The Autoxidation of Hydrazobenzene

by William C. Stwalley[1]

Abstract

The autoxidation of hydrazobenzene has been studied in methanol from 30-45°C. The reaction in neutral solution was found to be one-half-order with respect to hydrazobenzene and three-halves-order with respect to oxygen. The energy of activation was found to be 13 ± 1 kcal/mole and the entropy of activation was found to be -34.5 ± 2.5 eu. The kinetics of the base-catalyzed and the ferrous-catalyzed autoxidations were also studied. The effects of certain autoxidation inhibitors were investigated. These results are compared with other kinetic studies of oxidations of hydrazobenzene to azobenzene. Possible mechanistic courses of the autoxidation are considered on the basis of this kinetic and extrakinetic evidence.

Introduction

The autoxidation of hydrazobenzene to form azobenzene and hydrogen peroxide was noted by Manchot and Herzog in 1901[2]; the first kinetic measurements of the reaction were made by Walton and Filson in 1932.[3] Since 1956, four additional kinetic studies of this autoxidation and related oxidations have been reported.[4-7]

Three general mechanistic schemes have been proposed. Blackadder and Hinshelwood[4] proposed a mechanism for the autoxidation in basic solution involving the second conjugate base of hydrazobenzene, in analogy with postulation of the second conjugate acid in the benzidine rearrangement. They further proposed that the catalysis by metal ions was due to interception of the first conjugate base by the higher oxidation state of the metal ion, e. g. cupric, producing azobenzene, a proton, and the lower oxidation state, e. g. cuprous.

Kwart and Zubyk[5] were reported[6] to have proposed a one-step mechanism for the autoxidation "at least under certain conditions". May and Halpern[6] proposed a one-step mechanism also for the oxidation by I_2 and I_3^-; they suggested a cyclic activated complex was most likely while mentioning the possibility of hydride transfer to I_2 as an alternative one-step mechanism.

Whalley, Evans and Winkler[7] proposed a radical chain mechanism for the peroxydisulfate oxidation of hydrazobenzene, involving the α,β-diphenylhydrazyl radical. An analagous mechanism for the autoxidation is readily formulated.

The kinetic and extrakinetic evidence for the various mechanisms is discussed in detail below.

Experimental

Materials:

Aldrich Chemical sym-diphenylhydrazine (hydrazobenzene) was recrystallized from 60-100° petroleum ether (pure white crystals, m.p. 125-126°C) and was stored under vacuum.

Trans-azobenzene was obtained from Dr. Chin-Hua Wu (orange-red crystals, m.p. 68°C).

K&K Laboratory N,N'-diphenyl-para-phenylenediamine (DPPD) was recrystallized from 85-100°C petroleum ether (gray crystals, m.p. 144.5-145.5°C)

Ferrous chloride dihydrate was obtained from Dr. Chin-Hua Wu in high purity.

Redistilled (middle fraction) reagent methanol was used in kinetic solutions; for spectral measurements, dilution was made with spectro grade methanol.

Other chemicals were reagent grade.

Kinetic Measurements:

The rate of uptake of oxygen was measured on the apparatus of Dr. Chin-Hua Wu. It consisted of a rxn. vessel, a volumetric (40ml) column, a U-tube sealed at one end, a cell for electrolysis of oxalic acid, and various lines of connection. When the system was sealed at one atmosphere pressure, the pressure at the sealed end of the U-tube was also one atmosphere and thus a contact was maintained with the mercury in the U-tube. When the pressure in the system fell slightly, the mercury level at the sealed end fell also and thereby broke contact.

Meanwhile, the cell containing the oxalic acid had a pressure equal to the pressure in the system plus the weight of the oil in the volumetric column. When the mercury contact was broken, the evolution of CO_2 from the electrolysis began to

raise the pressure in the cell and thus the oil level; when the oil level raised, the volume of the system decreased, raising the pressure, and the mercury made contact again.

This mechanism was set in motion either by uptake of O_2 in the reaction vessel or by release of pressure in the electrolytic cell. Values were generally reproducible to .02 ml.

The volumetric column and the mercury U-tube (approximately 85% of system outside of reaction vessel) were kept at a constant temperature by a circulating bath system at 30°C. The reaction vessel was connected to an independent bath whose temperature was readily variable. Differences in temperature were measured by a Philadelphia Differential Thermometer and were reproducible to .02°C.

Iron Analysis:

Iron (II), iron (III), and total iron were analyzed by procedures developed by Dr. Chin-Hua Wu.

Iron (II) was analyzed by determining the optical density at 5100Å of a buffered pH 2.8 ortho-phenanthroline solution on a Beckman DU Spectrophotometer. The extinction coefficients had been previously determined by Dr. Chin-Hua Wu as follows:

$$\epsilon_{5100\text{Å}}(\text{Ferrous-o-phenanthroline}) = 1.118 \times 10^4$$

$$\epsilon_{5100\text{Å}}(\text{Ferric-o-phenanthroline}) = .03 \times 10^4$$

The total iron was determined by the same procedure following the total reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride.

The Fe(III) was analyzed by determining the optical density at 4780Å of a pH 1.5 ammonium thiocyanate HCl solution on a Beckman DU Spectrophotometer. The extinction coefficient, as determined by Dr. Chin-Hua Wu, was 7.98×10^3 for the ferric thiocyanate complex at 4780Å.

Spectra:

All UV and visible spectra were taken on a Cary 14 Spectrophotometer using matched quartz cells, except for a very few spectra of secondary importance which were taken on a Cary 11. Baselines were checked repeatedly.

Peroxide Analysis:

The standard thiosulfate (standardized by iodate) titration of hydrogen peroxide was used.[8] It should be noted that the solutions from which the samples which were titrated were taken were not homogeneous due to formation of considerable orange-red crystalline floc (presumably azobenzene) and some cloudiness within the liquid phase, since hydrazobenzene and azobenzene are only very slightly soluble in water.

pH Measurements:

All measurements were made with a Leeds and Northrup 7664 pH meter and were reproducible to better than .05 pH units. The measurements of "pH" in methanol containing tetramethylammonium hydroxide were, of course, not in any simple way related to the actual hydrogen ion concentration; nevertheless, with neutral redistilled methanol set arbitrarily at 7.80 pH units, a graphical correlation was made between hydroxide concentration and "pH" which served to indicate the correct hydroxide concentration when the "pH" was known.

Results

Stoichiometry:

The stoichiometry was generally reasonable although not quantitative. Using experimentally determined extinction coefficient of azobenzene at 3160Å of 20020, one obtained a spectrophotometrically determined final azobenzene concentration; on four of five high conversion runs, this value agreed within 10% with the oxygen uptake. Titration of the hydrogen peroxide indicated that only 70-80% of the stoichiometric amount was present, but, as noted above, the lack of homogeneity in the solutions from which the titration samples were taken makes the procedure somewhat questionable.

In the ferrous-catalyzed autoxidation, it was noted that practically no measurable Fe(III) was formed until all the hydrazobenzene had been converted to azobenzene. Of the five runs in which hydrazobenzene was completely oxidized, four showed agreement within 3% of the initial hydrazobenzene concentration and the final azobenzene concentration, determined by weight and by spectrophotometry, respectively. The initial iron (II) agreed with the final total iron to within 10%; the difference between the o-phenanthroline determinations of Fe(II) and total iron agreed with the thiocyanate determination of Fe(III) to within .007M for total iron concentrations of ~.155M. Due presumably to solvent oxidation to formaldehyde (normal tests for formaldehyde simply don't work in the presence of azobenzene), the azobenzene and Fe(III) formed usually corresponded to only about 75-80% of the oxygen uptake.

Kinetics:

The rates of autoxidation of hydrazobenzene in methanol at 30°C and one atmosphere oxygen were determined with no additives present and with ferrous chloride dihydrate, tetramethylammonium hydroxide, disodium EDTA, formaldehyde, N,N'-diphenyl-para-phenylenediamine, or di-tert-butyl-para-cresol added. In addition, rates of the pure autoxidation were determined at 35, 40 and 45°C, and at .21 atm. oxygen (dried air). These results are summarized in Table I.

The pure autoxidation was found to be one-half-order with respect to hydrazobenzene from initial rate data and from plots of the integrated rate expression such as shown in Figure 1. The rate of autoxidation was found to be three-halves-order with respect to oxygen by comparing the rate at .21 atm. with that at 1.00 atm. The rate constant for this kinetic stoichiometry was found to be 9.1×10^{-5} ml O_2/ml soln-sec-$M^{1/2}$-atm.$^{3/2}$ from initial rate constant data and 9.7×10^{-5} from the integrated rate expressions as shown in Table II. It should be noted that in the initial rate data there seems to be a slight tendency for the rate constant to increase with hydrazobenzene concentration.

Trace amounts of formaldehyde seem to have no effect on the rate constant. Disodium EDTA seems to inhibit the reaction to only a very limited extent; thus it is highly doubtful that a significant amount of the autoxidation without additives is due to trace amounts of catalytic metal ions.

A small amount of N,N'-diphenyl-para-phenylenediamine decreased the rate constant by about a third while a high concentration of 2,6-di-tert-butyl-para-cresol decreased the rate by only about a fourth.

The addition of 2.2×10^{-4} M tetramethylammonium hydroxide caused perhaps a slight decline in the rate constant; a five-fold increase in the hydroxide concentration produced a three-fold increase in rate compared to neutral solution.

The addition of ferrous chloride dihydrate greatly increased the rate of autoxidation. Since the iron (II) concentration was found to be constant until the complete disappearance of hydrazobenzene, the rate expression could be integrated to determine the pseudo-order with respect to hydrazobenzene; excellent plots for pseudo-half-order in hydrazobenzene for four ferrous chloride runs and good plots for the other two runs indicated strongly that the ferrous-chloride-catalyzed autoxidation was also half-order with respect to hydrazobenzene; see Figure 2.

The pseudo-order with respect to ferrous chloride is not clearcut. If the most dilute hydrazobenzene run is neglected and the others are corrected for autoxidation in the absence of ferrous chloride, the data are best fitted by assumption of second-order with respect to ferrous chloride as shown in Table III. The oxygen dependence was not investigated.

Reaction rates at 35, 40 and 45°C provided a basis for calculation of the energy of activation, E_a, and the entropy of activation, $\Delta S^{\ddagger}$, as defined by the equation (CONC. UNITS OF MOLES/LITER)

(1) $$k = \frac{eRT}{hN_o} e^{\Delta S^{\ddagger}/R} e^{-E_a/RT}$$

R-gas constant
N_o-Avogadro's number
h-Planck's constant
k-rate constant

E_a was found to be 13 ± 1 kcal/mole and $\Delta S^{\ddagger}$ was found to be -34.5 ± 2.5 e.u., when the important effect of change of O_2 solubility in methanol with temperature was taken into account.[9]

Discussion

Before consideration of mechanistic courses of the autoxidation of hydrazobenzene, one should review the results of the other studies of hydrazobenzene oxidation as summarized in Table IV. The results of Walton and Filson[3] are very hard to accept in light of more recent studies. It seems that something is radically different in that study and henceforth it will simply be disregarded. The results of Blackadder and Hinshelwood[4] seem hardly sufficient to justify the complex mechanisms and rate laws; for instance, kinetic measurements are made at only two "pH" values, the "pH" not being an accurate measure of (H^+) in 44% ethanol, and thus the (H^+) dependence is at best educated speculation. The precise results of Kwart and Zubyk[5b] have not yet been received and thus only the abstract[5a] and references[6] to their work were available.

The last four studies in Table IV suggest that the oxidations of hydrazobenzene have rates of the form:

$$\text{Rate} = k(AH_2)(Ox) + k'(AH_2)^{\frac{1}{2}}(Ox)^{3/2}$$

AH_2-hydrazobenzene; Ox-oxidizing agent

Such kinetics are perhaps most easily explained by a mechanism such as shown here for O_2:

$$AH_2 + O_2 \xrightarrow{k_1} AH\cdot + HO_2\cdot$$

$$AH\cdot + O_2 \xrightarrow{k_2} A + HO_2\cdot$$

$$AH_2 + HO_2\cdot \xrightarrow{k_3} AH\cdot + H_2O_2$$

$$AH\cdot + AH\cdot \xrightarrow{k_4} A + AH_2$$

with kinetics:

$$\frac{d(A)}{dt} = k_1(AH_2)(O_2) + k_2(k_1/k_4)^{\frac{1}{2}}(AH_2)^{\frac{1}{2}}(O_2)^{3/2}$$

where termination steps involving $HO_2\cdot$ are neglected. Thus, according to this mechanism, the autoxidation in methanol from roughly .02-.22 M in hydrazobenzene is a chain reaction involving step 1 for initiation.

Autoxidation in other solvents and at possibly higher concentrations as observed by Kwart and Zubyk[5] would proceed presumably with step one as the rate-limiting step; concerted processes as proposed by Kwart and Zubyk[5] and May and Halpern[6] would be essentially indistinguishable from geminate recombination of AH· and HO_2·.

Such a mechanism tacitly assumes that step four is the correct termination step and that thus the steady-state concentration of AH· is probably greater than that of HO_2· by a significant factor. Such will be the case if $k_2(O_2)$ is considerably less than $k_3(AH_2)$, which is somewhat reasonable considering the high reactivity of HO_2·. Once step one is rate-limiting, one no longer need require that step four be the only termination step, i.e. that the steady-state concentration of HO_2· be less than that of AH·. Thus this mechanism does serve to tie together the two kinetic forms of the autoxidation and related oxidations.

Consideration of the thermodynamics agrees in an interesting fashion with the general assumptions of the mechanism as shown in Table V; for a value of 54 Kcal/mole for ΔH of the reaction $AH_2 \rightarrow$ AH· + H· one seems to be tending toward a favorable step one and the results of Kwart and Zubyk[5]; while for a higher value of 65 Kcal/mole, the tendency seems to be toward a more favorable chain reaction. A study of the solvent dependence of such reactions might be rewarding. The assumption $k_2(O_2) \ll k_3(AH_2)$ certainly seems more reasonable in light of these approximate thermodynamics. An activation energy, E_a, for the chain reaction, as defined by equation (1), of 13 Kcal/mole can be seen to correspond roughly to a ΔH of $AH_2 \rightarrow$ AH· + H· of 65 Kcal/mole; while an E_a of 5 Kcal/mole for the reaction rate-limited by step one corresponds to ΔH of 41 Kcal/mole.

The exceedingly high entropy of activation presents something of a problem to the above mechanistic interpretation. This entropy could be taken to imply that either the reaction is polar or that it involves neutral structures of high entropy, such as the cyclic intermediate postulated by May and Halpern[7]. It has been suggested that HO_2 might be in the form of an isosceles triangle[10]; this could account for a significant negative entropy (compare with +23.6 for ΔS^o of $H_2 \rightarrow 2H\cdot$[11]). Any free radical complexing would contribute to the high negative entropy; there is some evidence for a weak complex between hydrazobenzene and azobenzene in that a small peak in the UV spectrum appears in mixtures but not in the spectrum of either individually - AH· might complex even better. Thus the entropy of activation does not as yet invalidate the combined mechanism; it does leave some room for doubt.

The fact that the addition of anti-oxidants only inhibited the reaction by about 25-35% cast further doubt on the existence of a free-radical mechanism for the autoxidation. It should be noted, however, that hydrazobenzene itself is commonly used as an anti-oxidant and therefore might simply be more efficient than 2,6-di-tert-butyl-para-cresol, which was added in high concentration. Since the N,N'-diphenyl-para-phenylenediamine was only slightly soluble and yet had a significant effect may indicate that this anti-oxidant is comparable to hydrazobenzene in reactivity toward O_2, $O_2H\cdot$, etc. A run in a solvent in which more of the latter anti-oxidant is soluble might be worthwhile.

The base-catalyzed autoxidation is of particular interest due to the discovery of the hydrazobenzene radical anion by ESR in this reaction by Russell and coworkers.[12] However, because of lack of data on the work by Russell et al and by Kwart and Zubyk,[5b] the reaction will not be further discussed here.

The ferrous-catalyzed autoxidation is also of particular interest as Wu and Hammond have recently succeeded in unravelling the mechanism of the autoxidation of $FeCl_2 \cdot 2H_2O$ in methanol[13]:

$$FeCl_2 + O_2 \rightleftharpoons Cl_2FeO_2$$

$$Cl_2FeO_2 + FeCl_2 \rightleftharpoons Cl_2FeOOFeCl_2$$

$$Cl_2FeOOFeCl_2 \longrightarrow 2\ Cl_2FeO \longrightarrow \text{products(Fe(III))}$$

By replacing O_2 in the mechanism postulated for the uncatalyzed autoxidation with Cl_2FeO_2 and making certain assumptions, one obtains via a rate law, Rate = $k\,(AH_2)^{\frac{1}{2}}(FeCl_2)^{3/2}(O_2)^{3/2}$. If it is assumed that Cl_2FeO reacts in place of O_2 in step one and Cl_2FeO_2 reacts in place of O_2 in step three, one obtains a rate law, Rate = $k\,(AH_2)^{\frac{1}{2}}(FeCl_2)^{2}(O_2)$. Thus preliminary agreement with experiment is obtained by superposition of the two mechanisms.

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REFERENCES

[1] NSF Summer Undergraduate Research Fellow, 1963.

[2] Manchot and Herzog, Ann., 316, 331 (1901).

[3] Walton and Filson, J. Am. Chem. Soc., 54, 3228 (1932).

[4] a) Blackadder and Hinshelwood, J. Chem. Soc., 1957, 2898.
b) " " " , " , " , 2904.

[5] a) Kwart and Zubyk, Abstracts of Papers, 135th Meeting, Am. Chem. Soc., 17-O, #25.
b) Zubyk, Ph. D. Thesis, University of Delaware, 1957.

[6] Whalley, Evans and Winkler, Can. J. Chem., 34, 1154 (1956).

[7] May and Halpern, Can. J. Chem., 39, 1377 (1961).

[8] Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, Macmillan, New York, 1952; Chapter XXXIX, sep. p. 600.

[9] Seidell, Solubilities of Inorganic and Metal Organic Compounds, Van Nostrand, New York, 1940; Vol. 1, p. 1357.

[10] Boyd, J. Chem. Phys., 37, 1317 (1962).

[11] Wall, Chemical Thermodynamics, Freeman. San Francisco, 1958; p. 402ff.

[12] Russell, Janzen and Strom, J. Am. Chem. Soc., 84, 4155 (1962).

[13] Wu and Hammond, personal communication.

TABLE I

Rates of Autoxidation of Hydrazobenzene

Initial Conc. Hydrazo. (moles/liter)	Special Conditions (additives; other than 30°C, 1 atm. O_2)	Exp. Rate ($\frac{ml\,O_2}{15ml\text{-}soln\text{-}min}$)	Rate Constant x 10^5 (ml O_2 per ml soln per sec $M^{1/2}$ per atm.$^{3/2}$)
.01855	-	.0098	8.00
.0359	-	.0151	8.85
.0576	-	.0183	8.48
.1123	-	.0264	8.75
.22	-	.0381	9.02*
.2250	-	.0456	10.69
.0368	.21 atm. O_2	.00145	8.75
.2265	.21 atm. O_2	.0043	10.40*
.0378	1.0 x 10^{-4} M HCHO	.0154	8.81
.1120	DisodiumEDTA-saturated soln	.0232	7.70
.0368	7.8 x 10^{-4} M N,N'-diphenyl-para-phenylenediamine	.0101	5.86
.0368	.242 M 2,6-di-tert-butyl-para-cresol	.0114	6.61
.0359	30°	.0151	8.85
.0367	35°	.0168	9.87
.0363	40°	.0203	11.85
.0368	45°	.0196	11.39
.0359	zero M $N(CH_3)_4OH$	.0151	8.85
.0371	2.20x10^{-4}M "	.0134	7.74
.0372	1.10x10^{-3}M "	.0538	27.9
.0576	zero M $FeCl_2.2H_2O$	.0183	8.48
.0566	.0390 M "	.033	15.4
.0574	.0767 M "	.064	29.7
.0566	.1551 M "	.255	119.1
.1132	.1514 M "	.284	93.9
.0285	.1562 M "	.162	106.7
.0147	.1538 M "	.161	147.4*

*-runs which are considered less reliable

TABLE II

Integrated Rate Expression Results

Initial conc. hydrazo. (moles/liter)	ΔV_∞ (ml O_2)	$2(\Delta V^{1/2} - V_t^{1/2})$ ($V_t = \Delta V_\infty - \Delta V_t$) vs. time in minutes: the slope	Rate Constant (ml O_2 per ml soln-sec-$M^{1/2}$-atm.$^{3/2}$)	% conversion to which plot is good
.0359	9.00	3.67×10^{-3}	9.40×10^{-5}	90(last pnt.)
.1123	43.58	3.85×10^{-3}	9.75×10^{-5}	98+(" ")
.0578	14.37	3.81×10^{-3}	9.86×10^{-5}	78 (" ")
		Average k =	9.7×10^{-5}	

TABLE III

Determination of Pseudo-order of Ferrous Chloride

Initial conc. hydrazo. (moles/liter)	Initial conc. $FeCl_2 2H_2O$ (moles/liter)	Exp. Rate (ml O_2/15 ml soln-min)	Calc. Rate in absence of $FeCl_2$ (ml O_2/15 ml soln-min)	Difference over (hydrazo)$^{\frac{1}{2}}$ x $(FeCl_2 \cdot 2H_2O)^n$ n=1	n=3/2	n=2
.0566	.0390	.033	.018	1.62	8.2	41.5
.0574	.0767	.064	.018	2.51	9.1	32.7
.0566	.1551	.255	.018	6.42	16.3	41.4
.1132	.1514	.284	.027	5.06	13.0	33.4
.0285	.1562	.162	.012	5.69	14.4	36.4
.0147	.1538	.161	.007	8.24	21.0	53.6

TABLE IV

Summary of Kinetic Results of Oxidations of Hydrazobenzene

AH_2-hydrazobenzene

Reference	Solvent	Temp. (°C)	Suggested Rate Law	E_a (Kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
3	95% EtOH, etc.	30	$k(AH_2)^2(O_2)$?	---	---
4a	44% EtOH	25	$\frac{k(AH_2)(O_2)/(H^+)}{a(H^+) + b(O_2)}$ *	---	---
4b	"	"	$\frac{k(AH_2)(O_2)(Cu^{++})/(H^+)}{a(O_2) + b(AH_2)/(H^+)}$	---	---
5a	EtOH, ? $HCO\text{-}N(CH_3)_2$, alcoholic NaOH, etc.		$k(AH_2)(O_2) + k'(AH_2)(O_2)(OH^-)$	<5**?	-42 to -52
6	100ml acetonitrile/ 12.5ml H_2O	25-45	$k(AH_2)(S_2O_8^=) + k'(AH_2)^{\frac{1}{2}}(S_2O_8^=)^{3/2}$	17**	-15**
7	60% EtOH, also 0-85%	0-25	$k(AH_2)(I_2)$	10.0	-7**
			$k'(AH_2)(I_3^-)$	16.4	-8**
this work	MeOH	30-45	$k(AH_2)^{\frac{1}{2}}(O_2)^{3/2}$ ***	13	-34.5
			$k'(AH_2)^{\frac{1}{2}}(Fe^{++})^{\sim 2}(O_2)$?	---	---

* This rate law does not agree with the experiments from which it was obtained; it would predict that in the limit $b(O_2) \gg a(H^+)$, (rate at pH13/rate at pH10) would be the order of one thousand-in fact, the experimental ratio is only five.

** Calculation by the present author.

*** Possibly plus a small term $k'(AH_2)(O_2)$.

TABLE V

Thermodynamics of the Combined Mechanism*

$AH_2 \rightarrow A + H_2$: ΔH = Ht. of Combust.$_A$ - Ht. of C.$_{AH_2}$ (a)

+ Ht. of Form.$_{H_2O}$ = 1545.9-1597.3+57.8 = 6.4 Kcal/mole

$H + HO_2 \rightarrow H_2O_2$: ΔH = -102 Kcal/mole (b)

$H + O_2 \rightarrow HO_2$: ΔH = -36 Kcal/mole (b)

$C_6H_5NH_2 \rightarrow$

$C_6H_5NH\cdot + H\cdot$: ΔH = 54 ± 3 Kcal/mole (c)

$AH_2 \rightarrow AH\cdot + H\cdot$: ΔH =

	41	54	65	75	Kcal/mole
ΔH(step one)	5	18	29	39	
ΔH(step two)	33	20	9	-1	
ΔH(step three)	-61	-48	-37	-27	
ΔH(step four)	28	2	-20	-40	
ΔH(AH-O_2H term.)	-33	-46	-57	-67	
ΔH(O_2H-O_2Hterm.)	-66	-66	-66	-66	

* Values are for gas phase and are therefore only approximate

a) Handbook of Chem.&Phys., Chem. Rubber Publishing Co. Cleveland, 1958.

b) Uri,"Inorganic Free Radicals in Solution and Some Aspects of Autoxidation", in Free Radicals in Inorganic Chemistry, American Chem. Soc., Washington, 1962.

c) Gowenlock and Snelling, "The Reactions of Alkyl-Substituted Amino Radicals", in ibid.

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(AUTO-OXIDATION OF HYDROBENZOIN)

FIG. 1

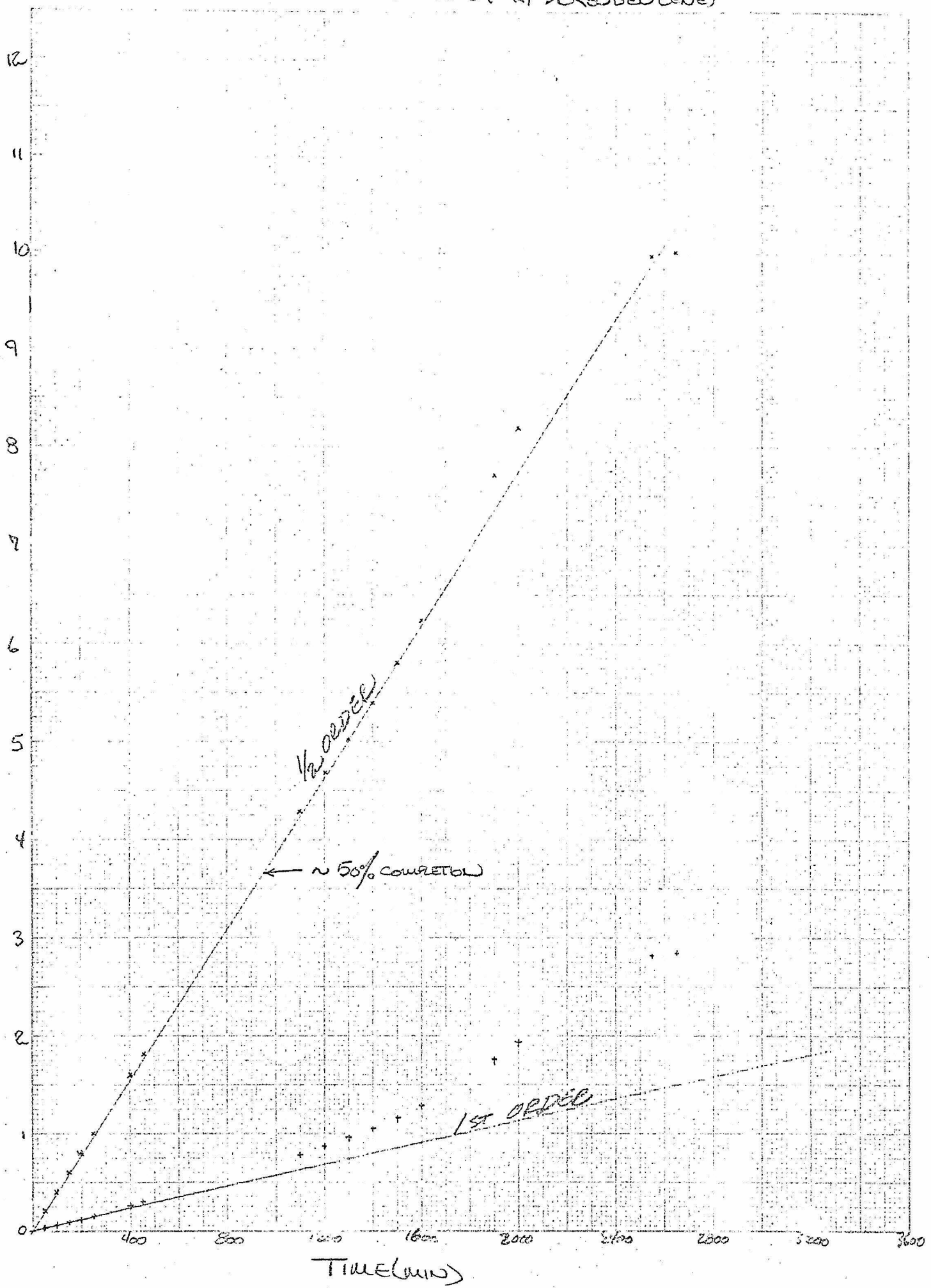

FIG. 2

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($FeCl_2 \cdot 2H_2O$ + O_2 + HYDRAZO)