

TABLE II
BULK POLYMERIZATION OF STYRENE^a

Temp., °C.	Catalyst Concn., Molar	Polymer Obtained, Grams	
		Benzoyl peroxide	Com- pound ^b
41	0	0.011	0.011
	2×10^{-4}	0.023	0.070
	2×10^{-3}	0.069	0.195
61	2×10^{-2}	0.214	0.493
	0	0.058	0.058
	2×10^{-4}	0.180	0.384
82	2×10^{-3}	0.486	1.067
	2×10^{-2}	1.574	2.820
	0	0.522	0.522
	2×10^{-4}	1.385	1.216
	2×10^{-3}	2.581	2.263
	2×10^{-2}	Solid	3.900

^a Nine g. of freshly distilled styrene heated in the dark under nitrogen for 6 hr. ^b The compound is *tert*-butyl *N,N*-pentamethyleneperoxycarbamate.

hydrochloric acid to a phenolphthalein end point and found to contain 0.01 equivalent of base. The polymer, 32 g., was brittle and possessed the following properties: molecular weight by boiling point elevation of benzene, 2360; nitrogen by Dumas' method, 0.9%; nitrogen by titrating the amino groups with perchloric acid in benzene, 0.73%. The former value for the nitrogen content calculates to 1.5 amino groups per molecule, assuming that 2360 is the molecular weight of the polymer.

Since it was possible that amino-containing impurities had been occluded in the polystyrene, 12 g. of the polymer was dissolved in benzene and reprecipitated with methanol and this process was repeated three times in all. The final dry polymer weighed 5.6 g. and contained 0.85% nitrogen by Dumas method, indicating that the polymer molecules contained amino groups as substituents.

The polystyrene prepared under the same conditions without the initiator did not contain nitrogen.

Vigorous reactions. The following mixtures gave violent reactions: 1.8 g. ethyl isocyanate, 2.78 g. perbenzoic acid, 50 ml. benzene, and 4 drops triethylamine when most of the solvent had been removed under reduced pressure; 3.15 g. toluene-2,4-diisocyanate, 3.0 g. 60% *tert*-butyl hydroperoxide and 10 ml. benzene after standing at room temperature for 2 hr. Isolated products which spontaneously decomposed very rapidly at room temperature were obtained from the following reactions: 0.7 g. *p*-nitrophenyl isocyanate, 0.6 g. perbenzoic acid, 15 ml. benzene, and 1 drop triethylamine; 3.2 g. *p*-nitrophenyl isocyanate, 4.2 g. 72% α -cumyl hydroperoxide, 500 ml. petroleum ether, and 3 drops triethylamine. These mishaps did not cause any bodily harm because adequate protective measures had been taken ahead of time.

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WILMINGTON, DEL.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND COMPANY, INC. ORGANIC CHEMICALS AND ELASTOMER CHEMICALS DEPARTMENTS, RESEARCH DIVISIONS]

Thermal Decomposition of Crystalline *tert*-Butyl *N*-Methyl-*N*-(*p*-nitrophenyl)peroxycarbamate

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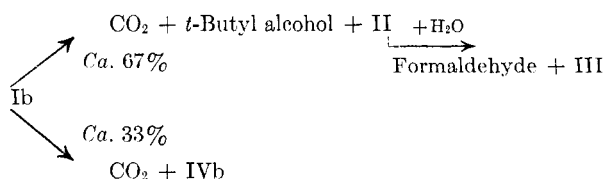
The decomposition of crystalline *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate at 30° proceeds by two different mechanisms: about 67% by an intramolecular concerted reaction giving carbon dioxide, *N*-methylene-*p*-nitroaniline, and *tert*-butyl alcohol; and the remainder by a homolytic scission followed by partial recombination of free radicals to give carbon dioxide and *O*-(*tert*-butyl) *N*-(*p*-nitrophenyl)hydroxylamine. The *N*-methylene-*p*-nitroaniline is rapidly converted to formaldehyde and *N,N'*-methylenebis(*p*-nitroaniline) by the moisture in the atmosphere.

This behavior is contrasted to that of crystalline *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate. The action of these compounds in aromatic solvents and styrene is briefly discussed.

During an investigation of the properties of the esters of *N*-substituted peroxycarbamic acids,¹ *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate, Figure 1, (Ia), and *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate, (Ib), were synthesized. Stability tests on the crystalline compounds stored in the open air at room temperature showed that Ia is rather stable, but Ib decomposes quietly and nearly completely to a yellow crystalline residue in about four days.

Identification of the products indicates that the

decomposition of crystalline Ib at 30° may be represented as follows:



Every product was definitely identified except II, but its transient existence was suggested by the infrared spectrum (C=N band present) of the residue obtained by decomposing Ib in the absence of

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(1) C. J. Pedersen, *J. Org. Chem.*, **23**, 253 (1958).

TABLE I
 THERMAL STABILITY OF PEROXYCARBAMATES

Compound	State	Stability
Ia	Crystalline	Rough estimate of half-life: 600 days at room temperature. ^a
Ib	Cumene solution ^b	Decomposes at 50–80° to produce (VIa) free radicals in high yield.
	Crystalline	Decomposes at 30° by two different mechanisms. Approximate half-life: 2 days at 30°.
	Cumene solution ^b	Decomposes at 50° to produce (VIb) free radicals in high yield.
$(\text{CH}_3)_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$	Liquid	Approximate half-life: 65 days at room temperature. ^a
$\text{C}_2\text{H}_5-\overset{\text{H}}{\underset{\text{O}}{\parallel}}{\text{N}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$	Crystalline	Rough estimate of half-life: 800 days at room temperature. ^a

^a 24–28°. ^b At 0.03 to 0.04 molar concentration.

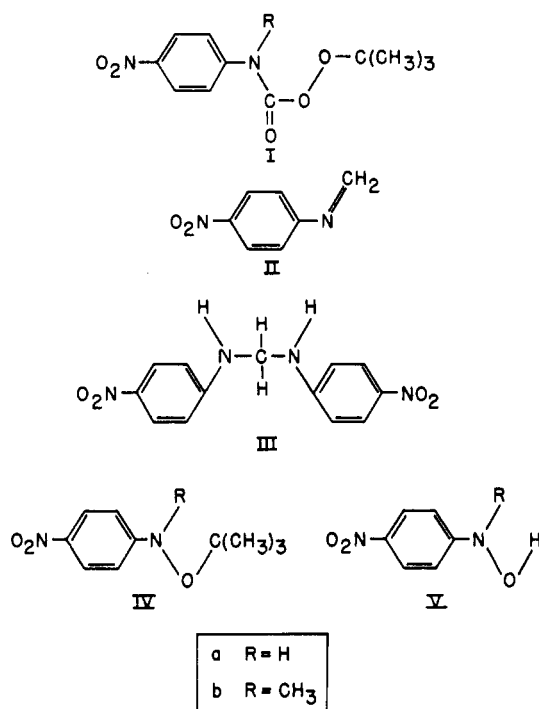
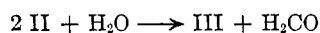


FIG. 1. STRUCTURES OF COMPOUNDS.

moisture. *N,N'*-Methylenebis(*p*-nitroaniline), (III) is formed by the following reaction:



No formaldehyde is released while Ib is decomposing in the absence of moisture.

In cumene solutions at 50–80°, however, both Ia and Ib decompose by homolytic scission as indicated by the formation in high yields of carbon dioxide and *p*-nitroaniline, (VIIa), and carbon dioxide and *N*-methyl-*p*-nitroaniline, (VIIb), respectively. These facts and some data from prior work¹ are summarized in Table I. The listed peroxy carbamates were obtained in high purity by crystallization or by distillation under reduced pressure.

Discussion. A satisfactory mechanism for the thermal decomposition of crystalline Ib will have to account for the facts given in Table I.

It seems likely that the decomposition of Ia and

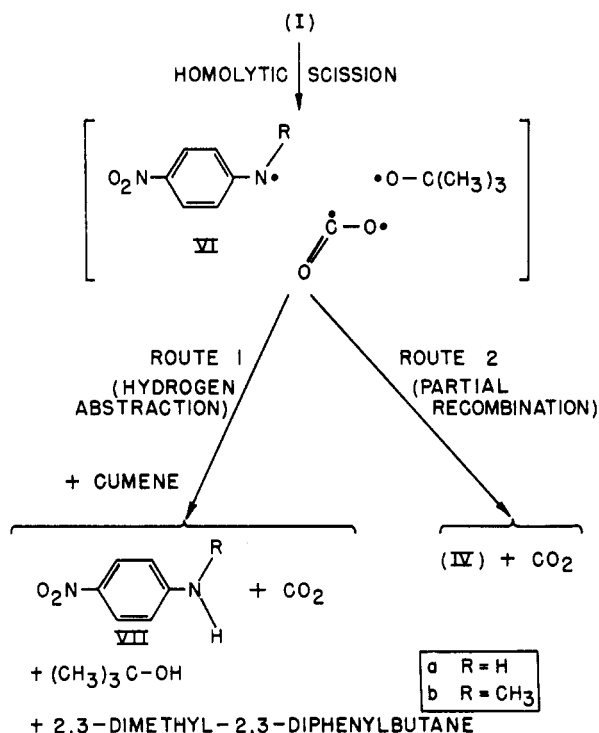


FIG. 2. FREE RADICAL DECOMPOSITION OF PEROXYCARBAMATES.

Ib in cumene solutions at 50–80° proceeds as shown in Figure 2, Route 1, the relatively weak O—O bond breaking first. The reactions in Route 2 occur to some extent as side-reactions and, in the case of Ib, a small amount of III is also formed (possibly from the crystals of Ib while they are dissolving). The expected products, except tertiary butyl alcohol, were isolated and identified. The fate of the *tert*-butoxy free radicals was not determined in these experiments, but they are presumed to have reacted with cumene to give tertiary butyl alcohol and 2,3-dimethyl-2,3-diphenylbutane. At least, no significant quantity of acetone was formed to suggest that the *tert*-butoxy radicals had decomposed into the ketone and methyl free radicals.

If the breaking of the O—O bond is the mainspring for the thermal decomposition of crystalline per-

oxycarbamates, there is no reason to conclude from structural considerations that Ia and Ib would differ greatly in stability. Since, however, the stability of these compounds is so widely different, some reaction besides homolytic scission must intervene in the crystals of Ib to render it so much less stable than crystalline Ia.

It is proposed that the cause of the decreased stability of Ib is the occurrence of an intramolecular concerted reaction resulting in the production of three stable² compounds as shown in Figure 3.

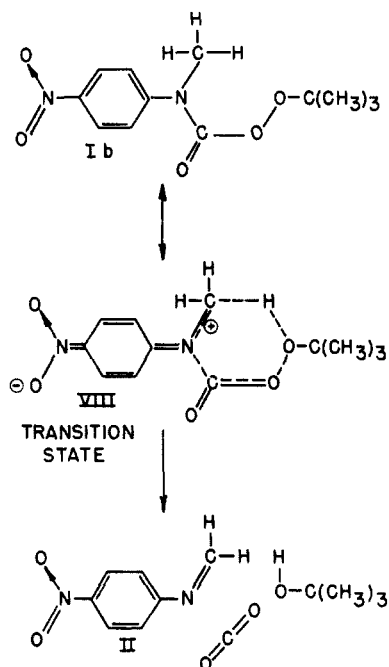


FIG. 3. DECOMPOSITION OF CRYSTALLINE Ib BY A CONCERTED REACTION.

This reaction is favored by three conditions: (a) the formation of "quasi six-membered ring;"^{4,5} (b) the maintenance of this favorable configuration in the crystal; and (c) the relatively high electronegativity of the nitrogen atom linked to the methyl group because of its attachment to the *p*-nitrophenyl group. These conditions facilitate the attainment of the transition state and subsequent

(2) *N*-Methylene-*p*-nitroaniline is not reported in the literature. In spite of this it is called a stable compound because its apparent nonexistence must be due to its extreme reactivity in regard to hydrolysis and polymerization, and not to thermodynamic instability. It is likely that *tert*-butyl *N*-benzyl-*N*-(*p*-nitrophenyl)peroxycarbamate would react like Ib and yield *N*-benzylidene-*p*-nitroaniline instead of II. Since *N*-benzylidene-*p*-nitroaniline is an isolable compound,⁸ its formation would have provided direct evidence for the reaction mechanism proposed above. The preparation of the desired peroxycarbamate was prevented by the refusal of *N*-benzyl-*p*-nitroaniline to react with phosgene to give the carbamoyl chloride required for its synthesis.

(3) W. v. Miller, J. Plöchl, *et al.*, *Ber.*, **25**, 2020 (1892).

(4) R. T. Arnold and W. W. Lee, *J. Am. Chem. Soc.*, **75**, 5396 (1953).

(5) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950).

reaction in which the breaking of the O—O bond and the C—H bond of the methyl group, the binding of the hydrogen to the oxygen of the *tert*-butoxy group, and the elimination of carbon dioxide proceed simultaneously. Note that independent ions or free radicals are not formed during this process.

The stability of *tert*-butyl *N,N*-dimethylperoxycarbamate at room temperature (Table I) is probably due to the higher electron density on the nitrogen atom attached to two methyl groups, and to its liquid state in which the configuration favorable for the concerted reaction is less readily attained and maintained.⁶

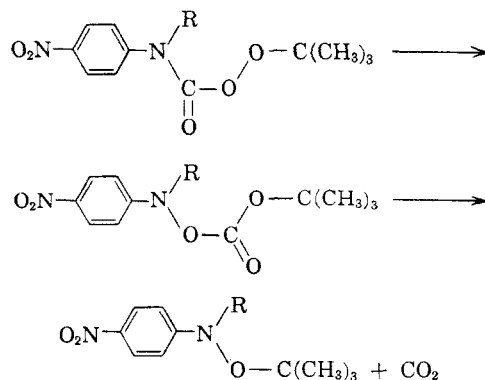
The concerted reaction discussed above must be exothermic, and possibly it is the heat generated by it that causes roughly one third of the molecules of Ib in the crystal to decompose by a free radical mechanism and proceed according to Figure 2, Route 2. The nearly quantitative yield of IVb is attributable to: (a) the production of *tert*-butoxy radicals of low energy content with a reduced tendency to decompose into acetone and methyl radicals; and (b) the super-"cage-effect"⁷ of the crystal lattice which compels the combination of *tert*-butoxy and VIb radicals to form IVb. The *tert*-butoxy radicals, and also VIb, are of low energy content because the heat supplied for their production is delicately regulated by the balance between the heat given off by the spontaneous, exothermic, concerted reaction, and the heat taken up to initiate the induced, endothermic, free radical reaction.⁸

The contrasting stability of Ia must depend on something besides its physical state, since it is also crystalline. It is apparent from Figure 4 that only a five-membered ring can be formed in this case and

(6) In order to test the first point without involving the second, an attempt was made to prepare *tert*-butyl *N*-methyl-*N*-(*p*-tolyl)peroxycarbamate which should be a solid, but without success.

(7) J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(8) A referee has suggested an alternative mechanism for the production of (IV) in high yield. It involves the carboxy inversion of the peroxy compound,⁹ followed by the elimination of carbon dioxide from the carbonic ester-anhydride.¹⁰



(9) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950).

(10) R. Boschan, Abstr. Papers, ACS Meeting, September 1956, p. 10-O.

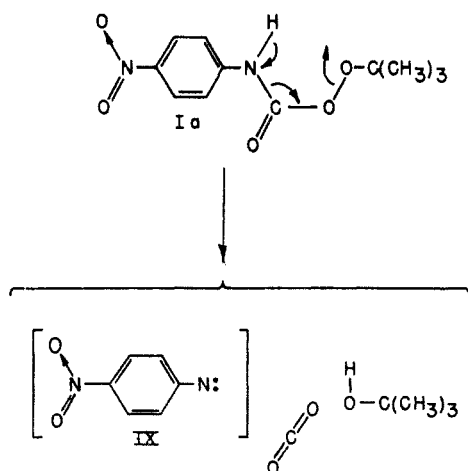


FIG. 4. HYPOTHETICAL REACTION FOR THE DECOMPOSITION OF CRYSTALLINE Ia.

not the six-membered ring which is favorable for the concerted reaction. Moreover, even if the reaction were to proceed, one of the products is IX which cannot be considered a stable entity. It might be suggested that two IX's could combine to form *p,p'*-dinitroazobenzene, but this compound was never found among the Ia decomposition products obtained under any condition.

There is another possibility, however, the formation within Ia crystal of intermolecular hydrogen-bonds between the hydrogen atom linked to the nitrogen and the oxygen atom of the carbonyl group. Such an arrangement will not only tend to prevent the occurrence of an intramolecular concerted reaction, but it would not weaken the O—O bond since these oxygen atoms are not involved in the hydrogen bond. This type of hydrogen-bonding might be thought to resemble that existing in amides or dimers of carboxylic acids.

It will be noted (Table I) that the two *N*-mono-substituted peroxy-carbamates, even the one having the electron-releasing ethyl group, are much more stable than the *N,N*-dimethyl derivative. This probably indicates that hydrogen-bonding is an important factor contributing to the stability of the *N*-monosubstituted compounds.

It has been stated that the intramolecular, concerted reaction does not yield free radicals, hence, that portion of Ib decomposing by this mechanism should be incapable of initiating radical polymerization. If Ib behaved similarly in solution as in the crystalline state, the occurrence of the concerted reaction would be revealed by its low effectiveness as an initiator of polymerization at relatively low temperatures, and by the formation of III. Data from experiments on the bulk polymerization of styrene are shown in Table II. At the end of 211 hours at 30° the freshly distilled styrene containing no initiator was 1.3% polymerized; that containing Ia was 61% polymerized (molecular weight about 9,000);

TABLE II
BULK POLYMERIZATION OF STYRENE^a

No.	Condition	Polymer Formed:		
		g. per 10-ml. sample		
		Control (Ia) ^b	(Ib) ^b	(Ib) ^b
1	Original samples	Nil	Nil	Nil
2	After 66 hr. at 30°	0.025	0.755	4.200
3	After 66 hr. at 30° followed by 24 hr. at 50°	0.110	4.510	4.660
4	After 211 hr. at 30°	0.114	5.500	4.610
5	After 211 hr. at 30° followed by 20 hr. at 80°	1.130	5.590	4.630

^a Heated under nitrogen in the dark. ^b Concentration of additive: 0.02 mole per liter.

and that containing Ib was 51% polymerized (molecular weight about 4,500).

Three interesting points issue from all these facts: (a) that Ib is an effective initiator and does not undergo the concerted reaction in styrene solution (confirmed by the absence of the insoluble III in the system); (b) that Ia decomposes much faster in styrene solution than would be expected (from the relative stability of the crystalline compounds and cumene solution) to initiate polymerization at 30°; and (c) that both compounds decompose in styrene mainly by a free radical mechanism which appears to be autocatalyzed (the polymer radical induces the decomposition of a molecule of initiator and generates a single free radical to start another polymer chain).

At any rate, both Ia and Ib behave differently when dissolved in styrene than when in the crystalline state. The more random orientation of the molecules in solution: (a) hinders the formation of the hydrogen bonds which stabilize Ia; and suppresses the concerted reaction of Ib by making the attainment of the favorable configuration less likely. Hence, the decomposition of Ib by a combination of the mechanisms represented in Figure 2, Route 2, and Figure 3 is conditioned on its crystalline state and is an example of a topochemical reaction.¹¹

EXPERIMENTAL

Decomposition of crystalline Ib in the absence of moisture. The material balance for the decomposition of crystalline Ib in a representative experiment is shown in Table III, and the corresponding experimental procedure is described below. Analytical results and other data concerning authentic compounds and recovered decomposition products are given in Table IV, nitrogen contents and melting points; Table V, ultraviolet absorption peaks; Table VI, infrared absorption bands; and Table VII, x-ray diffraction angles.

Crystalline *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxy-carbamate, (Ib), was placed in a vacuum-tight glass system (343 ml. free-space) in a constant temperature bath at 30°. The container was protected from light, evacuated, closed off from the atmosphere at 0.1 mm., and the rate of gas evolution was measured during the following 7 days by

(11) W. Feitknecht, *Fortschr. Chem., Physik. u. physik. Chem.*, 19, No. 2, 56 (1930).

TABLE III

MATERIAL BALANCE FOR THE DECOMPOSITION OF CRYSTALLINE Ib AT 30° IN THE ABSENCE OF MOISTURE

Products	Weight, g.	Mole $\times 10^3$	Yield, % ^a	Remarks
Original (Ib)	2.000	7.46	...	Vol. of sample, 18 ml.
Carbon dioxide	0.297	6.74	90	Identified by mass spec. and x-ray pattern of resulting barium carbonate.
Tertiary butyl alcohol	0.343	4.64	62	Identified by mass spec.
Isobutylene ^b	0.0013	0.022	0.3	Identified by mass spec.
Residue after high evacuation	1.277	...	64 ^c	Vol. of residue, 2 ml. ^d 5.98- μ band present in the infra-red spectrum. No peroxide value.
Recovered from the residue after exposure to moisture for 3 days.				
Formaldehyde	Identified by smell and alkaline resorcinol test. ^e
III (Benzene insoluble)	0.719	2.50	33.5	Identified by analysis, melting point and x-ray diffraction.
IVb (Benzene soluble)	0.546	2.44	32.7	Structure established by analysis, physical properties, and conversion to Vb with concentrated sulfuric acid.

^a 100 (mole of product)/[mole of (Ib)]. ^b This compound must have been produced by either dehydration of tertiary butyl alcohol or dehydroxylation of tertiary butoxy group, possibly during the main reaction. ^c 100 (weight of residue)/[weight of (Ib)]. ^d When a similar experiment was run under nitrogen at 50% relative humidity, the volume of the residue was 20.4 ml. although the yields of (III) and (IVb) remained nearly the same. Formaldehyde was formed during this experiment. ^e Ref. 12.

TABLE IV

NITROGEN CONTENTS AND MELTING POINTS^a OF COMPOUNDS

Compound	Isolated Decomposition Product		Authentic Sample		
	M.P., °C.	% N, Found	% N, Calcd.	% N, Found	M.P., °C.
Ia	11.0	10.9	93 ^{b,c}
Ib	10.5	10.6	64-5 ^{b,c}
<i>p</i> -Nitroaniline (VIIa)	147	...	20.3	20.5	147
<i>N</i> -Methyl- <i>p</i> -nitroaniline (VIIb)	151-2	...	18.4	18.6	151-2
III	230-2	19.6	19.5	19.7	230-2
IVb	138-40	12.6	12.5
<i>N</i> -(<i>p</i> -Nitrophenyl)hydroxylamine (Va)	18.2	18.2	107 ^{b,d}
2-Hydroxy-4-nitroaniline	18.2	18.1	201-2 ^e

^a Determined on a bronze block and are uncorrected. ^b Melting with decomposition. ^c Ref. (1). ^d Ref. (13). ^e Ref. (14).

TABLE V

SPECTRAL ABSORPTION MAXIMA OF COMPOUNDS

Compound	Decomposition Product		Authentic Sample	
	$m\mu^a$	ϵ^b	$m\mu^a$	ϵ^b
Ia ^c	292	13,000
Ib ^c	295	12,000
<i>p</i> -Nitroaniline (VIIa)	370	14,000	368	16,000
<i>N</i> -Methyl- <i>p</i> -nitroaniline (VIIb)	382	18,000	381	18,000
III	380	66,000
IVb	352	12,000
<i>N</i> -(<i>p</i> -Nitrophenyl)hydroxylamine (Va)	356	12,000
IVa ^d	348	10,000
2-Hydroxy-4-nitroaniline	390	13,000

^a Absorption peaks in methanol (unless otherwise noted) with a Cary Model 11 recording spectrophotometer. ^b Extinction coefficients. ^c In iso-octane instead of methanol. ^d Not pure.

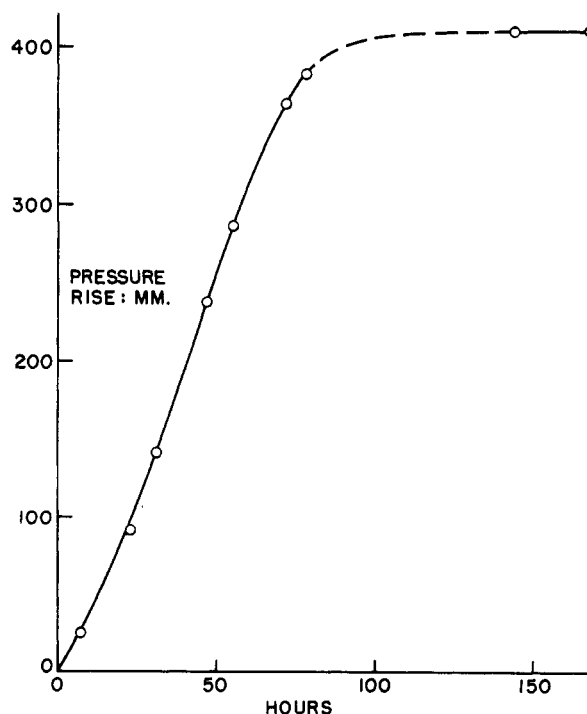


FIG. 5. EVOLUTION OF GAS FROM *t*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate (Ib).

TABLE VI
 INFRARED ABSORPTION BANDS OF COMPOUNDS AND PRODUCTS^a

Compound	Absorption Band in Microns			
	O—H	N—H	C=O	C=N
$(\text{CH}_3)_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$	5.73	...
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{C}_2\text{H}_5\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3 \end{array}$...	3.01	5.78	...
Ia	...	2.99	5.75	...
Ib	5.75	...
Dry residue from Ib ^b	...	3.00	5.73	5.98
Moist residue from Ib ^c	...	3.00	5.73	...
IVb	2.99 ^d
Vb from IVb with sulfuric acid	3.01
<i>N</i> -(<i>p</i> -Nitrophenyl)hydroxylamine (Va)	2.96	3.04
III	...	3.03
2-Hydroxy-4-nitroaniline	2.96	3.00

^a Absorption bands in smear of Nujol mull with a Perkin-Elmer Model 21 spectrophotometer. The well known bands for alkyl, aromatic, and nitro groups, as well as many ambiguous bands have been omitted. ^b This was the residue obtained by decomposing crystalline (Ib) in the absence of moisture and pumping off to constant weight. The band at 6 μ indicates the presence of the C=N bond. No other sample had this band. Even with careful handling moisture caused the formation of some (III) as shown by a weak band at 3 μ . According to iodometric analysis (Ib) had been completely decomposed, but a weak band at 5.73 μ persisted. The compound responsible for this band was not identified. ^c This was the residue obtained by decomposing crystalline (Ib) in the presence of moisture and pumping off to constant weight. The 6- μ band was no longer present, the 3- μ band was stronger and the 5.73- μ band was weaker than for the dry residue. ^d This band was very weak and is thought to be due to the presence of a small amount of either (III) or (Vb) as an impurity.

 TABLE VII
 X-RAY DIFFRACTION PATTERNS OF COMPOUNDS

Compound	Bragg Angle ^a	Relative Intensity ^b
Ib	5.8	100
	11.7	46
	25.5	34
III	14.0	100
	19.3	55
	16.0	40
IVb	20.4	100
	21.3	83
	23.8	83

^a With a Norelco Wide Range diffractometer using Cu K α radiation. ^b Three strongest.

periodically observing the internal pressure by means of a manometer. The resulting data are plotted in Figure 5. The composition of the evolved gases (185 ml. at 30° and 760 mm.) was determined with a mass spectrograph and found to consist of (in mole %): carbon dioxide, 90.8; *tert*-butyl alcohol, 8.9; and isobutylene, 0.3. No trace of methane, ethane, formaldehyde, or acetone was found in the gas mixture. It is assumed that all the carbon dioxide was in the gas mixture but that much of the *tert*-butyl alcohol was retained in the greasy-looking residue which smelled of the alcohol. The quantity of *tert*-butyl alcohol given in Table III was arrived at by adding the amount in the gas mixture (0.049 g.) to the weight lost by the residue under high evacuation to constant weight. The final residue no longer had the odor of *tert*-butyl alcohol. It is likely, however, that some carbon dioxide was dissolved in the residue, and some *tert*-butyl alcohol was condensed on the walls of the equipment, thus accounting for the deficiencies in the material balance.

The infrared spectrum of the residue at this stage (before exposure to moisture) had an absorption band at 5.98 μ indicating the presence of the C=N bond, and suggesting that (II) still persisted in the residue.

The residue was then submitted to a stream of nitrogen

at 50% relative humidity for 3 days. During this time the sample became loosely crystalline and increased in volume about tenfold, and formaldehyde was evolved. The infrared spectrum of the residue at the end of the 3 days no longer had the band at 6 μ .

The moist residue was treated with cold benzene and separated into soluble and insoluble fractions. The yellow crystals insoluble in benzene were found to be *N,N'*-methylenebis(*p*-nitroaniline) (III), as shown by analysis and a comparison of their x-ray diffraction pattern with that of an authentic sample. The benzene soluble compound has been identified as the *O-tert*-butyl ether of *N*-methyl-*N*-(*p*-nitro-

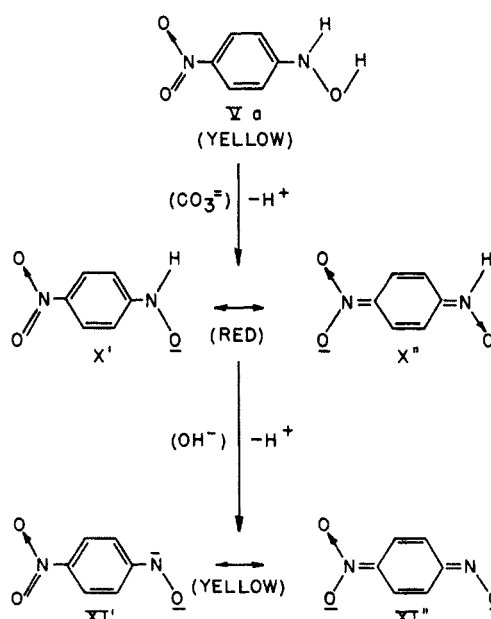
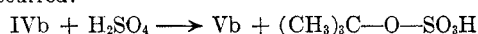


FIG. 6. STRUCTURES OF *N*-(*p*-NITROPHENYL)HYDROXYLAMINE AND ITS IONS.

phenyl)hydroxylamine, (IVb). This conclusion is based on the facts discussed below.

Structure of IVb. The benzene soluble portion, when evaporated to dryness, was an oil which gradually solidified. Orange crystals were obtained from petroleum ether (30–60°). They are soft and readily smeared with a spatula in spite of the fact that they melt at 138–140° on a bronze block. The odor of this compound is reminiscent of nitrobenzene and cinnamaldehyde. As seen in the tables, the analysis and the infrared spectrum are in agreement with the proposed structure. Its ultraviolet spectrum is similar to that of *N*-(*p*-nitrophenyl)hydroxylamine (Va), whose structure and those of its ions obtained by treatment with 2% aqueous sodium carbonate and 2% aqueous sodium hydroxide, respectively, are shown in Figure 6. Note that its univalent anion is red but its divalent anion is yellow, the latter due probably to the unfavorable charge distribution on resonance form XI'.

IVb is soluble in neither alkaline solution, since it has no readily ionizable hydrogen. When IVb was treated with cold concentrated sulfuric acid for 2 min. and poured on ice, a yellow solution was obtained which gave a red color with both alkaline solutions. The following reaction is thought to have occurred:



The resulting *N*-methyl-*N*-(*p*-nitrophenyl)hydroxylamine, (Vb), gives a red color with both alkaline solutions because it can be converted to X-type ions but not to XI-type ions due to the absence of a hydrogen on the nitrogen atom.

It was thought remotely possible that sulfuric acid might have caused the rearrangement of Vb to *N*-methyl-2-hydroxy-4-nitroaniline. It is seen, however, that the ultraviolet spectrum of 2-hydroxy-4-nitroaniline, which should closely resemble that of the *N*-methyl derivative, is entirely different, and whereas the red color obtained by dissolving 2-hydroxy-4-nitroaniline in either sodium carbonate or sodium hydroxide persists for a long time, the red colored carbonate and hydroxide solutions of Va and Vb fade within an hour or so.

Decomposition of cumene solution of Ib at 51°. Seventy-five ml. of a 0.025 molar solution of Ib in purified cumene were heated for 72 hr. in a constant temperature bath at 51° while a slow stream of nitrogen was passed through it and a connected flask containing aqueous barium hydroxide. The latter was protected from the atmosphere with a tube of Ascarite. The barium carbonate formed during this time (identified by x-ray diffraction) accounted for 90% of theory of carbon dioxide. The yellow cumene solution was found to contain 0.02 g. of III, 0.251 g. of *N*-methyl-*p*-nitroaniline (89% of theory), 0.07 g. of IVb, and much less than the expected amount of 2,3-dimethyl-2,3-diphenylbutane (mixed melting point with an authentic sample: 115°).

Note that the decomposition in this case is mainly by Figure 2, Route 1.

Decomposition of cumene solution of Ia at 51° and 80°. One hundred ml. of a 0.037 molar solution of Ia in purified cumene were heated at 51° for 21 days in the same way as in the previous experiment. The barium carbonate formed during this period accounted for only 28% of theory of car-

bon dioxide. The temperature was then raised to 80° and heating was continued for 3 more days. The total evolution of carbon dioxide was 87% of theory. The clear red solution was found to contain 0.233 g. of *p*-nitroaniline (45% of theory), and a considerable amount of a material listed as IVa in Table V. It gave no red color with either sodium carbonate or sodium hydroxide solution, but on treatment with concentrated sulfuric acid, a yellow solution was obtained which became red in sodium carbonate and yellow in sodium hydroxide. This behavior is that of *N*-(*p*-nitrophenyl)hydroxylamine.

Ninety ml. of a 0.02 molar solution of Ia in purified ethylbenzene was found to decompose completely in 10 days at 30°. In this case, the yield of *p*-nitroaniline was 95% of theory.

The much faster rate of decomposition of Ia in ethylbenzene than in cumene may be due to the fact that whereas *alpha*-cumyl radical is relatively inert and dimerizes, *alpha*-phenethyl radical behaves like the polystyrene radical and induces the decomposition of Ia. The rate of decomposition in ethylbenzene is about one half that in styrene. This ratio holds also for the rates of decomposition of Ib in ethylbenzene and styrene.

Bulk polymerization of styrene. Freshly distilled styrene, 400 ml., containing 0.008 mole of Ia or Ib was placed in a 430-ml. brown glass bottle which was swept with nitrogen, stoppered with cork, and kept in a constant temperature bath at 30°. Samples (10 ml.) were taken periodically and analyzed for peroxide content iodometrically, and for degree of polymerization by the following method.

The sample was poured into 50 ml. of 95% alcohol and allowed to stand overnight at room temperature. The precipitated polymer was filtered through a tared asbestos-matted Gooch crucible, washed with 25 ml. of methanol, dried at 80°, and weighed. The molecular weights were determined by the elevation of the boiling point of benzene.

Some of the samples taken from the 30° reservoir were heated at a higher temperature before analysis for polymer formation, in order to show that if the extent of polymerization was low at this stage, it was due to the fact that all the initiator had not yet reacted rather than that the initiator had been decomposed without initiating polymerization.

As control, styrene containing no additive was treated in the same way. The data obtained are given in Table II and discussed in the text.

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