

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 non-volatile 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

Acknowledgments. The author is deeply grateful to Professor Paul D. Bartlett for his guidance in this work and for valuable comments on the manuscript, and to Professor Leon B. Gortler for helpful discussions.

(39) (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960); (b) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963).

(40) T. G. Traylor, *J. Amer. Chem. Soc.*, **85**, 2411 (1963).

(38) L. Horner and W. Jürgeleit, *Justus Liebigs Ann. Chem.*, **591**, 138 (1955).

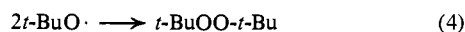
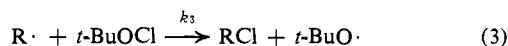
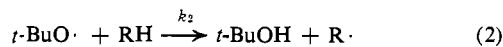
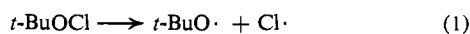
Radicals and Scavengers. VI. The Absolute Rate Constant for Reaction of *tert*-Butoxy Radical with Toluene by a Competition Technique¹

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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 $ca. 0.9 \times 10^6 M^{-1} \text{sec}^{-1}$, 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



their kinetics and those reported by Walling and Kurkov.⁴ These have recently been resolved by Zavitsas

(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).

(2) Address correspondence to this author at the Department of Chemistry, Central Michigan University, Mt. Pleasant, Mich. 48859.

(3) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4891 (1967).

(4) C. Walling and V. P. Kurkov, *J. Amer. Chem. Soc.*, **89**, 4895 (1967).

and Blank,⁵ who eliminated chlorine atom chains⁶ by addition of tetrachloroethylene. The kinetics now corresponded clearly to termination by reaction 5, rather



than (4). The authors⁵ also asserted that of the two propagation steps, (3) was rate determining, rather than (2). From the literature value⁷ 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 = $k_3(t\text{-BuOCl})(R_1/2k_5)^{1/2}$, where R_1 = 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 Kurkov⁴ attempted to estimate k_2 , using cage effect data for *tert*-butoxy radicals to arrive at a value of k_2 and thence k_3 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.

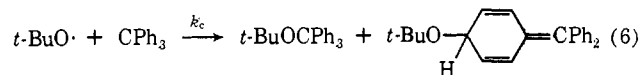
(5) A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, **94**, 4603 (1972).

(6) C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, **91**, 2053 (1969).

(7) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

In the only other report known to us, Weiner and Hammond⁸ obtained, for reaction 4 in neat di-*tert*-butyl peroxide, the value $k_4 = 1.3 \times 10^9 M^{-1} \text{sec}^{-1}$, by applying the rotating sector method to the decay of the esr signal of photolytically generated *tert*-butoxy radicals. It is significant that their value is fully an order of magnitude greater than that of Carlsson and Ingold.³

We have developed a new method of estimating k_2 which does not require measuring any reaction rates. Our method is not revolutionary, but is an extension of classical competition kinetics to include one diffusion-controlled reaction, in particular reaction 6, for which



the rate constant, k_c , should be calculable by means of a good theory. We use the von Smoluchowski equation,⁹ believed to be accurate to within a factor of 2,¹⁰ but modify the calculated rate constant through knowledge of a cage effect involving reaction 6, as described below. We now present our results in order to begin to fill the void created by the failure of hypochlorite kinetics to afford a value of k_2 .

Conditions for the success of this method become apparent upon comparing the rate laws of reactions 2 and 6 (RH = PhCH₃)

$$\frac{\text{rate}(2)}{\text{rate}(6)} = \frac{\text{yield}(2)}{\text{yield}(6)} = \frac{k_2(t\text{-BuO}\cdot)(\text{PhCH}_3)}{k_c(t\text{-BuO}\cdot)(\text{Ph}_3\text{C}\cdot)} \quad (7)$$

$$k_2 = \frac{\text{yield}(2) k_c(\text{Ph}_3\text{C}\cdot)}{\text{yield}(6) (\text{PhCH}_3)} \quad (8)$$

("Rate(2)" and "yield(2)," etc., refer to eq 2 and 6, respectively.) (1) The triphenylmethyl radical must be present at an observable concentration which remains fairly constant. Its concentration may easily be measured by virtue of its λ_{max} 515 nm (ϵ 656). (2) Reaction 6 must take place in bulk solution in part, so that reactions 2 and 6 will compete kinetically. (3) There must exist an initiator which generates *tert*-butoxy and triphenylmethyl radicals as a geminate pair, and a cage effect must be demonstrable. The probability, f , of the cage reaction may be identified with the probability that the bulk species (as well as the geminate pair) will react during an encounter. It is then possible to express k_c by eq 9, in which k' is the maximum possible

$$k_c = fsk' \quad (9)$$

second-order rate constant given by eq 10, the

$$k' = 6\pi\rho D'N/1000 \quad (10)$$

ρ = encounter diameter of radical pair
(sum of radii)

D' = relative diffusion coefficient of the pair
($D' = D_1 + D_2$)

N = Avogadro's number

von Smoluchowski equation, and s is a spin correction factor (*vide infra*). The diffusion coefficients, D_i , are

(8) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 2182 (1969).

(9) M. von Smoluchowski, *Z. Phys. Chem. (Leipzig)*, **92**, 129 (1917).

(10) (a) R. M. Noyes, *J. Amer. Chem. Soc.*, **86**, 4529 (1964); (b) J. P. Lorand in "Inorganic Reaction Mechanisms," Vol. 2, J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 207-325.

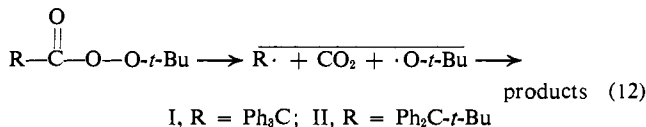
calculated by the Stokes-Einstein equation (eq 11)

$$D_i = kT/4\pi\eta r_i \quad (11)$$

r_i = radius of radical i

modified as suggested by Edward and others to fit existing data for small molecules.¹¹

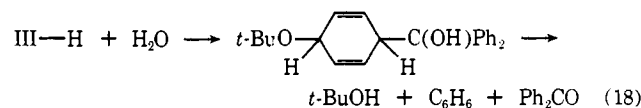
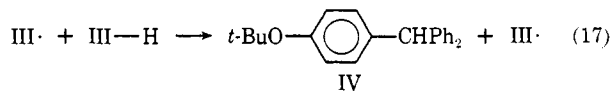
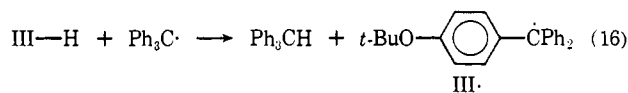
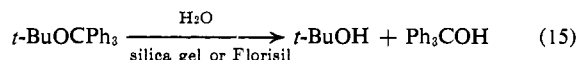
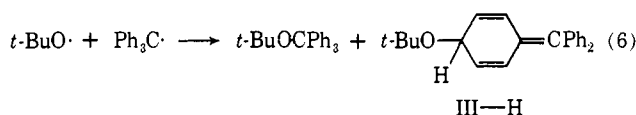
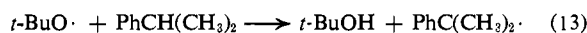
An initiator, the decomposition of which fulfills these conditions, *tert*-butyl triphenylperacetate (I), has already been described.¹² Its thermal decomposition in cumene has $t_{1/2} = 1$ hr at 25°, and follows eq 12.



A second *tert*-butyl perester, *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate (II), $t_{1/2} = 8$ hr in cumene at 26°, has been described;¹³ its decomposition generates the similar, stable 1,1-diphenylneopentyl radical. We now report the extension to toluene solution of our studies of their decompositions and the calculation of k_2 . If our method is valid, both I and II should lead to the same value of k_2 .

Results and Discussion

Our approach will be illuminated by a brief consideration of the products of decomposition of I. In cumene,¹² these include CO₂ (95%), *tert*-butyl alcohol (42%), triphenylmethanol (20%), benzophenone (14%), *p*-*tert*-butoxytriphenylmethane (16%), triphenylmethane (36%), and α -methylstyrene (13%). The triphenylmethanol appeared only after chromatography; the nmr spectrum of the crude product before chromatography showed a sharp singlet attributable to the *tert*-butyl protons of *tert*-butyl triphenylmethyl ether, which was assumed to be hydrolyzed on the chromatographic adsorbent (eq 15). No acetone was detected by glpc, nor was there any dicumyl or 1,1,1,2-tetraphenyl-2-methylpropane. Equations 13-18 have



(11) (a) J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970); (b) E. Mc-Glaughlin, *Trans. Faraday Soc.*, **55**, 28 (1959).

(12) J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 3294 (1966).

(13) J. P. Lorand and R. W. Wallace, *J. Amer. Chem. Soc.*, **96**, 1402 (1974), paper IV in series.

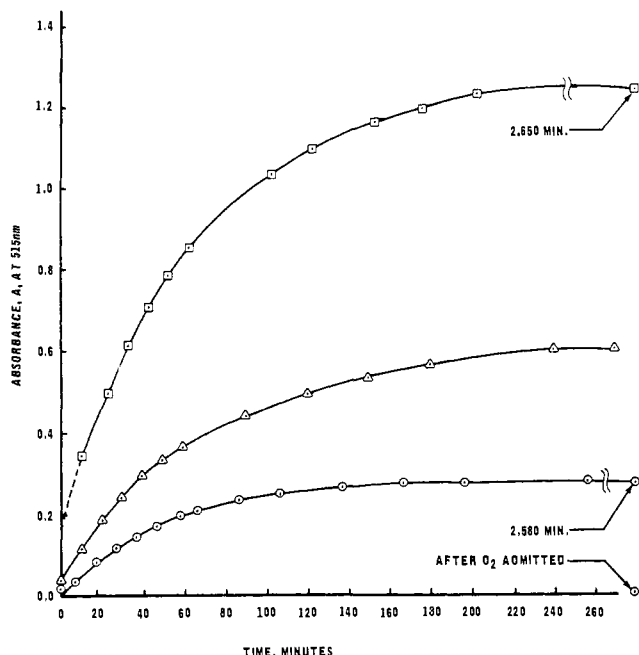


Figure 1. Absorbance at 515 nm of triphenylmethyl radical from thermal decomposition of perester I at 25° in toluene vs. time. Initial concentration of I: (□) 0.166 M; (△) 0.059 M; (○) 0.0336 M.

been proposed to explain the products. The coupling of cumyl radicals to dicumyl (2,3-dimethyl-2,3-diphenylbutane) cannot compete with reaction 14 because of the high observed concentration of triphenylmethyl radicals. Reaction 16 is postulated to explain the greater yield of triphenylmethane than α -methylstyrene; reactions 16 and 17 convert III-H to IV. This product distribution shows that a small but significant contribution is made by reaction 13, and that a very considerable amount of cross-coupling, reaction 6, must take place.

Most of reaction 6 was found to involve bulk radicals, rather than geminate ones. Addition of 0.5 M *tert*-dodecanethiol (RSH) led to 94% of *tert*-butyl alcohol (based on the yield of CO₂).¹² This suggests that only



6% of coupling is "cage effect" (involves geminate radicals fresh from the homolysis of one molecule of I). This conclusion has been confirmed by the finding¹³ that decomposition of both I and II in highly viscous solutions in the presence of thiol gives much lower yields of alcohol, consistent with the expectation that the cage effect is increased by viscosity.

Toluene was chosen as solvent for the present study, not only for the sake of relevance to previous work, but also because of simplicity: benzyl radicals arising from reaction 2 (RH = PhCH₂H), having no β hydrogen, cannot give olefin, but can only couple with triphenylmethyl radicals to form either 1,1,1,2-tetraphenylethane or its isomer, *p*-benzyltriphenylmethane. In the cumene study,¹² resolution of α -methylstyrene from cumene by glpc was difficult.

Cage Effects in Toluene. We have recently¹³ determined the cage effects in the decompositions of peresters I and II at 25° in toluene by extrapolating back to the viscosity of toluene plots of $1/f$ vs. $1/\eta^{1/2}$ for mixtures of mineral oil and toluene. The reported

values of 11.5% for I and 4.5% for II may be upper limits because curvature of such plots in the low-viscosity region is usually observed.¹⁴ With I and II, however, curvature was not clearly evident.

Concentration of Stable Radicals. These measurements and the determinations of product yields were carried out using the same initial concentrations of I and II. Triphenylmethyl formed by the thermolysis of I was monitored at 515 nm; absorbances in a solution initially 0.0336 M in I are presented in Table I,

Table I. Concentration of Triphenylmethyl during Decomposition of Perester I^a in Toluene at 25°

| Time, min | Absorbance, 515 nm | Concn, M ^b |
|-------------------|--------------------|-----------------------|
| 0 | 0.025 | 0.38×10^{-4} |
| 7 | 0.038 | 0.58 |
| 17 | 0.088 | 1.34 |
| 27 | 0.123 | 1.88 |
| 37 | 0.150 | 2.29 |
| 47 | 0.176 | 2.68 |
| 58 | 0.200 | 3.05 |
| 67 | 0.214 | 3.26 |
| 87 | 0.240 | 3.66 |
| 107 | 0.257 | 3.92 |
| 137 | 0.270 | 4.12 |
| 167 | 0.279 | 4.25 |
| 197 | 0.279 | 4.25 |
| 257 | 0.285 | 4.35 |
| 1080 | 0.285 | 4.35 |
| 2580 | 0.269 | 4.10 |
| 2580 ^c | 0.009 | (0.14) |

^a Initial concentration = 0.0336 M. ^b ϵ 656; cf. ref 12. ^c After exposure to air.

while those for all three experiments are plotted in Figure 1. For the decomposition of II, it was impossible to monitor the stable radical concentration similarly, since no distinct visible absorption maximum was found for 1,1-diphenylneopentyl radical, but only end absorption.¹³ Instead, epr spectra were integrated with respect to both triphenylmethyl and DPPH as external standards. After complete decomposition of 0.19 M II in toluene at 25°, the concentration of radical was found to be *ca.* 5.5×10^{-4} M, a value believed accurate within 50%.

It is clear from Table I and Figure 1 that the concentration of triphenylmethyl is far from constant during the first few half-lives of decomposition of I, when most of the product is formed. Presumably the same is true of the decomposition of II. Considering the assumptions already inherent in the method, it was deemed adequate to choose a single value of radical concentration, that attained after 1 half-life, *i.e.*, 65 min in the case of I. In all three runs with I, the radical concentration after 65 min was very nearly $2/3$ of that after 10 half-lives. Therefore, the concentration of 1,1-diphenylneopentyl radical from II was assumed to be $2/3$ of that measured, or 3.6×10^{-4} M after 1 half-life at 25°. These values, presented in Table II, are used in the calculation of k_c (*vide infra*).

Product Yields. The yields of H-atom transfer and coupling, reactions 2 and 6, respectively, were determined indirectly, the former because there were additional sources of *tert*-butyl alcohol, and the latter be-

(14) (a) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **90**, 7014 (1968); (b) T. Koenig, *ibid.*, **91**, 2558 (1969).

Table II. Products of Decomposition of I and IV in Toluene at 25°

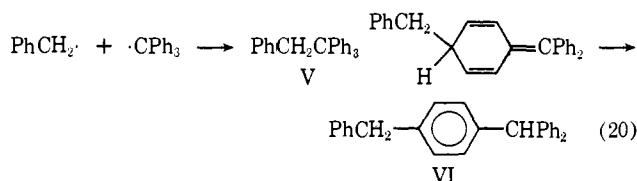
| Perester | (Perester), <i>M</i> | Yield, % ^a | | | |
|----------|-------------------------|-----------------------|--------------------|------------------|----------------------------------|
| | | <i>t</i> -BuOH | Ethers | | PhCH ₂ R ^d |
| | | | Gross ^b | Net ^c | |
| I | 0.0336 | 71 | 29 | 17.5 | 53 |
| I | 0.059 | 63 | 37 | 25.5 | 36 |
| I | 0.166 | 40 | 60 | 48.5 | 25 |
| II | 0.190 | 91 | 9 | 4.5 | 12 |

^a Based on yield of CO₂. ^b 100 - % *t*-BuOH. ^c 100 - % *t*-BuOH - 100^f. ^d I, R = Ph₃C; II, R = Ph₂C-*t*-Bu.

cause determination of all coupling products was tedious, and possibly unreliable because of their variety. The yield of reaction 2 was taken to be that of products containing the benzyl radical. The yield of reaction 6 was assumed to be 100% - % yield of *tert*-butyl alcohol, if all *tert*-butoxy radicals not converted to alcohol underwent coupling.

Yields of alcohol in decompositions of I and II appear in Table II together with their complement, the total yield of ethers, as well as the latter less the cage effect, *i.e.*, the net yield of ethers formed in bulk solution. For I, the yield of ethers is seen to increase with increasing (I)₀, consistent with the mechanism and the fact that (Ph₃C·) also increases with increasing (I)₀ at any given time.

The nmr spectrum of the nonvolatile products from the decomposition of I in toluene showed a sharp singlet at δ 3.85 ppm, which could arise from the benzyl protons of either 1,1,1,2-tetraphenylethane (V) or its



isomer, *p*-benzyltriphenylmethane (VI). A sample of IV previously prepared¹⁵ from benzylmagnesium chloride and triphenylmethyl chloride in ether had shown a sharp singlet at 3.85 ppm and no trace of absorption at 5.4 ppm, characteristic of triphenylmethanes. Addition of diphenylmethane to the solution of decomposition products did not result in enhancement of the 3.85-ppm signal, but produced a new singlet at 3.95 ppm. Since VI would be expected to show benzyl proton absorption virtually superimposable upon that of diphenylmethane, this evidence supports the assignment of the 3.85-ppm signal to V. It should be recalled that triphenylmethane is one of the products, so it will give rise to absorption at 5.4 ppm whether or not VI is present. Integration of the 3.85-ppm signal relative to the integral of a known concentration of anisole gave the yields of V shown in Table II.

Similar absorption was found for the products of decomposition of perester II and attributed to the coupling product, 1,2,2-triphenyl-3,3-dimethylbutane. Its yield is presented in Table II.

An alternative fate of the benzyl radical might be H-atom abstraction from III-H to give toluene, identical with the solvent; the yield of V would then underestimate that of reaction 2. Although reaction of tri-

phenylmethyl with III-H has been postulated to account for the excess triphenylmethane, this pathway is not likely to be significant for benzyl radicals. These have a far shorter lifetime than triphenylmethyl, which is expected to trap them at a diffusion-controlled rate. Furthermore, benzyl radicals are expected to be orders of magnitude less reactive in H-atom abstraction than *tert*-butoxy radicals.¹⁶ These probably react with III-H to the extent of 15-27%, the range of the difference in yields between *tert*-butyl alcohol and V in the three runs with I. The disappearance of benzyl radicals by reaction with III-H can, therefore, certainly be neglected.

Calculation of *k_c*. Two procedures for applying eq 10 and 11 have been employed; diffusion coefficients required for (10) have also been evaluated by the empirical equation of Wilke and Chang (eq 21), which is

$$d = 7.4 \times 10^{-8} T(xM)/\eta V^{0.6} \quad (21)$$

M = solvent molecular weight

x = solvent association parameter (*x* = 1 usually)

V = molal volume of solute at normal boiling point

reported to reproduce a wide variety of diffusion data.¹⁸

The first procedure for applying eq 10 and 11 involves the simplifying assumption that the two different radicals have the same radius; thus, ρ (eq 10) = $2r_i$ (eq 11), and $D' = 2D_i$; this leads to eq 22 (where η' is

$$k' = 4RT/1000\eta = 4RT/\eta' \quad (22)$$

in mP), which does not contain the radius or encounter diameter of the diffusing species. As the viscosity of toluene at 25° is reported¹⁹ to be 5.5 mP the simplification gives $k' = 1.80 \times 10^{10} M^{-1} \text{sec}^{-1}$.

The second procedure utilizes eq 23, derived with

$$k' = (RT/\eta')(r_1 + r_2)^2/r_1r_2 \quad (23)$$

the assumption that $\rho = r_1 + r_2$, as well as that $D' = D_1 + D_2$, where η' is in mP. Substitution of $r_1 = 2.5 \text{ \AA}$ (*tert*-butoxy) and $r_2 = 4.2 \text{ \AA}$ (mean of longitudinal and transverse radii for triphenylmethyl) gives $k' = 1.95 \times 10^{10} M^{-1} \text{sec}^{-1}$. With these values, the factor $(r_1 + r_2)^2/r_1r_2$ is 4.3, while if $r_2 = 1.8 \text{ \AA}$, the transverse radius, the factor is 4.1.

For eq 21, molal volumes of 292.5 for triphenylmethyl and 100.5 for *tert*-butoxy^{1b} lead to *D* values of 12.4×10^{-6} and $24 \times 10^{-6} \text{ cm}^2/\text{sec}$, respectively. Substitution into eq 10 with $r_1 = 2.5$ and $r_2 = 4.2 \text{ \AA}$ gives $k' = 1.82 \times 10^{10} M^{-1} \text{sec}^{-1}$.

For these few available means of evaluating k' the resulting values are essentially the same, and we shall employ their mean, $1.86 \times 10^{10} M^{-1} \text{sec}^{-1}$. A possible pitfall in this procedure should be noted. Burkhart and coworkers²⁰ have measured experimentally *D* values for primary alkyl radicals in cyclohexane at 25°. Their values are smaller than those predicted by eq 11 by factors ranging from 3 to 27. It remains to be seen

(16) Benzylic radicals in cumene and toluene, in the absence of triphenylmethyl, survive to undergo self-coupling;^{17a} *tert*-butoxy radicals do not.^{1c, 17b}

(17) (a) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963); (b) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 5175 (1970).

(18) C. R. Wilke and P. Chang, *Amer. Inst. Chem. Eng. J.*, **1**, 264 (1955).

(19) "Handbook of Chemistry and Physics," 49th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1968, p F42; interpolated between 20 and 30°.

(20) R. D. Burkhart, R. F. Boynton, and J. C. Merrill, *J. Amer. Chem. Soc.*, **93**, 5013 (1971).

(15) J. P. Lorand, Ph.D. Thesis, Harvard University, 1964.

Table III. Values of k_2 from Equation 8 for I and II at 25°

| Perester | (Perester) ₀ , <i>M</i> | Yield(2) ^a /yield(6) | k_c /[PhCH ₃] | [R·] ^b , <i>M</i> | k_2 , <i>M</i> ⁻¹ sec ⁻¹ |
|----------|------------------------------------|---------------------------------|-----------------------------|------------------------------|--|
| I | 0.0336 | 3.03 | 1.13×10^8 | 3.0×10^{-4} | 1.03×10^5 |
| I | 0.059 | 1.41 | 1.13×10^8 | 5.8×10^{-4} | 0.93×10^5 |
| I | 0.166 | 0.515 | 1.13×10^8 | 13.0×10^{-4} | 0.75×10^5 |
| II | 0.192 | 2.7 | 0.44×10^8 | 3.6×10^{-4} | 0.41×10^5 |

^a From Table II; yield(2) = % PhCH₂R; yield(6) = net % ethers. ^b From I, R· = Ph₃C·; from II, R = Ph₂C(*t*-Bu)·; cf. text.

whether the discrepancies are real or arise out of the chemistry involved in their measurements. In any case we would not know what correction factor to choose, and are therefore leaving our own estimate of k' unchanged.

The Spin Correction Factor, *s* (Eq 9). Values of k' calculated for fluid solvents probably require adjustment for the fact that not all encounters between bulk radicals will give a singlet state.²¹ In the gas phase, encounters are identical with single collisions, and one collision in four generates a singlet state. In solution encounters are longer lived, and some spin inversion from triplet to singlet might occur. Studies by Fox and Hammond²² of the triplet photosensitized decomposition of *N*-1-cyanocyclohexylpentamethyleneketimine in cumene showed a cage effect one-third that of the direct photolysis, presumably involving an excited singlet state. Thus, one part in three of triplet pairs cross over fast enough to react, and one of every two random encounters can give reaction. We shall thus choose the value of 0.5 for the spin correction factor, *s*. For toluene at 25°, $sk' = 0.93 \times 10^{10} M^{-1} \text{ sec}^{-1}$. Finally, from eq 9, with $f = 0.115$, $k_c = 1.07 \times 10^9 M^{-1} \text{ sec}^{-1}$. For II, with $f = 0.045$, $k_c = 0.42 \times 10^9 M^{-1} \text{ sec}^{-1}$.

Calculation of k_2 . Values of k_2 calculated by eq 8, with (PhCH₃) = 9.5 *M*, appear in Table III. The results for all three initial concentrations of perester I are closely similar, supporting the proposed mechanism and suggesting that cage effects and product yields are reasonably precise. The precision of these measurements is indicated by maximum and minimum values of k_2 calculated for 0.059 *M* I with limits of ± 0.03 for the *tert*-butyl alcohol yield, ± 0.05 for the 1,1,1,2-tetra-phenylethane yield, and ± 0.025 for the cage effect, *f*: these are 1.95 and $0.37 \times 10^5 M^{-1} \text{ sec}^{-1}$, respectively. These limits indicate that the single measurement with perester II, although only about one-half that for I, is the same as the latter within the experimental uncertainty. The uncertainty in k_2 from II is probably greater than that from I considering the small yield values involved. The mean of the results for I is then $k_2 = 0.9 \times 10^5 M^{-1} \text{ sec}^{-1}$.

In addition to the sources of error just considered, one must bear in mind the following: the unknown accuracy of eq 10; the applicability of eq 11 to small radicals; the rather arbitrary spin correction factor *s* of 0.5 (eq 9); the variation in concentration of the stable radicals during perester decomposition; and most important, our basic assumption that bulk radicals have the same reactivity as caged, geminate radical pairs, *i.e.*, the applicability of eq 9. The variation in stable radical concentrations could be treated by monitoring

the product yields with time, but we doubt that this is a serious source of error.

With regard to the comparison between caged and bulk radicals, three possible points of difference have been discussed previously: spin, rotational orientation, and solvation.^{10b,28} We have corrected for spin; the second is inscrutable but possibly insignificant for geminate radicals initially separated by a small molecule;^{10b} but the third point may be serious. Evidence has been presented, for example, that primary alkyl radicals in aromatic solvents undergo coupling with much lower rate constants than in cyclohexane, a fact accountable by solvation of bulk radicals.²⁴ If *tert*-butoxy radicals in our system are solvated by toluene, their reactivity may be diminished. Equation 9 would then be valid only for a much smaller value of *f*, by how much smaller can only be guessed at.

It should be noted, however, that our value of k_2 was used successfully by Zavitsas and Blank⁵ to explain the predominance of alkyl radical coupling as the terminating step in *tert*-butyl hypochlorite chlorinations of hydrocarbons. Had a smaller value of k_2 been used, the estimated *tert*-butoxy radical concentration would have been comparable to the alkyl radical concentration, not 60–100 times smaller; some termination by *tert*-butoxy radical coupling would then be expected. Our value of k_2 is therefore consistent with experiment.

Attempts have been made^{10b,25} to compare the reactivities of caged and bulk radicals by comparing experimental values of *f* with those calculated by eq 9, using eq 10 and 11 to obtain k' . For several radicals the agreement was good, and in two cases low calculated *f* values could be explained away by solvation of bulk radicals.^{10b} The situation has encouraged us in the present work, but clearly more rate constants and cage effects must be obtained for further tests to determine whether the agreement noted so far is fortuitous or not.

Finally, we reiterate our recommended empirical alternative to the use of eq 10 and 11 for estimation of k' .^{10b} In cases where termination rate constants are directly measurable, determinations over a wide range of viscosities must generate a relationship which may be extrapolated to a low viscosity characteristic of a solvent of interest. Alkyl radical coupling rate constants are already known to be viscosity dependent,²³ and this procedure would eliminate at one stroke the need for eq 10 and 11 and the spin correction.

Experimental Section

Materials. Toluene was shaken with concentrated sulfuric acid, washed with water, followed by bicarbonate solution, dried

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over magnesium sulfate, distilled from sodium, and stored under nitrogen. Nujol was obtained from Plough, Inc., and *tert*-dodecanethiol from Phillips Petroleum Co.; both were used as received. *tert*-Butyl alcohol was distilled from calcium hydride. *tert*-Butyl triphenylperacetate (I) was prepared from recrystallized triphenylacetyl chloride and fresh sodium *tert*-butyl peroxide as described previously.¹² The slightly greenish yellow crystals were assayed by CO₂ yield on thermal decomposition in cumene solution at 25°; it has previously been reported that other methods of assay, such as combustion analysis, melting point, or even iodometry, are misleading or useless for the more reactive peresters. A modified Warburg manometer,¹³ which had been calibrated with standard sodium carbonate solution acidified with excess hydrochloric acid, was used to measure the volume increase. This apparatus required only microliter amounts of dilute solutions. Samples of I were used if they evolved 95% or more of the theoretical amount of CO₂.

Stable Radical Concentrations. The triphenylmethyl radical was readily detected by its esr spectrum which was identical with published spectra.²⁶ Its concentration was measured over 2 days by the absorbance at its sharp λ_{\max} 515 nm (ϵ 656). The apparatus consisted of a quartz esr tube linearly sealed to a 1-cm² Pyrex cell, and had a T-joint with a stopcock. Into the Pyrex cell was placed 4 ml of a cold toluene solution of I, the solution flushed with nitro-

gen for several minutes through a syringe needle, and the stopcock closed. The solution in the quartz cell was warmed for 10 min at 25°, dried, and placed into the Cary 14 spectrophotometer. The 1,1-diphenylneopentyl radical was generated by decomposition of II in the same apparatus; its concentration was determined by cutting and weighing first derivative spectra and comparing with results for solutions of triphenylmethyl which had been standardized at 515 nm.

Decomposition Products. The same stock solutions were used as for measuring radical concentrations. *tert*-Butyl alcohol was determined by glpc (F&M Model 700 instrument with thermal conductivity detector and disc integrator) using standard solutions of the alcohol for calibration.

To determine nonvolatile products, solutions of decomposition products were stripped of solvent on a rotary evaporator with a vacuum pump and the residues made up to 1 ml with CCl₄. The nmr spectra of these solutions and a standard solution of anisole were integrated using the same instrument settings, on a Jeolco C-60HL spectrometer. This somewhat hazardous procedure was validated by obtaining the same integral for two aliquots of the same solution in different tubes.

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Molecular Structure of Ion Pairs from Electric Dipole Moments. II. Complexing of Potassium *p*-Toluenesulfonate and Lithium Chloride with Macrocyclic Polyethers in Octanoic Acid¹

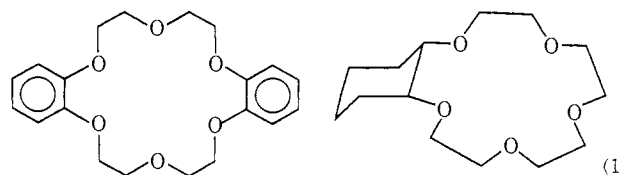
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Abstract: Measurements of the permittivity of dilute solutions of potassium *p*-toluenesulfonate (KTs), LiCl, dibenzo-18-crown-6 ether (crown-6), cyclohexyl-15-crown-5 ether (crown-5), and of their mixtures in octanoic acid at 25° led to the following electric dipole moments (μ , D) and association constants (K , M⁻¹): crown-6, μ = 1.37, crown-5, μ = 4.00; KT_s-crown-6, μ = 8.27, K = 50,000; KT_s-crown-5, μ = 8.92, K = 13,000; LiCl-crown-5, μ = 9.97, K = 6,000; LiCl + crown-6, no detectable association. For KT_s-crown-6, the association constant was confirmed by spectrophotometry. Application of Böttcher's model to the dipole moments identified the most stable ion-pair isomers and led to the following electrostatic interaction energies (W , kcal/mol): KT_s-crown-6, axial contact ion pair, W = -89.9; KT_s-crown-5, axial contact ion pair, W = -87.4; LiCl-crown-5, ligand-separated ion pair, W = -101.4. From the distances between the ionic electrical centers it is inferred that the K⁺...Ts⁻ distance is stretched (relative to that in uncomplexed KT_s ion pairs) by 0.5 Å in KT_s-crown-6 and by 0.15 Å in KT_s-crown-5.

In a recent paper² we showed that electric dipole moments of ion pairs involving noncentric ions can be analyzed to define the sites of attachment of the ions and to estimate the distance between the electrical centers. Because of the current interest in the complexing of alkali and alkaline earth metal ions with macrocyclic polyethers^{3,4} and its effect on ion-pair structure,⁵ we now extend this work to the complexes

of lithium chloride and potassium *p*-toluenesulfonate (KT_s) with cyclohexyl-15-crown-5 ether⁶ (crown-5) and of KT_s with dibenzo-18-crown-6 ether⁶ (crown-6) in octanoic acid. Solutions of lithium chloride and crown-6 in this solvent showed no interaction. The structural formulas of the crown ethers are shown below.



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