Cage Reactions of *t*-Butoxy Radicals. Effects of Viscosity and of Intervening Molecules[1]

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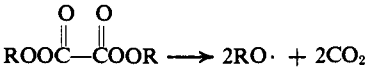
Abstract: The effects of changes in viscosity on amounts of cage DPB (*t*-BuOO-*t*-Bu) produced from DBPO (*t*-BuOOCOCOOO-*t*-Bu), from DBH (*t*-BuON=NO-*t*-Bu), and from DBP itself are reported. The presence of a nitrogen molecule or two carbon dioxide molecules in the cage causes the efficiencies of radical production to increase in the order DBP < DBH < DBPO. That these initiators maintain a constant ratio of efficiencies over a wide range of viscosities is presented as evidence that secondary recombination does not occur in these cases. Large cage effects have been demonstrated in DBP decompositions. However, no simple function of viscosity adequately describes the changes in cage effects with solvent changes even in simple hydrocarbons. Finally DBH is used as a model for the elusive tetroxide in a discussion of autoxidation termination.

Decomposition of free-radical initiators in solution produces a pair of radicals in a solvent cage.[2a,b] Extensive theoretical discussions[3] and limited experimental studies[2b–d,3c,4,5] have been devoted to the elucidation of the behavior of such cage radical pairs.

Alkoxy radicals may be produced from a wide variety of precursors and are subject to an unprecedented

$$\mathrm{ROOR} \longrightarrow 2\mathrm{RO}\cdot \qquad (1)^{6}$$

$$\mathrm{RONNOR} \longrightarrow 2\mathrm{RO}\cdot + \mathrm{N_2} \qquad (2)^{7}$$



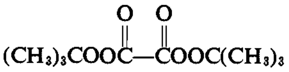
$$\mathrm{ROO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OOR} \longrightarrow 2\mathrm{RO}\cdot + 2\mathrm{CO_2} \qquad (3)^{8}$$

variation in cage effect with changes in viscosity.[9] We have therefore begun a systematic study of the effects of radical size and structure, viscosity, solvent structure, and nature and number of intervening molecules on the cage collapse of alkoxy radicals.

In this paper we report the effect of viscosity on the cage collapse of *t*-butoxy radicals generated thermally and photolytically from di-*t*-butyl peroxide (DBP),[6] di-*t*-butyl hyponitrite (DBH),[7] and di-*t*-butyl peroxyoxalate (DBPO).[8]

$\mathrm{(CH_3)_3COOC(CH_3)_3}$
(DBP)

$\mathrm{(CH_3)_3CON{=}NOC(CH_3)_3}$
(DBH)



$$\mathrm{(CH_3)_3COO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OOC(CH_3)_3}$$

(DBPO)

Experimental Section

Isooctane (Eastman Spectral Grade), *n*-pentane, *n*-hexane, and *n*-heptane (Phillips Reagent), *n*-octadecane (99% olefin free, Matheson), and Nujol (Plough, Inc.) were used without purification. The ultraviolet cutoff point of Nujol was found to be 230 mμ. Di-*t*-butyl peroxyoxalate (DBPO) and di-*t*-butyl hyponitrite (DBH) were prepared as previously described.[7,8] Di-*t*-butyl peroxide was distilled under nitrogen at 80 torr, bp 47.5°. Mixed solvents were prepared by weight.

Viscosities were measured at 45.0 ± 0.01° in modified Ostwald, Cannon-Fenske (ASTM) viscosimeters.[10] Densities were measured at the same temperature when not available from literature. Literature values for pentane, hexane, heptane, and octadecane were used.[11]

Products of thermal or photochemical decompositions of DBH or DBPO were determined by glpc (as previously described)[7,9] except in solvents containing Nujol or octadecane where the infrared method was used. The two methods gave identical results in isooctane. The concentrations of *t*-butyl alcohol (TBA) and di-*t*-butyl peroxide (DBP) were read from concentration *vs.* peak area curves or from concentration *vs.* log I_0/I curves obtained from known mixtures. Infrared analyses were carried out in 0.1-mm cells on a Cary-White Model 90 infrared spectrophotometer. The 875-cm^{-1} peak of DBP and the 915-cm^{-1} peak of TBA were used in these analyses. Standard log I_0/I *vs.* concentration of TBA and DBP plots were linear and identical in isooctane and 40% Nujol–isooctane. The glpc and infrared methods were accurate to ±3 and ±5%, respectively, of values determined.

In a typical run, an approximately 0.1 *M* solution of DBH was decomposed completely (thermally or photolytically) and the solution subjected to the analyses described above. The products were TBA and DBP with less than 1% biproducts (*e.g.*, acetone) in all solvents. The cage effects were therefore calculated as

$$\text{fraction of cage collapse} = \frac{[\mathrm{DBP}]}{[\mathrm{DBP}] + ([\mathrm{TBA}]/2)} \qquad (4)$$

Photodecompositions were carried out in an apparatus which rotated small quartz test tubes around a central light source at 60 rpm. The light was a General Electric H85A3 ultraviolet lamp with the Pyrex envelope removed. The lamp was placed in a quartz test tube in the center of a rotating circle of 10-mm diameter by 50-mm long tubes. The light was parallel to the test tubes and the distance of tubes from the light center was 3.5 cm. The whole apparatus was submerged in a constant-temperature water bath to maintain the tubes at temperature ±0.01°. A Vycor sleeve was fitted over the central quartz tube as a filter.

To determine the rates of photodecomposition the quartz tubes were filled to identical heights with the solutions, capped with

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(1) Supported by the Air Force Office of Scientific Research Grant AF-AFOSR-514-66.

(2) (a) T. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934); (b) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955); (c) G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964); (d) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964); (e) C. S. Wu, G. S. Hammond, and J. M Wright, *ibid.*, **82**, 5386 (1960); (f) G. S. Hammond, C. S. Wu, O. D. Trap, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960); (g) S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 827 (1962).

(3) (a) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); (b) *ibid.*, **78**, 5486 (1956); (c) *ibid.*, **82**, 1868 (1960); (d) "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press Ltd., London, 1961.

(4) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 3486 (1955).

(5) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962), and other references quoted there.

(6) J. H. Raley, F. F. Rust, and W. E. Vaughn, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

(7) H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, **49**, 6163 (1966).

(8) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(9) (a) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965); (b) R. Hiatt, private communication.

(10) L. Ubbelohde, "Zur Viskosimetrie," S. Hirtzel, Ed., 7th ed., S. Hirzel Verlag, Stuttgart, 1965.

(11) R. R. Dreisbach, Ed., "Physical Properties of Chemical Compounds," Advances in Chemistry Series, No. 22, American Chemical Society, Washington, D. C., 1959, p 47.

Table I. Cage Combinations (*F*) of *t*-Butoxy Radicals from DBPO, DBH, and DBP at 45.0° in Various Solvents[a]

Solvent	Density, g/ml	Viscosity (centistokes)	η, cp	Fraction of cage collapse, *F* DBPO[e]	 DBH[c]	 DBP[d]	R_{DBPO}/R_{DBH}	R_{DBH}/R_{DBP}
n-Pentane	...	...	0.20[b]	(0.039)	(0.037)	[0.04][e]	1.0	1.0
n-Hexane	...	0.3936[b]	0.250[b]		(0.063)			
n-Heptane	...	0.4923[b]	0.326[b]		(0.084)			
Isooctane	0.6737	0.562	0.379	0.086(0.081)	(0.098)	0.12	1.23	1.26
n-Octadecane	...	3.626[b]	2.774[b]	...	0.30	...		
20% Nujol	0.7086	0.865	0.613	0.13	0.16	0.19	1.27	1.23
40% Nujol	0.7474	1.52	1.14	0.18	0.21	0.28	1.22	1.46
60% Nujol	0.7839	3.52	2.76	0.26	0.30	0.34	1.22	1.20
70% Nujol	0.8041	5.85	4.70	0.31	0.36	0.48	1.26	1.64
80% Nujol	0.8249	10.6	8.74	0.40	0.46	0.60	1.27	1.76
90% Nujol	0.8466	25.6	21.7	0.43	0.56	0.70	1.69	1.83
100% Nujol	0.8683	92.0	79.9	0.54	0.68	0.76	1.80	1.50
100% Nujol	0.8683	92.0		...	0.65,[f] 0.67	...		

[a] The mixed solvents contained isooctane and Nujol. [b] Reference 11. [c] Cage collapse in DBH and DBPO decompositions were measured by the infrared method except those in parentheses which were determined by glpc. [d] From kinetic data. See following section. [e] Assigned a value of $F = 0.04$ arbitrarily (see text). [f] Photodecomposition. All other DBH and DBPO were from thermal decomposition. [g] $R = (1 - F)/F$. [h] In 90% chlorobenzene–10% cumene at 45.0°, $\eta = 0.6$ cp, $F_{DBH} = 0.091$.

syringe caps, and placed in the apparatus. A metal sleeve was inserted around the lamp to prevent photodecomposition, the lamp turned on, and after 15 min the metal sleeve removed to begin the photolysis. Tubes were removed at intervals, cooled, and analyzed as described above (or elsewhere).[9]

The Vycor sleeve was used to remove differences in self absorptions between Nujol and isooctane due to the differences in end absorptions. To test the constancy of light sources in these solvents with the Vycor filter DBH was photodecomposed in each solvent at 45.0°. The observed rates were 4.25×10^{-4} sec^{-1} in isooctane and 4.33×10^{-4} sec^{-1} in Nujol using the Vycor filter. In isooctane the rate was 6.5×10^{-4} sec^{-1} without the Vycor sleeve. Most of the rates of DBP photodecomposition were determined in duplicate or triplicate and the deviations are listed in the tables.

Rates of thermal decompositions of DBP were determined approximately by placing ampoules containing 0.1 *M* solutions of DBP in Nujol and in isooctane in an oven at 135 ± 1°. Ampoules of Nujol and isooctane solutions were removed simultaneously and analyzed by the infrared method. The rates were 3.6×10^{-6} sec^{-1} in Nujol and 5.2×10^{-6} sec^{-1} in isooctane, and the viscosities at 135° were ~4 and ~0.2 cp, respectively.

Results

Cage effects in carbon radical pairs are generally determined by the use of inhibitors which prevent solution recombination of radicals. However, the presence of DPPH or cumene hydroperoxide as *t*-butoxy radical traps failed to decrease the yields of DBP[9a] indicating that all DBP is cage product in hydrocarbon solvents. We may therefore determine cage combination of *t*-butoxy radicals from the yields of DBP. We have corroborated Hiatt's[9b] finding that DBP + TBA constitute 95–100% of products from *t*-butoxy groups in saturated hydrocarbons and that negligible amounts of isobutylene oxide are formed under these conditions. We have therefore used the ratio of DBP to *t*-butyl alcohol to calculate cage effects.

Cage effects in DBH and DBPO decompositions are given by the equation

$$F = \text{fraction cage collapse} = [1 - \text{efficiency}] = \frac{\text{concn of DBP}}{\text{initial concn of initiator}} \qquad (5)$$

which may be approximated within about 1% by the equation

$$F = \frac{\text{DBP}}{\text{DBP} + (t\text{-BuOH}/2)} \qquad (6)$$

The values of *F* determined in this way for DBH and DBPO are listed, along with those for DBP (determined as described below), in Table I.

Rates of photodecomposition of di-*t*-butyl peroxide (DBP) were used to determine cage collapse because the usual methods are not applicable. Since we wished to compare DBP with DBPO and DBH in this cage reaction, it was necessary to measure the kinetics of decomposition at 45° where the half-life for thermal decomposition is over 10 years.[6] We therefore developed a method for determining rates of photodecomposition in the solvents of Table I, tested this method with DBH, and applied it to DBP. A comparison of cage collapse from thermal and photodecomposition of DBH (Table I) shows that the two methods produce radicals which behave identically.

The kinetic data for photodecomposition of DBP at 45° are shown in Table II and the cage collapse calculated from these data (by eq 7 below) appear in Table I.

Table II. Rates of Photodecomposition of DBP in Various Solvents at 45.0° [a]

Solvent[b]	[DBP], *M*	$k \times 10^6$, sec^{-1}
Pentane	0.20	4.75 ± 0.00
Isooctane	0.20	4.35 ± 0.02
20% Nujol	0.20	4.00
40% Nujol	0.20	3.55 ± 0.08
60% Nujol	0.20	3.26 ± 0.08
70% Nujol	0.20	2.59 ± 0.08
80% Nujol	0.20	1.96 ± 0.04
90% Nujol	0.20	1.50
100% Nujol[c]	0.10	1.17 ± 0.00

[a] Initial rates observed for 10–15% decomposition. Deviations listed for two or three runs. Within a run the average deviation was about 2% and the maximum deviation 7%. [b] Mixed solvents were isooctane–Nujol. [c] Identical rate constants were obtained with and without the Vycor filter.

Clearly, an absolute value of cage collapse in DBP decomposition is not available. Because the differences in cage collapse between DBPO and DBH disappeared in pentane we assumed that DBP would also show cage collapse equal to that of the other two initiators in this solvent. We then assign a value of 4% cage collapse

(F = 0.04) to DBP in pentane at 45.0°. Having made this assignment we may calculate the rate of photodecomposition of DBP in the absence of cage collapse to be: $k_0 = 4.75 \times 10^{-5}/0.96 = 4.94 \times 10^{-5}$ sec^{-1}. The cage effect in a given solvent(s) is then given by the equation

$$F = (k_0 - k_s)/k_0 \tag{7}$$

Discussion

Current theories of diffusion such as the cubic cell model of Houghton[12] or the continuum model used by Noyes[3d] require that the diffusion coefficient be inversely proportional to viscosity

$$D = C\rho/\eta \tag{8}$$

For the reaction

$$\mathrm{R_2} \underset{k_c}{\overset{k_1}{\rightleftharpoons}} \overline{\mathrm{R\cdot\cdot R}} \xrightarrow{k_d} 2\mathrm{R}\cdot \tag{9}$$

Booth and Noyes[3c] have expressed the fraction of cage collapse (F)

$$F = k_c/(k_d + k_c) \tag{10}$$

as a function of viscosity by the equation

$$1/F = C[1 + (A/\eta)] \tag{11}$$

where C and A are constants.

With reasonable values for C and A, eq 11 describes the behavior of iodine atoms in hydrocarbons of rather low viscosity.[3c] This relationship fails at high viscosities, and in fact the quantum yield ($1 - F$) of iodine atoms appears to reach a limiting value at a viscosity of about 1 poise. Furthermore, chlorinated solvents cause larger cage effects (F) than was predicted by their viscosity. These results prompted Booth and Noyes to suggest that specific solvent–radical interactions were important in determining cage behavior of radicals.

Our data for DBP, DBH, and DBPO are plotted by eq 11 in Figure 1. These results differ somewhat from those of Booth and Noyes in that there is no sign of reaching a limiting value of F with increasing viscosity. However, we, like Nelson and Bartlett[13] and Koenig and Deinzer,[14] agree with Booth and Noyes that no simple function of viscosity will describe our results accurately.[15]

We have used both pure and mixed solvents in this work and can exclude any special effects due to the use of mixed solvents (see Figure 1). There are apparently important differences in the ability of different sized hydrocarbons to solvent radicals. We have previously recorded 25% faster rates of decomposition of DBH in Nujol than in isooctane. We now wish to offer this as evidence for solvent stabilization of DBH by isooctane in excess of that provided by Nujol.

$$(\text{+ONNO+})\ \text{solvated} \rightarrow (\text{+O—NN—O+})^{\ddagger} \rightarrow \overline{\text{+O}\cdot\quad \mathrm{N_2}\quad \cdot\text{O+}} \tag{12}$$

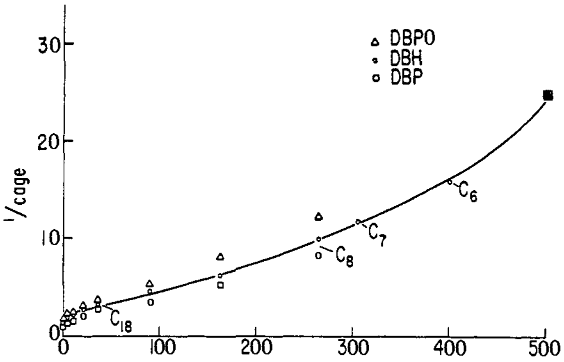

Figure 1. Plots of the reciprocal of the fraction cage product as a function of reciprocal of absolute viscosity for the decompositions of the following initiators: △, di-*t*-butyl peroxyoxalate (DBPO); ○, di-*t*-butyl hyponitrite (DBH); □, di-*t*-butyl peroxide (DBP).

Since solvation is less in the transition state in both solvents, the faster rate in Nujol is explicable. Similarly, after formation of the cage, the radical pair will be solvated differently by solvents of different size and structure, and these specific interactions must be considered.[17]

Cage collapse of *t*-butoxy radicals in DBP decomposition are clearly predicted by our previous results on DBH[7] and DBPO[9,18] but the data recorded here comprise the first clear demonstration of this cage collapse.[19,20] We have assumed that the cage effect (F) is 0.04 for DBP in pentane because DBH and DBPO give this cage effect. If we assume somewhat larger or smaller cage effects in DBP decomposition the arguments presented here are not affected. We cannot compare solution decompositions of DBP with gas-phase reactions because the latter are about 30% slower.[22] This difference undoubtedly rests in solvent effects although we would have expected the solvation to retard the rate.

Pryor and Smith have recently derived an equation from the effect of viscosity on the rates of decomposition of initiators which reform by cage collapse.

$$\log k_{\text{obsd}} = \log k_1 + \frac{C}{\eta} + C' \tag{13}$$

The C and C' are constants and k_1 is that in eq 9. They have extrapolated the plots of data[5] for decomposition of acetyl peroxide (DAP) and *p*-nitrophenylazotriphenylmethane (NAT) decompositions to infinitely high viscosity to obtain k_1. Figure 2 compares their plots for acetyl peroxide with a plot of our DBP data. Plots of ($1 - F$) or $\log(1 - F)$ *vs.* η^{-1} for DBH and DBPO show the same behavior as that illustrated for DBP decomposition rates. Although we apparently cannot use the

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[12] G. Houghton, *J. Chem. Phys.*, **40**, 1628 (1964).

[13] S. E. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

[14] T. Koenig and M. Deinzer, *ibid.*, **88**, 4518 (1966).

[15] Plots of these data according to the equations derived by Braun, Rajbenbach, and Eirich,[5] or by Pryor and Smith[16] also show severe discrepancies. Plots of F against $\log \eta$ are reasonably straight.

[16] W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **89**, 1741 (1967).

[17] We are currently measuring $\Delta H^{\ddagger}$ for cage combination of *t*-butoxy radicals in various solvents in order to estimate these solvent effects.

[18] A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).

[19] C. Walling, private communication, has recently found that thermal decomposition of DBP is slower in Nujol than in *t*-butylbenzene. W. A. Pryor, private communication, has also observed such viscosity effects.

[20] Cage collapse of acetoxy radicals from acetyl peroxide has been demonstrated both by changes of rate with viscosity[5] and by oxygen labeling experiments.[21]

[21] J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966).

[22] See P. Molyneux, *Tetrahedron*, **22**, 2929 (1966), for a summary.

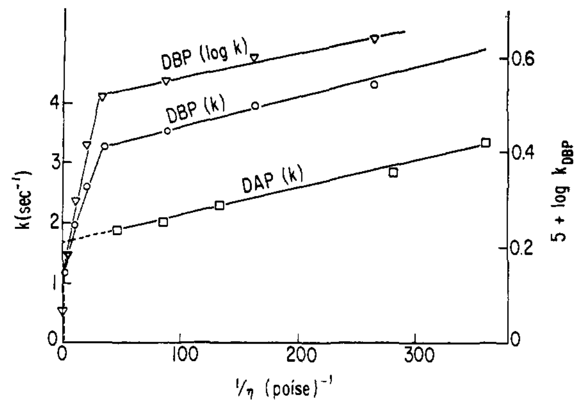
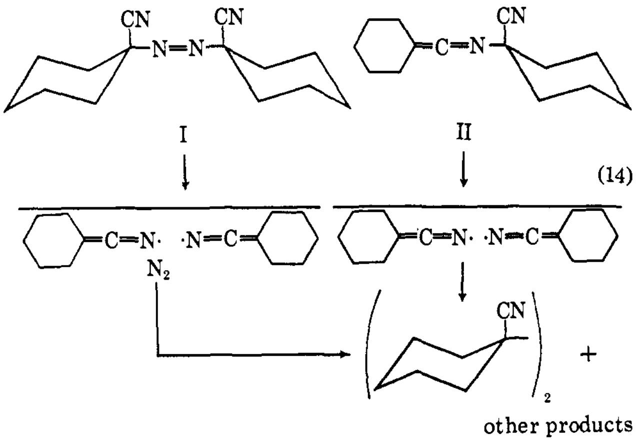


Figure 2. Plots of decomposition rates for DBP (Table II) and diacetyl peroxide (DAP)[6] *vs.* reciprocal viscosity ($k \times 10^6$ for DAP and $k \times 10^5$ for DBP).

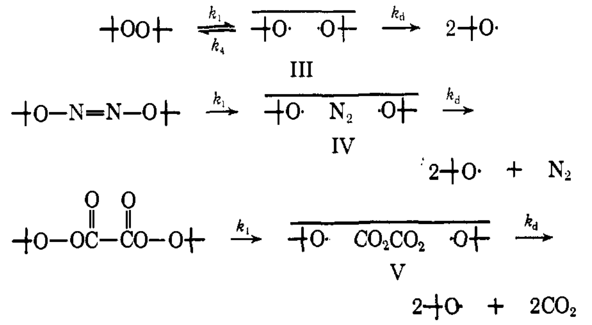
method of Pryor and Smith to obtain accurate values of k_1 for DBP, we corroborate their suggested use of a viscosity–rate relationship such as eq 13 to differentiate between one-bond and two-bond initiators. The rate of (one-bond) decomposition depends upon viscosity whereas those of DBH (two-bond) and DBP (three-bond)[8] do not.[7,9] It is also clear that rate dependence upon viscosity may be used to exclude cyclic processes as well.[5]

The influence of inert molecules between radical pairs has been studied previously by Hammond and coworkers.[2e] They observed that the efficiency of radical production from I was about 1.5 times that from II in chlorobenzene.



(14)

We have also observed an influence of inert molecules upon the extent of cage collapse (Figure 1).



(15)

(16)

(17)

The efficiency of production of *t*-butoxy radicals increases in going from reactions 15 to 16 to 17. There is excellent evidence[8] for concerted cleavage of all bonds indicated in reactions 16 and 17, and we may therefore attribute these differences to behavior of the indicated cage clusters. However, II gave twice as much cage product as did I, and III gave only 20% more cage product than did IV. This could be ascribed to the higher exothermicity of alkyl radical combinations or to the occurrence of a molecular rearrangement of II.

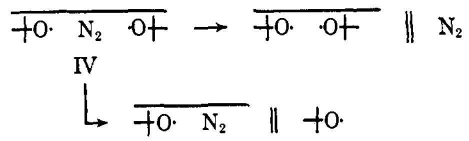
Primary *vs.* Secondary Cage Recombination. Waits and Hammond[2d] concluded from their study of effects of high scavenger concentrations on cage reactions that either the suggested[3] primary and secondary cage reactions could not be separated experimentally or that the secondary cage collapse did not exist. The effects of these inert molecules inside the cage might be used to differentiate primary from secondary cage effects.

We have listed in Table I the quantity

$$R_{\mathrm{DBPO}}/R_{\mathrm{DBH}} = (k_d/k_c)_{\mathrm{DBPO}}/(k_d/k_c)_{\mathrm{DBH}} \tag{18}$$

and similar ratios for DBH *vs.* DBP. These are comparisons of the ratios of diffusion to cage recombination in DBPO decomposition to the same ratio for DBH decomposition and this comparison is made at several viscosities.

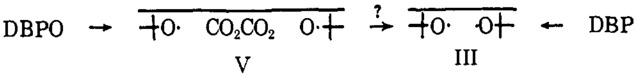
If there were secondary recombination, then the nitrogen or carbon dioxide should also diffuse out of the cage and should do so somewhat faster than do *t*-butoxy radicals.



(19)[23]

(20)

Because the diffusion of N_2 or CO_2 will depend upon viscosity, then, as the viscosity is decreased there should be a steady change so as to make cages V and IV more like cage III.



But the constant ratio $R_{\mathrm{DBH}}/R_{\mathrm{DBPO}}$ over a rather wide viscosity range indicates that this is not the case. That is, cage nitrogen and carbon dioxide are not involved in diffusion during the competition between cage collapse (k_c) and cage destruction (k_d). There are only two ways in which this situation may arise. The inert molecules must either diffuse out completely[24] prior to the competition between k_d and k_c or else they remain in place during this competition. Since the difference in diffusion between CO_2 (molecular weight 44) and *t*-butoxy (molecular weight 75) is finite, the former assumption may be discarded. We therefore suggest that, in most solvents, there is only primary cage collapse of *t*-butoxy radicals.[26,27]

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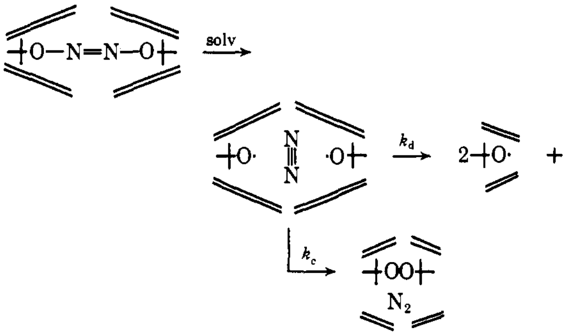
[23] We represent a cage cluster by a bar above the components[3d] and solvent molecules by parallel lines.

[24] Cage effects should be proportional to the inverse of the distance (r_0) separating the newly formed radicals (fraction cage = A/r_0),[25] and this is qualitatively (although not quantitatively) consistent with our results at one viscosity. However, this proportionality assumes isotropic diffusion which would require that solvent molecules replace the CO_2 or N_2 molecules before the diffusion *vs.* collapse competition. This seems unlikely for reasons stated above.

[25] T. C. Vogt, Jr., and W. H. Hammill, *J. Phys. Chem.*, **67**, 292 (1963).

[26] We have recently found large $\Delta E^{\ddagger}$ values for k_d/k_c ratios which are consistent with this conclusion.

This interpretation presents a picture of the solvent cage having much more structure than is usually assumed.[3]

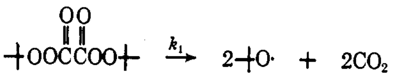


(21)

In this scheme any diffusion out of the cage simply destroys it.

At the extreme of zero viscosity, the differences between DBPO, DBH, and DBP will disappear since there is no cage. In fact we observed $R_{\mathrm{DBPO}}/R_{\mathrm{DBH}} = 1$ before zero viscosity (in pentane).

Tetroxides have been implicated[28,29a] as intermediates[29c] or transition states in the termination of autoxidation[28] and in hydroperoxide decompositions.[18,29c] The mechanism of chain decomposition of tertiary hydroperoxides proposed by Hiatt, Clipsham, and Visser[30] is shown below.[18]



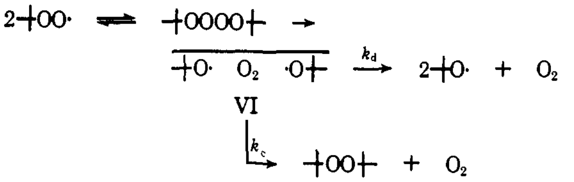
$$+\mathrm{OOC(=O)C(=O)OO}+ \xrightarrow{k_i} 2+\mathrm{O}\cdot + 2\mathrm{CO_2} \quad (22)$$

$$+\mathrm{O}\cdot + +\mathrm{OOH} \rightarrow +\mathrm{OO}\cdot + +\mathrm{OH} \quad (23)$$

$$2+\mathrm{OO}\cdot \rightarrow 2+\mathrm{O}\cdot + \mathrm{O_2} \quad (24)$$

$$2+\mathrm{OO}\cdot \rightarrow +\mathrm{OO}+ + \mathrm{O_2} \quad (25)$$

It has been suggested that both steps 24 and 25 proceed through the tetroxide and that the chain length, $[(k_{24}/k_{25}) + 1]$, is just the efficiency of *t*-butoxy radical production[18] from reversibly formed tetroxide.[29c]



(26)

(27)

Some evidence for this formulation derives from limited studies of viscosity effects on chain length.[18]

However, we may now make a more direct test of this postulate. Cage VI is sterically very similar to cage IV from DBH, the only difference being the presence of oxygen instead of nitrogen. Then

$$\left(\frac{k_d + k_c}{k_c}\right)_{\mathrm{VI}} \equiv \text{chain length} = \left(\frac{k_d + k_c}{k_c}\right)_{\mathrm{IV}} \equiv \frac{1}{F_{\mathrm{IV}}} \quad (28)$$

In chlorobenzene at 45.0° the chain length for *t*-butyl hydroperoxide decomposition is 10.2 and $1/F$ for DBH is 11.[31] We submit that this is strong evidence for reactions 26 and 27. This mechanism also accounts for the observation that cumyl peroxy radicals terminate faster than do *t*-butyl peroxy radicals[32,33] and yet the chain length for cumene hydroperoxide decomposition is about the same as that for decomposition of *t*-butyl hydroperoxide.[18]

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[27] This does not exclude secondary cage effects for other radicals with higher rate constants for combination.

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[31] The *t*-butyl hydroperoxide decomposition (10.2) was observed in 90% chlorobenzene–10% *t*-butyl hydroperoxide whereas the solvent for DBH decomposition ($1/F = 11$) was 90% chlorobenzene–10% cumene. A correction for this slight solvent difference would probably bring these two cage effects even closer together.

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