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AUTOXIDATION OF 1,1-DIMETHYLHYDRAZINE

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ABSTRACT. The autoxidation of 1,1-dimethylhydrazine I gives formaldehyde dimethylhydrazone II, nitrogen, and water as its major products. Minor ones are ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde. This reaction is of first order in I and of zero order in oxygen. It is catalyzed by metals and metal salts, inhibited by added 1,3-butadiene, and accelerated by ultraviolet light. A free-radical chain mechanism is postulated as the rate-determining reaction sequence. The 1,1-dimethylhydrazyl-2-hydroperoxide so formed is presumed to give the products II, hydrazine, and hydrogen peroxide via a rapid sequence of wall reactions (established in the study of liquid-phase autoxidations of 1,1-dialkylhydrazines). Nitrogen and most minor products probably result from further wall reactions of hydrogen peroxide with I, II, and hydrazine. Autoxidations of hydrazines resemble those of hydrocarbons.

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FORWORD

This report is a comprehensive study of the autoxidation of 1,1-dimethylhydrazine which has been conducted over several years.

This report was reviewed for technical accuracy by R. A. Henry and R. H. Knipe.

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INTRODUCTION

The facile autoxidation of 1,1-dimethylhydrazine I provides an interesting example for the study of such reactions of nitrogen compounds. Most related research has involved autoxidation of hydrocarbons. The mechanisms of autoxidation of nitrogen compounds remain to be elucidated.

From a practical standpoint, these studies show that I stored with access to air accumulates formaldehyde dimethylhydrazone II and water, with smaller amounts of dimethylnitrosamine, dimethylamine, and ammonia. Nitrogen is evolved as the reaction proceeds. Other products (see below) are found in even smaller yields. Such accumulation is much more rapid in the light, and in metal containers. Commercial samples of I that had been stored for even short periods of time were found by analysis with vapor phase chromatography and nuclear magnetic resonance spectrometry to contain the above autoxidation products in significant amounts.

RESULTS

Previous workers (Ref. 1 and 2) claimed that the vapor-phase autoxidation of I gave methyl azide since they observed absorption in the 4.7- μ region of infrared spectra of these reaction mixtures. The current investigation shows that this absorption (doublet--4.72 and 4.78 μ) is due to diazomethane, a minor product that is formed and then destroyed. The infrared spectrum of methyl azide prepared for comparison is different in the region of interest (doublet--4.55 and 4.76 μ). Figure 1 shows sequential infrared spectra of the reaction mixture (initial composition: I, 100 mm, and oxygen, 605 mm, in a 10-cm Herkin-Elmer gas cell with sodium chloride windows, Ref. 3-4). Periodic scans of the 4- to 5- μ region of its infrared spectrum (Fig. 2 and 3) illustrated the growth and eventual disappearance of the diazomethane absorption. In the presence of barium oxide (see Fig. 3), the reactions consuming diazomethane are slower. Hence, its concentration reaches a higher maximum, and its disappearance takes a longer time. For comparison, Fig. 4 shows infrared spectra (4- to 5- μ region) of diazomethane taken at various pressures. Accordingly, even in the autoxidation of I where diazomethane is partially protected from further reaction by barium oxide, its maximum concentration is less than 5.9 mm (from 100 mm of I; cf. Fig. 3 and 4).

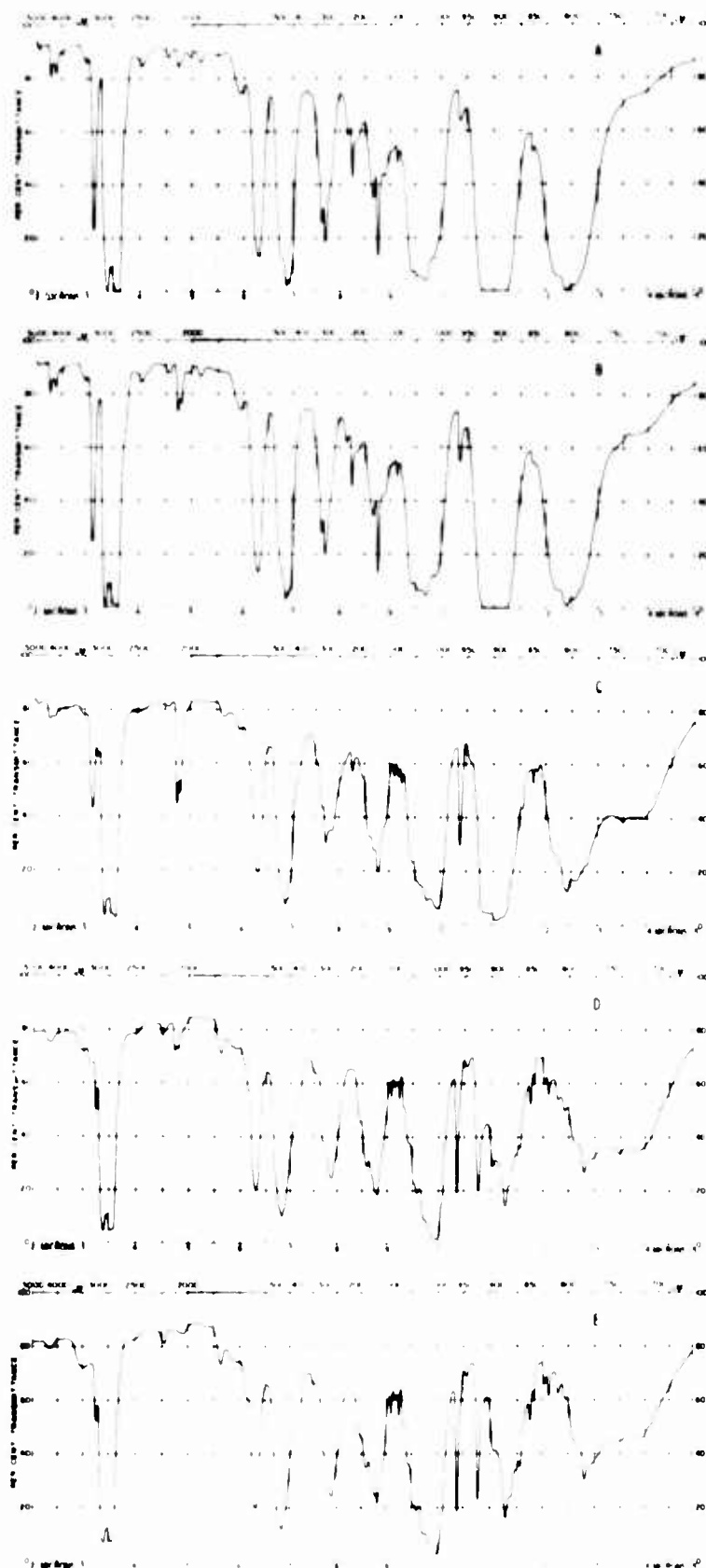


FIG. 1. Infrared Spectra of Reaction Mixture (Initially 100 mm of I and 605 mm of O₂) Taken at Successive Reaction Times: A after 1 hr, B after 3 hr, C after 7 hr, D after 14 hr, and E after 23 hr.

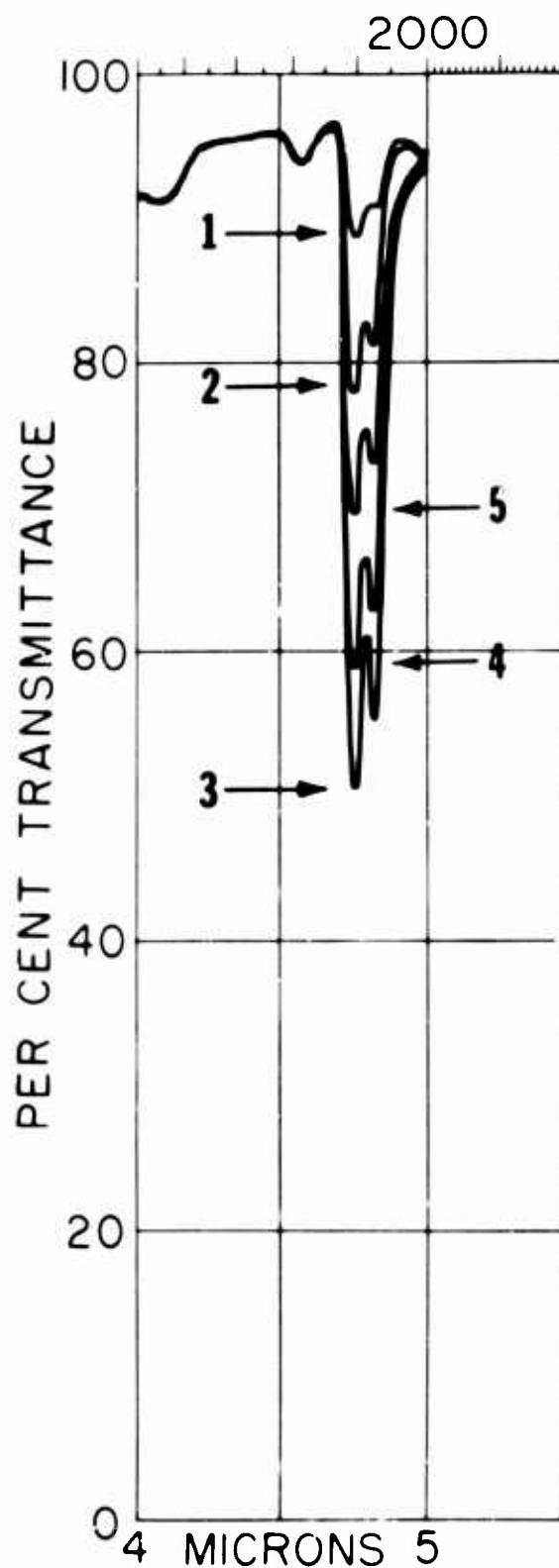


FIG. 2. Main Absorption Band (4.72 and 4.78 μ) of Diazomethane in a Reaction in an Infrared Gas Cell of I (100 mm) With O_2 (600 mm): 1 after 2 hr, 2 after 5 hr, 3 after 21 hr, 4 after 26 hr, and 5 after 34 hr.

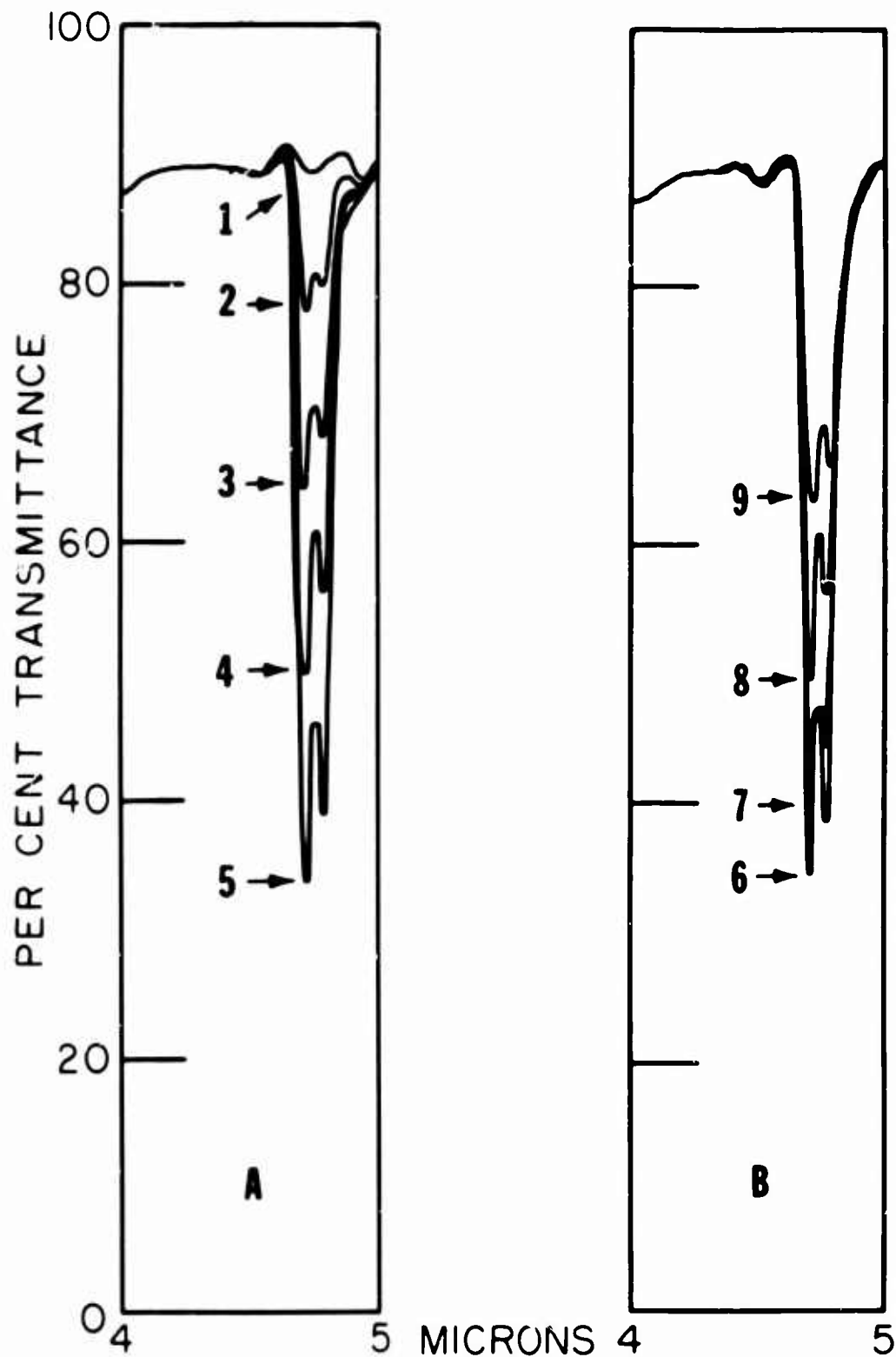


FIG. 3. History of the Principal Infrared Band of Diazomethane During the Reaction of I (100 mm) With O_2 (605 mm) in a Cell With a Cup Filled With BaO: 1 initial, 2 after 1 hr, 3 after 3 hr, 4 after 7 hr, 5 after 22 hr, 6 after 46 hr, 7 after 68 hr, 8 after 114 hr, and 9 after 162 hr.

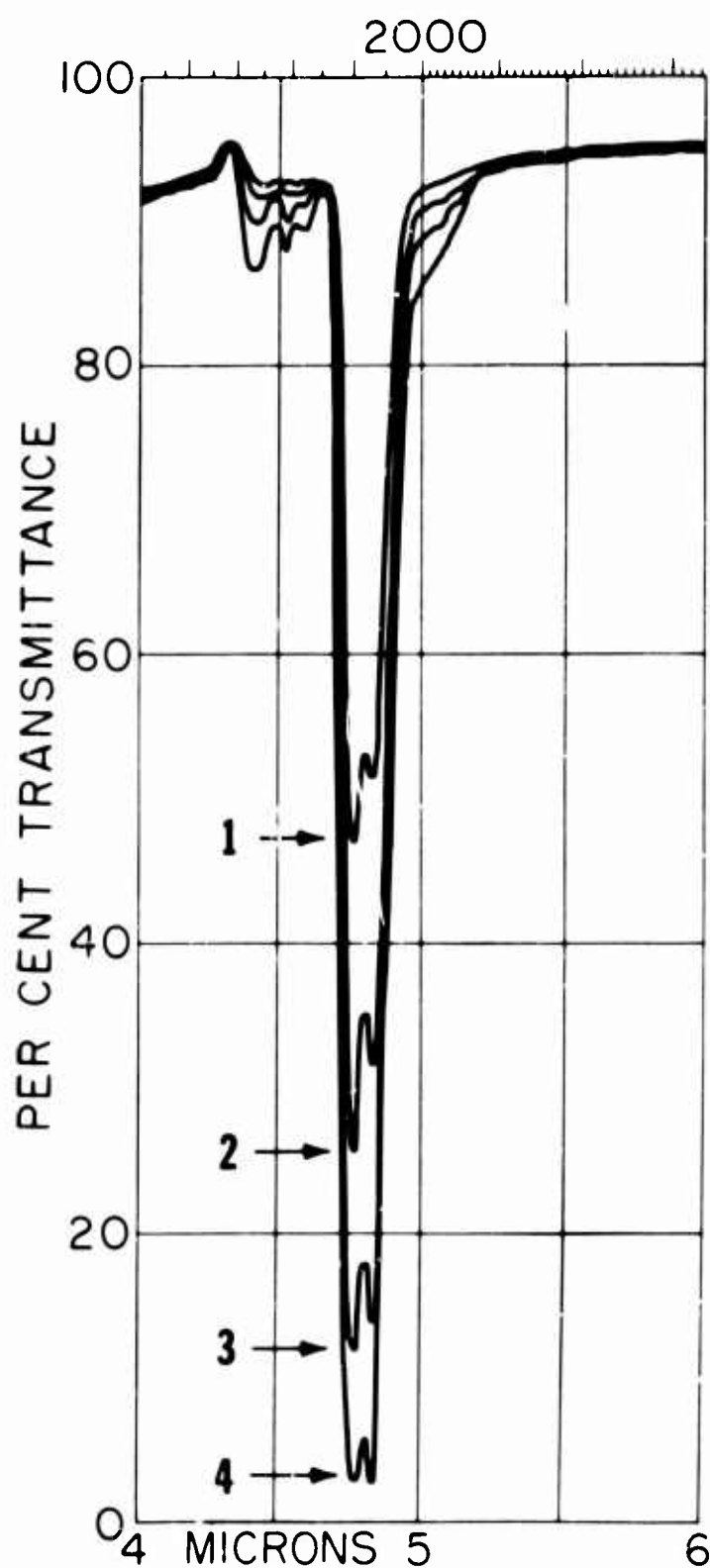


FIG. 4. Vapor Phase Infrared Spectra of the Principal Absorption Band of Diazomethane at Various Pressures: 1 = 3.6 mm, 2 = 5.9 mm, 3 = 10 mm, and 4 = 18 mm.

Such sequential infrared spectra permit approximate estimation of the concentration change of I and products in the latter experiment ($I + O_2$ in the presence of BaO, see Fig. 5). Apparently, II is formed during the entire reaction but diazomethane, ammonia, and dimethylamine seem to be produced only during the first half of it. From I (100 mm), yields are II (61 mm), ammonia (20 mm), dimethylamine (8 mm), diazomethane (4.5 mm), and nitrogen (21 mm, see below). Other benefits in addition to the preservation of diazomethane result when the water and presumably hydrogen peroxide formed are partially removed by barium oxide. No condensate collects on the cell walls, the reaction is slower than in the absence of BaO, and change of the logarithm of the concentration of I with time is linear (see Fig. 6) throughout the entire reaction (see below for description of kinetics in the presence of condensate). The reaction is, therefore, of first order in I (zero order in O_2 , see below).

When reaction is complete, its infrared spectrum (Fig. 1E) closely resembles that of the major reaction product II (Fig. 7) with that of dimethylamine (13.4-14 μ), and many sharp peaks of the ammonia spectrum (most prominent ones at 10.38 and 10.77 μ) superimposed. In nearly all of these reactions of I with oxygen, the product nitrous oxide (doublet--4.46 and 4.52 μ) is observed in small amount. Sequential infrared studies have shown that it is usually formed in the later stages of "normal" reactions. With reactions catalyzed in various ways (light, ammonia, sodium chloride with barium oxide, circulating cell--see Table 1), it is formed in larger amounts; in some of these experiments, no diazomethane was observed. A small peak (5.77 μ) probably due to formaldehyde appears in the later stages of the reaction. Infrared absorptions of carbon monoxide and carbon dioxide are not visible in spectra of these reaction mixtures.

Studies of the autoxidation of I with infrared spectroscopy show that the rate of the reaction between I and oxygen is highly erratic (Table 1). With no apparent differences in experimental procedure, the times for these reactions to reach completion ranged from 24 to 72 hr (cf. experiments 1 and 2, Table 1). The apparent reason for such behavior is that the reaction is subject to various catalytic effects. It is markedly accelerated by light (experiment 8, Table 1), and by the introduction of various materials into the reaction cell--metals, glass helices, ground glass, and even ground sodium chloride prepared from the window material of the cells. Butadiene in the gaseous mixture of I and O_2 is not consumed in an amount great enough to be detected, but the autoxidation of I is inhibited (see Experimental section).

Products were isolated and identified by various experimental procedures. First, oxygen was bubbled through liquid I. Excess oxygen and product vapors were passed through a long spiral condenser ($-20^\circ C$), and all volatile products except nitrogen were condensed in a trap ($-80^\circ C$). In the latter, diazomethane, dimethylamine, and ammonia were shown to

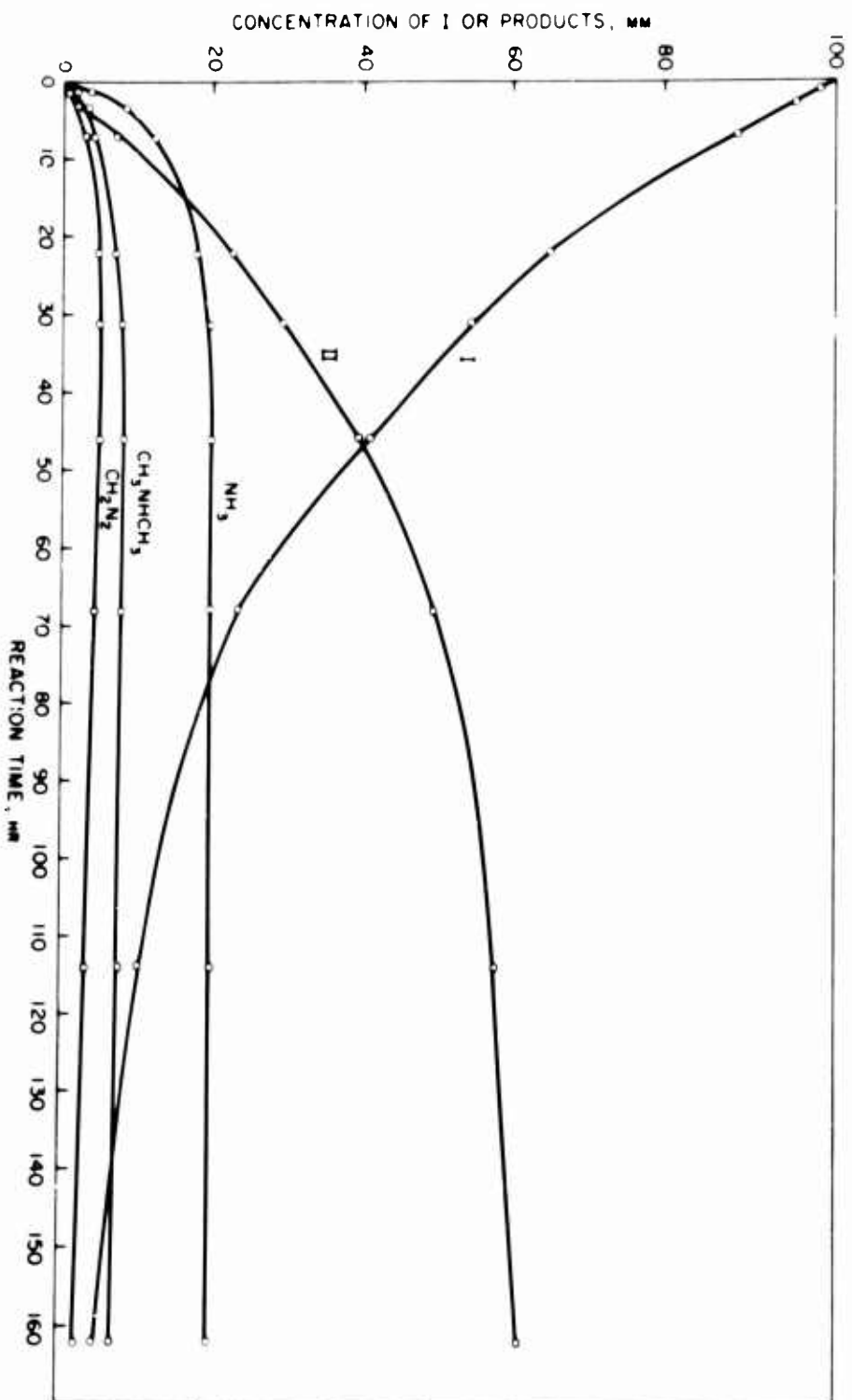


FIG. 5. Reactant I and Products in the Reaction of I (100 mm) and Oxygen (605 mm) at 25°C in the Infrared Cell with an Attached Chamber Filled with BaO. Relative concentrations were estimated from heights of peaks for I at 3.12 μ , II at 3.24 μ , CH₂N₂ at 4.72 μ , NH₃ at 10.35 μ , and (CH₃)₂NH at 13.75 μ . Total concentrations were determined from infrared calibration spectra of each substance at various pressures in the cell.

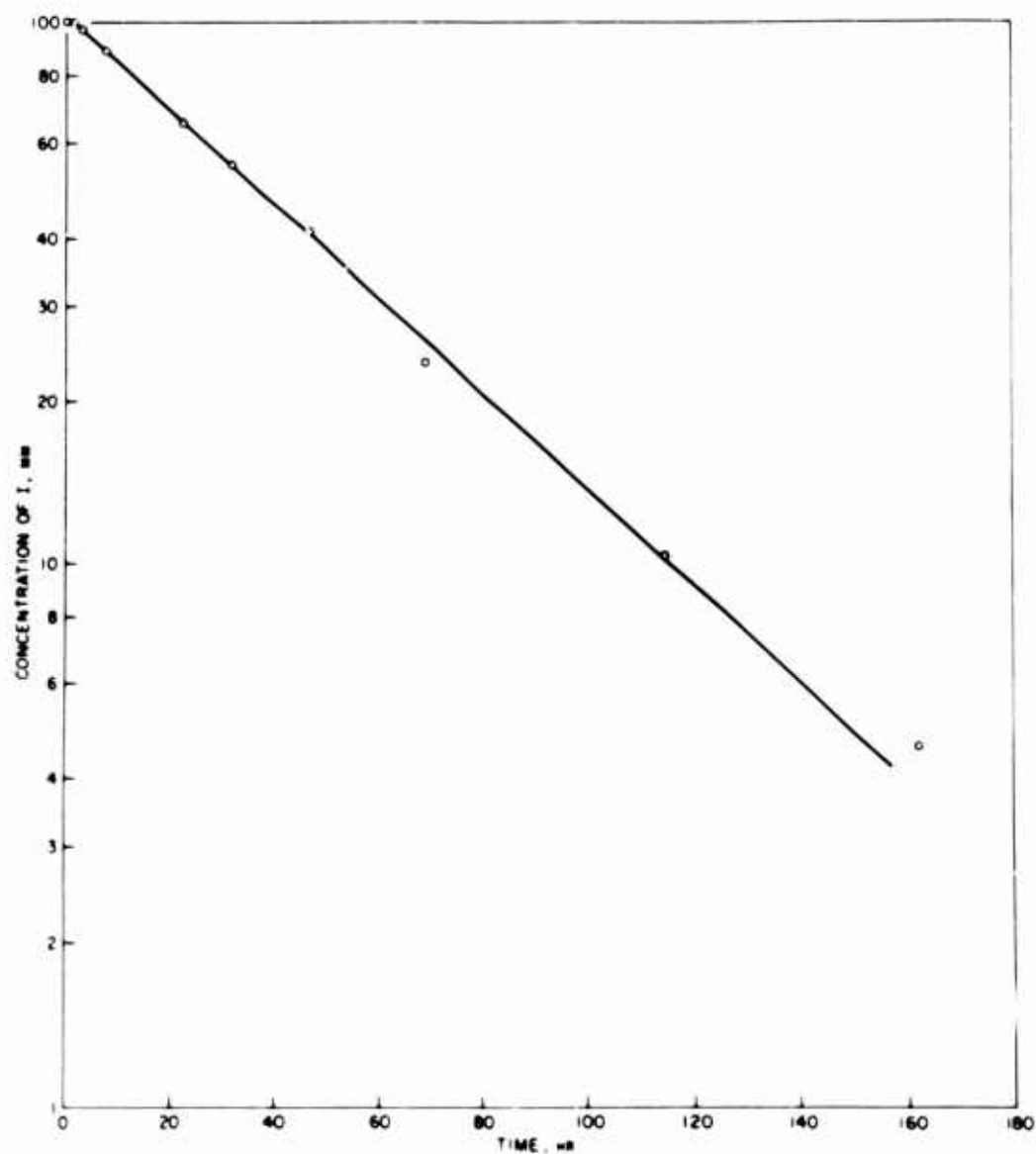


FIG. 6. Concentration of I (from Fig. 5) vs. Time in the Reaction of I (100 mm) With O_2 (605 mm) in the Presence of BaO in the Infrared Gas Cell at $25^\circ C$.

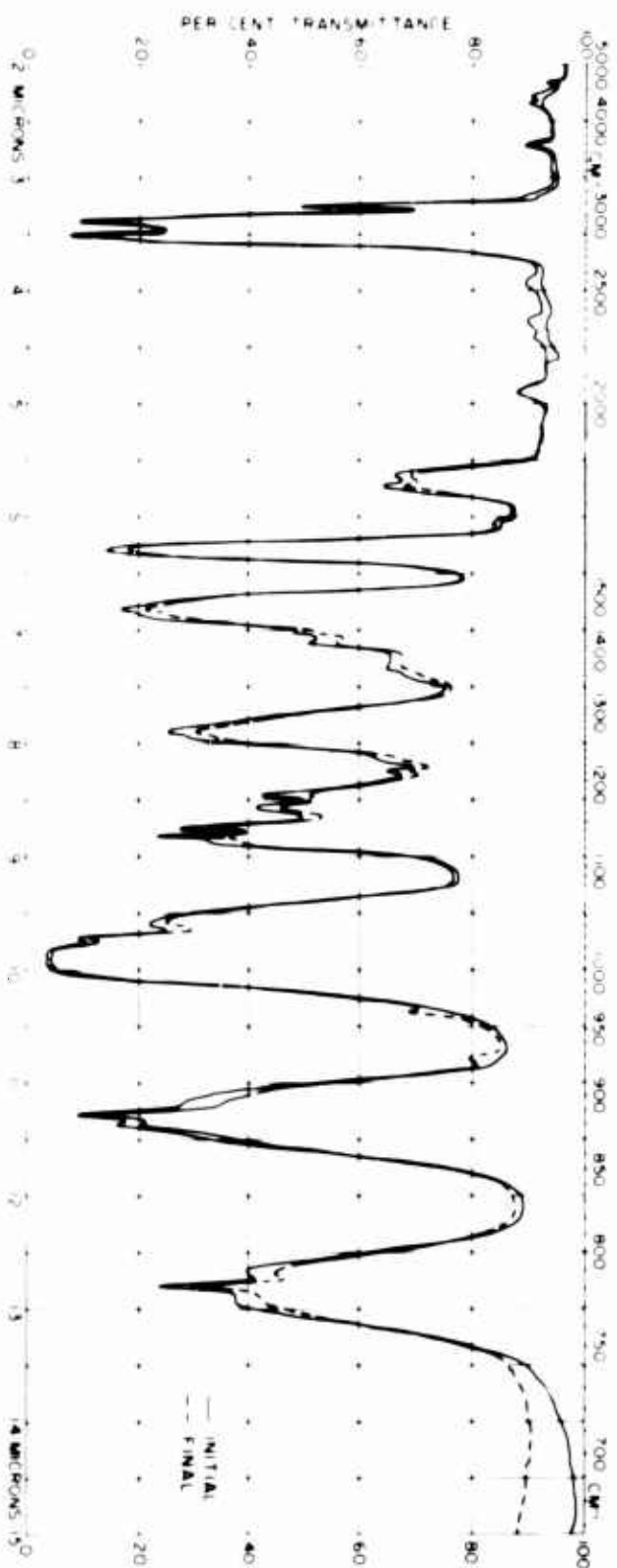


FIG. 7. Infrared Spectra of a Gaseous Mixture of II (50 mm), and O₂ (655 mm). Final scan (dotted line) was taken after 21 days.

be present. The yellow condensate became colorless when it was treated with 3,5-dinitrobenzoic acid in ether, and dimethylammonium and ammonium 3,5-dinitrobenzoates precipitated. Methyl 3,5-dinitrobenzoate was recovered from the ether filtrate. Part of the salt mixture was recrystallized from ethanol until pure dimethylammonium 3,5-dinitrobenzoate was obtained. The remainder of the salt was dissolved in sodium hydroxide solution, and the solution was partly distilled. Ammonium chloride (identified by its X-ray powder pattern) was isolated when the distillate was made acidic with hydrochloric acid, the latter solution was evaporated to dryness, and the resulting mixture of hydrochlorides was extracted until all dimethylammonium chloride had been removed.

The dark brown liquid remaining in the reaction vessel was shown to contain II and dimethylnitrosamine. The dominant product II (b.p. 65-68°C infrared spectrum identical with known) was isolated by vacuum distillation through calcium chloride (to absorb amines and water). Its reaction with 2,4-dinitrophenylhydrazine reagent gave the 2,4-dinitrophenylhydrazone of formaldehyde; with aqueous oxalic acid, it gave dimethylhydrazinium oxalate. The identity of II was further verified by polarography. Dimethylnitrosamine was extracted from the distillation residue. It was identified by its spectrum, vapor phase chromatography (v.p.c.), and by reduction to I. Analysis (v.p.c.) of yellow condensates in vapor-phase autoxidation showed that it is also a trace product under these conditions.

The product mixture from the reaction of I (96 mm) and oxygen (594 mm) in a gas reaction vessel (650 ml) was washed with sulfuric acid to remove basic products. Mass spectrometric analysis of the remaining mixture of gaseous products showed that it contained unreacted oxygen (96.25%), nitrogen (3.22%, 63% yield based upon reaction 1 below), methane (0.19%), carbon dioxide (0.36%), and hydrogen (0.03%). Yields of these products differed. In another experiment in which the oxygen was also removed from the gas sample, the analysis was nitrogen (90.0%), methane (0.51%), ($N_2:CH_4$ ratio approximately ten times that in the previous experiment), and carbon dioxide (0.23%).

Nitrous oxide was identified, and its yield estimated, in a reaction mixture prepared by the irradiation of I (100 mm) and oxygen (605 mm) in a quartz infrared cell. The gas isolated as above contained oxygen (96.7%), nitrogen (2.85%), and nitrous oxide (0.46%).

More precise kinetic investigation of the vapor-phase autoxidation of I confirms that it is of first order. In the experiments illustrated in Fig. 8 with gaseous mixtures of I (initial concentrations: 43, 63, and 78 mm) and oxygen (625, 247, and 287 mm, respectively) at 25°C the plot of the logarithm of II formed against reaction time shows two essentially linear regions--one prior to the appearance of a condensed phase on the vessel walls and the other subsequent to it. Linear consumption of I is apparent after condensation. This more rapid reaction in the two-phase system seems to have the same rate constant in all three experiments since the three lines are parallel.

TABLE 1. Infrared Study of 1,1-Dimethylhydrazine Autoxidation^a

Expt. no.	Conditions ^b	Approx. half-life, hr	Comments
1	Cell in dark when not in spectrophotometer	20	Diazomethane formed early. N ₂ O and H ₂ CO visible after 48 and 71 hr, respectively.
2	Cell in dark when not in spectrophotometer	7	N ₂ O developed as CH ₂ N ₂ declined.
3	Cell in infrared beam continuously	10	Product spectrum same as Fig. 1E.
4	With room light and temperature	24	Product spectrum same as Fig. 1E.
5	Temperature held at 45-46°C	12	Product spectrum same as Fig. 1E.
6	Quartz cell held at 50°C	32	CH ₂ N ₂ and N ₂ O develop simultaneously.
7	Quartz cell in infrared beam during reaction	9	CH ₂ N ₂ peak 45% transmittance at 7 hr. Some N ₂ O formed later.
8	Quartz cell - Hanovia lamp without filter 0.3 m from cell	2	More NH ₃ , (CH ₃) ₂ NH than usual. N ₂ O observed instead of CH ₂ N ₂ .
9	Cell fitted with cup containing BaO	32	Fig. 3 shows CH ₂ N ₂ increase and decrease.
10	NH ₃ (5 mm added)	18	N ₂ O and CH ₂ N ₂ formed.
11	NH ₃ (10 mm added)	6	N ₂ O formed, but no CH ₂ N ₂ .
12	Tetramethyltetrazene, TMT, (5 mm added)	3	Product spectrum same as Fig. 1E.
13	Control (no TMT)	11	Product spectrum same as Fig. 1E.
14	TMT (3 mm)	No reaction in 3 hr.
15	Circulating cell ^c BaO in weighing cup gained 0.0251 g	5	Some NH ₃ in I used. N ₂ O formed faster than CH ₂ N ₂ . Latter gone after 22 hr.

See footnotes at end of table.

TABLE 1. (Contd.)

Expt. no.	Conditions ^b	Approx. half-life, hr	Comments
16	Cell with NaCl window pieces and BaO in cup	1.5	Some NH ₃ in I used. N ₂ O, no CH ₂ N ₂ . Abnormal product - little II and large amounts of NH ₃ .
17	Ground glass helices in cup	2	Products as in Fig. 1E. CH ₂ N ₂ , no N ₂ O.
18	NaCl pieces in cup	0.5	Reaction complete in 0.5 hr. CH ₂ N ₂ , no N ₂ O.
19	Mercury in cup	0.25
20	Control for 15-19, nothing in cup	Less than 10% reaction in 20 hr.

^a Representative examples of many such experiments.

^b Except as noted, the infrared cell (Perkin-Elmer, 10 cm, NaCl windows sealed with a Glyptal bead outside) was filled with I (100 mm) and oxygen (605 mm). Perkin-Elmer Infrared spectrophotometer, Model 21, was used. All experiments at 25°C except as noted.

^c Described in Ref. 41.

When the reaction vessel is immersed in an oil bath (dark) at 41°C (illuminated by a 100-w Mazda lamp, see Experimental section), a much longer reaction time is observed, and condensation of a liquid phase on the vessel walls is delayed. Here, an induction period of over 100 hr, a slow first-order rate for the gas-phase reaction (120 to 540 hr), and a faster rate (first order) for the two-phase reaction are observed (see Fig. 9).

Experimental procedures as used with I have shown that 1,2-dimethylhydrazine and trimethylhydrazine undergo rapid and complete autoxidation in the vapor phase at 25°C, methylhydrazine gives a rapid initial reaction that seems to stop suddenly, and tetramethylhydrazine does not react. Reaction products from 1,2-dimethylhydrazine are azomethane and water (see Fig. 10), and with trimethylhydrazine are II and water (see Fig. 11).

When mixtures of methylhydrazine and oxygen were mixed in the infrared cell, the initial rapid autoxidation gave products that condensed upon the cell walls and so made it impossible to determine the infrared spectrum of the reaction mixture. A 3-liter flask was filled with methylhydrazine (34 mm) and dry air (570 mm), and the condensate appeared.

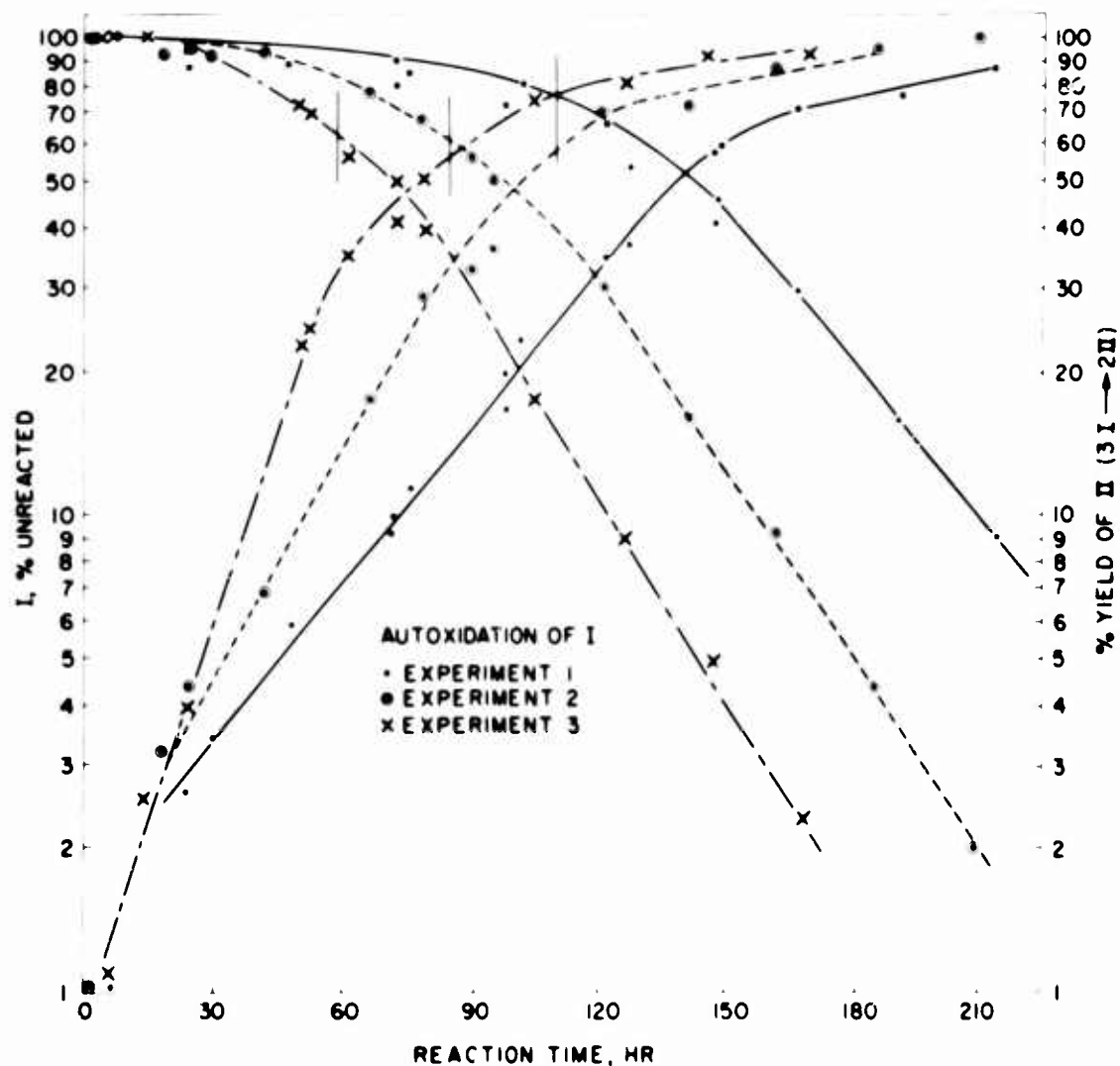


FIG. 8. Experiment 1 With I (43 mm) and O_2 (625 mm); Experiment 2 With I (63 mm), O_2 (247 mm), and N_2 (390 mm); and Experiment 3 With I (78 mm), O_2 (287 mm), and N_2 (331 mm), all at $25^\circ C$ and in Room Light. Ascending curve, II formed; and descending curve, I consumed. Vertical lines indicate reaction time at which condensation of a liquid phase was observed.

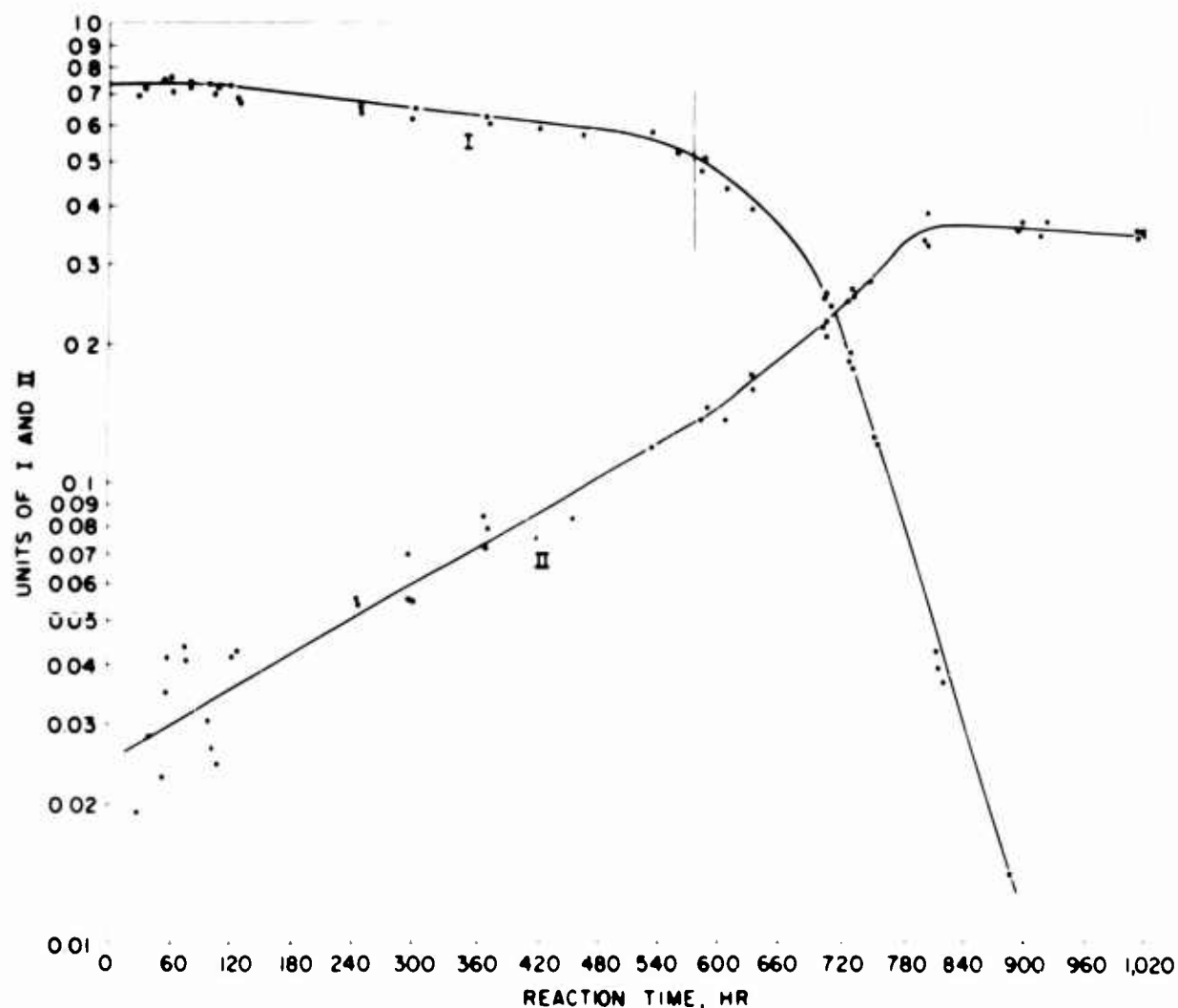


FIG. 9. Reaction Mixture Contained Initially I (60 mm), O_2 (205 mm), and He (428 mm) at $41^\circ C$ in an Oil Bath (Dark). Descending curve records I consumed, and scattered points are the data for II formed. Vertical line indicates reaction time at which condensation of liquid products on the reaction vessel walls was observed.

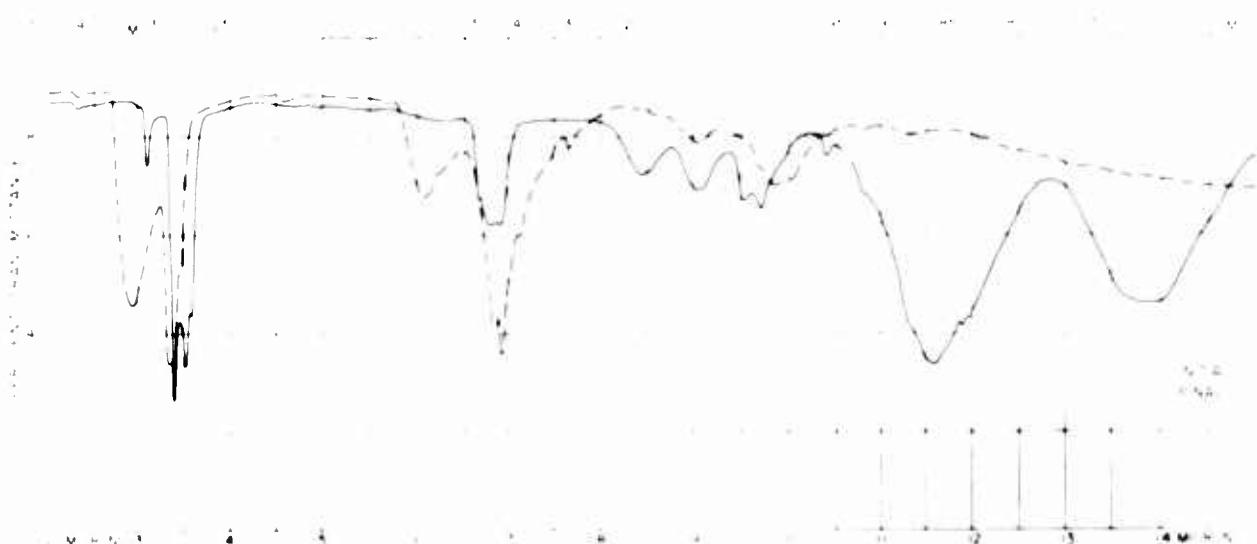


FIG. 10. Infrared Spectrum of 1,2-Dimethylhydrazine (46 mm) and of the Reaction Mixture Taken 1 hr After O₂ (668 mm) Had Been Added. Products are azomethane and water.

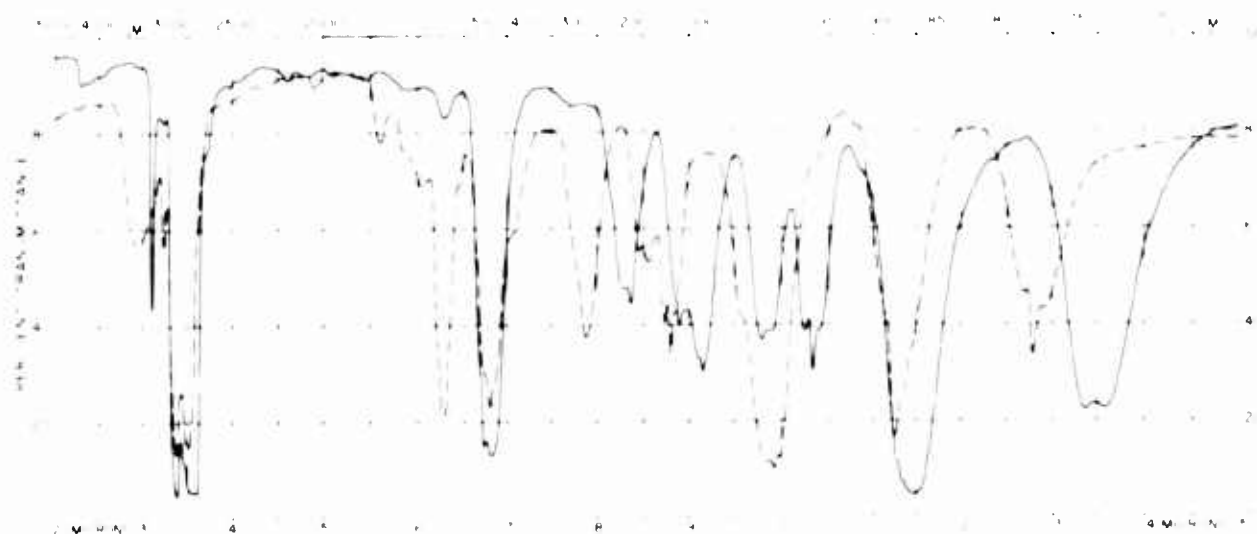


FIG. 11. Autoxidation of Trimethylhydrazine. The infrared gas cell was filled with this hydrazine (50 mm) and O₂ (658 mm). Solid line is the initial spectrum. The spectrum of the products (after 42 hr, dotted line) indicates II and water (broad bands at 2.94 μ and 6.06 μ).

A sample of the reaction mixture pumped into an infrared cell gave the spectrum of pure methylhydrazine. Dry, carbon dioxide-free oxygen was bubbled through methylhydrazine for 21 days. A very small amount of volatile product condensed at -80°C contained methyl azide, ammonia, and methyl amine (see Fig. 12), and the residual liquid in the bubbler reaction vessel was unreacted methylhydrazine.

Mixtures of tetramethylhydrazine or tetramethyltetrazene with oxygen were unchanged after long periods of time (Fig. 13 and 14).

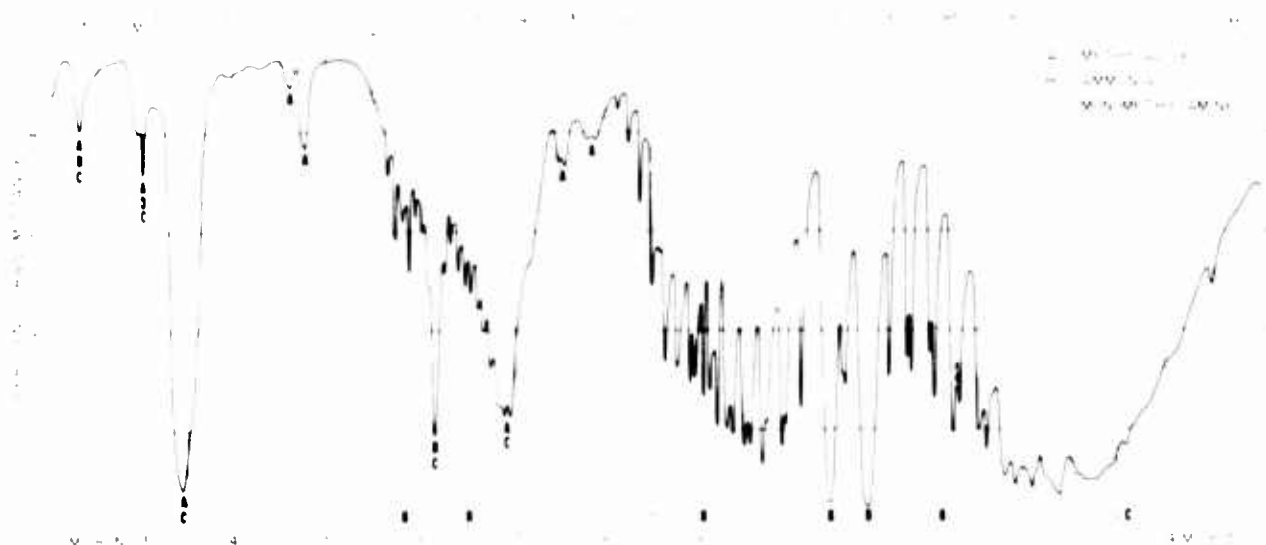


FIG. 12. Infrared Spectrum of Condensate of Volatile Products Obtained When O_2 is Bubbled Through Methylhydrazine.

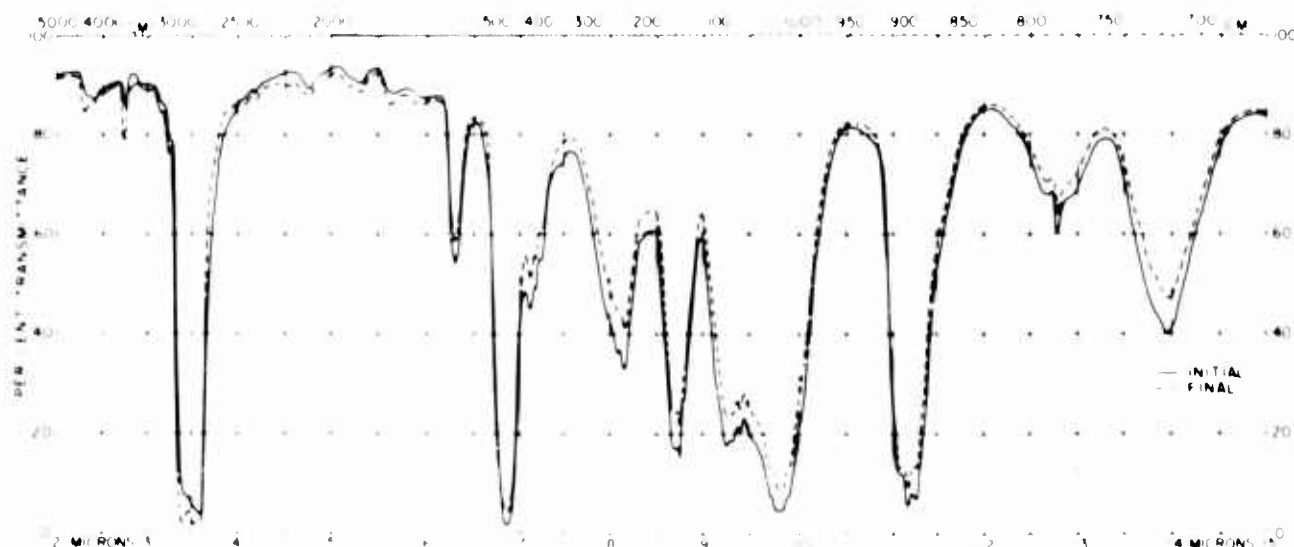


FIG. 13. Infrared Spectra of a Gaseous Mixture of Tetramethylhydrazine (70 mm) and O_2 (635 mm) Immediately After Mixing and After 170 hr (Dotted Line) at 25°C .

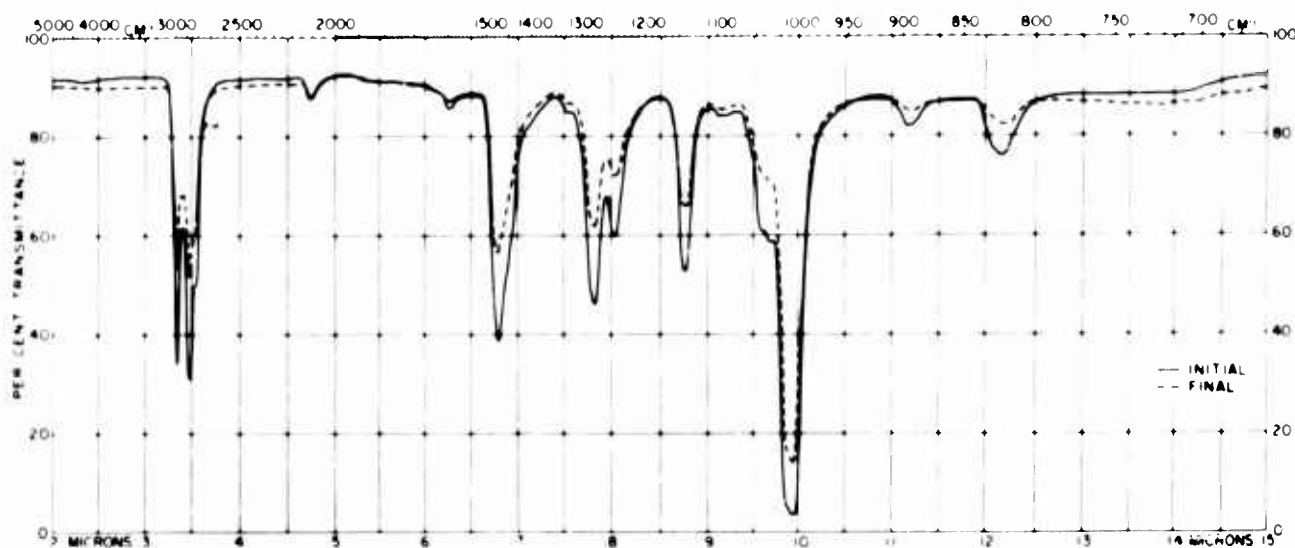
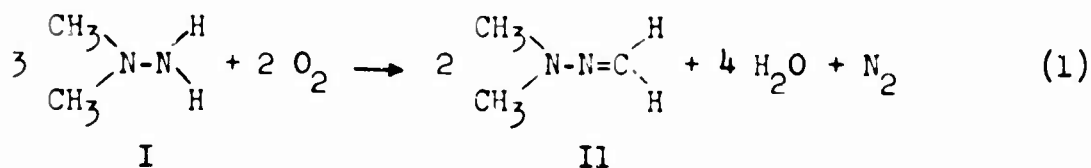


FIG. 14. Gas Infrared Spectra of a Mixture of Tetramethyltetrazene (8 mm) and O₂ (697 mm) Before and After (Dotted Line) Standing for 66 hr.

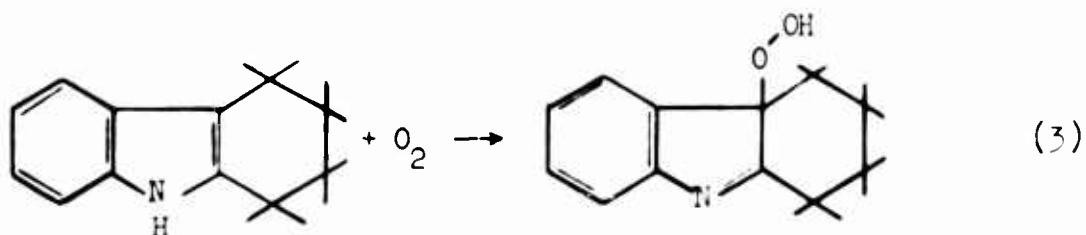
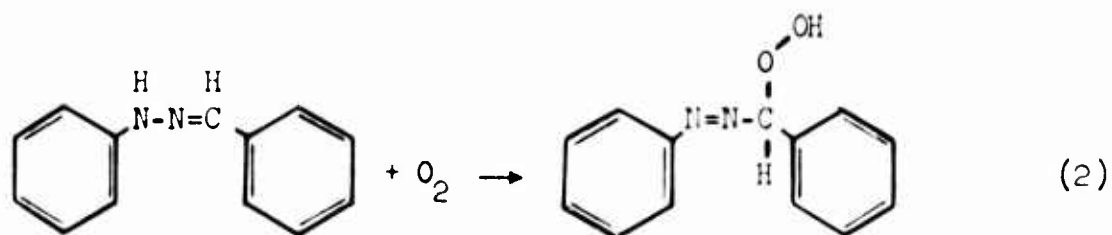
DISCUSSION

The autoxidation of 1,1-dimethylhydrazine I gives formaldehyde dimethylhydrazone II, water, and nitrogen as the dominant products, and the stoichiometry of Eq. 1 is approached. Numerous other products (dimethylamine, ammonia, diazomethane, dimethylnitrosamine, and formaldehyde) are formed in small amounts.



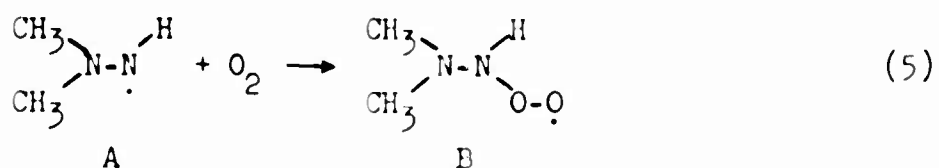
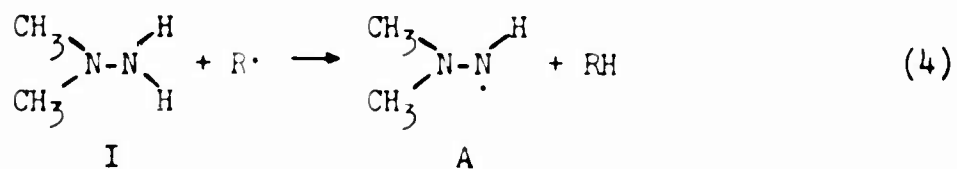
Kinetic studies have shown that this reaction is of first order in I (Fig. 6, 8, and 9), and probably of zero order in oxygen (cf. experiments 1 and 2, Fig. 8). Reactions of first order in the substances being oxidized, and of zero order in oxygen (above a limiting oxygen concentration) are common in the autoxidations of hydrocarbons and aldehydes (Ref. 5-7).

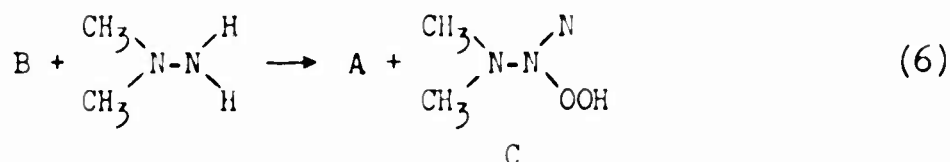
First-order dependence of rate upon substrate concentration has also been observed in the autoxidation of phenylhydrazones (Ref. 8-11, Eq. 2), and in the autoxidation of 1,2,3,4-tetrahydrocarbazole, and other substituted indoles, in solution (Ref. 12-21, Eq. 3).



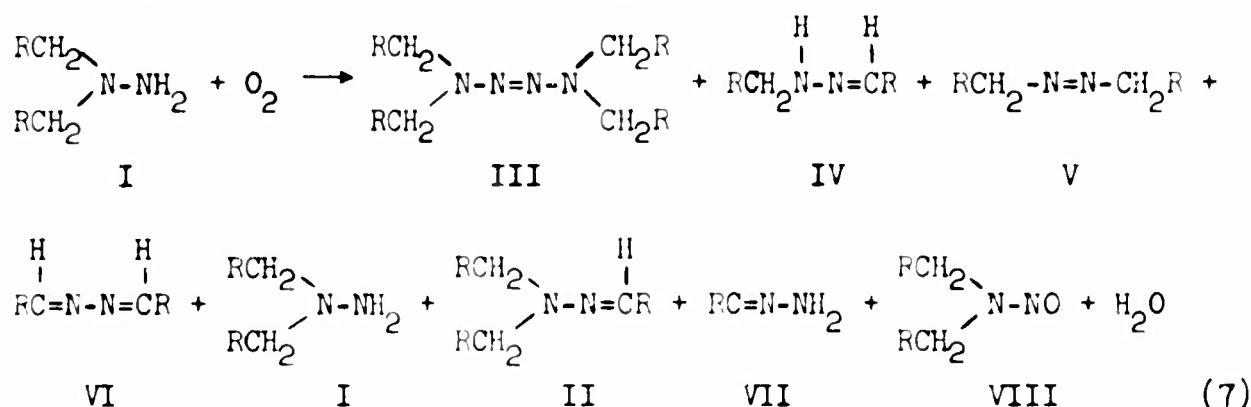
Since these studies of hydrazone and indole autoxidation have involved the measurement of oxygen uptake at constant pressure, the kinetic order with respect to oxygen was not determined.

These results suggest that the rate-determining sequence in the autoxidation of I resembles the free-radical chain reaction established for the autoxidation of cumene (Ref. 22-25). Reaction initiation would involve the free-radical decomposition of hydrazine hydroperoxides C (slowly accumulated during the induction period) shown below. Equation 4 represents the last step in initiation [$\text{R}\cdot = \text{HO}\cdot$ or $(\text{CH}_3)_2\text{N-NHO}\cdot$]. Reactions 5 and 6 represent the chain-propagating sequences. The indicated attack upon hydrogen atoms attached to nitrogen is supported by the fact that substances without this functional group (tetramethylhydrazine, tetramethyltetrazene, or II) do not oxidize under these mild conditions while all hydrazines with N-H groups (hydrazine, methylhydrazine, I, 1,2-dimethylhydrazine, or trimethylhydrazine) do. Chain termination probably involves mutual destruction of two radicals such as B. Qualitative observations supporting this hypothesis are that the autoxidation of I is induced by light; it has an induction period; its rate is markedly enhanced by trace impurities, notably metals and metal salts, known to react with hydroperoxides to give radicals; and it is inhibited by butadiene-1,3.





Although the hydroperoxides derived by the related autoxidations of hydrazones and indoles are stable enough to be isolated, C is not. Its fate is suggested by recent parallel studies (see Table 2 below, from Ref. 26) of oxidative reactions of 1,1-dialkylhydrazines in solution. The products observed (Ref. 26) in the autoxidation of such hydrazines in the liquid phase are the following:

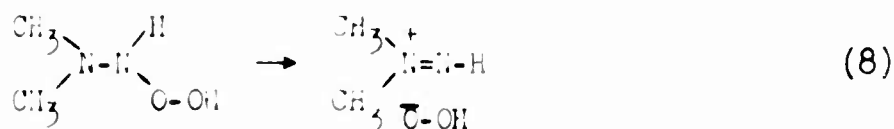


I - VII, R = H-

Ia - VIIa, R = CH₃CH₂-

Ib - VIIb, R = CH₃CH₂CH₂-

Products II through VII, but not VIII, also are obtained in (1) reactions of 1,1-dialkyl-2-p-toluenesulfonylhydrazides with base, (2) mercuric oxide-oxidation of 1,1-dialkylhydrazines, and (3) reactions of acidic solutions of 1,1-dialkyldiazonium salts with base. It is postulated that a common intermediate, the 1,1-dialkyldiazene, is formed first in all four reactions. Hence, one mode of decomposition of C is presumed to give the diazene via the 1,1-dimethyldiazonium hydroperoxide (Ref. 27-30). Since such ionic reactions are unlikely to occur in the vapor phase and since II is the major product in both liquid and gas autoxidations, these reactions (8 and 9) probably occur on reaction vessel walls in the latter. Accordingly, addition of materials of large surface area (cf. experiment 1 with experiments 16-18, Table 1) markedly increases the reaction rate.



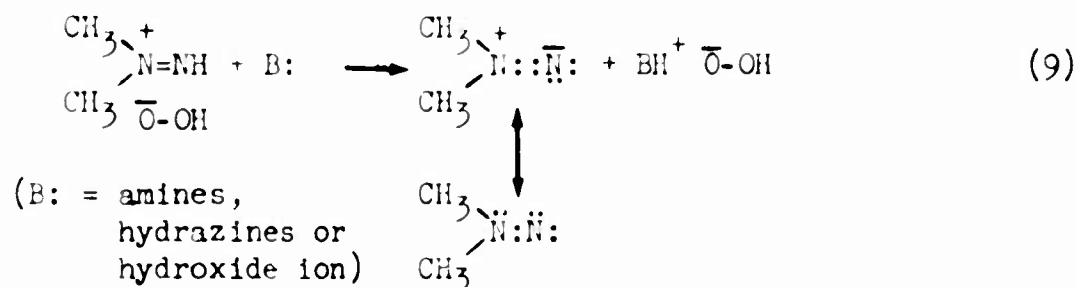


TABLE 2. Products From Liquid-Phase Autoxidation of 1,1-Dialkylhydrazine (mole %)

I-VII, R = H-; Ia-VIIIa, R = CH₃CH₂-; Ib-VIIIb, R = CH₃CH₂CH₂-.

Expt. no.	A. Products From 1,1-Dipropylhydrazine Ia							
	IIIa	IVa	Va	VIa	Ia	IIa	VIIa	VIIIa
1 ^a	0.6	0.3	0.2	0.4	... ^b	41	5.7	52
Expt. no.	B. Products From 1,1-Dibutylhydrazine Ib							
	IIIb	IVb	Vb	VIb	Ib	IIb	VIIb	VIIIb
2 ^a	12.5	4.4	... ^b	... ^b	0.3	57.6	1.1	24.4
3 ^{c,f}	... ^d	... ^b	... ^b	... ^b	... ^b	71.5	... ^b	28.5
4 ^{e,f}	... ^d	6.9	... ^b	... ^b	... ^b	69	... ^b	24.1

^a Liquid hydrazine stirred in oxygen (1 atm) at 25°C. Induction period (1.5 hr) observed.

^b Trace products observed (v.p.c.).

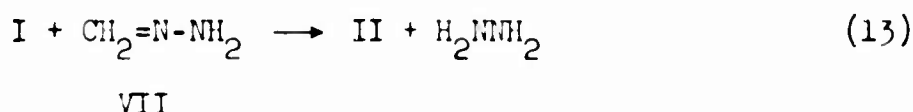
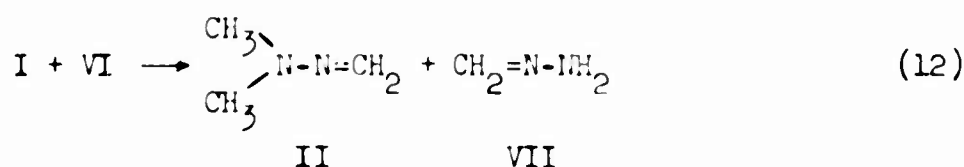
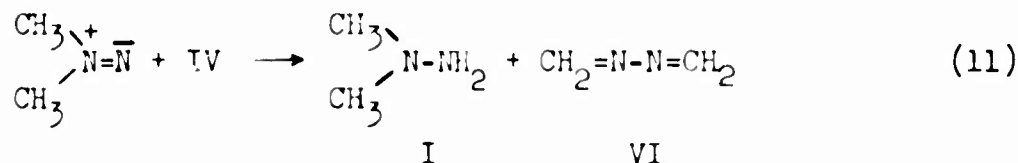
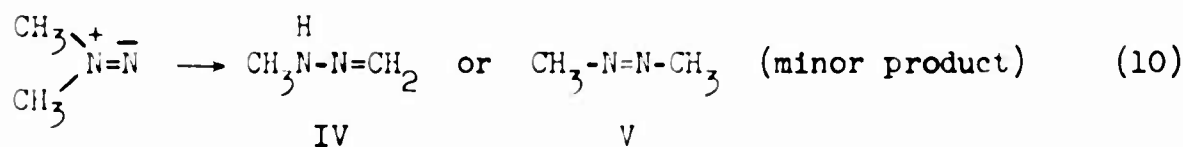
^c Methanol:hydrazine solution in 3:1 molar ratio. Long induction period (3 hr).

^d Not determined.

^e Water:hydrazine mixture in 6:1 molar ratio.

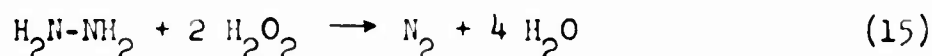
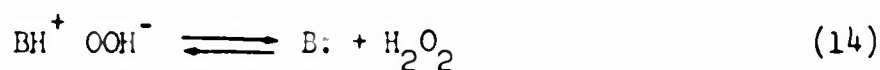
^f Relative molar percentages of products IVb, VIIIb, and IIb determined (v.p.c.). Tetrazene not measured.

The reaction mechanism confirmed (Ref. 26) for liquid-phase reactions probably is operative (on reaction vessel walls) in the vapor-phase autoxidation of I. Accordingly, diazenes dimerize, rearrange (reaction 10), and oxidize the rearrangement product IV (reaction 11). Reactions of I with formaldazine VI or from formaldehyde hydrazone VII (reactions 12 and 13) then occur to give the major product II.

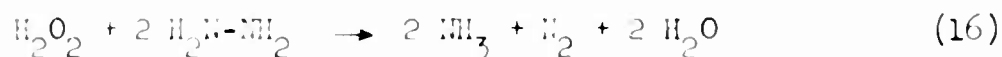


Tetramethyltetrazene (diazene dimerization product) is not observed as a product of gas-phase autoxidation of I. These reaction rates are so slow that the average concentration of diazene is low. Therefore, the unimolecular rearrangement (reaction 10) predominates over the bimolecular dimerization. In the more rapid autoxidations of 1,1-dialkylhydrazines in solution described above, tetrazenes are minor products (Table 1). Rearrangement reactions of the type proposed (reaction 10) were first observed (Ref. 31-32) in the autoxidation of N-benzyl-N-arylhydrazines with mercuric oxide to give benzaldehyde arylhydrazones. The same products are obtained when 1-benzyl-1-aryl-2-tosylhydrazides are heated with aqueous alkali (Ref. 33). Such rearrangements of 1,1-dialkylhydrazines and their derivatives have recently been studied (Ref. 26 and 34). The oxidation of IV by the diazene (reaction 11) has been demonstrated; and the reactions of hydrazines with hydrazones (reactions 12 and 13) are well known, and have been shown to be rapid (Ref. 26).

Reactions 5-13 would give stoichiometric Eq. 1 if hydrazine (product of reaction 13) were oxidized completely by the hydrogen peroxide produced in this reaction sequence on reaction vessel walls (b.p. of hydrogen peroxide 150°C and b.p. of hydrazine 114°C) to give only nitrogen and water (reaction 15).



However, the yield of nitrogen (based upon Eq. 1) in the vapor-phase oxidation of I is only 63%. Three reasons probably are responsible for this low yield. First, the reaction of hydrogen peroxide with hydrazine in basic aqueous solution has been shown to give ammonia as well as nitrogen, and water (Ref. 35-38); and ammonia has been observed as a product, in addition to nitrogen and hydrogen peroxide in the autooxidation of hydrazine in dilute, basic aqueous solutions (Ref. 39). To the extent that reaction 16 occurs, the nitrogen yield would be reduced.



Second, this reaction on the vessel walls is not complete since qualitative tests of condensates from these experiments show that they contained unreacted peroxides and hydrazines. Third, the hydrogen peroxide is partly consumed by reactions with I and II. Interpretation of the mechanisms of all autooxidations of hydrazines is complicated by the fact that the reaction with oxygen gives hydrogen peroxide (Ref. 39-40), and then subsequent oxidation of the hydrazines by the hydrogen peroxide occurs. Further, both reactions are catalyzed by traces of metal salts.

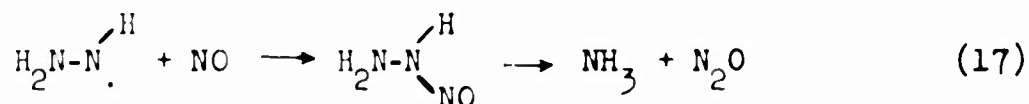
Accordingly, the reactions of hydrogen peroxide with I and II in deuterium oxide were studied with nuclear magnetic resonance (n.m.r.) spectrometry. Neutral solutions of 1,1-dimethylhydrazinium oxalate do not react with hydrogen peroxide. In contrast, the basic solutions of I or II react rapidly with this oxidizing agent. With I, dominant products are dimethylnitrosamine and II; while with II, dimethylamine, methylamine, ammonia, their formate and carbonate salts, and formaldehyde are produced. In such oxidations in water solutions containing both I and II, the former is consumed first (dimethylnitrosamine is formed, and the concentration of II increases). Only after most of the I has been oxidized do products of oxidation of II appear. These oxidation reactions seem to stop with I; II and excess hydrogen peroxide remain unreacted. However, when such reaction mixtures (pH 8 and 9) are made more basic by the addition of dimethylamine, rapid completion of the reaction occurs.

These results suggest reasons for curious features observed in the autooxidation of I. Dimethylamine and ammonia are formed only in the early stages of the reaction (Fig. 5). They are probably products of the hydrogen peroxide oxidation of II and hydrazine on the reaction vessel walls. Similar wall reactions of I probably give dimethylnitrosamine and some of the II formed. These reactions stop when carbonic and formic acids, also formed, partially neutralize the wall film. Then unreacted hydrazines and peroxide accumulate in the condensate. Gordon (Ref. 41) has shown that the reaction of hydrazine with hydrogen peroxide in dilute aqueous solutions is very slow when they are acidic or neutral (pH 1-7), its rate increases to a maximum at pH 10, and then it decreases in more strongly basic solutions. He suggested that the reaction occurs between hydrazine and hydrogen peroxide, but not between ions derived from them.

Since I is a stronger base than hydrazine, the reaction of hydrogen peroxide with I stops with less decline in basicity of the reaction mixture (to pH 9) than that of hydrazine (to pH 7).

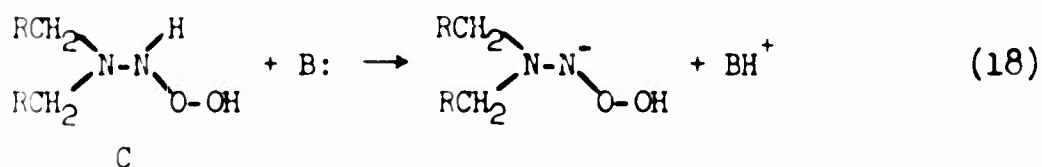
Diazomethane appears in the first part of the autoxidation of I, and then it disappears. Again, its early limited formation suggests that it results from a wall reaction of hydrogen peroxide with formaldehyde hydrazone VII or methylhydrazine that also ceases when the condensate is reduced in basicity. Its slow reaction with water, or hydrogen peroxide, probably is responsible for its disappearance. Reagents that remove water (BaO) preserve the diazomethane (cf. Fig. 2 and 3). Further, diazomethane has been shown to react slowly with alcohols to give methyl ethers (Ref. 42).

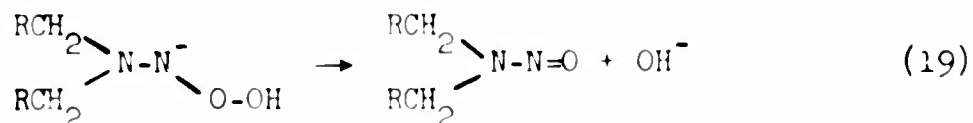
Nitrous oxide is another minor product in the autoxidation of I. Its yield is greatest when ammonia is added to the initial reaction mixture (Table 1, experiments 10, 11, and 15), and when more rapid autoxidation occurs (Table 1, experiments 6, 15, and 16). It is probably formed by the autoxidation of ammonia to give nitric oxide (Ref. 43) followed by its reaction with hydrazine or dimethylhydrazine. Bamford (Ref. 44) has postulated that unit reactions in photolysis of hydrazine in the presence of nitric oxide are



The vapor-phase autoxidation of I differs in two important ways from the reactions of other 1,1-dialkylhydrazines in the liquid (Table 2). First, only in the former case are dialkylamine, ammonia, and diazoalkane formed in the first part of the reaction. Second, in the former the dialkylnitrosamine is a trace product but in the latter case it is an important one. These effects may be attributed to the competing oxidations by hydrogen peroxide. It undergoes wall reactions with products (II and hydrazine) and intermediates to give dimethylamine, ammonia, and diazomethane in the gaseous autoxidation of I. These reactions cease when the wall film is reduced in basicity. On the other hand, liquid-phase reaction mixtures contain high concentrations of the 1,1-dialkylamines. Hence, they react with the hydrogen peroxide to give the dialkylnitrosamines VIIa, b and the aldehyde dialkylhydrazones IIa, b as major products.

The strongly basic reaction mixtures in the liquid phase autoxidations may also give a base-catalyzed decomposition of the hydrazine hydroperoxide C.





This mechanism is analogous to those suggested for the base-catalyzed reactions of primary and secondary hydroperoxides and peroxides (Ref. 45-47).

Kinetic studies of the vapor-phase autoxidation of I (Fig. 6, 8, and 9) show that it is of first order in I and independent of oxygen concentration both before and after the appearance of wall condensate. However, the reaction increases in rate after products begin to condense upon the reaction vessel walls. These observations suggest that this reaction has the same rate-determining sequence in both phases, but is much more rapid in the condensed phase. After condensation, the three experiments of Fig. 9 give the same rate constants for the consumption of I and formation of II (straight lines of the semilog plot are parallel). However, before liquid product appears on the walls, the first-order formation of II seems to be dependent upon the initial concentration of I. Slopes of these lines (Fig. 9) are approximately proportional to the initial pressure of I. These results suggest that in the "one-phase reaction" the rate is also proportional to product P formed.

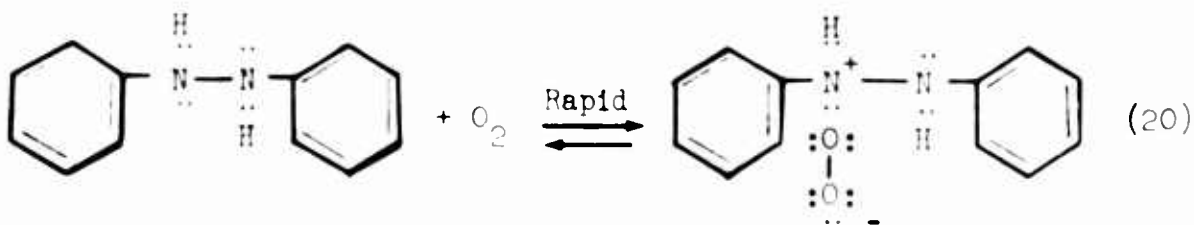
$$\frac{dP}{dt} = k [I] [P]$$

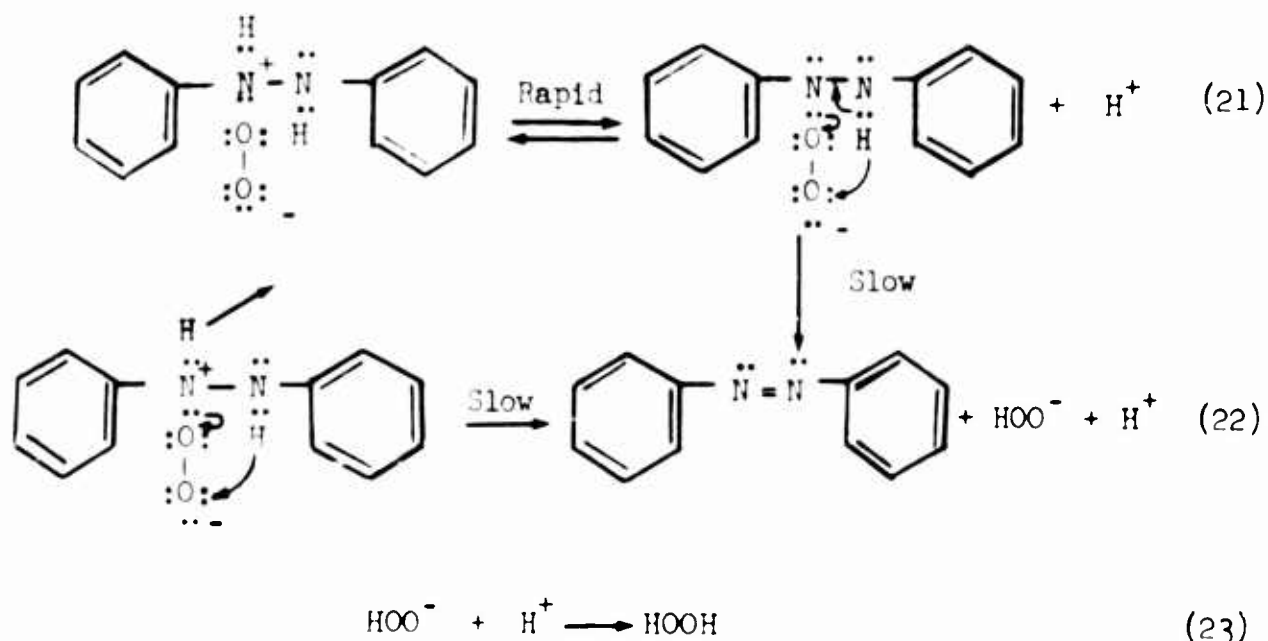
Since the early change of the concentration of I is small ($[I]$ assumed constant), integration gives (initial, $t = 0$)

$$\ln P = k [I] t.$$

Such a kinetic result is expected if products, such as hydrazine or formaldehyde hydrazone, undergo autoxidation much more easily than I to give higher concentrations of peroxides, resulting in more rapid initiation. The rate then becomes proportional to the concentration of product.

The autoxidations of hydrazines with at least one hydrogen atom on each nitrogen atom seem to occur by a different mechanism. The reaction of hydrazobenzene with oxygen studied in dimethyl formamide (Ref. 40) is of first order in each reactant (over-all second order). High negative entropies, general base catalysis, and marked substituent effects in substituted hydrazobenzenes were also observed. The following mechanism, that features a rigid, highly ordered transition state, was suggested.





Less comprehensive studies of the autoxidation of hydrazine in solution suggest that it is similarly second order (Ref. 39 and 43).

This difference of reaction mechanism--first order, free-radical chain reactions with 1,1-disubstituted, and probably trisubstituted hydrazines, and second-order multicenter reactions with hydrazine, 1,2-disubstituted, and possibly mono-substituted hydrazines--is clearly of fundamental importance. Further study is needed to substantiate this dichotomy, and to determine if these reactions are mutually exclusive or competing. The significance of these research questions is emphasized by indications that two similar mechanisms may operate in the reactions of hydrocarbons with oxygen. At moderate temperatures (to 200°C), the free-radical chain mechanism to give hydroperoxides as initial products has been established for the autoxidations of alkanes, alkenes, and alkylbenzenes. However, Knox has recently shown (Ref. 48) that in the reaction of propane with oxygen at higher temperatures (over 300°C) the dominant initial products are propene and hydrogen peroxide. This reaction may proceed via a multicenter mechanism similar to that suggested above for the hydrazobenzene autoxidation.

EXPERIMENTAL

Continuous Large-Scale Reaction of 1,1-Dimethylhydrazine (I) With Oxygen. I (30 ml, Westvaco, dried over sodium hydroxide pellets, and distilled through a 50-plate column packed with single-turned glass helices) was placed in a trap with a lead-in tube fitted with a sintered-glass bubbler. Oxygen (Airco, purified by passage through a liquid nitrogen trap) was slowly bubbled (3 ml per min) through the hydrazine.

Volatile products were carried by the excess oxygen through a spiral condenser (0.3 m, cooled to -15°C by ethylene glycol from an Aminco cold bath). Products were condensed from the gas stream in a trap cooled to -80°C . Permanent gases then flowed through a calcium chloride tube protecting the trap.

This reaction was continued (10 days) until the liquid condensed in the -80°C trap remained constant in amount. This bright yellow condensate was mixed with ether at -80°C and the solution was allowed to warm to room temperature. An ether solution of 3,5-dinitrobenzoic acid (recrystallized) was added to part of it. The yellow color disappeared, gas was evolved, and a white solid precipitated.

The latter was removed on a filter and was shown to contain dimethylammonium and ammonium 3,5-dinitrobenzoates. After three recrystallizations of part of this solid from ethanol, pure dimethylammonium 3,5-dinitrobenzoate (m.p. $188-190^{\circ}\text{C}$, mixture m.p. $188-190^{\circ}\text{C}$) was isolated. The remainder of the solid was added to sodium hydroxide solution (5%, 35 ml), and the resulting reaction mixture was distilled. The distillate (15 ml) was made acidic with hydrochloric acid, and the solution was evaporated. The moist mixture of hydrochloride salts was dried by repeated (three times) evaporations of anhydrous ethanol from it. The salt mixture was then extracted (five times) with ethanol. Ammonium chloride (X-ray powder pattern identical with known) remained.

The ether filtrate was washed with sodium bicarbonate solution, and was dried over anhydrous magnesium sulfate. Methyl 3,5-dinitrobenzoate (m.p. $106-108^{\circ}\text{C}$ from ethanol; mixture m.p. with authentic sample, $106.5-108^{\circ}\text{C}$; X-ray powder patterns identical) was obtained by evaporation of the ether solution. This product indicates that diazomethane is a component of the yellow ether solution, and hence it probably is responsible for the absorption in the infrared spectra (4.72 and $4.78\ \mu$) of gaseous reaction mixtures.

The liquid remaining in the gas bubbler tube was distilled under vacuum through a calcium chloride tube (80% of it so distilled). The infrared spectrum of this distillate was identical with that of authentic II. A polarographic study of this product confirmed its identity. In boric acid solution (0.5 molar), its half-wave potential was 1.12. Known II (b.p. $69-70^{\circ}\text{C}$), prepared by the reaction of I with formaldehyde, gave the same half-wave potential in a separate experiment. The solution containing known II, and that of unknown II, then were mixed, and the polarogram again gave a single wave ($E^{1/2}$, 1.12).

The dark liquid remaining from the distillation above was extracted with ether. The resulting yellow solution contained dimethylnitrosamine. Its visible spectrum (λ_{max} , 368, ϵ 120 in hexane) and behavior in v.p.c. (Perkin-Elmer Model 154, 42- by 1/4-in. column packed with 28.5% squalane-glycerin on neutral C-22 firebrick, isothermal 61°C , helium flow rate

77 ml/min, retention time, 13.35 min) were identical to those of authentic nitrosamine. The nitrosamine was similarly identified as a trace product in the yellow condensates obtained in gas-phase rate experiments described below. Its yield was not determined, but it was obviously low since the yields of other products (II and dimethylamine) account for nearly all of the I used.

Identification of Permanent Gaseous Products. A gas sampling bulb (1 liter) was filled with I (100 mm, Westvaco, purified by distillation from sodium hydroxide pellets; 1 peak with v.p.c.) and oxygen (600 mm). This reaction mixture was allowed to stand for 24 hr (room light and temperature). The gas then was washed with hydrochloric acid solution (500 ml, 5%), with water (500 ml), with sodium hydroxide solution (500 ml, 5%), and again with water. Oxygen was absorbed by washing it with Oxsorbent. The gas sample remaining was transferred under vacuum to a gas sample bulb, and it was analyzed with a Consolidated Engineering Mass Spectrometer (Model 21-103; ionizing current, 10.5 μ a; magnet current, 0.540 amp; ion source temperature, 250°C). It contained nitrogen (89.98%), methane (0.51%), carbon dioxide (0.23%), argon (4.29%, impurity in O₂ used), and water (4.9%).

In a second experiment, a gas reaction vessel (graduated, 650 ml) was filled on a vacuum line with I (96 mm) and oxygen (594 mm) to give an initial total pressure of 690 mm. This reaction mixture was allowed to stand at room temperature, and successive pressure readings were taken on a mercury manometer attached to the system. After 1 hr, the pressure in the vessel had increased to 702 mm, and after 2 hr, to 710 mm. Then, liquid condensate appeared on the walls of the reaction vessel, and the pressure fell. After 19 hr, the pressure was 656 mm.

Stopcocks on the bulb were then closed, and it was removed from the vacuum line. Its gas contents were washed with dilute sulfuric acid solution (5%) to leave a gas volume of 585 ml at 702 mm. The gas then was washed twice with water. Mass spectrometric analysis showed that it contained: oxygen, 96.25%; methane, 0.19%; nitrogen, 3.22%; carbon dioxide, 0.36%; and hydrogen, 0.03%. From the I used (75.7 ml S.C.), nitrogen (16.1 ml 63% yield according to Eq. 1), methane (0.95 ml), carbon dioxide (1.8 ml), and hydrogen (0.15 ml) were obtained.

A quartz infrared gas cell (150-ml capacity) was filled with I (100 mm) and oxygen (605 mm), with vacuum line apparatus equipped with a manometer and a storage vessel for I and for oxygen. The gaseous reaction mixture was irradiated (Hanovia lamp, filter removed) for 8 hr. An infrared spectrum of this reaction mixture indicated that the autoxidation of I was complete, and the doublet absorption peak due to N₂O was present. The gas in the cell was transferred to a gas buret, and was washed with 5% sulfuric acid solution, water, 5% sodium hydroxide solution, and again with water. Mass spectrometric analysis indicated that it contained oxygen (96.69%), nitrogen (2.85%), and nitrous oxide (0.46%).

The experiment was repeated with I (75 mm) and oxygen (630 mm) in the gas infrared cell. Mass spectrometric analysis after the same gas recovery procedure was: oxygen (98.06%), nitrogen (1.59%), and nitrous oxide (0.35%).

Maximum Diazomethane Yield. In most of the reactions followed with infrared procedures the doublet (4.72 and 4.78 μ) due to diazomethane increased for about 15 to 20 hr and then decreased (see Fig. 1-3). Since the maximum height of this peak frequently approached 50% transmission, diazomethane initially was considered to be a major primary product. Determinations of the diazomethane infrared spectrum at various pressures (Fig. 4) showed that its maximum amount (3.6 mm from 90-100 mm of I) is low.

Diazomethane was prepared by the reaction of Diazald (N-methyl-N-nitroso-p-toluenesulfonamide, 3 g) in anisole (17 ml) with a solution containing potassium hydroxide (25 g), water (30 ml), and 2-ethoxyethanol (120 ml). This reaction mixture was stirred vigorously with a magnetic stirrer, and nitrogen was bubbled through it. Diazomethane was swept with the nitrogen through a spiral condenser at -10°C , a U-tube packed with KOH pellets, and a -80°C trap. It was condensed in a trap cooled with liquid nitrogen.

The trap containing the solid diazomethane (at -196°C) was transferred to the vacuum line and was subjected to three freeze-pump-melt sequences. The diazomethane was then allowed to warm, and its vapor was conducted to an infrared vapor cell. Nitrogen was then added. Initial pressures in the cell were diazomethane (102 mm) and nitrogen (595 mm). Infrared spectrophotometer scans were taken at various pressures. The absorption of the diazomethane doublet was total when its pressure was above 20 mm. The pressure-transmittance data are shown in Fig. 4.

Reaction of 1,1-Dimethylhydrazine With Oxygen in the Presence of Butadiene-1,3. A gas infrared cell of the usual type was filled with butadiene-1,3 (51 mm), 1,1-dimethylhydrazine (43 mm), and oxygen (559 mm). This filling of the cell was interrupted to take an infrared spectrum of butadiene at the pressure given. Infrared spectra of the reaction mixture were then taken at various intervals. Little change was apparent after 19 hr; but after 92 hr the diazomethane doublet at 4.72 and 4.78 μ was apparent, and other features of the spectrum suggested that the autoxidation of the hydrazine had reached its half-life. However, no visible change had occurred in that portion of the spectrum due to butadiene-1,3. Apparently, the butadiene is not consumed, but it may decrease the rate of reaction by its chain-breaking action.

Rate Studies. In each of the first three experiments (data, Fig. 8), a 3-liter, spherical Pyrex reaction vessel with a single tube fused to it, equipped through a vacuum stopcock (silicone lubricant) with a standard-taper, ground-glass joint, was washed carefully (concentrated

nitric acid, three times; water, three times; 6N-ammonium hydroxide, three times; and distilled water, ten times). It then was attached to the vacuum line (pumps, cold traps, manifold with storage vessel for I, and attached to oxygen supply and manometers), and was flamed under vacuum. I (purified as previously described, one peak with v.p.c.) was added (experiment 1, 43 mm; experiment 2, 63 mm; and experiment 3, 78 mm), and then oxygen was introduced (experiment 1, 625 mm; experiment 2, 247 mm; and experiment 3, 287 mm). With the latter two experiments, nitrogen was also added (experiment 2, 390 mm; and experiment 3, 331 mm). Each reaction mixture was held at 25°C in a thermostatted room in room light.

Periodic analyses of the reaction mixture (Perkin-Elmer, Model 154, Vapor Fractometer with thermistor detector, a Leeds and Northrup 6-mv span, 1-sec response recorder--chart speed, 12.7 mm per min; isothermal, 61°C; 109-cm column packed with 28.5% of a mixture of squalane (84.7%), and glycerol (15.3%) on C-22, 20-60 mesh neutral firebrick; helium flow rate, 77 ml/min; and retention times: I, 9.6 min and II, 4.1 min) were made with v.p.c. Calibration experiments showed that the pressures (mm) of I and II were proportional to peak heights (with I, peak height in recorder units x attenuation setting x 0.169 = mm of I; and with II, peak height x attenuation x 0.130 = mm of II).

Samples for this analysis were taken with a Pyrex U-tube gas buret (volume between vacuum stopcocks, 4.31 ml) equipped with a standard-taper, ground-glass joint which fitted the reaction vessel. With the sampling device so attached to the reaction vessel, and, with its two stopcocks open, the volume up to the reaction vessel stopcock was evacuated to 0.01 mm (Hyvac oil pump) for 15 min. Then the outer stopcock of the buret was closed, and that of the reaction vessel was opened (1 min allowed for gas flow into sampling buret). Then, the stopcocks of the reaction vessel and the buret were closed, the buret was quickly transferred to an attachment to the inlet of the chromatograph, and a by-pass valve and the stopcocks of the buret were opened to sweep the sample into the fractometer with the helium stream. The time required for the last operation was held to 3 min. This regime was followed strictly to obtain reproducible results since changes in procedure gave errors due to the solubility of I and II in the silicone grease on the stopcocks.

In preliminary work, it was found that a stainless-steel gas buret could not be used. The metal surface so catalyzed the reaction that it was virtually complete when a mixture of I and oxygen in the device was allowed to stand for 30 min.

With experiment 4, the reaction vessel above was equipped with another tube closed by a rubber syringe cap held by a metal clamp. Its preliminary treatment was the same as before; and, with the previous procedure, it was filled with I (59.5 mm), oxygen (204.5 mm), helium

(428 mm), and benzene (73 mm). It was immersed in a dark oil bath held at 41°C, and light from a 100-w Mazda lamp (152.4 mm from flask) illuminated part of the reaction mixture through the neck of the reaction vessel.

Samples (4.0 ml) for analysis of the reaction mixture were taken with a Hamilton gas syringe with a sealed-on needle through the syringe cap. They were injected immediately into the sample port of the above chromatograph. The quantitative analysis (183-cm column packed with 9.45% Apiezon L on Fluoropak 80; isothermal, 50°C; helium flow rate, 41 ml/min; and retention times: I, 5.60 min; and II, 12.0 min) involved integration of peak areas (Perkin-Elmer, Model 194, Printing Integrator). Since flow of air, or reaction mixture, through the syringe needle occurred, sample size varied. Hence, benzene was used as a nonreactive internal standard. The data plotted (Fig. 10) are in arbitrary units, and quantities involved are fractions that are ratios (area of I peak/area of benzene peak; and area of II peak/area of benzene peak).

Peaks due to minor products (dimethylamine-retention time, 2.9 min) and water (retention time, 1.8 min) increased in area at rates proportional to the rate of formation of II during the reaction period prior to the appearance of condensate upon the vessel walls.

One observation illustrates the sensitivity of this reaction to accidental impurities. An experiment, prepared and carried out seemingly the same as the above, gave no reaction in 600 hr. Apparently, either a trace inhibitor was present, or necessary catalytic metal salts were essentially absent.

Autoxidation of Other Methyl Hydrazines. The reactions of all the other methylhydrazines were studied with the infrared method described above. In several experiments, various mixtures of methylhydrazine (24-80 mm) and oxygen (100-580 mm) were admitted to the infrared vapor cell. In all cases, rapid reaction with condensation of liquid products on the cell walls occurred. Damage to the sodium chloride windows made it impossible to determine the infrared spectrum of the product mixture. Accordingly, oxygen was bubbled for 15 days through methylhydrazine in the apparatus described for the large-scale autoxidations of I. Only a small amount of volatile reaction products condensed in the -80°C trap. The infrared spectrum of this mixture of volatile products, with its analysis (methylazide, ammonia, and methylamine) is shown in Fig. 12. A rough estimate of relative amounts in this infrared gas sample is: methyl azide, 3 mm; ammonia, 45 mm; and methylamine, 40 mm. These amounts probably result from the relative volatilities: methyl azide, b.p. 20°C, ammonia, b.p. -33°C, and methylamine, b.p. -6°C. The vapor infrared cell was filled by freezing the condensate, the trap and the attached infrared cell were evacuated, and then the condensate was allowed to warm until the pressure in the system was 90 mm. Nitrogen was then added until a pressure of 705 mm was attained.

The products above are minor ones (little condensate was obtained). The liquid remaining in the reaction vessel was nearly the same in volume as that of the methylhydrazine initially added. The initial rapid reaction seems to produce an inhibitor since even after the 15 days of treatment with oxygen, much methylhydrazine remained in the reaction mixture (KIO_3 test positive; oxalate of methylhydrazine, m.p. $167-168^\circ\text{C}$, obtained from it). After oxygen had been bubbled through for another 7 days (total 22 days), the liquid in the reaction vessel was dried over sodium hydroxide pellets, and was then distilled. The infrared spectrum of the distillate was identical with that of methylhydrazine except for minor superimposed peaks due to ammonia.

The autoxidation of 1,2-dimethylhydrazine, however, was rapid and complete. An infrared cell was filled with this hydrazine (46 mm) and oxygen (668 mm), and the infrared spectrum taken after 15 min showed that much reaction had occurred. After 1 hr of reaction time, the infrared spectrum was that of a mixture of azomethane and water (see Fig. 10).

With trimethylhydrazine, the autoxidation rate seemed to be intermediate between that of 1,2-dimethylhydrazine (very rapid) and that of I. In an experiment with trimethylhydrazine (30 mm) and oxygen (685 mm) in the infrared cell, the reaction half-life (estimated from growth of peak at 6.29μ due to II) was approximately 18 hr; and reaction was complete after 90 hr to give only II and water. With trimethylhydrazine (50 mm) and oxygen (655 mm), a half-life of 3 hr was observed (see Fig. 11).

Tetramethylhydrazine does not undergo autoxidation under these conditions. The infrared spectrum of a mixture of this hydrazine (70 mm) and oxygen (635 mm) was unchanged after 170 hr at 25°C (see Fig. 13).

Reactions of 1,1-Dimethylhydrazine (I) and Formaldehyde Dimethylhydrazine (II) With Hydrogen Peroxide. When an aqueous solution of II is treated with hydrogen peroxide (30% in water), a vigorous exothermic reaction occurs with evolution of gas. This reaction and its water-soluble products were studied with n.m.r. spectrometry. A solution of II in deuterium oxide (^1H n.m.r. with DDS: N-CH_3 peak at 2.738; and methylene AB quadruplet at 6.408, J 9.5 cps, area ratio, 3:1) was treated with hydrogen peroxide (30%, Baker and Adamson). After 30 min, the n.m.r. spectrum of the reaction mixture showed that II had been consumed (above methylene quadruplet had vanished). A small peak due to formate (8.248), and many other peaks in the 2.6-3.058 region (N-methyls), had appeared.

Tentative n.m.r. analysis of this reaction mixture (addition of authentic samples of probable products, and observed peak enhancement) showed that a small amount of unreacted II (2.738) remained and methylamine (2.618), dimethylamine (2.888), I (3.058), formate (8.248), and other products not so identified are formed. Ammonium hydroxide is not visible (exchanges rapidly--part of DOH peak) in these experiments.

Carbonates were also formed since carbon dioxide was evolved when the reaction mixture was made acidic. The complexity of the reaction products is probably due to the formation of various products of reaction of the amines and hydrazine with carbon dioxide, formic acid, and formaldehyde (probably also present). In accordance with this interpretation, n.m.r. peaks for the methylamines are at the higher δ values of their salts.

To identify basic products, II (6.29 g, 0.087 mole) in water (25 ml, apparatus swept with N_2) was treated with aqueous hydrogen peroxide solution (30%, 20.42 g, 0.18 mole). The reaction mixture became yellow (λ_{max} . 325 m μ with a shoulder at 280 m μ indicates dimethylnitrosamine and tetramethyltetrazene), and gas was evolved (150 ml). Mass spectrometric analysis indicated: nitrogen (sweep gas, 94.7%), carbon dioxide (2.3%), hydrogen (2.4%), methane (0.36%), and oxygen (0.22%). Sodium hydroxide solution (5%, 250 ml) was added to the reaction mixture, and it was distilled. The basic distillate (200 ml) was treated with stirring with phenylisothiocyanate until the odor of the latter persisted. A solid mixture of phenylthioureas (7.6 g) precipitated. It was removed on a filter, and dried overnight in a desiccator. Analysis by n.m.r. showed that it contained phenylthiourea (46 mole %). 1H n.m.r. in CCl_3 with TMS: phenyl multiplet at 7.30 δ), 1,1-dimethyl-3-phenyl-2-thiourea (36 mole %). 1H n.m.r.: 6H methyl singlet at 3.20 δ , and 5H phenyl singlet at 7.20 δ), 1-methyl-3-phenyl-2-thiourea (15 mole %). 1H n.m.r.: 3H methyl doublet at 3.07 δ , J 5 cps, and 5H phenyl multiplet at 7.33 δ), and 1,1-dimethyl-4-phenyl-3-thiosemicarbazide (3 mole %). 1H n.m.r.: 6H methyl singlet at 2.58 δ ; and 5H phenyl multiplet at 7.25 δ). These n.m.r. spectra were identical with those of the known substances. A small amount of phenylthiourea (m.p. 152-154°C; mixture m.p. 153-154°C) did not dissolve in the deuteriochloroform.

Further qualitative n.m.r. studies showed that no reaction occurred in 100 hr with a solution of 1,1-dimethylhydrazinium oxalate and hydrogen peroxide in deuterium oxide (n.m.r. spectrum unchanged). This lack of reaction in neutral solution is striking since I reacts vigorously with hydrogen peroxide in water. A study of this latter reaction mixture showed that it contained dimethylnitrosamine (55 mole %). 1H n.m.r. with DDG: equal singlets at 3.17 and 3.81 δ). Peaks enhanced upon addition of authentic dimethylnitrosamine. Yellow color of solution, λ_{max} . 325 m μ . Solution of dimethylnitrosamine in H_2O containing I, λ_{max} . 328 m μ , and II (39 mole %). 1H n.m.r.: methyl singlet at 2.75 δ , methylene quadruplet at 6.42 δ). Trace peaks not identified were also present. With more hydrogen peroxide, the II is consumed.

Hydrogen peroxide (30% in H_2O) was added slowly to a solution containing equimolar amounts of I and II in deuterium oxide. The n.m.r. spectra taken at successive times during the addition showed that I was oxidized first (peaks due to II and dimethylnitrosamine increased but that due to I decreased). Appreciable oxidation of II occurred only when the I was completely consumed. The oxidation of II then ceased

(pH of reaction mixture, 8) even when excess hydrogen peroxide was added. When this reaction mixture was made more basic by the addition of dimethylamine, vigorous oxidation occurred and II was consumed.

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13. ABSTRACT The autoxidation of 1,1-dimethylhydrazine I gives formaldehyde dimethylhydrazone II, nitrogen, and water as its major products. Minor ones are ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde. This reaction is of first order in I and of zero order in oxygen. It is catalyzed by metals and metal salts, inhibited by added 1,3-butadiene, and accelerated by ultraviolet light. A free-radical chain mechanism is postulated as the rate-determining reaction sequence. The 1,1-dimethylhydrazyl-2-hydroperoxide so formed is presumed to give the products II, hydrazine, and hydrogen peroxide via a rapid sequence of wall reactions (established in the study of liquid-phase autoxidations of 1,1-dialkylhydrazines). Nitrogen and most minor products probably result from further wall reactions of hydrogen peroxide with I, II, and hydrazine. Autoxidations of hydrazines resemble those of hydrocarbons.			

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