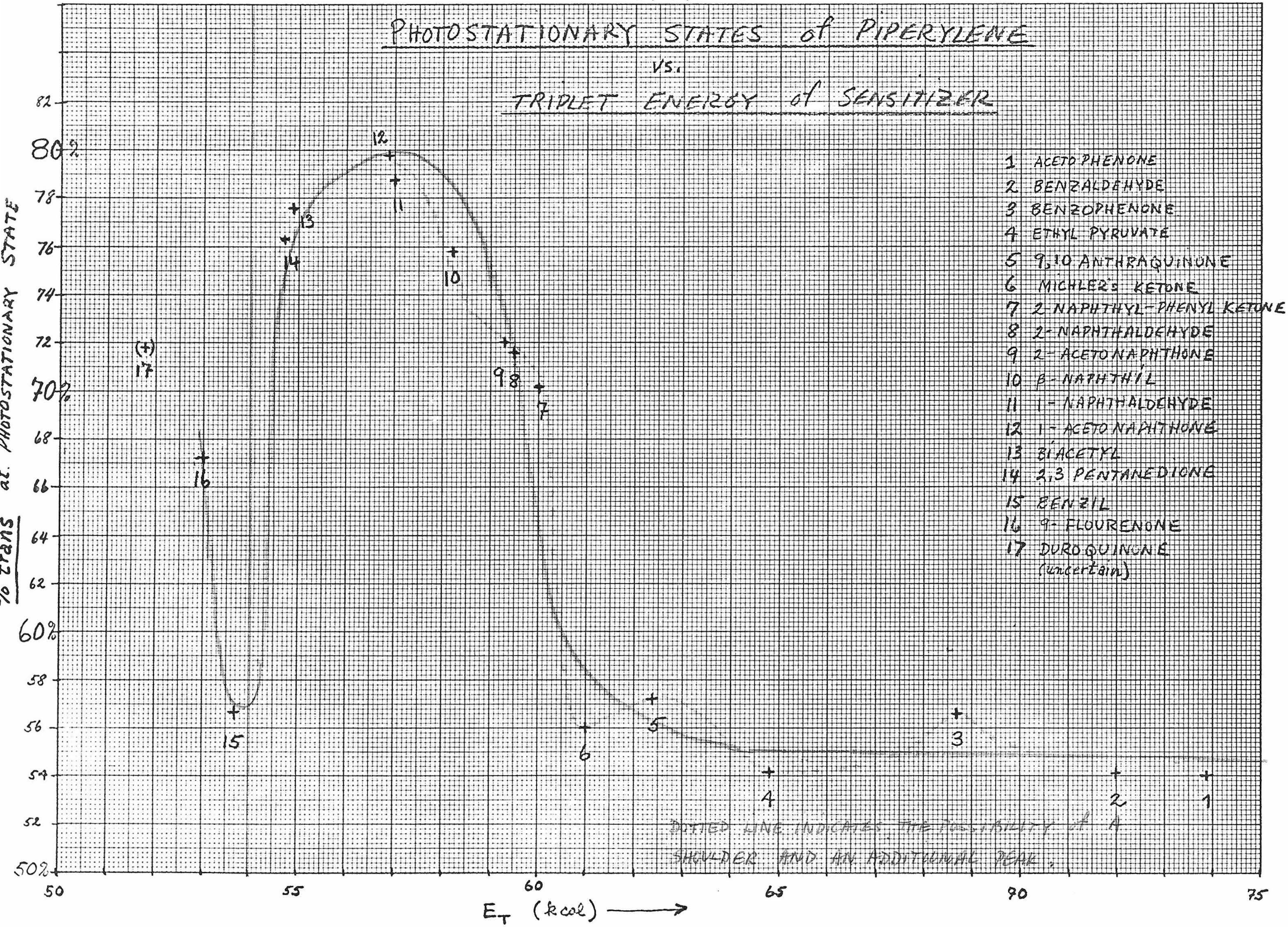
The same abbreviations and format as Table I is used.

sitizer	#	hrs. photo.	filter	area	% t	BAV % t	E_t	cons. of sens.	comments
hthylphenyl	11A	36	(c)	129	76.2		~~57.7~~	little	9 July 62
ketone	11B	"	"	141	73.7	revised	60.0		"
	48A	19½	3200 ?	~~[illegible]~~	71.8	70.1			22 Aug. 62. diff. column
	48B	"	"		70.3				in any case
nthral-	12A	36	(c)	153	74.8			nearly complete cons.; turns	
ehyde	12B	"	"	146	57.5			colorless	
	31A	48	3200	104	79.3				
	31B	"	"	117	<56.2				
	41A	20	blue sol.		ca.95				(f)
	41B	"	"	155	40				note these values
zal	13A	36	(c)	134	55.8	55.4	~~xx~~	~95%	
tophenone	13B	"	"	126	55.1				
rone	14A	"	"	187	92.3			little	
	14B	"	"	160	12.2				
ityl	15A	"	"	188	95			little	see ~~xxxx~~ notebook for
ide	15B	"	"	202	6.2				further figures
lo-	18A	"	none	163	59.3	58.0		little	new abs. prod. with
ntanone	18B	"	"	167	56.7				intense new odor
lo-	19A	"	"	193	59.4	58.8		very	
xanone	19B	"	"	206	58.2			little	
ethyl cyclo	20A	"	"	185	58.9±3	58.0		little	rxn. prod. above 320mμ.
xanone	20B	"	"	204	57.0				
enzal	32A	24	2300 ?	91	99			~95%	see Table III for further
cetone	32B	"	"		9				figures
henyl	34A	48	"	142	92.4				no UV analysis
lfone	34B	"	"		---				impure <u>cis</u> again
hiocol	37A	24?	3600 ?		95.3				
	37B	"	"		7.5				
	37A	20	blue filter	131	99			9%	
	37B	"	solution	144	1				
oquinone	42A	1	2300	57	76.8	(71.8)	~ 51.8[a]		presumably diels-alder
	42B	"	"	86	65.6				addition; reject value

TABLE II- continued

sitizer	#	hrs. photo.	filter	area	% t	BAV % t	E_t	cons. of sens.	comments
ctopyrene	43A	24	2300		88		45.2 (h)	little	some new abs. prod.
	43B	"	"	139	15.3				
	55A	79	2300-3600	143	78.3			>8%	" ;time split between filters
	55B	"	"	172	26.5				
tonin	47A	24	2300	ca.145	96				no UV analysis
	47B	"	"	ca.145	4				
bromo phthylene	49A	13	"	136	71 peak ht; 63 area		[illegible]	>80%	new peak before trans. new products; colorless sample turns amber
	49B	"	"	22	80 peak ht.				
iodo- aphthylene	50A	"	"	49	73.0			(g)	new prods.; colorless sample turns blue-black opaque; 2 new peaks VPC
	50B	"	"	58	79.3				
nzanthrone	51A	12	"	155	92.3		46.0 (h)		
	52B	"	"	159	17.8				
	51A	37	"	141	80.8			ca. 5%	some new products
	51B	"	"	100	29.4				
nzidine	52B	3 3/4	"	124	17.5				
	52A	19½	"	94	86.5				reaction prods.; peach color turns deep reddish
	52B	"	"	71	50.3				
nitro aphthylene	53A	12	"	110	75.3	74.8		(g)	rxn. prods.; light yellow to reddish
	53B	"	"	117	74.3				
bromo nthracene	57A	50	"	152	59.0	58.8	40.2 (h)	some cons.;	rx. Prods., light yellow to darker yellow
	57B	"	"	150	57.6				
ANK: iperylene	54A	39	"	168	89.3				
	54B	"	"	159	20.1				

GRAPH I



PHOTOSTATIONARY STATES of PIPERYLENE
vs.
TRIPLET ENERGY of SENSITIZER
% trans at PHOTOSTATIONARY STATE
50%
52
54
56
58
60%
62
64
66
68
70%
72
74
76
78
80%
82
50
55
60
65
70
75
E_T (kcal) ⟶
1 ACETOPHENONE
2 BENZALDEHYDE
3 BENZOPHENONE
4 ETHYL PYRUVATE
5 9,10 ANTHRAQUINONE
6 MICHLER'S KETONE
7 2-NAPHTHYL-PHENYL KETONE
8 2-NAPHTHALDEHYDE
9 2-ACETONAPHTHONE
10 β-NAPHTHIL
11 1-NAPHTHALDEHYDE
12 1-ACETONAPHTHONE
13 BIACETYL
14 2,3 PENTANEDIONE
15 BENZIL
16 9-FLOURENONE
17 DUROQUINONE (uncertain)
(+)
DOTTED LINE INDICATES THE POSSIBILITY OF A SHOULDER AND AN ADDITIONAL PEAK.

TABLE III

Attempt to establish photostationary values

for two low energy sensitizers indirectly.

sensitizer	#	hrs. photo.	area	%trans	cons. of sens.	Comments
9-anthraldehyde	58A	2½	152	57.8	>35%	new abs. product..Note both of these sensitizers were photolyzed through 3600 filter -soltion did not change color appreciably.
	58A	BLANK	165	56.8		
	58B	2½	140	67.8		
	58B	BLANK	175	67.3		
	58C	2½	137	81.2		
	58C	BLANK	167	78.5		
	58D	2½	131	86.3		
	58D	BLANK	151	89.9		
dibenzal acetone	59A	2½	96	67.3	90%	slightly lighter yellow
	59A	BLANK	145	66.0		
	59B	2½	99	75.1		
	59B	BLANK	130	76.9		
	59C	2½	110	82.8		
	59C	BLANK	152	82.8		
	59D	2½	95	90.0		
	59D	BLANK	141	89.4		
	59E	2½	72	57.8		
	59E	BLANK	108	55.3		

Note that the blanks are not intended for calibration of VPC, since time shortage permitted only a rough approximation of 60:40, 70:30, etc. trans:cis.

TABLE IV

Solvent Effects

All figures from pure "ββ" column unless noted otherwise. Abbreviations: p = poor; f = fair; g = good. More than one entry for one time and one solvent indicated the same sample was run through the VPC again. All solvents are 0.05 in 2-acetonaphthone except isopentane, mineral oil, and ethylene glycol, which are 1/5 saturated.

solvent	hrs. photo.	reliability of tracing	area % t	peak ht. % t	comments	cons. of sensitizer
isopentane	½	p	94.1	96.1	peaks too small, too	
	1	g	88.8	89.0	much evaporation for	
	24	f-g	69.6	72.8 ←	UV analysis	
chlorobenzene	½	p		86.7	run together	2%
	½	"		85.2		
	1	"		82.7		
	1	f-g	84.4	86.7		
	24	"	65.4	71.5 ←		
acetonitrile	½	p-f	84.7	88.1		
	1	f	79.8	85.4	area interpolated	
	24	p-f		72.5 ←		-½% ?
ethanol	½	p-f		91.0		
	1	f	83.8	86.8	area interp.	
	24	g	69.9	73.0 ←		6.5%
Ethylene glycol	½	p		76.7		
	1	f		72.7 ←	piperylene about 95%	
	24	p		55.6	consumed	30%
mineral oil	½	v.p		63.3		
	½*	p	87.2	91.8	* ββ-$AgNO_3$	
	1*	f	83.4	89.4	* ββ-$AgNO_3$	
	24	p		55.3	piperylene ca. 50% consumed.	
	24	p-f		54.5		
benzene	½	f	90.7	92.3		
	1	f	83.8	86.2		
	24	p		76.2 ←	value too high because of bad base line.	

REFERENCES (for pinacalone decomposition)

The following contain most of the interesting information on photolysis of simple ketones in solution. Unfortunately, all experiments described were run in hydrocarbon solvent, which provides the possibility of hydrogen abstraction by radicals. Pinacalone is not dealt with in any of the papers.

1 Bamford and Norrish, J. Chem. Soc., p. 1531 (1938).

2 W. Davis, Jr., Chem. Revs., 40, 201 (1947).

3 J.N. Pitts, J. Chem. Educ., 34, 112 (1957).

4 H. Waits, CIT chem seminar, Notes, 3 Feb. 1961.

REFERENCE - for the theory of the excitation process:

G.S. Hammond, J. Saltiel, A. Lamola, N. Turro, J. Bradshaw, D. Cowan, R. Counsell, V. Vogt, & C. Dalton, "Mechanisms of Photochemical Reactions in Solution. XXI. Photochemical cis-trans Isomerization.", submitted for publication in J. Am. Chem. Soc.