products showed that the high mass cut-off point was 246 corresponding to icosaborane-26 or $B_{10}H_{13}–B_{10}H_{13}$, two decaborane units coupled by a B–B bond. A typical mass spectrum is shown in Fig. 2. No mass peaks higher than 246 were observed although one might expect such coupling reactions to continue further. However, the volatility of the products presumably would be too low to observe mass spectroscopically under our conditions.

During the course of these studies, it was found that if a mixture containing diborane-6, tetraborane-10 and pentaborane-9 was irradiated with deuterons, both liquids and solids of low volatility were formed in the cell. The volatile hydrides remaining after irradiation contain small amounts of hexaborane-10 in addition to the starting materials. When the resulting solids or solutions of the solids were introduced into the gas chromatograph, results such as the ones in Fig. 3 were obtained. Mass spectroscopic measurements showed several groups of peaks displaying shapes characteristic of boron hydrides. The m/e values ranged from 10 to 246 and included decaborane-14. It was possible to collect some of the individual separated materials by trapping them from the exit flow gas and then to analyze them mass spectroscopically. The identity of the peaks or their mass cut-offs are indicated in the figure. In addition to the m/e's indicated above, 226 has also been observed. It therefore appears that there is a host of boron hydrides with molecular weights greater than decaborane which appear to possess reasonable stabilities and which are amenable to study by modern techniques.

In conclusion, therefore, just as it is possible under appropriate conditions to couple two pentaborane-9 molecules to form decaborane-16, two decaborane-14 molecules can be combined to give icosaborane-26. In addition, some of the hydrides with molecular weights between 126 and 246 also show some indication of this type of coupling behavior. For example, mass 138 could correspond to a pentaborane-9 and hexaborane-10 joined by a B–B bond across the apical borons, and 186 may result from a decaborane-14 and a pentaborane-9 combination. The evidence in the latter cases, of course, is not as convincing as in the former cases; however, it is suggestive. It is planned to explore these indications further by irradiation of other purified boron hydrides and by studies of some of the purified crystalline products.

We are indebted to Mr. Jeffrey L. Sanders for his assistance in making the mass spectroscopic measurements.

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, O.]

The Photoöxidation of 2,2'-Azoisobutane at 25°

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A rate study of the photoöxidation of 2,2'-azoisobutane has been made in an oxygen-rich atmosphere at 25°. Long-path infrared spectrophotometry was used to identify the major products of the *tert*-butyl free radical–oxygen reaction as acetone, formaldehyde, *tert*-butyl hydroperoxide and *tert*-butyl alcohol; methanol and carbon dioxide were minor products. Reasonably good mass balances were obtained. From a consideration of the initial rates of product formation and azoisobutane disappearance, a detailed mechanism was proposed. The results suggested that for this oxygen-rich system at 25° the radical–radical disproportionation reactions are the origin of hydroperoxide and alcohol products, and that H-abstraction from azoisobutane, formaldehyde or other H-containing products in the system was unimportant here. The rate data are consistent with a value of about 5 sec.$^{-1}$ for the first-order rate constant for the decomposition of the *tert*-butoxyl radical at 25°.

Our knowledge of the nature of the products and the reactions of alkyl free radicals in an oxygen-rich atmosphere at 25° is very limited today. Air pollution workers and health authorities are particularly concerned with this information as it bears on the light-initiated free radical oxidations in auto-exhaust-polluted atmospheres. It is not uncommon for an investigator to suggest mechanisms for the oxidation of alkyl free radicals for the low temperature, oxygen-rich systems by extrapolation of high temperature oxidation results obtained from the combustion of near stoichiometric mixtures of hydrocarbons and oxygen. Results obtained with the simple methyl radical show that this procedure may lead to the incorrect mechanism choice.[1-3] For example, the methyl peroxyl radical formed in the oxidation of methyl radicals at 25° in oxygen-rich media does not take part in the H-abstracting reactions generalized by 1, although reactions of this sort are often suggested as dominant chain-propagating reactions in high temperature combustions. The hydroperoxide

$$CH_3O_2 + RH \longrightarrow CH_3O_2H + R \qquad (1)$$

formed in this system is derived from radical–radical interactions.

The mechanism of oxidation of the higher alkyl free radicals in oxygen-rich media at 25° has received little attention. Quantitative studies are very difficult since the complex mixture of reaction products may contain many compounds of high reactivity so that the conventional analytical procedures cannot be used. The success of the long-path infrared techniques in the previous studies of the methyl radical reactions[1-3] encouraged us to extend the method to the more complicated *tert*-butyl radical system. A very complex mixture of reaction products is expected

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(1) N. R. Subbaratnam and J. G. Calvert, Chapter 7, "Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishers, Inc., New York, N. Y., 1961, p. 109.

(2) N. R. Subbaratnam and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 1113 (1962).

(3) D. F. Dever and J. G. Calvert, *ibid.*, **84**, 1362 (1962).

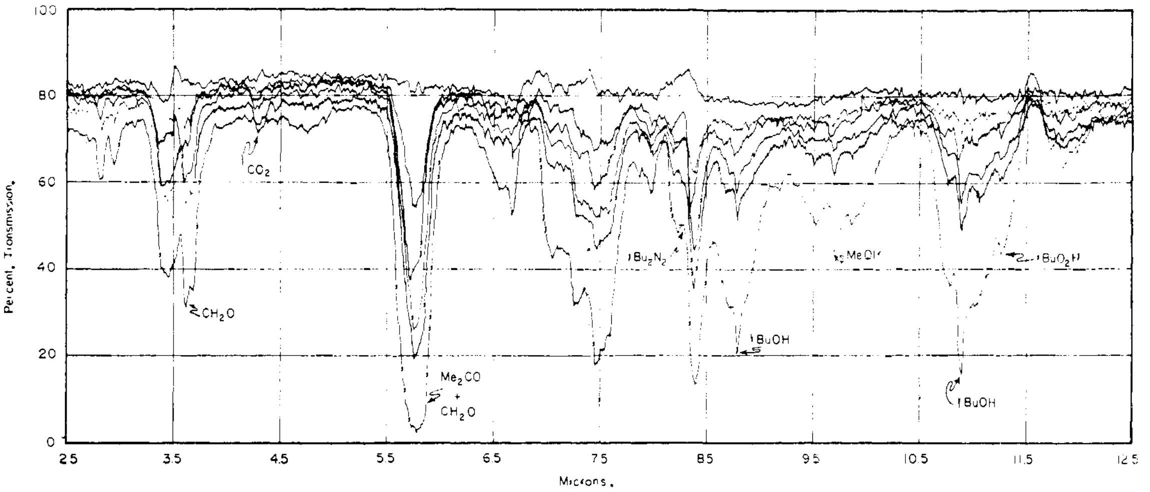

Fig. 1.—Infrared absorption spectra of products of the photolysis of 2,2′-azoisobutane–oxygen mixtures at 25° (run 3 of Table I); the spectrum was rescanned after each of four consecutive 2-min. exposures, and after 30 min. total exposure time.

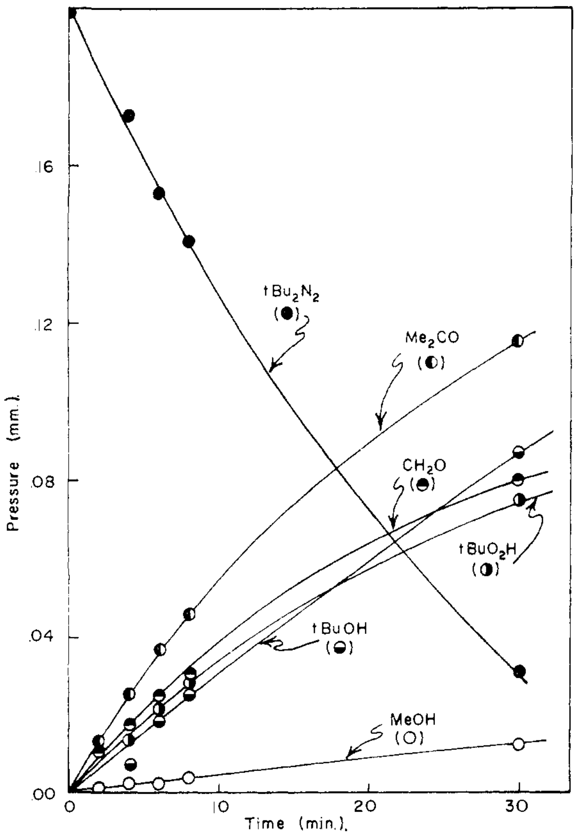

Fig. 2.—The time dependence of the pressure of 2,2′-azoisobutane and its photoöxidation products at 25° (run 3 of Table I) calculated from the spectral data of Fig. 1. Initial rates reported in Table I were estimated from these and similar data from other runs.

from previous studies of the *tert*-butyl peroxyl radical systems. McMillan and Wijnen[4] report that the photodecomposition of oxygen-free di-*tert*-butyl peroxide gives acetone, *tert*-butyl alcohol, ethane, methane, methyl *tert*-butyl ether and isobutylene oxide. At wave lengths below 2300 Å., Frey[5] also found neopentane, isobutane and isobutene among the products. Raley, Porter, Rust and Vaughan[6] found that the thermal decomposition of di-*tert*-butyl peroxide in oxygen gave methanol, formic acid, formaldehyde, acetone, carbon monoxide, carbon dioxide, water and traces of *tert*-butyl alcohol. In addition to these products Blake and Kutschke[7] recently identified methyl hydroperoxide as an important product in the thermal decomposition of di-*tert*-butyl peroxide in oxygen-containing mixtures.

In consideration of the known photochemical properties of the simple alkyl-azo-compounds, we have chosen the photolysis of 2,2′-azoisobutane as the source of *tert*-butyl radicals. We have utilized the analytical method of infrared spectrophotometry, incorporating long-path techniques, to follow concentrations of the reactant and the products without condensation or separation. Although the product mixtures are very complex, the infrared data are easily resolvable, and initial product rate data have been determined. Several interesting aspects of the *tert*-butyl radical–oxygen reactions found in this work are reported here.

Experimental

Materials.—2,2′-Azoisobutane was a product of Merck and Co. Ltd., Montreal, Can. The alkyl groups were found to be 99% of the *tert*-butyl structure by n.m.r. analysis. The *tert*-butyl hydroperoxide was a product of K. and K. Laboratories, Jamaica, N. Y. All other chemicals were from the usual commercial sources. Purification of all samples was accomplished by vacuum distillation and fractionation at reduced temperatures.

Equipment.—All of the photoöxidation studies were carried out in a 70-liter Pyrex cell which housed the long-path multiple reflection system of a modified Perkin–Elmer model 21 double beam infrared spectrophotometer. The multiple reflection system was adjusted to provide a path length of 20 m. A metal collar about the flanged open end of the cell secured it to the instrument. In order to obtain a vacuum seal a rubber gasket was inserted between the instrument and the flat ground edge of the open end of the cell. The majority of the weight of the cell was supported

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

(5) H. M. Frey, *Proc. Chem. Soc.*, 385 (1959).

(6) J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 15 (1951).

(7) A. R. Blake and K. O. Kutschke, *Can. J. Chem.*, **39**, 278 (1961).

TABLE I

INITIAL RATES OF PRODUCT FORMATION IN THE PHOTOÖXIDATION OF 2,2′-AZOISOBUTANE AT 25°

	Pressure, mm.			Initial rates, mm./min. $\times 10^2$							Rate functions					
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
Run	t-Bu_2N_2	O_2	Added gas	$-R_{t\text{-}Bu_2N_2}$	$R_{t\text{-}BuOH}$	$R_{t\text{-}BuO_2H}$	R_{Me_2CO}	R_{MeOH}	R_{CH_2O}	R_{CO_2}	6/5	7/5	$12 \times 8^{1/2}$	$\frac{5+6+7}{4+4}$	$\frac{7}{8+9+10}$	$\frac{5+6+8}{9}$
1	2.00	740	....	..	29	32	61	..	32	..	1.1	2.1	...	..	..	..
2	0.406	740	....	20	8.7	9.7	17	1.5	16	1.0	1.1	2.0	0.078	0.88	0.92	1.2
3	.200	740	....	7.4	3.3	3.9	6.6	0.53	4.7	0.73	1.2	2.0	.046	0.93	1.1	1.6
4	.110	740	....	2.9	1.2	1.7	3.1	.23	2.3	.27	1.4	2.6	.039	1.0	1.1	1.4
5	.0889	740	....	3.3	1.6	1.7	3.5	.43	2.2	.51	1.1	2.2	.046	1.0	1.1	1.7
6[a]	.0923	740	....	2.4	0.80	0.96	2.5	.29	1.3	..	1.2	3.1	.053	0.89	1.6	1.6
7[b]	.0958	740	....	1.1	0.31	.50	1.5	.13	1.2	..	1.6	4.8	.053	1.1	1.1	0.78
8	.0923	740	0.297 (CH_2O)	..	1.8	2.4	..	..	..	..	1.3	..	...	..	..	..
9	.0889	10	730 (N_2)	..	0.71	1.0	..	..	..	..	1.4	..	...	..	..	..
10	.0889	19	721 (He)	2.7	1.3	1.3	2.9	0.32	2.8	..	1.0	2.2	...	1.0	0.93	1.0
11	.0889	19	721 (N_2)	2.6	1.4	1.7	3.2	.31	2.8	..	1.2	2.3	...	1.2	1.0	1.2
12	.0889	19	721 (CO_2)	2.2	0.76	1.3	3.1	.31	2.5	..	1.7	..	...	1.2	1.1	1.0
13	.0889	19	721 (CO_2)	1.4	0.63	1.0	2.4	.17	1.9	..	1.6	..	...	1.4	1.2	1.0

[a] Light intensity incident on the reaction vessel was two-thirds that in other runs. [b] Light intensity incident on the reaction vessel was one-third that in other runs.

from below by an adjustable metal stand. Arranged with equal spacing above the cell in a water-cooled Pyrex condenser were three 550-watt Hanovia type A (S-500) medium pressure mercury arcs. The effective radiation was limited to the 3660 Å. region by the filtering action of the Pyrex cell and condenser. An aluminum reflector was placed above the condenser to concentrate the radiation in the reaction cell. A removable aluminum shutter was placed between the cell and the arcs to block out the radiation when necessary.

Several experiments were carried out in an oxygen-free photolysis system of a more conventional design described previously.[8]

Procedures.—Small quantities of 2,2′-azoisobutane (usually 0.1 mm. pressure) were introduced in the reaction cell. The total pressure was then brought up to 740 mm. by addition of oxygen or another gas. In each experiment the absorption of the azoisobutane was blanked by the addition of an equivalent amount of the reactant to the reference cell. In a typical experiment the entire spectrum was scanned before starting the reaction. Then an exposure of 4 min. duration was made, the shutter interposed, and the spectrum rescanned. The shutter was again removed and the cycle was repeated four or five times. The spectrum showed evidence of the products: formaldehyde, methanol, acetone, *tert*-butyl alcohol, *tert*-butyl hydroperoxide and, in some runs, carbon dioxide. Presumably methyl hydroperoxide, carbon monoxide and formic acid are also present in these runs of short duration, but they are only detectable in long exposures, and they are relatively minor products. Formaldehyde was determined through the absorption band at 3.58 μ, methanol at 9.67 μ (spike only used), acetone at 5.76 μ (after subtraction of the contribution of formaldehyde), *tert*-butyl alcohol at 8.78μ (spike only), *tert*-butyl hydroperoxide at 11.25 μ (after subtracting the contribution due to *tert*-butyl alcohol), carbon dioxide at 4.3 μ, 2,2′-azoisobutane loss at 8.23μ (after correction for acetone, *tert*-butyl alcohol and *tert*-butyl hydroperoxide absorptions). Figure 1 shows the spectrum obtained from a typical photolysis run. Figure 2 shows the time dependence of the pressure of the reactant and products of the run as calculated from the spectrum of Fig. 1. The results of the experiments were quite consistent and reproducible and could be used to obtain initial rate data of good reliability. For each run curves of the type of Fig. 2 were constructed from the spectral data, and by extrapolation to zero time initial rates were determined for azoisobutane loss and products formed. These results are summarized in Table I.

Discussion of the Results

Proposed Mechanism for the Photoöxidation of 2,2′-Azoisobutane in Oxygen-rich Media at 25°.—It will be instructive to consider the following mechanism in explanation of the initial rate data summarized in Table I.

$$(t\text{-}C_4H_9)_2N_2 + h\nu \longrightarrow (t\text{-}C_4H_9)_2N_2^* \qquad \text{(I-a)}$$

$$(t\text{-}C_4H_9)_2N_2^* + M \longrightarrow (t\text{-}C_4H_9)_2N_2 + M' \qquad \text{(I-b)}$$

$$(t\text{-}C_4H_9)_2N_2^* \longrightarrow 2t\text{-}C_4H_9 + N_2 \qquad \text{(I-c)}$$

$$t\text{-}C_4H_9 + O_2 \longrightarrow t\text{-}C_4H_9O_2 \qquad (2)$$

$$2t\text{-}C_4H_9O_2 \longrightarrow 2t\text{-}C_4H_9O + O_2 \qquad (3)$$

$$(+M)t\text{-}C_4H_9O \longrightarrow CH_3 + CH_3COCH_3\,(+M) \qquad (4)$$

$$CH_3 + O_2 \rightleftarrows CH_3O_2'\,(+M) \longrightarrow CH_3O_2\,(+M') \qquad (5)$$

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (6)$$

$$CH_3O_2 + t\text{-}C_4H_9O_2 \longrightarrow CH_3O + t\text{-}C_4H_9O + O_2 \qquad (7)$$

$$t\text{-}C_4H_9O + CH_3O \longrightarrow t\text{-}C_4H_9OH + CH_2O \qquad (8)$$

$$t\text{-}C_4H_9O_2 + CH_3O \longrightarrow t\text{-}C_4H_9O_2H + CH_2O \qquad (9)$$

$$2CH_3O \longrightarrow CH_3OH + CH_2O \qquad (10)$$

$$CH_3O_2 + CH_3O \longrightarrow CH_3O_2H + CH_2O \qquad (11)$$

The Primary Process in 2,2′-Azoisobutane Photolysis at 3660 Å.—The quantum yield of nitrogen

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[8] J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.* **79**, 5921 (1957).

was determined in several experiments using 3660 Å. radiation and a conventional photochemical apparatus.[8] Azomethane photolysis was used as an actinometer.[9,10] In an oxygen-free system at 25° and 19.5 mm. of 2,2′-azoisobutane pressure, $\Phi_{N_2} = 0.63$. The inefficiency of the primary process is consistent with that observed for azoethane,[11–13] azoisopropane[14,15] and azo-*n*-propane[16] photolyses, and suggests that an excited molecule mechanism I-a, b, c is operative in azoisobutane photolysis at 3660 Å. This conclusion is supported by the rates of photodecomposition of azoisobutane in the experiments with different added gases shown in Table I (runs 9–13). The rate of loss of azoisobutane in experiments at equal intensities of absorbed light (0.0889 mm. of the azo-compound) was about the same for O_2, He or N_2 atmospheres: 2.4×10^{-3} mm./min. for 740 mm. of O_2 present (average of runs 3, 4 and 5 corrected to 0.0889 mm. of the azo-compound); 2.7×10^{-3} for 721 mm. of He and 19 mm. O_2; 2.6×10^{-3} for 721 mm. N_2 and 19 mm. O_2; and 1.8×10^{-3} mm./min. for 721 mm. CO_2 and 19 mm. of O_2. In terms of the suggested mechanism, collisional deactivation of excited azoisobutane molecules by helium in I-b is about 33% less efficient than by CO_2.

Products and Mass Balance.—Through the observed products, *tert*-butyl alcohol, *tert*-butyl hydroperoxide, formaldehyde, methanol, acetone and carbon dioxide, a reasonably good account can be made of all the *tert*-butyl radicals formed in the primary process. Within the experimental error the rate of *tert*-butyl radical formation ($2 \times -R_{t\text{-Bu}_2\text{N}_2}$) is equal to the summation of the rates of formation of the C_3 and C_4 oxidation products in accord with the suggested mechanism and the expected relation 12; see column 14, Table I. If reactions which degrade the primary

$$-2R_{t\text{-Bu}_2\text{N}_2} = R_{\text{Me}_2\text{CO}} + R_{t\text{-BuOH}} + R_{t\text{-BuO}_2\text{H}} \quad (12)$$

product formaldehyde are unimportant, then in terms of the suggested mechanism the rate of formaldehyde formation should be related to the summation of the rates of the alcohols and the hydroperoxide products. The data of column 16 of

$$R_{\text{CH}_2\text{O}} = R_{\text{MeOH}} + R_{t\text{-BuOH}} + R_{t\text{-BuO}_2\text{H}} \quad (13)$$

Table I show the test of this mass balance. In the runs at 19 mm. of oxygen pressure with added excess of nitrogen, helium or carbon dioxide gases, the relation 13 is followed reasonably well. In most of the runs at high oxygen pressures $R_{\text{CH}_2\text{O}}$ is significantly lower than that suggested by 13. Carbon dioxide is evident in these runs, and it is likely that carbon monoxide is also present, although its very low absorption coefficient makes our analysis for it unreliable here. The amount of carbon monoxide necessary to account completely for the mass unbalance in the high O_2-pressure runs yields an absorption peak which is near the noise level of the instrument. It is our interpretation that the partial destruction of formaldehyde occurs in the runs at high O_2 pressure; reactions of a vibrationally excited formaldehyde molecule, formed in the very exothermic disproportionation reactions 8, 9, 10 and 11, may occur in an early collision with an O_2 molecule in the O_2-rich systems; however, the excited molecules may be thermalized in the CO_2, N_2 or He-rich systems before reaction with O_2 is possible. Recent results of Dever and Calvert also suggest the importance of degradative processes of this sort from a study of the methyl radical in an O_2-rich system.[3]

Through the mechanism which has been suggested, a further mass balance is expected: the sum of the rates of formation of products of the methyl radical should equal the rate of formation of acetone, relation 14. In column 15 of Table I

$$R_{\text{Me}_2\text{CO}} = R_{\text{CH}_2\text{O}} + R_{\text{MeOH}} + R_{\text{CO}_2} \quad (14)$$

good agreement of the data with relation 14 can be noted.

Although the mass balances suggest that at least the major products have been found, the infrared spectrum of the products was examined carefully for indication of several other possible products of the reaction of *tert*-butyl radical with oxygen. At the end of a photochemical run the products acetone and *tert*-butyl alcohol were blanked in the reference cell, and the regions characteristic of di-*tert*-butyl peroxide were scanned; there was no indication of this product. Furthermore the infrared spectrum of a standard sample of this peroxide was unchanged after 45 minutes of irradiation in the photolysis cell. Thus di-*tert*-butyl peroxide cannot be a significant product here. This result is in accord with the predicted very low rate constant for the *tert*-butoxyl radical association reaction.[17,19] Isobutylene oxide was also below the detection limits in the 12.5 μ region.[18] Isobutane, isobutene, methane and ethane were absent. Nitrogen analysis was not possible with the infrared system employed in the majority of the work.

The Reactions of the *tert*-Butyl Free Radical in an Oxygen-rich Medium at 25°; (a) Reaction with Oxygen.—With the 7000-fold excess of oxygen used in most of these experiments, it is reasonable to expect that *tert*-butyl free radicals will react predominantly with oxygen to form alkyl peroxyl radicals in reaction 2. Although the possible reaction mode 15 may be slightly exothermic ($\Delta H^\circ_{298} \cong -1.6$ kcal./mole), it apparently has sufficient activation energy so that it is unimportant compared to 2 at 25°.

$$t\text{-C}_4\text{H}_9 + \text{O}_2 \longrightarrow \text{iso-C}_4\text{H}_8 + \text{HO}_2 \quad (15)$$

(b) **The Disproportionation and H-Abstraction Reactions of the *tert*-Butyl Peroxyl and the *tert*-Butoxyl Free Radicals.**—*tert*-Butyl peroxyl radicals formed in 2 could conceivably participate in the H-abstraction reactions (generalized by 16) involving 2,2′-azoisobutane, or formaldehyde, espe-

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[9] M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

[10] G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1955).

[11] J. L. Weininger and O. K. Rice, *J. Am. Chem. Soc.*, **74**, 6216 (1952).

[12] P. Ausloos and E. W. R. Steacie, *Bull. soc. chim. Belg.*, **63**, 87 (1954).

[13] H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

[14] R. W. Durham and E. W. R. Steacie, *ibid.*, **31**, 377 (1953).

[15] R. H. Riem and K. O. Kutschke, *ibid.*, **38**, 2332 (1960).

[16] J. A. Kerr and J. G. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961).

[17] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 242 (1951).

[18] W. A. Patterson, *Anal. Chem.*, **26**, 823 (1954).

cially in experiments with added formaldehyde.

$$t\text{-}C_4H_9O_2 + RH \longrightarrow t\text{-}C_4H_9O_2H + R \quad (16)$$

That this is not the case under our conditions is evident in the relative constancy of the ratio of the rate of *tert*-butyl hydroperoxide formation to that of *tert*-butyl alcohol under varied experimental conditions; see column 11 of Table I. Since the *tert*-butoxyl radical can be formed only from the *tert*-butyl peroxyl radical in this system, it follows that if 16 were of increasing importance as RH increased then the ratio $R_{t\text{-}BuO_2H}/R_{t\text{-}BuOH}$ should increase. The opposite trend, a small decrease in the ratio, is observed in runs with increasing azoisobutane or formaldehyde pressure, and the unimportance of reaction 16 is suggested. These results are consistent with the methyl radical–oxygen-rich system reported previously.[1-3] Reactions 3, 6 and 7 between alkyl peroxyl radicals seem to be the most reasonable source of alkoxyl radicals in these systems. The reactions 3 and 6 are analogous to 7 first suggested by Raley, *et al.*[6,17] Other possible alkyl peroxyl-to-alkoxyl conversion steps are not ruled out but seem much less likely. For example, $t\text{-}C_4H_9O_2 + O_2 \rightarrow t\text{-}C_4H_9O + O_3$, may occur, but the enthalpy change for the over-all reaction is probably about +25 kcal./mole so that thermally equilibrated $t\text{-}C_4H_9O_2$ radicals would not react measurably by this path at 25°.[3] The possible product ozone is below the detection limits of our equipment in this system.

The approximate mass balance between the formaldehyde rate and the hydroxylic products expressed by 13 is in accord with the occurrence of 8, 9 and 10; 11 is also included in the mechanism by analogy with the results of previous studies; R_{MeO_2H}/R_{MeOH} was about 0.1 in the methyl radical system and it would be expected to be at least this small and the MeO_2H well below the detection limits in the present work. A high exothermicity of reactions 8–11 and a very low activation energy are likely.[3] The analogous disproportionation reactions in which $t\text{-}C_4H_9O_2$ and $t\text{-}C_4H_9O$ act as H-atom sources are expected to be unimportant at 25°; since no stable unsaturated compound such as formaldehyde can be formed and can contribute to the lowering of the activation energy for these reactions, activation energies may be about equal to that expected for 16.

The ratio $R_{t\text{-}BuO_2H}/R_{t\text{-}BuOH}$ shows a slight increase as the azoisobutane pressure is lowered by a factor of 20 and as the light intensity is lowered by a factor of three. Such a trend would be expected in terms of the suggested mechanism since the rate of the first-order decomposition reaction of *tert*-butoxyl, reaction 4, should increase in importance compared to reaction 8, second order in radical concentration, as the steady state radical concentrations are lowered in experiments at lower absorbed light intensities. The slight increase in $R_{t\text{-}BuO_2H}/R_{t\text{-}BuOH}$ in runs with added carbon dioxide may indicate the effect of varied M on reaction 4. Recently Batt and Benson[19] have suggested a second-order character to this decomposition reaction. The importance of the hydroperoxide product in the *tert*-butyl radical–oxygen system is in striking contrast to the results found in the methyl radical–oxygen system[1-3]; here $R_{t\text{-}BuO_2H}/R_{t\text{-}BuOH} \cong 1$, while $R_{MeO_2H}/R_{MeOH} \cong 0.1$ in the methyl radical–oxygen system. There are several possible factors which might contribute to this difference. There are obvious steric differences between the radicals: there is a relatively available O-atom in the CH_3O, CH_3O_2 and $t\text{-}C_4H_9O_2$ radicals, favoring 9, 10 and 11, and a less available O-atom in the $t\text{-}C_4H_9O$ radical which would possibly slow reaction 8. Furthermore, the importance of the decomposition reaction of the $t\text{-}C_4H_9O$ radical would result in a relatively lower steady-state radical concentration of this radical than that of the CH_3O in the methyl radical–O_2 system where decomposition of the alkoxyl radical is unimportant.

Estimation of the Rate Constant for the Thermal Decomposition of the *tert*-Butoxyl Radical at 25°.—The appearance of acetone in the products suggests its formation from the thermal decomposition of the *tert*-butoxyl radical. The ratio of

$$(+ M) + t\text{-}C_4H_9O \longrightarrow CH_3COCH_3 + CH_3 (+ M) \quad (4)$$

the rates, $R_{Me_2CO}/R_{t\text{-}BuOH}$, increases with decreasing intensity for runs at constant azoisobutane pressure; the ratio is 2.2, 3.1 and 4.8 (runs 5, 6 and 7 of Table I) for full, two-thirds and one-third intensity, respectively. The trend is in accord with the suggested mechanism which demands increasing importance of 4, compared to 8, as the steady-state radical concentrations are lowered at the lowered intensities. If one assumed the suggested mechanism for acetone, methyl alcohol and *tert*-butyl alcohol formation, these product rates should satisfy the theoretical rate law 17

$$R_{Me_2CO}/R_{t\text{-}BuOH} = k_4k_{10}^{1/2}/k_8 \; R_{MeOH}^{1/2} \quad (17)$$

In Fig. 3, $R_{Me_2CO}/R_{t\text{-}BuOH}$ is plotted *vs.* $1/R_{MeOH}^{1/2}$. Although the rates of methanol formation are very small and subject to considerable uncertainty, the data do fit the theoretical relation 17 within the large experimental error. The bars through each point represent the maximum error in the estimates. They were arrived at by drawing a line from the origin to the highest and the lowest of the early experimental points used to construct the pressure–time curves from which initial rate data were determined. These are the least accurate of all of the points and only suggest the maximum error. From the slope of the least-squares line through the data of Fig. 3 it is estimated that $k_4k_{10}^{1/2}/k_8 \cong 0.51$ mm.$^{1/2}$ min.$^{-1/2}$ $= 1.5 \times 10^{-6}$ (moles/cc.-sec.)$^{1/2}$. It is reasonable to assume k_{10} and k_8 to be of the magnitude of the rate constants for alkyl radical association and disproportionations. Assuming $k_8 = 2.2 \times 10^{13}$ cc./mole-sec.,[20] and from purely statistical reasoning, $k_{10} = 2k_8$, we estimate $k_4 \cong 5.1$ sec.$^{-1}$ at 25°. Due to the polar nature of the alkoxyl and peroxyl radicals, an orientation favorable to reaction 10 or 8 would be assumed as the radicals approach one another, so that k_{10} and k_8 may be somewhat larger than the estimates used here, and the estimated value for k_4 somewhat smaller than the actual value. However, our estimate of k_4 is in reasonable agreement

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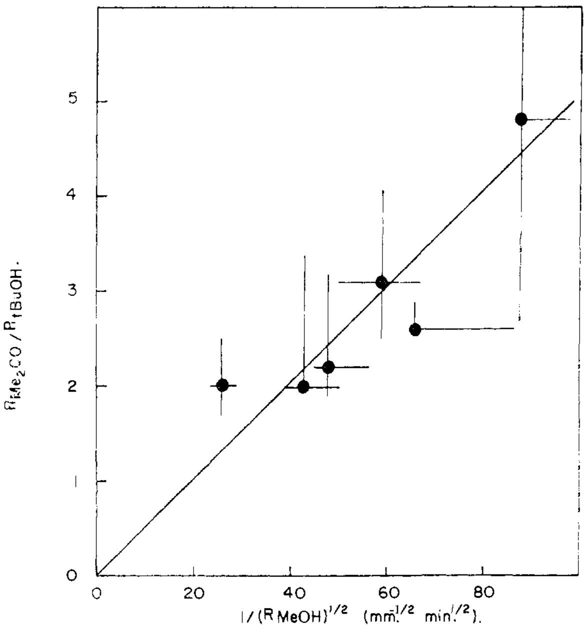

Fig. 3.—Plot of R_{Me_2CO}/R_{t-BuOH} *vs.* $1/(R_{MeOH})^{1/2}$; the slope of the plot is theoretically equal to the rate function $k_4k_{10}^{1/2}/k_8$.

with the extrapolation of higher temperature thermal data for reaction 4 obtained by other workers. With similar assumptions concerning the rate constants for radical reactions, Hinshelwood's data from the pyrolysis of di-*tert*-butyl peroxide–nitric oxide mixtures at 160° suggest $k_4 \cong 21$ sec.$^{-1}$ at 25°.[21] Batt and Benson's[19] thermal data for di-*tert*-butyl peroxide decomposition in the 130–160° temperature range give $k_4 \cong 27$–97 sec.$^{-1}$ at 25°. In view of the approximations and uncertainties involved in the present estimate and the estimates from the Hinshelwood's and Batt and Benson's data, the agreement is satisfactory and adds credence to the reaction mechanism suggested here. Data for reaction 4 based on photochemical decomposition of di-*tert*-butyl peroxide lead to values for k_4 at 25° which are about 10^2 to 10^3 times higher than those from thermal experiments; this may be the result of fragmentation of non-thermally equilibrated radicals formed in the primary act.[22,23]

Our mechanism has not incorporated the reaction 18 which was suggested recently by Hoare and Wellington in explanation of di-*tert*-butyl peroxide thermal and photodecompositions in the 50–135° temperature range.[24] Reaction 18 cannot be important in this system at 25° since the ratio $R_{Me_2CO}/R_{t\text{-}BuOH}$, column 12 of Table I, is invariant with change in O_2 pressure from 19 to 740 mm.; compare values for runs 5, 10 and 11. If 18 were important here a dramatic change in this ratio would be expected. If association between alkoxyl radicals and oxygen occurs, it must involve a very weak interaction at room temperature since the ultimate fate of the radicals is not altered by oxygen pressure variation.

$$(CH_3)_3CO + O_2 \longrightarrow (CH_3)_3COO_2 \longrightarrow CH_3O_2 + CH_3COCH_3 \quad (18)$$

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[Contribution from the Instrument Division, Varian Associates, Palo Alto, California and the Department of Chemistry, University of Kansas, Lawrence, Kansas]

Electron Paramagnetic Resonance of Aromatic and Aliphatic Nitro Anions in Aqueous Solution[1]

By L. H. Piette, Peter Ludwig and Ralph N. Adams

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A wide variety of aromatic and aliphatic nitro anion radicals can be generated in aqueous media. The lifetimes are reasonably long. The e.p.r. spectra can be interpreted with ease in most cases. One of the most significant findings is that a relatively large solvent effect on the N^{14} coupling constant exists for the aromatic compounds, whereas it is absent in the spectra of the aliphatic compounds.

The properties of aromatic nitro anion radicals generated electrochemically in acetonitrile have been dealt with thoroughly by Geske and Maki.[2,3] Recently it was reported that both aromatic and aliphatic nitro anion radicals could be generated in ordinary aqueous media[4]. We wish to summarize the aspects of the aqueous solution results which are of interest in electron paramagnetic resonance (e.p.r.) studies. Details of the electrogeneration technique in aqueous media are given elsewhere.[5]

Experimental

All e.p.r. studies were carried out with a Varian V-4500 spectrometer employing 100-kc. field modulation. The cells for electrogeneration were rectangular Varian cells with an inner thickness of *ca.* 0.5 mm. Generations were performed

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