of the favorable resonance distribution. The ability to develop ionic charge in the transition state varies with the cation and with the solvent as well as with the organic group. Thus, organometals undergo proton abstraction and nucleophilic substitution reactions much more easily in polar solvents like dimethyl sulfoxide[63] and hexamethylphosphoramide[64] than in THF or ether. Benzyllithium appears to react faster than phenyllithium[47,65] in processes requiring large charge separation, whereas the opposite may be the case[66] when the activated complex for a reaction requires relatively little charge separation, such as in a transition state resembling reactants.

In summary, it has been demonstrated that isotope effects in reactions of an organometallic compound with hydrocarbon acids in THF change with the rate of the reaction. The variation of the isotope effect for proton transfer from weakly acidic hydrocarbons to a given organometal supports the theoretical prediction of a maximum in isotope effects for a series of closely related reactions. The position of the maximum in the isotope effect and the shape of the curve may be an indication of the effect of the cation or the organic group on the ionic nature of these organometallic compounds.

(63) J. T. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Amer. Chem. Soc.*, **89**, 1728 (1967).

(64) H. Normant and T. Cuvigny, *Bull. Soc. Chim. Fr.*, 1881 (1965).

(65) E. Grovenstein, Jr. and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 1852 (1967).

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Radiation-Induced Oxidation of 2-Propanol by Dialkyl Peroxide[1a]

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Contribution from the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556. *Received May 20, 1968*

Abstract: Solutions of di-*t*-butyl peroxide in 2-propanol have been subjected to ^{60}Co γ irradiation. Under alkaline conditions di-*t*-butyl peroxide was reduced to *t*-butyl alcohol and the solvent oxidized to acetone according to the stoichiometry $(t\text{-BuO})_2 + \text{Me}_2\text{CHOH} \rightarrow 2t\text{-BuOH} + \text{Me}_2\text{CO}$. Yields were independent of alkali concentration when the latter exceeded about 2×10^{-2} *M*, but were first order in peroxide concentration. The magnitudes of the yields indicate a chain reaction. It is proposed that the chain is initiated by radiolytic intermediates that undergo hydrogen abstraction reactions with the solvent to produce dimethylhydroxymethyl radicals (I). The latter ionize, and the resulting radical anions (II) undergo a redox reaction with di-*t*-butyl peroxide, decomposing it to *t*-butoxide and a free radical (*t*-butoxy) that can regenerate I from the solvent. The chain reaction exhibits a dose-rate dependence that is consistent with termination being second order in chain carrier. Retardation and inhibition were observed in the presence of compounds that may be expected to undergo nondissociative electron transfer with II (nitrobenzene, benzophenone, oxygen, sulfur hexafluoride, perfluorocyclobutane) but were not observed in the presence of neutral free radical scavengers (1-hexene, benzene) or compounds that may be expected to dissociate on electron capture (methyl bromide, bromobenzene, carbon tetrachloride, nitrous oxide).

In a recent study of the base-catalyzed chain decomposition of nitrous oxide in alcoholic solution, the photolysis of dissolved di-*t*-butyl peroxide (DTBP) was used as a source of initiating free radicals.[3] Incidental to this study was the observation that, in the absence of nitrous oxide, decomposition of DTBP and the concomitant oxidation of the solvent were increased by the presence of alkali. The suggested cause of this increase was that DTBP itself enters into a chain reaction in which propagation involves a redox reaction with the ionized form of the solvent α-hydroxyalkyl radical (the latter being oxidized to the ketone, while DTBP is reduced to a *t*-butoxy radical and a *t*-butoxide ion). This type of reaction is an interesting extension of the chemistry of dialkyl peroxides,[4] and therefore worthy of more detailed study. Toward this end the present communication reports further experiments on the chain decomposition of DTBP in alkaline 2-propanol in which the chain-initiating species are generated by the absorption of ^{60}Co γ rays in the solution.

Experimental Section

Materials. 2-Propanol (Baker reagent) was used as received. Acetone ($\sim 10^{-5}$ *M*) was the only detectable impurity in the sample used. Potassium hydroxide (Baker) and DTBP (K & K Laboratories) were similarly used as received. Nitrous oxide, sulfur hexafluoride, perfluorocyclobutane, and methyl bromide (Matheson) were purified from air by trap-to-trap distillation on a vacuum line. All other materials were of reagent grade and used without further purification.

Procedure. All solutions were freshly prepared directly before radiolysis to minimize any decomposition of the peroxide. Aliquots (5 ml) were placed in 13-mm o.d. Pyrex tubes fitted with standard-taper joints. These were attached to a vacuum line and thoroughly degassed by successive freeze-pump-thaw cycles. When a gaseous solute was to be added this was admitted into an evacuated bulb of known volume to a measured pressure, and then the gas was condensed into the reaction tube cooled in liquid nitrogen. The reaction tube was then sealed and allowed to warm to room temperature before irradiation. When a gaseous additive was present, the tube was vigorously shaken for at least 10 min to ensure equilibration.

Samples were irradiated at room temperature in a 4-kc ^{60}Co source. Dose rates received by Fricke dosimeter solutions, based on $G(\text{Fe}^{3+}) = 15.6$, were 1.57×10^{18} eV ml^{-1} min^{-1}. The dose received by a particular solution was calculated by correction for the

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(1) (a) Part IV: The γ Radiolysis of 2-Propanol. Part III: W. V. Sherman, *J. Phys. Chem.*, **71**, 1695 (1967); (b) address inquiries to Chicago State College, Chicago, Ill. 60621.

(2) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U.S. Atomic Energy Commission. This is AEC Document No. COO-38-608

(3) W. V. Sherman, *J. Am. Chem. Soc.*, **89**, 1302 (1967).

(4) For reviews see A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961, and A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954.

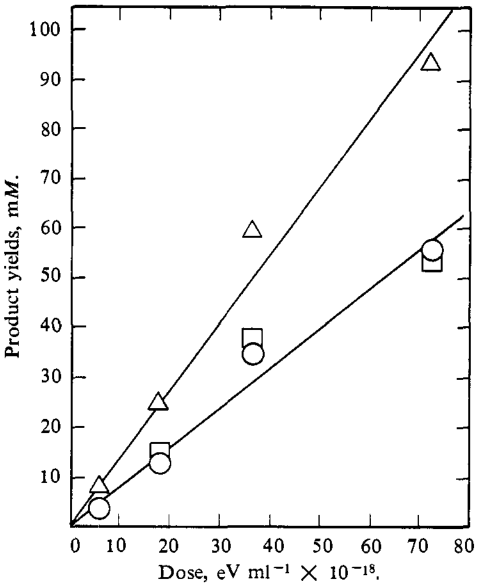

Figure 1. Product yields from alkaline DTBP solutions as a function of radiation dose: [KOH] = [DTBP] = 0.1 *M;* dose rate = 1.2 × 10^{18} eV ml^{-1} min^{-1}; △, *t*-butyl alcohol; ○, acetone; □, −DTBP.

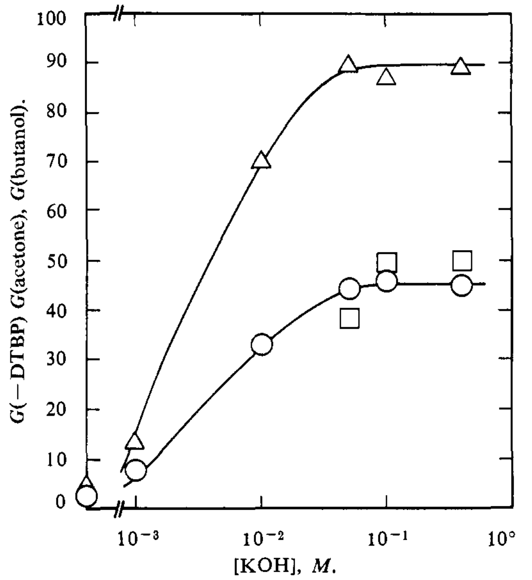

Figure 2. Product yields from DTBP solutions as a function of potassium hydroxide solutions: [DTBP] = 0.1 *M;* △, *t*-butyl alcohol; ○, acetone; □, −DTBP.

electron density of 2-propanol relative to that of the dosimeter (0.764).

After irradiation the reaction tubes were allowed to stand for 1 hr. They were then opened, and the contents analyzed by gas chromatography (F & M Model 609) using a column of 5% Carbowax 1500 on Chromosorb G at 50° with flame ionization detector. The relative elution times were DTBP, 0.40; acetone, 0.54; benzene, 0.80; *t*-butyl alcohol, 0.87; and 2-propanol, 1.00.

Results

The yield of acetone from pure 2-propanol (Table I) is in good agreement with that obtained by Schulte-Frohlinde and coworkers[5] at a similar dose. Addition of DTBP produced a small decrease in *G*(acetone) (Table I). *t*-Butyl alcohol was the only other liquid product identified.

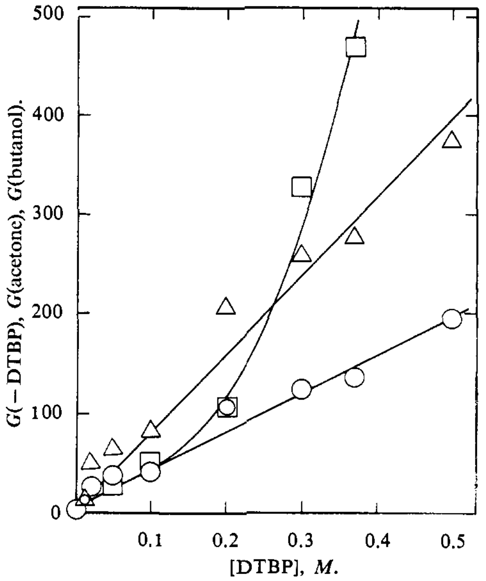

Figure 3. Product yields from alkaline solutions as a function of DTBP concentration: [KOH] = 0.1 *M;* △, *t*-butyl alcohol; ○, acetone; □, −DTBP.

Acetone and *t*-butyl alcohol were the only major liquid products observed in the gas chromatogram of irradiated alkaline solutions of DTBP. The yields of these products together with the amount of DTBP consumed increased linearly with dose over the range 6.0 × 10^{17} to 7.2 × 10^{19} eV ml^{-1} (Figure 1), with the highest dose corresponding to 56% consumption of DTBP.

Product yields are plotted as a function of potassium hydroxide concentration ([DTBP] = 0.10 *M*) and DTBP concentration ([KOH] = 0.10 *M*) in Figures 2 and 3, respectively. These yields were determined for a single dose (1.8 × 10^{19} eV ml^{-1}) except for the case [KOH] = [DTBP] = 0.10 *M* (see Figure 1). Product yields at three different dose rates are presented in Table II.

Table I. Radiolysis of Neutral DTBP Solutions[a]

[DTBP], *M*	*G*(−DTBP)	*G*(acetone)	*G*(*t*-butyl alcohol)
0		3.0	
1 × 10^{-2}	*b*	2.7	1.6
5 × 10^{-2}	*b*	2.7	3.1
1 × 10^{-1}	*b*	2.7	3.7
1 × 10^{-1}	1.4[c]	3.7[c]	3.1[c]
5 × 10^{-1}	*b*	2.7	8.0

[a] Dose = 3.6 × 10^{19} eV ml^{-1}. [b] Too small to be determined. [c] Dose = 1.1 × 10^{21} eV ml^{-1}.

Table II. Dose Rate Effect on Alkaline DTBP Solutions[a]

Dose rate, 10^{16} eV ml^{-1} min^{-1}	*G*(−DTBP)	*G*(acetone)	*G*(*t*-butyl alcohol)
120	50	46	87
7.2	87	78	145
1.2	240	167	339

[a] [KOH] = [DTBP] = 0.10 *M;* total dose = 6.0 × 10^{18} eV ml^{-1}.

In the solute effect study (Table III) three classes may be distinguished: (1) solutes that had little effect on

[5] D. Schulte-Frohlinde, C. v. Sonntag, and G. Lang, *Z. Physik. Chem.* (Frankfurt am Main), **45**, 257 (1965).

the oxidation of the solvent to acetone (1-hexene, benzene); (2) solutes that decrease solvent oxidation (nitrobenzene, benzophenone, oxygen, sulfur hexafluoride, perfluorocyclobutane); and (3) solutes that enhance solvent oxidation (nitrous oxide, methyl bromide, bromobenzene, carbon tetrachloride). Potassium bromide was present as a white precipitate in the methyl bromide and bromobenzene solutions after irradiation, and a precipitate of potassium chloride was similarly observed as a product of the radiolysis of the carbon tetrachloride solution. Quantitative determination was not attempted.

Table III. Solute Effects on Alkaline DTBP Solutions[a,b]

Solute	Concn, *M*	*G*(−DTBP)	*G*(acetone)	*G*(*t*-butyl alcohol)
None		50 ± 2[c]	46 ± 2[c]	87 ± 5[c]
1-Hexene	2×10^{-2}	50	55	94
1-Hexene	1×10^{-1}	32	39	62
Benzene	1×10^{-1}	55	43	*d*
Nitrobenzene	1×10^{-3}	<10	8.1	12
Nitrobenzene	1×10^{-2}	<10	8.8	7.0
Benzophenone	1×10^{-2}	23	28	45
Oxygen	*e*	≦5[f]	5.3[f]	4.5[f]
Sulfur hexafluoride	1×10^{-2}	17	28	11
Perfluorocyclobutane	1×10^{-2}	<10	18	10
Nitrous oxide	1×10^{-2}	57	78	112
Methyl bromide	1×10^{-2}	62	70	97
Bromobenzene	2×10^{-2}	57	105	*d*, *g*
Carbon tetrachloride	1×10^{-2}	266	105	~8

[a] [KOH] = [DTBP] = 0.1 *M*. [b] Dose = 3.6×10^{19} eV ml^{-1}, unless otherwise noted. [c] Linear over dose range 0.6–72 $\times 10^{18}$ eV ml^{-1}. [d] *t*-Butyl alcohol eluted in the tail of the large benzene peak and could not be accurately determined. [e] Air-saturated solution. [f] Dose = 1.1×10^{20} eV ml^{-1}. [g] Benzene identified as major product, *G*(benzene) = 72.

Discussion

The small values for *G*(−DTBP) in neutral solution (as measured by the formation of *t*-butyl alcohol) do not indicate a chain reaction of significant chain length. In contrast, Huyser and Bredeweg[6] obtained evidence for a chain in their study of the thermal decomposition of DTBP in primary and secondary alcohols at elevated temperatures. Under their experimental conditions hydroxyalkyl radicals cleaved DTBP at the oxygen–oxygen linkage to give *t*-butyl alcohol and a *t*-butoxy radical. It must therefore be concluded that under the present experimental conditions either the product of the lifetime and yield of dimethylhydroxymethyl radicals is small, or the activation energy for reaction with DTBP is too high to allow efficient reaction at ~30°.

The chemistry of alkaline solutions containing 0.2 *M* or less DTBP subjected to radiation intensities greater than $\sim 7 \times 10^{16}$ eV ml^{-1} min^{-1} conforms to the

$$(t\text{-BuO})_2 + \mathrm{Me_2CHOH} \rightarrow 2t\text{-BuOH} + \mathrm{Me_2CO} \qquad \text{(A)}$$

stoichiometry A. The dependence of product yields on the concentration of DTBP and potassium hydroxide closely parallels that observed in the radiation-induced chain oxidation of alkaline 2-propanol by nitrous oxide.[7] In both reactions *G*(products) is first order in the solute undergoing decomposition. Similarly, the onset of the chain occurs when the potassium hydroxide concentration exceeds $\sim 1 \times 10^{-3}$ *M*, and the yields reach limiting values when the hydroxide concentration exceeds $\sim 2 \times 10^{-2}$ *M*. By analogy it is proposed that the kinetically significant reactions in the DTBP chain are
initiation

$$\mathrm{Me_2CHOH} \rightsquigarrow \mathrm{X_1, X_2} \ldots\ldots\ldots \mathrm{X}_i + \text{other products} \qquad (1)$$

where X_i is any species (*e.g.*, $\mathrm{e_{solv}}^-$, H·, organic radical) that can undergo a hydrogen abstraction reaction with the solvent

$$\mathrm{X}_i + \mathrm{Me_2CHOH} \rightarrow \mathrm{X}_i\mathrm{H} + \underset{\mathrm{I}}{\mathrm{Me_2\dot{C}OH}} \xrightarrow{\mathrm{OH}^-} \underset{\mathrm{II}}{\mathrm{Me_2\dot{C}O^-}} \qquad (2)$$

$$\mathrm{X}_i + \mathrm{DTBP} \longrightarrow \mathrm{X}_i(-\mathrm{H}) + t\text{-BuOH} + t\text{-BuO}\cdot \qquad (3)$$

propagation

$$\mathrm{II} + \mathrm{DTBP} \longrightarrow \mathrm{Me_2CO} + t\text{-BuO}^- + t\text{-BuO}\cdot \qquad (4)$$

$$t\text{-BuO}\cdot + \mathrm{Me_2CHOH} \longrightarrow t\text{-BuOH} + \mathrm{I} \xrightarrow{\mathrm{OH}^-} \mathrm{II} \qquad (5$$

termination

$$2\mathrm{II} \xrightarrow{\mathrm{Me_2CHOH}} \mathrm{Me_2CO} + 2\mathrm{Me_2CHO^-} \qquad (6)^{8,9}$$

$$\mathrm{II} + \mathrm{M} \longrightarrow \mathrm{Me_2CO} + \mathrm{M^-} \qquad (7)$$

where M is an impurity.

If the principal termination step is second order in chain carriers (reaction 6) then, assuming steady-state kinetics

$$G(t\text{-BuOH}) = 2G(\mathrm{Me_2CO}) = 2\Sigma G(\mathrm{X}_i) + 2k_4[\mathrm{DTBP}][\Sigma G(\mathrm{X_1})/k_6 I]^{1/2} \qquad \text{(B)}$$

where *I* = dose rate.

The linear dependence of product yields on the reciprocal of the square root of the dose rate (Figure 4) is consistent with bimolecular termination as expressed by eq B. Assuming then that expression B pertains to the present experimental conditions, then the slope of the square root plot in Figure 4, $\mathrm{d}G(\mathrm{Me_2CO})/\mathrm{d}(1/I^{1/2})$, is given by expression C. Although k_6 is not known it

$$k_4[\mathrm{DTBP}][\Sigma G(\mathrm{X}_i)/k_6]^{1/2} \qquad \text{(C)}$$

may be expected to be not too dissimilar to the second-order rate constant for the disappearance of $(\mathrm{C_6H_5})_2\dot{\mathrm{C}}\mathrm{O}^-$ in alkaline 2-propanol. This has been determined to be 1×10^9 M^{-1} sec^{-1}.[10] Hence, $k_4 = 2.5 \times 10^3 \cdot (\Sigma G(\mathrm{X}_i))^{-1/2}$ M^{-1} sec^{-1}. A suitable choice for $\Sigma G(\mathrm{X}_i)$ would be *G*(*t*-BuOH) from a neutral solution containing the same concentration of DTBP where no chain is assumed (3.7, see Table I). Hence k_4 is tentatively estimated to be $\sim 1.3 \times 10^3$ M^{-1} sec^{-1}. This low value

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(6) E. S. Huyser and C. J. Bredeweg, *J. Am. Chem. Soc.*, **86**, 2401 (1964).

(7) See ref 1, part III.

(8) Additional termination reactions involving two radical species are given by reactions 6a–d. However, in view of the ionization of I to II

$$2\mathrm{I} \longrightarrow \mathrm{Me_2CO} + \mathrm{Me_2CHOH} \qquad \text{(6a)}$$

$$\longrightarrow \mathrm{Me_2C(OH)C(OH)Me_2} \qquad \text{(6b)}$$

$$\mathrm{I} + \mathrm{II} \longrightarrow \mathrm{Me_2CO} + \mathrm{Me_2CHO^-} \qquad \text{(6c)}$$

$$t\text{-BuO}\cdot + \mathrm{I} \longrightarrow t\text{-BuOH} + \mathrm{Me_2CO} \qquad \text{(6d)}$$

(reaction 2) being very fast and having a $\mathrm{p}K_\mathrm{a}$ of 12.2 (ref 9) the participation of I in chain termination may be expected to be kinetically unimportant.

(9) K. D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsenges. Physik. Chem.*, 70, 756 (1966).

(10) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

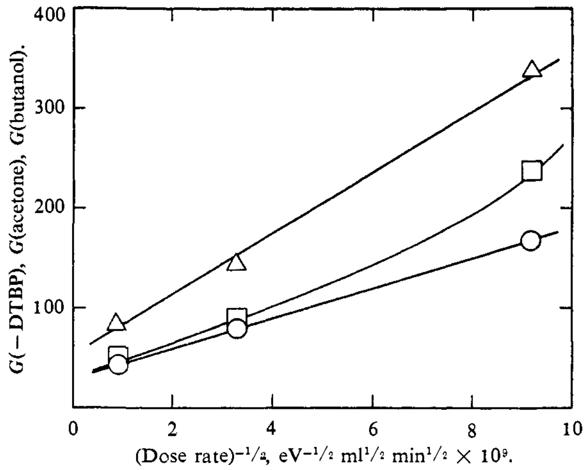

Figure 4. Product yield from alkaline DTBP solutions as a function of dose rate: [KOH] = [DTBP] = 0.1 M; dose = 6.0×10^{18} eV ml^{-1}; △, t-butyl alcohol; ○, acetone; □, −DTBP.

for k_4 is consistent with the small rate constant estimated for the dissociative electron capture by nitrous oxide from radical anion II ($10^{2\pm1}$ M^{-1} sec^{-1}).[7]

While for all radiolyses of alkaline DTBP solutions carried out in the absence of added solute $G(t\text{-BuOH}) \approx 2G(\text{Me}_2\text{CO})$, at high DTBP concentrations (>0.2 M) and low radiation intensities the disappearance of DTBP did not conform to the stoichiometry of A. $G(-\text{DTBP})$ progressively exceeded $G(t\text{-BuOH})/2$ with increasing DTBP concentration and decreasing radiation intensity, and it must therefore be concluded that under these conditions chain-carrying radicals in the system, in addition to undergoing reactions 2–7, react with DTBP to give other (unidentified) products.

The compounds used to study solute effects (Table III) may be classified as (i) compounds that are good free-radical scavengers, do not attach low-energy electrons in the gas phase, and react relatively slowly with electrons in solution[11] (1-hexene, benzene); (ii) compounds that attach low-energy electrons nondissociatively in the gas phase,[12] and undergo fast reaction with electrons in solution[11] (nitrobenzene, benzophenone, oxygen, sulfur hexafluoride, perfluorocyclobutane); and (iii) compounds that undergo dissociative electron capture with low-energy electrons in the gas phase,[13] and undergo fast reaction with electrons in solution[11] (nitrous oxide, methyl bromide, bromobenzene, carbon tetrachloride). Compounds of class ii and iii may be expected to undergo charge transfer with radical anion II, the former in a nondissociative process (reaction 8), the latter dissociatively (reaction 9).

$$\text{II} + \text{AB} \longrightarrow \text{Me}_2\text{CO} + \text{AB}^- \qquad (8)$$

$$\text{II} + \text{AB} \longrightarrow \text{Me}_2\text{CO} + \text{A} + \text{B}^- \qquad (9)^{14,15}$$

The inefficient inhibitory influence of compounds of class i on product yields is consistent with the rapid ionization of radical I, and II rather than I being the longer lived chain carrier (the reactivity of benzene toward the neutral free radical I should not be too dissimilar to that of the aromatic compounds of class ii and iii). Compounds of class ii can compete with DTBP for the charge on II. Since these compounds have high electron affinities, subsequent charge transfer between AB$^-$ and DTBP is inefficient, and retardation or inhibition of the chain is observed. The remarkable efficiency with which nitrobenzene acts as an inhibitor was noted previously with the nitrous oxide chain reaction in both 2-propanol[3,7] and methanol.[16] Although compounds of class iii compete with DTBP for the charge on II each successful electron capture by these solutes results in the formation of a free radical (a neutral radical in the case of the halides, a radical anion, O·$^-$, in the case of nitrous oxide) and hence the chain carrier II.

The operation of the last mentioned process by itself should result in no change in product yields and $G(-\text{DTBP})$. However, the presence of an additional electron scavenger at 10^{-2} M may be expected to increase the effective yield of "primary" radiolytic reactive intermediates (by scavenging electrons in the radiation spurs),[17] and hence $\Sigma G(\text{X}_i)$. This could account for the enhancement of DTBP disappearance and product formation in the presence of these solutes. The observed deviation from stoichiometry A is a consequence of radicals other than t-butoxy being the precursors of I and hence acetone.

In conclusion, the observation of a chain reaction involving DTBP affords further support for the generality of the rule, proposed previously,[15] defining the criteria for the observation of radical-initiated chain decomposition of a compound in alkaline alcoholic media. This is that the compound must (a) have an electron affinity sufficient to facilitate electron transfer from the ionized form of the solvent α-hydroxyalkyl radical, and (b) yield a free radical on electron capture which is capable of abstracting a carbinol hydrogen from the solvent to give an α-hydroxyalkyl radical.

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(11) M. Anbar and P. Neta, *Intern. J. Appl. Radiation Isotopes*, **18**, 493 (1967).

(12) R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966), for SF_6, $\text{C}_6\text{H}_5\text{NO}_2$; Report ORNL-TM-1409, 1966, for C_4F_8; *J. Chem. Phys.*, **43**, 4273 (1965), for O_2. Electron attachment experiments with benzophenone have not been reported, but it may be expected to be a nondissociative process.

(13) G. J. Schultz, *J. Chem. Phys.*, **34**, 1778 (1961), for N_2O; V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **54**, 127 (1955), for CH_3Br; L. G. Christophorou, R. N. Compton, G. S. Hurst, and R. W. Reinhardt, *J. Chem. Phys.*, **45**, 536 (1966), for $\text{C}_6\text{H}_5\text{Br}$; A. F. Gaines, J. Kay, and F. M. Page, *Trans. Faraday Soc.*, **62**, 874 (1966), for CCl_4.

(14) Evidence for this reaction for methyl bromide and bromobenzene is discussed in ref 15. Evidence for carbon tetrachloride and nitrous oxide is presented in ref 7.

(15) W. V. Sherman, *J. Phys. Chem.*, **72**, 2287 (1968).

(16) W. V. Sherman, *ibid.*, **71**, 4245 (1967).

(17) For a discussion see W. V. Sherman in "Advances in Free-Radical Chemistry," Vol III, G. H. Williams, Ed., Academic Press, London, 1968.