The low activation energy of the investigated propagation of styrene polymerization suggests that the reaction in tetrahydrofuran may involve two steps—a rapid equilibrium

$$\mathrm{S_n{\cdot}S^- + S \rightleftarrows S_n{\cdot}S^-,S}, \ldots, K_{\mathrm{as}}$$

in which a complex is formed with the monomer (*e.g.*, a charge transfer complex) followed by an irreversible rearrangement

$$\mathrm{S_n{\cdot}S^-,S \longrightarrow S_{n+1}{\cdot}S^-}, \ldots, k_{\mathrm{r}}$$

If $(\mathrm{S_n{\cdot}S^-,S}] \ll [\mathrm{S}]$, the kinetic result of this scheme would be identical with the conventional bimolecular reaction. However, the over-all activation energy E_{p} would be $E_{\mathrm{p}} = \Delta H_{\mathrm{as}} + E_{\mathrm{r}}$; and since ΔH_{as} is negative, E_{p} could be very low. Such a scheme may account for the observed dependence of k_{p} on [LE] if the complex is in equilibrium with its ions, *i.e.*

$$\mathrm{S_n{\cdot}S^-, S, Na^+ \rightleftarrows S_nS^-,S + Na^+}$$

and the rearrangement constant k_{r}' for $\mathrm{S_n{\cdot}S^-, S, Na^+}$ is lower than that for $\mathrm{S_n{\cdot}S^-, S}$ (k_{r}''). Since the concentration of $\mathrm{S_n{\cdot}S^-, S}$ is much lower than that of $\mathrm{S_n{\cdot}S^-, Na^+}$, its dissociation into free ions may be considerable. This scheme avoids all the difficulties of the previously considered suggestion, namely, $\mathrm{S_nS^-, Na^+ \rightleftarrows S_nS^- + Na^+}$, which made the latter unacceptable, as the explanation of the dependence of k_{p} on the concentration of living ends.

It is interesting to note that the rate constant of propagation in the anionic polymerization of styrene at 25° is greater only by a factor of 25 or 30 than the k_{p} of the radical polymerization. Hence, the large increase in the rate of anionic polymerization, when compared to the radical reaction, is due to a higher concentration of growing chains. As was pointed out, the stationary concentration of growing radicals is about 10^{-7}–10^{-8} *M*, while that of the growing anions is 10^{-3}–10^{-2} *M*.

Finally, let us compare the absolute propagation rate constants of styrene and α-methyl styrene polymerizations. The latter is smaller by a factor of 300, while the respective equilibrium constants of propagation differ by a factor of $\sim 10^6$. This indicates that the strain caused by the bulky groups present in the α-methyl styrene molecule is much more pronounced in the final state, *i.e.* in the polymer, than in the transition state. This point was clearly recognized by Alfrey.[9]

We wish to acknowledge the financial support of this investigation by the National Science Foundation (Grant No. G14393) and by the Quartermaster Corps (Grant No. DA-19-129-QM-1297).

[9] T. Alfrey in T. Alfrey, J. J. Bohrer and H. Mark, "Co-polymerization," Interscience Publishers, New York, N. Y., 1952; see also T. Alfrey and W. H. Ebelke; *J. Am. Chem. Soc.*, **71**, 3235 (1949).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, CELANESE CHEMICAL COMPANY, A DIVISION OF CELANESE CORPORATION OF AMERICA, CLARKWOOD, TEXAS]

Excited Alkoxy Radicals in the Photolysis of Dialkyl Peroxides[1]

BY G. R. MCMILLAN

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The decomposition of alkoxy radicals formed by photolysis (λ 2537 Å.) of diisopropyl, di-*tert*-butyl and isopropyl-*tert*-butyl peroxides is not completely suppressed by nitric oxide. This observation is discussed in terms of excited or "hot" alkoxy radicals formed in the primary process. In the di-*tert*-butyl peroxide–nitric oxide system, the excited radical effect appears to decrease as the peroxide pressure is increased or as propylene is added, suggesting a collisional deactivation process. Such a deactivation is evidence for the participation of excited radicals of finite lifetime, as it weighs against an alternative primary process involving concerted scission of two or three bonds in the peroxide molecule to form products directly. *tert*-Pentoxy radicals are known to decompose by two parallel reactions, a favored path to split off an ethyl radical, and a second path to split off a methyl. *tert*-Pentoxy radicals formed by photodecomposition of ethyl-*tert*-pentyl peroxide with λ 2537 Å. radiation show an increased randomness in the bond scission reaction compared with radicals formed by λ 3130 Å. radiation or by thermal decomposition of the peroxide, a result perhaps to be expected of excited radicals. Indirect evidence points to the absence of an excited radical decomposition of the ethoxy formed by photolysis of ethyl-*tert*-pentyl peroxide.

Introduction

Much of the information about reactions of alkoxy radicals in the vapor phase has been obtained from studies of the photolysis of dialkyl peroxides.[2–6]

It is known that isopropoxy radicals may decompose according to

$$\mathrm{(CH_3)_2CHO \longrightarrow CH_3 + CH_3CHO} \qquad (1)$$

but decomposition of the radicals formed by photolysis of diisopropyl peroxide by light of λ 2300–2900 Å. appeared to be complex.[6] In effect, the apparent rate of reaction 1 was expressible not as $k_1[\mathrm{(CH_3)_2CHO}]$ but as $K + k_1[\mathrm{(CH_3)_2CHO}]$. Furthermore, addition of nitric oxide, a scavenger of known effectiveness for alkoxy radicals, did not eliminate acetaldehyde formation; in fact, the acetaldehyde quantum yield was independent of

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[1] Presented in part at the 140th National Meeting of the Society, Chicago, Ill., September, 1961.

[2] L. M. Dorfman and Z. W. Salsburg, *J. Am. Chem. Soc.*, **73**, 255 (1951).

[3] D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

[4] G. R. McMillan and M. H. J. Wijnen, *Can. J. Chem.*, **36**, 1227 (1958).

[5] G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960).

[6] G. R. McMillan, *ibid.*, **83**, 3018 (1961).

nitric oxide pressure over a range of 9–33 mm. Finally, with nitric oxide present, the quantum yield of acetaldehyde was only weakly dependent on temperature.

Two explanations for these observations were examined. Either the primary process produces a certain fraction of excited isopropoxy radicals which decompose at an abnormally high rate, or the primary process is a combination of steps involving concerted scission of two or three bonds to form methyl and acetaldehyde directly. It was not possible to decide which mechanism was operating, but the excited radical description was adopted for convenience in presenting and discussing the data.

Excited radical decomposition might be expected in the photolysis of other peroxides as well, yet some studies of the di-*tert*-butyl peroxide photolysis do not disclose participation of excited *tert*-butoxy radicals. Volman and Graven found that butadiene at a pressure of a few hundred mm. scavenged at least 80% of the *tert*-butoxy radicals formed by photodecomposition of di-*tert*-butyl peroxide vapor with 2537 Å. radiation.[7] Henbest and Patton[7] reported that *tert*-butoxy radicals produced by photolysis of the peroxide in solution were quantitatively converted to *tert*-butyl alcohol.

To try to test the generality of the excited radical effect and to determine the influence of structure of the peroxide and of the alkoxy group on the excited radical effect, experiments have been carried out on diisopropyl, di-*tert*-butyl, isopropyl-*tert*-butyl and ethyl-*tert*-pentyl peroxides, using the technique of nitric oxide inhibition. Decomposition of alkoxy radicals not formed in a high energy state is thus prevented, and the decomposition of excited radicals can be studied directly.

Experimental

The di-*tert*-butyl peroxide was a Shell Chemical Co. product. The diisopropyl peroxide was the sample prepared previously.[6] Isopropyl-*tert*-butyl peroxide was prepared by the procedure of Dickey and Bell.[8] Ethyl-*tert*-pentyl peroxide was prepared from *tert*-pentyl hydroperoxide.[9] A mixture of 0.5 mole *tert*-pentyl hydroperoxide and 0.6 mole ethyl sulfate was stirred at 45°. Potassium hydroxide solution, 50%, was added at such a rate that the mixture was just basic as shown by the green-blue color of bromthymol blue, added as an internal indicator.[10] All peroxides were fractionated at reduced pressure and finally purified by gas chromatography on a column of bis-(2-ethylhexyl) sebacate on Celite.

Nitric oxide, obtained from Matheson Chemical Co., was purified by low temperature fractionation.

Propane and propylene were Phillips Research Grade samples.

The fused quartz photolysis cell had a diameter of 50 mm. and a volume of 236 ml.

A GE B-H6 mercury arc was used for irradiation of ethyl-*tert*-pentyl peroxide–nitric oxide mixtures at 3130 Å. The Hanovia Type *A* mercury arc was used for other irradiations.

A 5 mm. Pyrex filter placed in the light beam restricted the radiation absorbed by the peroxides largely to 3130 Å. Light of 2537 Å. was isolated by a filter combination consisting of a 1 cm. optical path of potassium tri-iodide solution[11] and a 12 cm. optical path of chlorine (275 mm. pressure), both in quartz vessels.

The reactants were degassed, then mixed by repeated expansion into a large mixing bulb. Completeness of mixing was indicated by the invariance of results obtained with or without subsequent interruptions of the illumination for frequent mixing periods.

The reaction products were analyzed by a combined gas chromatography–mass spectrometry technique. Small amounts of alkyl nitrites and nitrates are not decomposed on the chromatographic column of bis-(2-ethylhexyl) sebacate on Celite.

Results

(a) Di-*tert*-butyl Peroxide–Nitric Oxide Mixtures.—Illumination with 2537 Å. radiation produced acetone, *tert*-butyl nitrite, methyl nitrate and possibly nitrogen. A trace of *tert*-butyl alcohol may be formed. No methyl nitrite nor isobutylene oxide could be found. Nitromethane, if formed, would probably not be detected by the analytical method.

In two experiments at 77°, quantum yields of products were measured, taking the quantum yield of acetone in the photolysis of pure di-*tert*-butyl peroxide to be two at 77°. Acetone and *tert*-butyl nitrite were found to account for all the *tert*-butoxy radicals formed in the system containing nitric oxide.

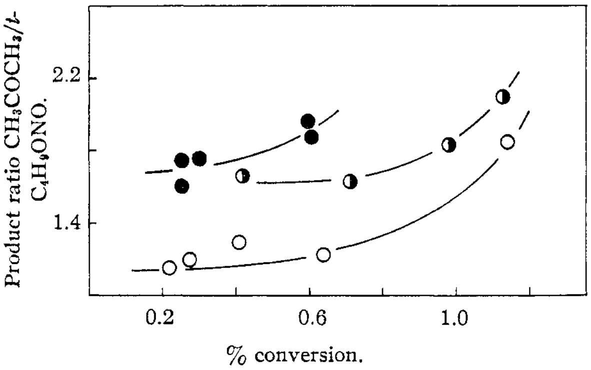

Fig. 1.—Photolysis of di-*tert*-butyl peroxide–NO mixtures with 2537 Å. light. Dependence of acetone/*tert*-butyl nitrite ratio on % conversion of peroxide: $T = 26°$, $P_{\text{NO}} =$ 15 mm., $P_{\text{peroxide}} = 23.5$ mm. (○), 7 ± 1 mm. (◑); $T = 77°$, $P_{\text{NO}} = 15$ mm., $P_{\text{peroxide}} = 23.0$ mm. (●).

Product yields under various conditions are given in Table I; mole ratios of products, acetone/*tert*-butyl nitrite, are plotted in Fig. 1. The rise in the ratio at higher conversions is probably due to secondary photodecomposition of the *tert*-butyl nitrite, since alkyl nitrites absorb strongly and presumably continuously[12] at 2537 Å. In a few experiments, small amounts of isopropyl nitrite, comparable to the amount of *tert*-butyl nitrite that might be produced in an ordinary photolysis, were mixed with di-*tert*-butyl peroxide and nitric

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[7] H. B. Henbest and R. Patton, ASTIA Report AD 246 579, November 28, 1960; also H. B. Henbest, J. A. W. Reid and C. J. M. Stirling, *J. Chem. Soc.*, 5239 (1961).

[8] F. H. Dickey and E. R. Bell, U. S. Patent 2,403,709, July 9, 1946.

[9] N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 643 (1946). Best yields were obtained by stirring the reaction mixture 24 hr. at room temperature.

[10] W. Eggerglüss, *Monograph, Angew. Chem. u. Chem.-Ing. Tech.*, No. 61 (1951).

[11] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 69.

[12] H. W. Thompson and C. H. Purkis, *Trans. Faraday Soc.*, **32**, 674 (1936).

Table I

Photolysis of Di-*tert*-Butyl Peroxide in the Presence of Nitric Oxide

λ, 2537 Å.

$P_{peroxide}$, mm.	P_{NO}, mm.	$P_{C_3H_6}$, mm.	% Decomp.	Yield, 10^8 moles		$\frac{CH_3COCH_3}{CH_3ONO_2}$	α
				CH_3COCH_3	$(CH_3)_3CONO$		
			T = 26°				
3	15	..	1.33	75	26	13	
6	15	..	0.71	67	41	6.1	0.62
6	15	..	.98	97	53	2.9	
6.5	15	..	.42	43	26	4.8	.62
7.5	15	..	1.13	146	70	15	
19.7	15	..	0.23	64	50	11	.56
19.7	15	..	.31	89	66	15	.57
23.5	15	..	.22	70	61	18	.53
23.5	15	..	.28	94	79	16	.54
23.5	15	..	.41	139	108	23	.56
23.5	15	..	.67	220	181	16	.55
23.5	15	..	1.14	441	240	6.2	
23.5	45	..	0.34	109	92	12	.54
23.5	60	..	.31	95	87	11	.52
23.5	15	70	.37	110	112	4.6	.50
23.5	15	135	.23	60	76	4.0	.44
23.5	15	185	.32	81	107	2.8	.43
23.5	15	135[a]	.40	120	118	5.0	.50
			T = 77°				
23.0	15	..	.26	80	50	11	.62
23.0	15	..	.26	82	47	14	
23.0	15	..	.31	98	56	25	
23.0	15	..	.60	196	100	25	
23.0	15	..	.61	198	106	22	

[a] Propane.

oxide. Illumination for a nominal time produced small amounts of acetaldehyde, proving that a secondary decomposition of alkyl nitrites in these systems may occur.[13]

In three experiments at 26°, mixtures of di-*tert*-butyl peroxide (20 mm.) and nitric oxide (15 mm.) were irradiated with the unfiltered light of the arc. The ratios of acetone/*tert*-butyl nitrite were 1.42, 1.42 and 1.83 at conversions of the peroxide of 0.24, 0.28 and 0.40%.

(b) **Diisopropyl Peroxide–Nitric Oxide Mixtures.**—Illumination with light of λ 2300–2900 Å. forms acetaldehyde, acetone, isopropyl nitrite, methyl nitrate, nitrous oxide and nitrogen.[6]

In six experiments (λ 2537 Å.; peroxide, 23.5 mm.; nitric oxide, 15 mm.; T = 26°), the following acetaldehyde/isopropyl nitrite ratios were found at the indicated extents of decomposition of the peroxide: 1.60 (0.26%); 1.72 (0.29%); 1.72 (0.33%); 1.73 (0.35%); 1.84 (0.43%); and 1.76 (0.45%).

In three experiments (full light of arc; peroxide, 23.5 mm.; nitric oxide, 15 mm.; T = 26°), the product ratios and corresponding extents of decomposition were: 1.91 (0.27%); 2.54 (0.55%); and 2.32 (0.62%).

In four experiments (λ 3130 Å.; nitric oxide, 15 mm.; T = 26°), the peroxide pressure, the measured ratios of acetaldehyde/isopropyl nitrite and the percentage decompositions were: 10.5 mm., 0.34 (0.34%); 18 mm., 0.31 (0.23%); 30 mm., 0.31 (0.16%); 0.41 mm., 0.27 (0.14%).

The acetaldehyde and isopropyl nitrite yields in these experiments are generally quite reproducible, but the small acetone yields show more scatter. The scatter is probably due mostly to small amounts of acetone initially present in the peroxide. The difficulties in removing the last traces of acetone from diisopropyl peroxide have been discussed.[6] In experiments at low conversion, these traces are particularly troublesome. Rather than attempt to make a blank correction to the acetone yield, the true yield of acetone will be calculated from the isopropyl nitrite yield by multiplying by the 0.15 factor already obtained.[6]

(c) **Isopropyl-*tert*-Butyl Peroxide–Nitric Oxide Mixtures.**—Photolysis products include acetone, acetaldehyde, *tert*-butyl nitrite, isopropyl nitrite and methyl nitrate. Some product ratios are given in Table II. The acetone has been corrected by subtracting the amount formed from isopropoxy radicals.

(d) **Ethyl-*tert*-Pentyl Peroxide–Nitric Oxide Mixtures.**—Photolysis products include ethyl nitrite, *tert*-pentyl nitrite, acetone, methyl ethyl ketone, acetaldehyde, ethyl nitrate and traces of methyl nitrate. Not more than traces of ethyl alcohol are formed. All the products were identified by examination of both mass spectra and gas chromatograms. Conversion of the peroxide was

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[13] Photodecomposition of *tert*-butyl nitrite to acetone in the presence of high pressures of nitric oxide implies a hot radical effect (or equivalent) in the nitrite photolysis. Details of the nitrite photolysis have been submitted for publication.

TABLE II

PHOTOLYSIS OF ISOPROPYL-*tert*-BUTYL PEROXIDE–NITRIC OXIDE MIXTURES

T, 26°; λ 2537 Å.; Pressure of Peroxide, 23.5 mm.; pressure of nitric oxide, 15 mm.

CH_3COCH_3/ *t*-C_4H_9ONO	CH_3CHO/ *i*-C_3H_7ONO	% Decomp.
1.88	2.69	0.28
1.47	2.79	.35
2.18	2.66	.36
1.73	2.44	.44
1.87	2.95	.50
2.15	3.09	.50

kept below about 0.5%. Some product ratios are given in Table III.

TABLE III

PHOTOLYSIS OF ETHYL-*tert*-PENTYL PEROXIDE–NITRIC OXIDE MIXTURES

Pressure of peroxide, 20 mm.; pressure of nitric oxide, 15 mm.

Wave length, A.	Temp., °C.	$CH_3COCH_3/CH_3COC_2H_5$	No. of expts.
3130	26	16 ± 1	3[a]
2537	26	10.0 ± 0.3	3[b]
2537	73	8.3	1

[a] A range of conversion of about a factor of 4. [b] A range of conversion of about a factor of 2.

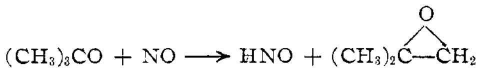
Thermal decomposition of the peroxide (20 mm.) in the absence of nitric oxide again formed acetone and methyl ethyl ketone in a ratio of 16 at 114° and 15 at 137°. Conversions were 1% or less.

Discussion

(a) **Di-*tert*-Butyl Peroxide–Nitric Oxide Mixtures.**—Birss, Danby and Hinshelwood[14] found that nitric oxide at a few mm. pressure scavenged most of the *tert*-butoxy radicals formed by pyrolysis of di-*tert*-butyl peroxide, at least at temperatures in the neighborhood of 160°. In the present study it was found that nitric oxide at 15 mm. pressure is sufficient to scavenge >99% of the *tert*-butoxy radicals formed by thermal decomposition of the peroxide vapor at 121°. Hence, in the photochemical system, all *tert*-butoxy radicals of normal energies will react according to

$$(CH_3)_3CO + NO \longrightarrow (CH_3)_3CONO \qquad (2)$$

Levy[15] concluded from studies of pyrolyses of alkyl nitrites that a corresponding disproportionation step, such as



$$(CH_3)_3CO + NO \longrightarrow HNO + (CH_3)_2\overset{O}{C{-}CH_2}$$

does not occur. The present results support this conclusion; $\Phi_{CH_3COCH_3} + \Phi_{t-C_4H_9ONO} = 2.0$ and isobutylene oxide is not a product.

The presence of acetone in the products of the photochemical reaction in the presence of nitric oxide at 2537 Å. is evidence that some of the *tert*-butoxy radicals decompose due to the excess of energy they bear at the moment of formation.

$$(CH_3)_3CO^* \longrightarrow CH_3COCH_3 + CH_3 \qquad (3)$$

The O–O bond dissociation energy in di-*tert*-butyl peroxide is <40 kcal.; therefore, about 70 kcal. excess of energy will be distributed between the two radicals.

This "hot radical" effect may be discussed in terms of α, defined as the fraction of alkoxy radicals decomposing in the presence of an excess of nitric oxide. The quantity $\alpha_{t-\text{butoxy}}$ is given simply by the rate of acetone formation divided by the sum of rates of acetone and *tert*-butyl nitrite. The dependence of product ratios on extent of decomposition of peroxide (Fig. 1) shows that the calculated α is a meaningful quantity only in the limiting region of low conversion.

(i) **Dependence of $\alpha_{t-\text{butoxy}}$ on Nitric Oxide Pressure.**—Over the range of nitric oxide pressure 15–60 mm., the quantity α (Table I) shows a maximum decrease of two parts in fifty, consistent with complete scavenging of unexcited radicals even at the lowest pressure. The small effect further indicates that nitric oxide is not efficient in deactivation of excited *tert*-butoxy radicals.

(ii) **Dependence of $\alpha_{t-\text{butoxy}}$ on Peroxide Pressure.**—The low conversion limits of the acetone/*tert*-butyl nitrite ratio at 26° (Table I, Fig. 1) correspond to α values of 0.62 at 7 ± 1 mm. peroxide pressure, 0.56 at 19.7 mm., and 0.53 at 23.5 mm. The decrease in α with increase of peroxide pressure can be rationalized by assuming a collisional deactivation of excited *tert*-butoxy radicals. Since the apparent primary quantum yield in the di-*tert*-butyl peroxide photolysis is about unity,[2,3] the energy transfer step does not ordinarily result in decomposition of the peroxide molecule accepting the energy.

Addition of propylene or propane (Table I) reduces α, presumably by the same mechanism. The observed deactivation is evidence for the presence of excited radicals of finite lifetime. The absorption of di-*tert*-butyl peroxide is thought to be continuous at 2537 Å.[3]; hence, there is no question of excited molecules. Observation of deactivation of *some* species lends favor to the excited radical picture and tends to exclude the alternative primary process of concerted decomposition to acetone and methyl.

The collisional deactivation process brings the present results into consistency with the observations of Volman and Graven and of Henbest and Patton mentioned in the introduction.

(iii) **Dependence of $\alpha_{t-\text{butoxy}}$ upon Temperature.**—From Fig. 1, the limiting acetone/*tert*-butyl nitrite ratio at 77° and 23.0 mm. peroxide does not exceed about 1.60, corresponding to an α of 0.62. At 26° and the same peroxide concentration (19.7 mm.), α is about 0.56. The temperature de-

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[14] F. W. Birss, C. J. Danby and C. Hinshelwood, *Proc. Roy. Soc.* (London), **A239**, 154 (1957).

[15] J. B. Levy, *Ind. Eng. Chem.*, **48**, 762 (1956).

pendence of α in the diisopropyl peroxide system is also slight.[6] In neither case may the temperature coefficient be assigned to any one process, since α is a complex function of the deactivation efficiency as well as other factors already discussed.[6]

(iv) **Dependence of $\alpha_{t-\text{butoxy}}$ upon Wave Length.**—The apparent values of α calculated for the three experiments using the full light of the mercury lamp are 0.59, 0.59 and 0.65 for peroxide conversions of 0.24, 0.28 and 0.40%. Thus, 2 × 0.6 may be taken as roughly the quantum yield of production of excited radicals in previous work on di-*tert*-butyl peroxide under similar conditions.[4,5]

(b) **Diisopropyl Peroxide–Nitric Oxide Mixtures.**—Quantum yield measurements[6] showed that the reactions

$$(CH_3)_2CHO^* \longrightarrow CH_3 + CH_3CHO \qquad (4)$$

$$(CH_3)_2CHO + NO \longrightarrow (CH_3)_2CHONO \qquad (5)$$

$$\longrightarrow CH_3COCH_3 + HNO \qquad (6)$$

could account for 93–98% of the isopropoxy radicals produced by photolysis (λ 2300–2900 Å.) of diisopropyl peroxide in the presence of nitric oxide. The quantity $\alpha_{\text{isopropoxy}}$ is then given by $R_{CH_3CHO}/[R_{CH_3CHO} + R_{i-C_3H_7ONO} + R_{CH_3COCH_3}]$. In the present work, the rate of acetone formation was computed from the rate of isopropyl nitrite and the previously determined value[6] of $k_6/k_5 = 0.15$ at 26°.

In the six experiments at 23.5 mm. peroxide, 15 mm. nitric oxide, and 26°, using light of wave length 2537 Å., α was 0.60 ± 0.004 (std. dev.) over a range of conversion 0.26–0.45%.

The experiments at various pressures at 3130 Å. give $\alpha = 0.19$–0.23. This α is an upper limit. Absorption by the peroxide is so weak at this wave length, no proper account could be taken of secondary photodecomposition of the isopropyl nitrite. However, the results indicate a definite wave length effect on α—a decrease as the wave length is increased.

(c) **Isopropyl-*tert*-Butyl Peroxide–Nitric Oxide Mixtures.**—The sum of yields of products derived from isopropoxy radicals was 1.03 ± 0.03 (std. dev.) times the sum of yields of products derived from *tert*-butoxy radicals. For the six experiments under the given conditions $\alpha_{\text{isopropoxy}}$ was 0.72 ± 0.004 and $\alpha_{t\text{-butoxy}}$ was 0.64 ± 0.01 (std. dev.).

(d) **Ethyl-*tert*-Pentyl Peroxide.**—The *tert*-pentoxy radical is known to decompose by two parallel paths involving carbon–carbon bond scission

$$C_2H_5(CH_3)_2CO \longrightarrow C_2H_5 + CH_3COCH_3 \qquad (7)$$

$$\longrightarrow CH_3 + CH_3COC_2H_5 \qquad (8)$$

Studies in which the *tert*-pentoxy radical was produced by thermal decomposition of peroxides indicate that k_7/k_8 is in the range 16–22 and is not strongly dependent upon temperature.[9,16]

The present results of the thermal decomposition of ethyl-*tert*-pentyl peroxide are consistent with a high value of k_7/k_8. The ratio of constants (calculated as $R_{CH_3COCH_3}/R_{CH_3COC_2H_5}$) was 16 at 114° and 15 at 137°.

In the photochemical experiments on this peroxide, nitric oxide was added to a pressure of 15 mm. to inhibit chain decomposition. A large fraction of the *tert*-pentoxy radicals decompose even in the presence of nitric oxide, indicating that the radicals are excited. When light of λ 3130 Å. was used, the ratio of rate constants k_7/k_8 was 16 ± 1, about the same as the ratio observed when the peroxide was thermally decomposed. When light of λ 2537 Å. was used, k_7/k_8 was 10.0 ± 0.3 at 26° and 8.3 at 73°. This increased randomness in the bond scission of the *tert*-pentoxy radical is consistent with a radical bearing higher than thermal energy at the moment of decomposition.

There is no indication that the ethoxy radicals undergo excited radical decomposition to methyl and formaldehyde. A direct test is not possible because formaldehyde, even if formed, could not be recovered from the vacuum line in use. However, formation of methyl radicals would lead to formation of methyl nitrate (section e). Since the yield of methyl nitrate is not greater than the amount expected from the number of methyls formed conjointly with methyl ethyl ketone, it is tentatively concluded that the ethoxy species does not undergo excited radical decomposition. The absence of significant amounts of ethyl alcohol in the products suggests that the excess of energy (if any) borne by the ethoxy radical does not usually lead to hydrogen abstraction.[17]

(e) **Formation of Alkyl Nitrates.**—Alkyl nitrates are observed as important products when alkyl radicals are formed in the presence of nitric oxide in all the peroxide–nitric oxide systems studied. Conversion of aliphatic nitroso compounds to nitrates was observed by Donaruma and Carmody.[18] Batt and Gowenlock[19] recently postulated such a transformation in a study of the reaction of nitric oxide with nitrosomethane vapor. Details of the conversion are not well understood; presumably there is addition of two molecules of nitric oxide to the nitroso compound, followed by rearrangement to a diazonium salt, which ultimately decomposes to give nitrate and possibly other organic nitrogen compounds. One or more steps in the conversion may be heterogeneous.

Decomposition of excited alkoxy radicals yields alkyl radicals which certainly form nitrosoalkanes in the presence of nitric oxide. Methyl nitrate was found to be an important product of the photolysis of diisopropyl peroxide–nitric oxide mixtures.[6] About one-third of the methyl radicals introduced eventually formed methyl nitrate. This proportion was rather independent of temperature and of concentration of peroxide and nitric oxide over narrow ranges.

In the di-*tert*-butyl peroxide–nitric oxide system (Table I), the ratio of methyl introduced to

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(16) J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88, 2767 (1948); J. H. Raley and D. O. Collamer, *ibid.*, **74**, 1606 (1952).

(17) Some ethyl alcohol, if formed, might not be found if transesterification with *tert*-pentyl nitrite occurred during product analysis.

(18) L. G. Donaruma and D. J. Carmody, *J. Org. Chem.*, **22**, 635 (1957).

(19) L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, **56**, 682 (1960).

methyl nitrate formed (equal to $R_{CH_3COCH_3}/R_{CH_3ONO_2}$) varies over almost a factor of ten. No explanation of this observation can be given. Neither methyl nitrate nor a methyl nitrate precursor is disappearing by reaction with acetone or *tert*-butyl nitrite; otherwise complete accountability of *tert*-butoxy radicals would not be obtained.

(f) **Influence of Structure on the Excited Radical Effect.**—The α quantities for isopropoxy and *tert*-butoxy radicals formed by photolysis of some peroxides (Table IV) differ but slightly. A small difference in α is consistent with available thermochemical data,[20] which indicates that the enthalpies of decomposition of the two species differ by less than 2 kcal./mole. The ratio of $\alpha_{\text{isopropoxy}}$ (from diisopropyl peroxide) to $\alpha_{t\text{-butoxy}}$ (from di-*tert*-butyl peroxide) is the same as the ratio of $\alpha_{\text{isopropoxy}}$ to $\alpha_{t\text{-butoxy}}$ (both from isopropyl-*tert*-butyl peroxide), showing that the relative α values of the two radicals are not primarily determined by the deactivation efficiency of the parent peroxide. The lifetime of the excited radical before decomposition is one factor surely important in determining the magnitude of α.

TABLE IV

α VALUES OF ALKOXY RADICALS FORMED BY PHOTOLYSIS OF SOME DIALKYL PEROXIDES

Peroxide pressure, 23.5 mm.; nitric oxide pressure, 15 mm.; λ 2537 Å., T, 26°

Peroxide	$\alpha_{i\text{-}C_3H_7O}$	$\alpha_{t\text{-}C_4H_9O}$
Diisopropyl	0.60	..
Di-*tert*-butyl	..	0.53
Isopropyl-*tert*-butyl	0.72	0.64

The tentative conclusion from this work is that ethoxy radicals from photolysis of ethyl-*tert*-pentyl peroxide do not decompose in the presence of an excess of nitric oxide—hence are not excited in the sense used in this paper. This result fits well with the observation by Wijnen[21] that isopropoxy radicals from photolysis of isopropyl propionate are excited but ethoxy radicals from photolysis of ethyl propionate are not excited.

Conclusions.—In vapor phase photolysis of dialkyl peroxides with *sec-* or *tert-* (possibly not *prim-*) alkyl groups, consideration must be given to the formation of excited alkoxy radicals—excited in the sense that they decompose (but do not abstract hydrogen) at an abnormally high rate. This effect introduces complications which make difficult an exact interpretation of some previous work on *tert*-butoxy reactions based on di-*tert*-butyl peroxide as a photolytic radical source. Some of the quantitative conclusions[4,5] are obviously rendered uncertain..

The observation of apparent collisional deactivation of excited *tert*-butoxy radicals suggests that the excited radical effect may not be important in the liquid phase.

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[CONTRIBUTION FROM THE RADIATION PHYSICS LABORATORY, ENGINEERING DEPARTMENT, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE]

Pulse Radiolysis of Aromatic Compounds

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Pulsed radiolysis of benzene, chlorobenzene, bromobenzene, toluene, *p*-xylene, anisole and mesitylene has led to the observation of transient absorptions. Product analysis, spectroscopic data and kinetic analysis indicate that the transients produced are free radicals, having a conjugated structure, derived from addition of reactive radicals to the parent aromatic compound. Bimolecular rate constants for the radical–radical reaction are calculated, and the rate of addition of phenyl radicals to chlorobenzene is estimated.

Introduction

Pulsed radiolysis has been shown to be a valuable technique for the production and observation of very reactive free radicals.[1,2,3] Previous publications from this Laboratory have reported the kinetics of benzyl radical dimerization,[1] the dimerization and disproportionation of ketyl radicals from cyclohexanol and the kinetics of some peroxy radical reactions, including cyclohexyl peroxy and octene peroxy radicals.[2,3] This paper summarizes an investigation of the nature of the transients observed when various aromatic compounds are pulse radiolyzed. Kinetic order and detailed product analysis are used to make assignments of product structure and for the calculation of absolute rate constants.

Experimental

Materials.—Benzene was Mallinckrodt analytical reagent; toluene was Merck reagent grade; anisole, bromobenzene, biphenyl and bibenzyl were Eastman white label chemicals; *p*-xylene, iodobenzene and phenylcyclohexane were Matheson, Coleman and Bell chemicals; 4,4′-dichlorobiphenyl and bicyclohexyl were obtained from the Aldrich Chemical Company; cyclohexane was Eastman Spectro

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[1] R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

[2] R. L. McCarthy and A. MacLachlan, *ibid.*, (in press).

[3] R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.* (in press).