acidity of a solution is increased. The reason for this lies in the fact that an increase in acidity also results in a decrease in the amount of water available for solvation and conjugate acids with high solvation requirements will consequently be formed less readily.

The most apparent indication of solvation requirements is the slope of plots of log I *vs.* $-H_0$. Compounds which form conjugate acids having lower solvation requirements than protonated anilines exhibit slopes greater than unity. For example, triphenylcarbinols which form carbonium ions on protonation give slopes of about 2 because such ions are not readily solvated by water.[10] On the other hand, the oxonium ion which forms when ethanol is protonated must be highly solvated and a slope of 0.25 is obtained.[4]

A similar tendency can be noted among the esters studied in this investigation. Compare, for example, ethyl acetate with phenylethyl acetate and ethyl benzoate. Of these three compounds, the conjugate acid which forms when ethyl acetate is protonated would be expected to have the greatest solvation requirements because the positive charge will be localized primarily on the two oxygen atoms. On the other hand, the charge on the conjugate acid of ethyl benzoate could be delocalized over the aromatic ring as well as on the two oxygens. Consequently, its requirement for solvation is much less and the slope much greater, being 1.3 for ethyl benzoate as compared to 0.51 for ethyl acetate, with phenylethyl acetate (where only partial delocalization is possible) having an intermediate value of 0.83.

In conclusion, it can be seen that the problem of determining quantitatively the basicity constants for aliphatic esters, particularly those with complex structures, may not be easily solved; each particular compound may have to be independently investigated. It can also be seen that aliphatic and aromatic esters do not conform to the same acidity functions. On the other hand, the protonation behavior of several simple unsubstituted aliphatic esters appears to be satisfactorily defined by the H_E function.

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Radicals and Scavengers. V. Steric Hindrance and Cage Effects in the Decompositions of Several *tert*-Butyl Peresters[1a]

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Abstract: Product isolation and scavenger methods have been used to study the cage effects in decompositions in cumene and chlorobenzene of several *tert*-butyl peresters, RCO_3-*t*-Bu, including the peracetate (I, R = CH_3), perpivalate (II, R = $(CH_3)_3C$), *p*-nitro- and *p*-methoxyphenylperacetates (III and IV, R = *p*-$O_2NC_6H_4CH_2$ and *p*-$H_3COC_6H_4CH_2$, respectively), α-phenylperisobutyrate (V, R = $C_6H_5C(CH_2)_3$), α,α-diphenylperpropionate (VII, R = $(C_6H_5)_2C(CH_3)$), and diphenylpermalonate (IX, $(C_6H_5)_2C(CO_3$-*t*-Bu$)_2$). As previously reported for the diphenylperacetate (VI, R = $(C_6H_5)_2CH$), reaction of *tert*-butoxy radicals with R· in bulk solution does not occur. For tertiary R, cage effects involving coupling are small, *ca.* 0–12%, but for primary R, *ca.* 30% or more. Disproportionation is *ca.* 5–10% per β-hydrogen atom of R. Steric repulsion is proposed as explanation for small or nil amounts of cage coupling.

The *tert*-butyl peresters are interesting initiators for studies of the cage effect, the mutual reaction of geminate radical in solution.[2] Since the *tert*-butoxy radical is formed by all homolytic decompositions of *tert*-butyl peresters,[3] the series presents an opportunity to study a structure–reactivity relationship.

We have carried out a series of scavenger studies of the thermal decompositions of II, IV, V, and VII, and product studies with I–V, VII, and IX, which supplement the studies of IV and its analogs,[4] V,[5] VI,[1,6] VIII,[1] and X[7] already reported. Scavenger studies of XI[8] and XII[9] have also been reported, as have photolytic studies of I, II, and an extensive series of their aliphatic analogs at 30°, and the thermolysis of I in decalin at 115°.[10] Data are therefore at hand for primary, secondary, and tertiary alkyl and aralkyl radicals between 25 and 115°.

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$$\mathrm{RCO_3\text{-}}t\text{-}\mathrm{Bu} \longrightarrow \mathrm{R}\cdot + \mathrm{CO_2} + \cdot\mathrm{O\text{-}}t\text{-}\mathrm{Bu} \longrightarrow \text{products} \quad (1)$$

I, R = CH_3
II, R = $(CH_3)_3C$
III, R = p-$O_2NC_6H_4CH_2$
IV, R = p-$H_3COC_6H_4CH_2$
V, R = $C_6H_5C(CH_3)_2$
VI, R = $(C_6H_5)_2CH$
VII, R = $(C_6H_5)_2C(CH_3)$
VIII, R = $(C_6H_5)_2CC(CH_3)_3$
IX, R = $(C_6H_5)_2C(CO_3$-t-Bu)
X, R = $(C_6H_5)_3C$
XI, R = t-BuO_2C
XII, R = t-BuO_3C

In all cases we find substantial cage effects, but essentially no bulk recombination of radical pairs from the perester, in contrast to results for VIII[1a] and X[7] and for azo compounds,[11] but in agreement with the reports for VI[1a,6] and for photolysis of aliphatic peresters.[10] Important differences are revealed between the reactivity of alkyl and aralkyl radicals with themselves and with *tert*-butoxy radicals.

Results

Peresters I–V, VII, and IX were prepared by standard methods,[3,7] and their infrared spectra, as well as melting points of crystalline peresters, were found to agree with those reported. The samples were not generally subjected to either combustion analysis or iodometric titration, since both methods have proven misleading for reactive peresters.[6,7] Rather, their purity was judged by the yields of CO_2 on thermal decomposition in degassed cumene solution. In this nonpolar solvent, with compounds prone neither to polar rearrangement nor to radical-induced decomposition, nearly quantitative CO_2 yields were frequently observed, including those for I–IV and VII, as shown in Tables I–IV. CO_2 yields and iodometric titers were in agreement for the relatively stable peresters I and III.

Table I. Products of Decomposition of *tert*-Butyl Perpivalate (II) at 70–80°

Product	Yield, mol/mol of CO_2, in Cumene	Chlorobenzene	Cumene + O_2 + PG[a]
CO_2	0.98[b]	0.99[b]	0.77[b]
tert-Butyl alcohol	0.79	0.63	
Acetone	0.00	0.30	
Di-*tert*-butyl ether	0.02	0.02	
Isobutene	0.41	0.26	0.50
Isobutane	0.30	0.22	0.00
Dicumyl	0.68		
O_2 absorbed			0.52[c]

[a] PG = pyrogallol. [b] Mol/mol of perester; different sample used in oxidation than in degassed runs in cumene and chlorobenzene. [c] Corrected; *cf.* text.

Table II. Products of Decomposition of *tert*-Butyl Peracetate (I) and *p*-Nitro- (III) and *p*-Methoxyphenylperacetates (IV) in Cumene

Product	Yield, mol/mol of CO_2, from I, 118°	III, 90°	IV, 80°
CO_2	0.97[a]	0.98[a]	0.99[a]
tert-Butyl alcohol	0.72	0.64	0.67
Acetone	0.11	0.03	0.03
Methyl *tert*-butyl ether	0.09		
Acetic acid	0.01[b]		

[a] Mol/mol of perester. [b] Estimated limit of detection.

Table III. Products of Decomposition of *tert*-Butyl α-Phenylperisobutyrate (V) at 60°

Product	Yield, mol/mol of CO_2, in Cumene	Chlorobenzene	Cumene + O_2 + PG,[a] 40°
CO_2	0.93[b]	0.96[b]	0.82[b]
tert-Butyl alcohol	0.92	0.58	
Acetone	0.00	0.18	
α-Methylstyrene	0.51	0.17	0.66
Dicumyl	0.92[c]	0.68[c]	
Cumyl *tert*-butyl ether	0.00	0.18	
O_2 absorbed			0.44[d]

[a] PG = pyrogallol. [b] Mol/mol of perester. [c] As moles of cumyl radicals. [d] Corrected; *cf.* text.

Table IV. Products of Decomposition of *tert*-Butyl α,α-Diphenylperpropionate (VII) in Chlorobenzene at 40–45°

Product	Yield, mol/mol of CO_2, at 45°	at 40°, + O_2 + PG[a]
CO_2	1.01[b]	1.00[b]
O_2 Absorbed		0.51[c]
tert-Butyl alcohol	0.47	
Acetone	0.18	
1,1-Diphenylethane	0.10	
1,1-Diphenylethylene	0.11	
2,2,3,3-Tetraphenylbutane	0.39[d]	
tert-Butyl 1,1-diphenylethyl ether	0.12	
Benzophenone	0.07	
Miscellaneous	250 mg[e]	

[a] PG = pyrogallol. [b] Mol/mol of perester. [c] Corrected; *cf.* text. [d] Calculated as moles of 1,1-diphenylethyl radicals. [e] Perester taken: 1.622 g.

Products of thermal decomposition in cumene and/or chlorobenzene, determined for all the peresters studied, are presented in Tables I–IV. For cumene solutions, *tert*-butyl ethers were found only in the cases of I and VII, but not II or V. In addition, III and IV must have produced ethers, although the nonvolatile products were not analyzed in the present investigation; ethers were found previously,[12] and the substantial deficit in *tert*-butyl alcohol yields requires the formation of ethers from both peresters.

The failure of V to produce cumyl *tert*-butyl ether in cumene stood in contrast to its reported formation in chlorobenzene.[3] We therefore repeated the decomposition in chlorobenzene, indeed obtaining a material identifiable by both infrared and nmr as cumyl *tert*-butyl ether, in a yield essentially the same as earlier reported. The yields of α-methylstyrene were confirmed in experiments utilizing glassware that had been base-washed, rinsed, and oven-dried to avoid catalyzed decomposition of ether to α-methylstyrene.

The thermolysis of I in cumene at 118° produced some methyl *tert*-butyl ether, but no acetic acid whatever, in contrast with the result reported for chlorobenzene,[3] and despite the superior H-atom donor ability of cumene. This result is consistent with several previous failures to trap acetoxy radical,[13] and suggests induced

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Table V. Zero-Order Galvinoxyl Kinetics of Several Peresters

Perester, R in R—CO_3-*t*-Bu	Solvent	Temp, °C	10^5k_1, sec^{-1} IR	10^5k_1, sec^{-1} Galv.[a]	Cage effect, *f*	*f*(temp, °C)
Me_3C (II)	Chlorobenzene	48.9	0.840	0.370[b,c]	0.560	
p-$MeOC_6H_4CH_2$ (IV)	Chlorobenzene	48.9	1.93	1.375[c]	0.290	
$PhCMe_2$ (V)	Chlorobenzene	34.1	3.26	1.805[b,c]	0.445	0.408 (41.3)[d]
	Cumene	34.1	2.48[e]	1.08[b,c]	0.565	0.410 (49.7)[d]
	Cumene	39.7	5.63	2.22[b]	0.605	
Ph_2CH (VI)[f]	Cumene	40.4	2.75	~2.02	~0.265	
Ph_2CMe (VII)	Chlorobenzene	34.1	7.76	4.43[g]	0.430	
Ph_3C (X)[h]	Cumene[i]	14.0	3.05	2.65	0.130	

[a] $(1 - f)k_1$; *cf.* text; corrected for perester purity: II, 90%; IV and VII, 100%; V, 88%; VI, *cf.* ref 6; X, 95% (*cf.* ref 7). [b] From final slope; plots curved owing to reaction with *tert*-butyl hydroperoxide impurity; *cf.* text. [c] Mean of duplicate runs. [d] Reference 5. [e] Extrapolated from 39.7° assuming E_a = 28.0 kcal/mol. [f] Reference 6. [g] Plot strictly linear from $A_0 = 1.3$ to $A = 0.3$; thereafter, slightly concave up; slope of linear portion used. [h] Reference 7. [i] Saturated with O_2.

decomposition in chlorobenzene solution as the source of the acetic acid.

Cage Effects. Three methods were used to estimate cage effects in decompositions of peresters in cumene and chlorobenzene.

(1) Product Yields in Presence or Absence of Scavengers. Yields of *tert*-butyl ethers from I, VI,[6] and VII were used directly; yields of *tert*-butyl alcohol were used for III (*vide supra*) and for VI[6] and X,[1,7] as previously reported, all cases in which cage formation of alcohol by H-atom transfer was precluded by the absence of β H-atoms in the hydrocarbon radicals. The cage effect, *f*, is given by $f = 1.0 - (\%\ tert\text{-butyl alcohol})/100$.

(2) Rate of Consumption of the Stable Free Radical Galvinoxyl. In the presence of a large excess of decomposing perester, galvinoxyl fades at a constant, or zero order, rate.[14] The cage effect is given by eq 2.

$$-dA^{770}/dt = 2(1 - f)k_1\epsilon_g^{770}[\text{perester}]_{av} \qquad (2)$$

A^{770} = absorbance of galvinoxyl at 770 nm

ϵ_g^{770} = molar absorptivity of galvinoxyl at 770 nm = 607

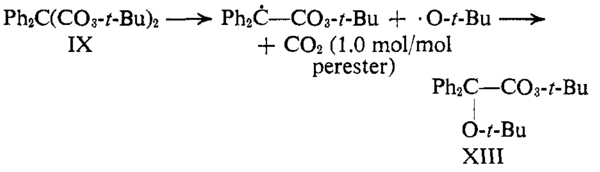
k_1 = first-order rate constant for perester decomposition

f = cage effect, as a decimal fraction

The results are presented in Table V for the peresters studied in this work, II, IV, V, and VII, as well as those studied previously, VI[6] and X.[7] Plots of A^{770} *vs.* time were generally strictly linear until complete disappearance of the radical; the plot for VII was linear to 75% disappearance. For II and V, plots were concave up, that is the rate decreased with time. It was found that *tert*-butyl hydroperoxide, a suspected impurity in these oily peresters, reacted very rapidly with galvinoxyl. In these cases, therefore, only final slopes were used for estimating *f*, values for which must be lower limits. In the case of V, the difference between initial and final slopes was less than 5% for chlorobenzene as solvent.

(3) Amount of Oxygen Consumed in the Presence of Pyrogallol. This method, applied previously in the cases of VI[6] and X,[7] was used for peresters II, V, and VII, and the results were combined with other data in Tables I, III, and IV, respectively. Oxygen can in theory react with every hydrocarbon radical which escapes the cage; pyrogallol served as a highly efficient inhibitor of autoxidation, presumably converting alkyl- and aralkylperoxy radicals rapidly to hydroperoxides, thus preventing chain autoxidation of cumene which would consume a large quantity of oxygen. As previously reported,[7] a control experiment with perester XII (DBPO, di-*tert*-butyl peroxyoxalate), which produces only *tert*-butoxy radicals, resulted in nearly nil consumption of oxygen. The amount actually consumed was used to correct values found for the other peresters. In other control experiments pyrogallol was found superior to all other inhibitors tried, including 2,6-di-*tert*-butyl-*p*-cresol. The cage effect, *f*, is given by $f = 1.0 -$ (mol of oxygen consumed/mol of CO_2 evolved), after correction as indicated above. This method was inspired by the work of Ziegler, *et al.*,[15] on rates of dissociation of highly substituted ethanes (actually isomers of the symmetrical structures); these workers found that very nearly 2 mol of oxygen/mol of hydrocarbon were consumed in the presence of pyrogallol.

In addition to the above methods, evidence for a cage effect in the case of IX was discerned in the CO_2 yield of 1.09 mol/mol of perester, and unexpectedly the formation of about 3% of a mixture of isobutane and isobutene. Since the principal product of decomposition of IX in cumene is known[16] to be the polyester of benzilic acid, only 1.0 mol of CO_2/mol of IX is to be expected. The mechanism of eq 3–5 illustrates the



$$\underset{\text{IX}}{Ph_2C(CO_3\text{-}t\text{-}Bu)_2} \longrightarrow Ph_2\dot{C}\text{—}CO_3\text{-}t\text{-}Bu + \cdot O\text{-}t\text{-}Bu + CO_2\ (1.0\ \text{mol/mol perester}) \longrightarrow \underset{\text{XIII}}{Ph_2C(O\text{-}t\text{-}Bu)\text{—}CO_3\text{-}t\text{-}Bu} \qquad (3)$$

$$\text{XIII} \longrightarrow Ph_2\dot{C}\text{—}O\text{-}t\text{-}Bu + CO_2 + \cdot O\text{-}t\text{-}Bu \longrightarrow Ph_2C{=}O + (CH_3)_3C\cdot \qquad (4)$$

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C{=}CH_2 \qquad (5)$$

inferred cage effect, and explains the formation of C_4 hydrocarbons. Consistent with this mechanism is the reported[16] formation of benzophenone.

Discussion

Table VI displays cage effect estimates for peresters I–X, as obtained by each of the three methods dis-

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Table VI. Cage Effects in Perester Decompositions[a]

Perester, R in RCO_3-*t*-Bu	Solvent	Temp, °C	Cage effect, *f*		
			Products[b]	Galvinoxyl[c]	O_2 absorption[d]
Me (I)	Cumene	118	0.09		
Me_3C (II)	Chlorobenzene	49		0.56	
	Cumene	70	0.50[e]		0.48
p-$O_2NC_6H_4CH_2$ (III)	Cumene	90	0.33[f]		
p-$MeOC_6H_4CH_2$ (IV)	Cumene	80	0.30[f]		
	Chlorobenzene	49		0.29	
$PhCMe_2$ (V)	Cumene	60	0.51		
	Cumene	49.7		0.41[g]	
	Cumene	40	0.66[e]	0.61	0.56
	Chlorobenzene	62	0.34		
		41.3		0.41[g]	
	Chlorobenzene	34.1		0.45	
Ph_2CH (VI)[h]	Cumene	60	0.16[i]		0.28
	Cumene	60	0.28[f]		
	Cumene	40	0.25–0.33	0.27	
Ph_2CMe (VII)	Chlorobenzene	45	0.12[j]		
		45	0.40–0.47[k]		
	Chlorobenzene	40			0.49
		34.1		0.43	
Ph_2C(*t*-Bu) (VIII)	Toluene	25	0.03[f,l]		
Ph_2CCO_3-*t*-Bu (IX)	Cumene	50	0.03–0.09[m]		
Ph_3 (X)[l,n]	Toluene	25	0.07[f,o]		
	Cumene	25			0.11
	Cumene	14		0.13	

[a] Data from Tables I–V and text unless reference given. [b] In absence of scavengers, unless otherwise noted. [c] Table V. [d] Corrected; *cf.* text. [e] With O_2 and pyrogallol. [f] 1.00 − (alcohol + acetone), mol/mol of CO_2. [g] *Cf.* ref 5. [h] *Cf.* ref 6. [i] Ph_2CHO-*t*-Bu only, all experiments. [j] *tert*-Butyl 1,1-diphenylethyl ether only. [k] Assuming diphenylethyl or *tert*-butyl (respectively) not accounted for to be isomeric cage product(s). [l] Reference 1a. [m] *Cf.* text. [n] *Cf.* ref 7. [o] In presence of thiol.

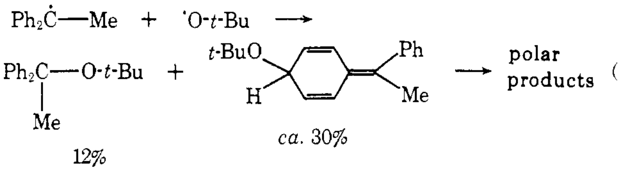
cussed. Since galvinoxyl experiments were generally carried out at lower temperatures than product studies or oxygen absorption experiments, it must be borne in mind that cage effects generally vary inversely with temperature;[2] however, over small temperature ranges such as 30°, the variation is small.

Pleasing agreement is found in cases II, IV, V, VI, and X, between results of product studies and galvinoxyl rates, and in some cases the latter are larger at lower temperatures (*vide supra*). Good agreement also exists in cases II, V, and X between the first two methods and oxygen absorption, further confirming the usefulness of oxygen as a radical counter under the proper conditions. Finally, the *f* value for IV agrees well with an ether yield of 0.25 mol/mol of perester inferred from data of Neuman and Behar:[4] these workers give the ratio of ether to alcohol (cumene, 80°, 1 atm) as 0.33, and the individual values follow from the assumption that their sum is 1.00. In further confirmation of the existence of a cage effect, Neuman and Behar found the ether–alcohol ratio to increase with pressure for all five *tert*-butyl phenylperacetates studied.

Certain discrepancies are found in cases V–VII: these can for the most part be explained away very plausibly. First, the average cage effect of 0.61 at 40° in cumene for V is in serious disagreement with the value reported[5] using the excess galvinoxyl method, 0.41 at 49.7°. It is conceivable that the cumene used in the experiments of ref 5 contained traces of cumene hydroperoxide sufficient to consume a significant amount of galvinoxyl, known to react rapidly with *tert*-butyl hydroperoxide. This would raise the *apparent* efficiency of radical production and suggest a low cage effect. The data are highly reproducible, as would be expected if all the experiments used the same sample of cumene and were performed in a short time interval. Clearly, however, the cage effect of V is large, of the order of 0.50 in cumene at 40–50°.

Second, a serious discrepancy exists in the case of VI between the yield of benzhydryl *tert*-butyl ether, *ca.* 17%, and the oxygen absorption estimate of cage effect, 28%, as has been remarked in the previous report.[6] The explanation given was that a second cage recombination product is formed in *ca.* 10% yield, but cannot be isolated by column chromatography because of its sensitivity to Florisil or silica gel. The "phantom" cage product is assumed, by analogy with the case of X, to result from attack of *tert*-butoxy radical at an ortho or para position of a ring of benzhydryl radical.

The third, more serious discrepancy can certainly be accounted for similarly. For VII in chlorobenzene, galvinoxyl and oxygen absorption estimates of *f* are in substantial agreement, 0.43 *vs.* 0.49, respectively, but only 12% of *tert*-butyl 1,1-diphenylethyl ether could be isolated. In view of the stability of benzhydryl *tert*-butyl ether toward chromatographic adsorbents,[6] it appears unlikely that 43–49% of the ether was formed originally, but dwindled to 12% after chromatography. Rather, para coupling of *tert*-butoxy radical with 1,1-diphenylethyl radical may have occurred, as shown in eq 6, leading ultimately to polar material incompletely eluted from the column and not identified. Similar phenomena have been noted in the radical copolymerization of 1,1-diphenylethylene and methyl meth-



(6)

acrylate.[17] The crucial point we stress is our belief that the 0.43–0.49 estimate of total cage effect is accurate.

In general, the yield of all products of the *tert*-butyl group is quantitative, and we have used the *tert*-butyl alcohol yield from III and IV to estimate cage effects. These results allow reinterpretation of data reported for III and galvinoxyl by Pryor and Smith,[18] who used the excess initiator, zero-order kinetics method, to measure decomposition rate. At 77.5° the observed rate constant decreased with increasing viscosity of the normal paraffin solvents; the more reactive peresters studied failed to show such a decrease, which was attributed to reversible, one-bond scission for III. The other systems, however, including VI, were studied at lower temperatures with excess galvinoxyl, which gives the true first-order rate constant. (The same method was not applicable to the more sluggish decomposition of III, because of the known instability of galvinoxyl at elevated temperatures.) For the case of III, eq 2 is applicable: k_{obsd} is, then, $(1 - f)k_1$, and the decrease in k_{obsd} is at least in part due to the anticipated *increase* in f, the cage effect involving *tert*-butoxy and *p*-nitrobenzyl radicals. Pryor and Smith report only two runs at 100° employing infrared monitoring of the perester carbonyl maximum: the rate constants in octane and dodecane were 160 and 131×10^{-6} sec^{-1}, respectively. The difference of *ca.* 19% between these values is of the order of the probable error of rate constants measured by this method. These considerations leave essentially unsupported the idea that III decomposes by reversible one-bond scission, reasonable though it is; they necessitate very accurate determinations of k_1 at a temperature much lower than 100° in the solvents used.

Reactivity of *tert*-Butoxy Radicals. The observed cage effects cast interesting light upon the reactivity of the *tert*-butoxy radical. First, *tert*-butoxy reacts with alkyl and aralkyl radicals *only* in the original cage, not in bulk solution. Second, *tert*-butoxy shows a marked preference for accepting hydrogen atoms from other radicals. Third, cage effects involving coupling of *tert*-butoxy with alkyl or aralkyl radicals appear to decrease, at moderate temperatures, in the order, primary > secondary > tertiary.

The first generalization follows from agreement between cage effects and product yields in the absence of scavengers. It also agrees with the finding of Sheldon and Kochi[10] that "crossover products" did not form when an equal mixture of *tert*-butyl peracetate and *tert*-amyl perpropionate was photolyzed in solution. The sole exceptions at present are the triphenylperacetate, X, and its analog, VIII; in each case the stable radicals triphenylmethyl and 1,1-diphenylneopentyl, respectively, attained very high concentrations such that they could act as scavengers of free *tert*-butoxy radicals.[1,7] The absence of bulk recombination appears to be general for *tert*-butyl peresters, and contrasts with the behavior in toluene or carbon tetrachloride of cyanoisopropyl radicals, which couple in a yield far exceeding the cage effect.[11]

The reason why bulk recombination of *tert*-butoxy and carbon radicals is not observed is the high reactivity of the former toward hydrocarbons, *e.g.*, cumene. The absolute rate constant for reaction 7 is of the order of 10^5 M^{-1} sec^{-1} (the value of *ca.* 10^4 previously reported[19] has recently been shown[20] to be incorrect).[20b] For the competing reactions in a typical perester decomposition, eq 7–9, assuming a steady-state radical concentration of 10^{-8} M, it may readily be shown that the rate of reaction 7 exceeds that of (8) by more than 10^4. It is clear that bulk recombination must be essentially completely suppressed, even in much less reactive solvents.

$$t\text{-BuO}\cdot + \text{PhCHMe}_2 \xrightarrow{k_H} t\text{-BuOH} + \text{Ph}\dot{\text{C}}\text{Me}_2 \qquad (7)$$

$$t\text{-BuO}\cdot + \text{R}\cdot \xrightarrow{k_c} \text{products} \qquad (8)$$

$$2\text{R}\cdot \longrightarrow \text{R–R} \qquad (9)$$

The Magnitudes of Cage Effects Involving *tert*-Butoxy Radical. The second and third generalizations stated above will now be discussed. The largest cage effect reported here, 0.60, involves H-atom transfer rather than coupling; this is for V in cumene at 40°. Likewise, a cage effect of about 0.50 is indicated for II in cumene at 70°, also involving H-atom transfer almost exclusively. These are about treble the value for the diphenylperacetate (VI) in cumene at 60° (considering only the formation of benzhydryl *tert*-butyl ether), or double the total cage effect inferred from oxygen absorption or from alcohol yield. Since the predominance of H-atom transfer over coupling for *tert*-butoxy radicals has been observed previously, we shall be more concerned with the reasons behind this, and behind the trends in cage coupling.

Cage effects in H-atom transfer are small if reckoned per available H-atom. Thus, they are *ca.* 0.10 per H-atom of cumyl radical (from V), and *ca.* 0.06 per H-atom of *tert*-butyl radical (from II). H-atom transfer is, however, enhanced by large statistical factors, there being, respectively 6 and 9 β hydrogens in the two radicals. It is not clear why perester VII in chlorobenzene does not show cage H-atom transfer. Conceivably, decomposition in cumene, as with V, would result in more H-atom transfer in the cage.

Coupling, on the other hand, is suppressed, particularly where the carbon radical R is tertiary, as for II, V, and VII–X. Coupling is appreciable only where R is primary or secondary, as for III, IV, and VI. With I cage coupling is certainly limited both by the low viscosity at 118° and the failure of all of the acetoxy radicals to fragment in the cage; the value of *ca.* 0.09 cannot be compared with values for other peresters.

Cage coupling is, however, not absolutely suppressed, if our inferences of ring attack in the cases of VI, VII, and X are correct. This additional possibility makes some cage effects, especially that of VII, much larger than they would otherwise be.

Because of the more accurately known values for "central atom" coupling, as opposed to "ring attack," and the interesting trend in central atom coupling cage effects, primary > secondary > tertiary, the following discussion will be concerned with central atom coupling

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(18) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

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(20) (a) A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, **94**, 4603 (1972); (b) J. P. Lorand and R. W. Wallace, *ibid.*, **96**, 2874 (1974), paper VI in series.

cage effects. Several factors might control the rate of cage coupling, as follows: (1) the rate of diffusion from the cage (dissipation of the cage); (2) the presence of a third product between the radicals, *e.g.*, N_2 or CO_2; (3) the spatial orientation and the multiplicity of the radical pair (whether singlet or triplet) as formed; (4) the "stabilities" of the radicals, measured perhaps by resonance or delocalization energy, or the corresponding CH bond dissociation energy; (5) steric hindrance to approach and bond formation. The last two are the conceivable contributors to activation energy for the coupling process. In addition, it has been suggested that *tert*-butoxy radicals react with cage solvent molecules,[10] a notion which we shall refute.

The first factor is probably unimportant, since diffusion rates are relatively insensitive to molecular size,[21] and cage effects of several simple alkyl radicals of different sizes are virtually identical.[22] The presence of CO_2 in the cage is common to all the peresters studied (except that with I, as noted, CO_2 is formed slowly after one-bond scission). The radical pairs are almost certainly in a singlet state at birth. Spatial orientation is an inscrutable factor, but some observations can be made. Stereochemical results for one-bond scissions, *i.e.*, retention of configuration in high degree,[23,24] imply that rotation is slowed compared to cage reaction; however, extensive racemization is observed for two-bond scissions,[25,26] and we infer that the corresponding radicals enjoy a greater opportunity for rotation prior to reaction. The azoalkanes of the latter example, possessing the trans configuration at the N=N bond, will serve as adequate models of *tert*-butyl peresters if these prefer the s-trans conformation at the C(carbonyl)–O single bond. In *tert*-butyl perester decomposition, then, the spatial orientation of caged radicals may well be randomized.

Factors which can lead to activation energy for cage coupling may be responsible for our observations. Radical stability might cause small coupling cage effects in tertiary systems, which are also the most stable. However, *tert*-butyl, from II, is probably less stable than diphenylmethyl, from VI, yet shows much less coupling. Further, the para-substituted benzyl radicals from III and IV are not any less stable than *tert*-butyl, yet they show cage coupling, $f = 0.30$. Even if we were to tabulate all the values of D(C–H) corresponding to these radicals, the differences would be insignificant in view of the exothermicity of coupling. Therefore, radical stability does not promise to explain our observations.

Steric hindrance to approach of the radical pair provides on the whole a more satisfying context in which to view cage effects involving *tert*-butoxy radicals. We consider the neopentyl-like *tert*-butoxy radical to have a large steric requirement, for the following reason. The approach of the alkyl or aralkyl radical must be pictured as occurring at an angle of 110° to the O–C bond of *tert*-butoxy. That is, to the extent that there is any activation energy for coupling, and hence any bond formation at the transition state, the C–O···C angle at that stage must be comparable to the final angle of 105–110°. The methyl groups of *tert*-butoxy are then as much in the way as in SN2 displacement on neopentyl chloride. The systems giving small or nil amounts of cage coupling are all the tertiary ones, in which there is no relative orientation of the two radicals free of steric interference. In the case of VI (the only secondary system investigated) steric hindrance is minimized if the *tert*-butyl group lies above the aliphatic hydrogen; the cage effect in cumene at 60° is 0.17. In the phenylperacetates III and IV there are two aliphatic hydrogens above which the *tert*-butyl group may lie, and the cage effects are *ca.* 0.30 at 80–90° in cumene.

Steric hindrance is usually more serious in couplings involving *tert*-butoxy radical, eq 11 and 12, than in those of alkyl or aralkyl radicals only, eq 10. Judging

$$2\mathrm{R}\cdot \longrightarrow \mathrm{R{-}R} \tag{10}$$

$$\mathrm{R}\cdot + \mathrm{O}\text{-}t\text{-}\mathrm{Bu} \longrightarrow \mathrm{R{-}O}\text{-}t\text{-}\mathrm{Bu} \tag{11}$$

$$2\cdot\mathrm{O}\text{-}t\text{-}\mathrm{Bu} \longrightarrow t\text{-}\mathrm{Bu{-}O{-}O}\text{-}t\text{-}\mathrm{Bu} \tag{12}$$

from cage effects, reactivity follows the order (10) > (11) > (12), except that for tertiary R, (12) > (11). Aliphatic radical pairs such as *n*-propyl, *n*-butyl, and *sec*-butyl have cage effects of *ca.* 0.33 in pentane, and 0.55 in decalin, at 30°, despite the presence of two CO_2 molecules between them.[22] Azomethane photolysis has cage effects of the order of 0.70 in ordinary solvents at ambient temperature.[13a] Pairs of diphenylmethyl radicals from the thermolysis of azodiphenylmethane at 34° in benzene couple with a cage effect of *ca.* 0.55,[9a] despite a likely significant degree of steric hindrance, and appreciable resonance energy; this result may be in small part due to slower diffusion from the cage (*vide supra*). On the other hand, *tert*-butoxy radicals couple in benzene with a cage effect of only 0.055.[9b]

Sheldon and Kochi point out[10] that the smaller cage coupling of alkyl–alkoxy pairs than of alkyl–alkyl pairs from diacyl peroxides is paradoxical, because the former cage contains only one CO_2 molecule, the latter, two. They postulate that alkoxy radical attacks the solvent cage competitively. This suggestion is entirely unfounded empirically. It is decisively ruled out by the fact that the rate constant for attack of *tert*-butoxy radical on cumene is only about $10^5\ M^{-1}\ \mathrm{sec}^{-1}$,[20b] while attack on cage solvent requires a value in excess of 10^8.[27] It is our feeling, instead, that the intrinsically lower reactivity of *tert*-alkoxy radicals toward other radicals, probably due to steric effects, is responsible.

It is important to compare the reactivities of older, bulk radicals from measured rate constants, with reactivities of geminate radicals from cage effects.[2] This is properly done by applying eq 13, where k_t is the

$$k_t = fk'' \tag{13}$$

coupling rate constant, f the cage effect, and k'' the

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[21] R. K. Dewan and K. E. VanHolde, *J. Chem. Phys.*, **39**, 1820 (1963); D for *n*-pentane is only twice that for *n*-hexadecane in CCl_4 at 20°.

[22] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970).

[23] N. A. Porter, M. E. Landis, and L. J. Marnett, *J. Amer. Chem. Soc.*, **93**, 795 (1971).

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[25] (a) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970); (b) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).

[26] P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

[27] The ratio of rates is, (solvent attack)/(coupling) = $k_S[\mathrm{S}]/k_c[\mathrm{R}_2]$, where S is solvent and R_2 the other radical. Taking their effective concentrations to be 10 and 3, respectively, and assuming $k_c = 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ (the value estimated by Sheldon and Kochi[10]), the ratio of rates is 1:3 if $k_S = 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.

Table VII. Comparison of Some Cage Effects with Bulk Rate Constants at 25°

Reactants	Solvent	$10^{-9}k_\mathrm{t}$[a]	$10^{-9}k''$[a,b]	Cage effect, f Calcd, $= k_\mathrm{t}/k''$	Obsd (temp, °C)
$2CH_3CH_2CH_2$	Cyclohexane	1.7[c]	3.0	0.57	~0.40 (30)[d]
$2Ph_2CH$	Benzene	~2.4[e]	4.5	0.53	0.55 (50)[f]
$2Me_3C$	Cyclohexane	1.1[g]	3.0	0.37	
t-BuO + Ph_2CH	Cumene		3.3		~0.28 (40–60)[h]
2*t*-BuO	Di-*tert*-butyl peroxide	1.3[i]		*j*	
	Isooctane		9.0		0.086 (45)[k]
	Benzene		4.5		0.055 (45)[l]
	CCl_4		2.5		0.14 (40)[m]

[a] M^{-1} sec^{-1}. [b] All values calculated as in ref 2, Table XXV. [c] R. D. Burkhart, *J. Phys. Chem.*, **73,** 2703 (1969). [d] Reference 10. [e] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91,** 986 (1969). [f] Reference 9a. [g] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90,** 7047 (1968). [h] References Ia and 6. [i] Reference 28. [j] Cannot be calculated, since viscosity not reported. [k] Reference 9c. [l] Reference 9b. [m] C. Walling and V. P. Kurkov, *J. Amer. Chem. Soc.*, **89,** 4895 (1967).

spin corrected rate constant for encounters of bulk radicals. Representative data in Table VII, displaying reported values of f and k_t/k'', show such comparisons are premature. Absolute rate constants for reaction 11 have not been reported, while that for (12) has been measured[28] in a solvent different from that used for alkyl radicals or for measurements of f for *tert*-butoxy radicals. The estimation of k'' is crucial, but the theoretical method which combines the von Smoluchowski and Stokes–Einstein equations is not capable of sufficient accuracy. Finally, Burkhart, *et al.*,[29] have shown that the von Smoluchowski equation gives rate constants for dimerization of primary alkyl radicals in cyclohexane that agree closely with experiment, when their measured diffusion coefficients for the radicals are used. This finding calls into question the application of eq 13. We reiterate here our proposal[2] that k'' be estimated by determining k_t through a range of viscosity high enough that $k_\mathrm{t} = k''$, and then extrapolating back to the viscosity of interest. This procedure would also eliminate the need for the arbitrary spin correction.

Although k_t values for most alkyl and aralkyl radicals in cyclohexane are virtually identical,[30,31] that for triphenylmethyl is nearly 10^5 smaller, or 3600 M^{-1} sec^{-1} as estimated from the dissociation rate and equilibrium constants of Ziegler and coworkers.[15] This spectacular exception, noted previously by Bartlett and McBride,[26] is all the more striking in light of more recent knowledge that the dimer of triphenylmethyl has the unsymmetrical, methylenecyclohexadiene structure.[32] Steric hindrance to formation of hexaphenylethane, which remains unknown, must be serious indeed.

In conclusion, the data, despite their rough edges, support the contention that steric hindrance is the major controlling factor in cage couplings involving *tert*-butoxy radicals, and in lesser degree those not involving them, provided comparisons are made at similar temperatures and viscosities.

Experimental Section

Detailed descriptions of the procedures used in this work are contained in the thesis of J. P. Lorand, Harvard University, 1964, available through University Microfilms, Ann Arbor, Mich.

Materials. Cumene and chlorobenzene were purified as described previously, and the cumene stored under nitrogen. The preparation and use of galvinoxyl have been described;[7,14] pyrogallol was reagent grade material and was used as received.

All peresters were prepared from their acid chlorides, which were obtained by briefly refluxing the acids with excess thionyl chloride in benzene and purified by distillation or recrystallization. *tert*-Butyl peracetate was prepared from *tert*-butyl hydroperoxide and pyridine,[3] while all the others were prepared from sodium *tert*-butyl peroxide suspended in dichloromethane at 0°.[7] *tert*-Butyl peracetate (I) was obtained in 70% crude yield; passage over Florisil in ligroin and bulb to bulb distillation raised the purity from 89 to 95% as determined by the iodometric method of Silbert and Swern.[33] *tert*-Butyl perpivalate (II), obtained in 70% crude yield, was passed through Florisil in ligroin and after removal of solvent evacuated to constant weight on a rotary evaporator at 0.5 mm; iodometric assay was 79.4%; subsequently, samples of II have been distilled *in vacuo*.[34] *tert*-Butyl *p*-nitrophenylperacetate (III) was obtained in 40% crude yield, chromatographed twice on Florisil, and recrystallized three times from benzene–petroleum ether; white plates; mp 54.5–56.0° (lit.[12b] 53.2–53.4°); iodometric assay, 97.1%. *tert*-Butyl *p*-methoxyphenylperacetate (V) was prepared in 34% yield after recrystallization to mp 39–42° (lit.[12b] 38.6–38.9°), iodometric assay 77.5 ± 0.2%. *tert*-Butyl α-phenylperisobutyrate (V), obtained in 55% crude yield, was dissolved in pentane, filtered from white precipitate, stripped of solvent, and maintained at 0° and 0.5 mm for several hours; the product assayed 66.6% (iodometry) and gave 93–95% yields of CO_2. The preparation of *tert*-butyl α,α-diphenylperpropionate (VII) was aided by an improvement in the preparation of the acid chloride: Refluxing α,α-diphenylpropionic acid (10.0 g, 0.0443 mol) with thionyl chloride (10.5 g, 0.088 mol) in 70 ml of benzene for 5 hr, rather than 24 hr as previously,[3] afforded 11.3 g of residue free of anhydride or 1,1-diphenylethylene, by ir. Cooling a solution in pentane to −78° caused separation of an oil which crystallized; two recrystallizations gave 7.8 g, 0.0319 mol, of product of mp 39.0–42.5°, in 72% yield. Reaction of the chloride with sodium *tert*-butyl peroxide for 3 hr at 0° gave the perester in 88.5% yield, mp 66–69.5° (lit.[3] 71–72°). *Anal.* Calcd for $C_{19}H_{22}O_3$: formula wt, 298.37; C, 76.47; H, 7.43. Found: C, 76.31; H, 7.35. Di-*tert*-butyl diphenylpermalonate (IX) was kindly supplied by Dr. R. D. Swigert, and had mp 71–71.5° (lit.[16] 66.4–67.6° dec). Di-*tert*-butyl diperoxyoxalate (DBPO, XII) was kindly supplied by Drs. A. J. Moye and H. Van Zwet, and consistently gave quantitative yields of CO_2 on solution thermolysis.

Di-*tert*-butyl Ether. This was prepared[35] from *tert*-butylmagnesium chloride and *tert*-butyl perbenzoate[36] in *ca.* 25% yield, bp 106° (lit.[37] 106.5–106.7°); ir no hydroxyl absorption; nmr δ 1.1 ppm (singlet); glpc retention time at 80° on UCON LB 550X on Chromosorb P was twice that of *tert*-butyl alcohol. The product

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of a previous preparation utilizing a different batch of magnesium to prepare the Grignard reagent was found by glpc to be an equal mixture of the ether with hexamethylethane. Attempts to convert di-*tert*-butyl peroxide to di-*tert*-butyl ether by the action of triphenylphosphine at 110° in an alkali-washed, baked sealed tube, as described by Horner, *et al.*,[38] led only to products of decomposition of the peroxide.

Determination of Perester Decomposition Products. Except for oxygen absorption experiments, product studies were carried out on degassed solutions in sealed Claisen flasks with a breakseal neck, as previously described.[39] The vacuum line used for fractionating the products was the same as that previously described and pictured.[39] Volatile products were determined by glpc, while the nonvolatile residue was subjected to column chromatography on Florisil or silica gel and the fractions were identified by nmr and ir. Oxygen absorption experiments were carried out with the apparatus and technique described by Traylor.[40]

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Radicals and Scavengers. VI. The Absolute Rate Constant for Reaction of *tert*-Butoxy Radical with Toluene by a Competition Technique[1]

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Abstract: The absolute rate constant, k_2, for the reaction of *tert*-butoxy radicals with toluene, $t\text{-BuO}\cdot + \text{PhCH}_3 \rightarrow t\text{-BuOH} + \text{PhCH}_2\cdot$, at 25° in toluene, is found to be *ca.* $0.9 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, by applying a competition technique to the decompositions of *tert*-butyl triphenylperacetate (I) and *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate (II). The stable radicals triphenylmethyl and 1,1-diphenylneopentyl are observed and evidently compete with toluene for *tert*-butoxy radicals. The rate constants for the latter reactions are evaluated theoretically and corrected with the aid of cage effects, under the critical assumption that geminate and bulk radicals have the same reactivity in coupling reactions. The new value of k_2 supersedes recently reported values based on unforeseen complications in the kinetics and mechanism of *tert*-butyl hypochlorite reactions. It is hoped, however, that better methods of evaluating diffusion controlled rate constants will be developed.

The importance of tertiary alkoxy radicals in organic free radical chemistry has elicited some interest in absolute rate constants for their reactions. Most of these reports have involved the chlorination of hydrocarbons by *tert*-butyl hypochlorite. Carlsson and Ingold,[3] applying the rotating sector method for the light-initiated reaction, obtained $k_2 = 1.07 \pm 0.34 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ for toluene in benzene solution at 24°; their kinetics had supported the mechanism of reactions 1–4. Discrepancies were, however, evident between

$$t\text{-BuOCl} \longrightarrow t\text{-BuO}\cdot + \text{Cl}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + \text{RH} \xrightarrow{k_2} t\text{-BuOH} + \text{R}\cdot \qquad (2)$$

$$\text{R}\cdot + t\text{-BuOCl} \xrightarrow{k_3} \text{RCl} + t\text{-BuO}\cdot \qquad (3)$$

$$2t\text{-BuO}\cdot \longrightarrow t\text{-BuOO-}t\text{-Bu} \qquad (4)$$

their kinetics and those reported by Walling and Kurkov.[4] These have recently been resolved by Zavitsas and Blank,[5] who eliminated chlorine atom chains[6] by addition of tetrachloroethylene. The kinetics now corresponded clearly to termination by reaction 5, rather

$$2\text{R}\cdot \longrightarrow \text{products} \qquad (5)$$

than (4). The authors[5] also asserted that of the two propagation steps, (3) was rate determining, rather than (2). From the literature value[7] for k_5 of $2.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, and their value for $k_3/(2k_5)^{1/2}$ (from the predicted rate law, rate $= k_3(t\text{-BuOCl})(R_i/2k_5)^{1/2}$, where R_i = rate of initiation), they calculated $k_3 = 6.3 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ for benzyl radical. It can readily be shown *via* the steady-state approximation that the rate law is independent of whether reaction 2 or 3, of the two propagation steps, is rate determining. Thus, k_3 may be considered to be known, while k_2 must be obtained by other means.

Walling and Kurkov[4] attempted to estimate k_2, using cage effect data for *tert*-butoxy radicals to arrive at a value of k_4 and thence k_2 from their kinetic data. Their value of $8 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ is unfortunately also invalid because reaction 4 was thought to be the principal terminating step.

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[1] (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract ORGN-138. (b) From the Ph.D. Thesis of R. W. W., Boston University, 1973. (c) Part V: J. P. Lorand, *J. Amer. Chem. Soc.*, **96**, 2867 (1974).

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