Registry No.—**2a**, 27415-49-2; **2a** HCl, 27415-50-5; **2b**, 27371-44-4; **2c**, 27415-51-6; **2c** HCl, 27415-52-7; **3a**, 27371-45-5; **3b**, 27415-53-8; **3b** HCl, 27415-54-9; **5a**, 27390-80-3; **5a** $^1/_2$-mucate, 27425-33-8; **5a** HCl, 27390-81-4; **5b**, 27390-82-5; **5b** $^1/_2$-mucate, 27494-97-9; *cis,cis*-**8**, 27390-83-6; *cis,cis*-**8** HCl, 27390-84-7; *cis,trans*-**8**, 27390-85-8; *cis,trans*-**8** HCl, 27390-86-9; **10**, 27371-46-6; **12**, 27371-47-7; **12** oxalate, 27371-48-8; **12** HCl, 27371-49-9; **15**, 27415-55-0; **15** HCl, 27415-56-1.

High Pressure Studies. VI. Polar Effects in Decomposition of Substituted *tert*-Butyl Phenylperacetates in Solution[1,2]

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The pressure dependences of the rates of thermal decomposition of the *m*-Cl-, *p*-Cl-, H-, *p*-CH$_3$-, and *p*-CH$_3$O-substituted *tert*-butyl phenylperacetates in cumene have been determined. The observed decomposition activation volumes are lower than expected for two-bond homolytic scission reactions and are also pressure dependent. The values of $\Delta V^*_{\mathrm{obsd}}$ are concluded to be a composite of contributions from bond stretching and solvation of a polar transition state. The data indicate that the polarity of the transition states varies with substituent and also that the pressure dependence of the values of $\Delta V^*_{\mathrm{obsd}}$ probably resides in the pressure dependence of solvent compressibility.

Activation volumes[3] for homolytic scission reactions in which the primary radical pair cannot return to starting material reflect the pressure dependence of the bond breaking process.[1a,3b,4] Examples of general systems which would be expected to fit this category are azo compounds and peresters, which decompose *via* simultaneous two-bond scission (eq 1 and 2). Activation volumes for representative cases (Table I) seem to fall within the range of +4 to +5 cc/mol, and they are relatively constant over a range of several thousand atmospheres.[1a,3b,5,6]

$$\mathrm{RN{=}NR} \longrightarrow \overline{\mathrm{R\cdot\ N_2\ \cdot R}} \tag{1}$$

$$\mathrm{RCO_2OR'} \longrightarrow \overline{\mathrm{R\cdot\ CO_2\ \cdot OR'}} \tag{2}$$

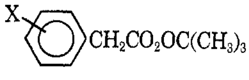
TABLE I

SOME ACTIVATION VOLUMES FOR HOMOLYTIC SCISSION[a]

Compd	*T*, °C	ΔV^*, cc/mol	Ref
$C_6H_{11}CO_3C(CH_3)_3$	79.6	+3.9	3b, 5a
$(CH_3)_3CON{=}NOC(CH_3)_3$	55.0	+4.3	1a
$C_6H_5C(CH_3)_2N{=}NC(CH_3)_2C_6H_5$	55.0	+4.9	*b*
$NCC(CH_3)_2N{=}NC(CH_3)_2CN$	70.0[c]	+4.0	6

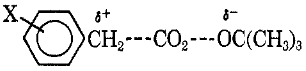
[a] Cumene solvent. [b] R. Neuman and M. Amrich, unpublished results. [c] Toluene solvent.

The ring-substituted *tert*-butyl phenylperacetates (**1**) are also thought to decompose by two-bond scission[7,8]



1

and would be expected to show similar behavior in pressure studies. However, we have previously reported that the low pressure activation volume for *tert*-butyl phenylperacetate (**1**, X = H) while positive is significantly lower (+0.5 cc/mol) than those for the compounds in Table I and is pressure dependent.[3b] We have suggested[3b,5] that this is due to the polar character of the homolytic scission transition state **2**.[7b] Formation of such a transition state should lead to an increase in solvent organization over that for the reactant. Such a process would be facilitated by pressure ($\Delta V^*_{\mathrm{solv}} < 0$) and might be expected to partially compensate for the positive activation volume associated with bond stretching.[9]



2

We now report the effect of ring substitution on the pressure dependence of the decomposition rates of *tert*-butyl phenylperacetate. The data are in agreement with the general conclusions previously outlined for the unsubstituted perester.[3b] Additionally they suggest that transition state polarity **2** varies with substituent, and they also provide a basis for explaining the pressure dependence of the observed activation volumes.

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[1] (a) Part V: R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970). (b) Support by the National Science Foundation (GP-4287, 7349, and 8670) is gratefully acknowledged.

[2] Taken from the Ph.D Dissertation of J. V. Behar, University of California, Riverside, 1969.

[3] (a) Activation volumes are related to the pressure dependence of reaction rate constants according to the equation $\partial \ln k/\partial P = -\Delta V^*/RT$. A detailed list of reviews has been presented.[3b] (b) See R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).

[4] For the general scheme for homolytic scission reactions, the observed

$$\text{initiator} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{geminate radicals} \xrightarrow{k_d} \text{free radicals}$$

decomposition rate constant is given by the equation $k_{\mathrm{obsd}} = k_1/(1 + k_{-1}/k_d)$. The quantity $k_{\mathrm{obsd}} = k_1$ (and $\Delta V^*_{\mathrm{obsd}} = \Delta V^*_1$) only when the geminate radicals cannot recombine to regenerate initiator ($k_{-1} = 0$).[1a,3b]

[5] (a) R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968); (b) *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

[6] A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1956).

[7] (a) On the basis of kinetic and product data for these[7b] and other peresters,[7c] Bartlett concluded that the peresters **1** decompose by simultaneous two-bond scission (eq 2). (b) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960). (c) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[8] For leading references to Bartlett's studies of peresters, see J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

[9] (a) Activation volumes expected for solvation or solvent electrostriction are reviewed by W. J. LeNoble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967); (b) see also M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 375 (1935).

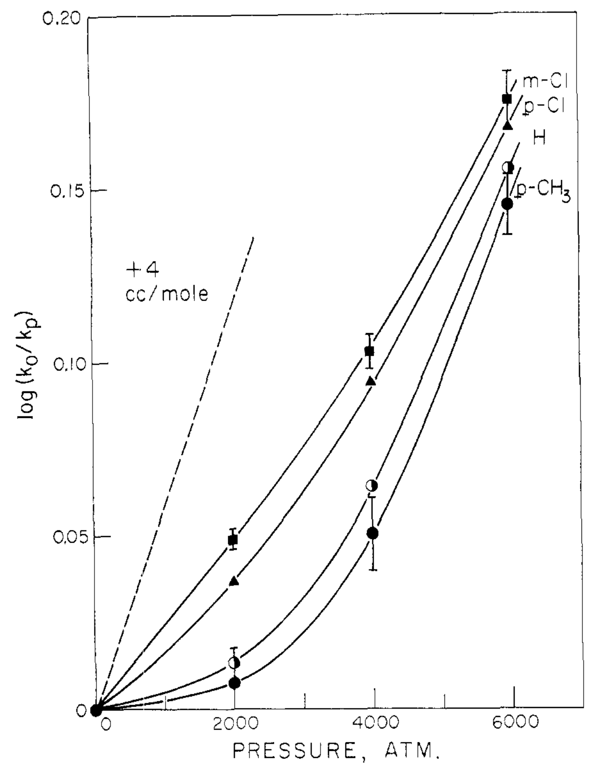

Figure 1.—Pressure dependence of the decomposition rate constants for the *m*-Cl- (■), *p*-Cl- (▲), H- (◐), and *p*-CH_3- (●) substituted *tert*-butyl phenylperacetates (cumene, 79.6°).

Results and Discussion

The rate constants for decomposition of 0.1 *M* cumene solutions of the *m*-Cl- (**1a**), *p*-Cl- (**1b**), H- (**1c**), *p*-CH_3- (**1d**), and *p*-MeO- (**1e**) substituted *tert*-butyl phenylperacetates at several pressures are given in Table II. Each high-pressure rate constant was determined using at least five sets of duplicate kinetic points and the errors shown are standard deviations arising from a least-squares analysis of all of the data for a perester at a given pressure. Each *kinetic point* for a high-pressure rate constant represents a separate experiment (see Experimental Section). The rates were determined by monitoring the decrease of the perester carbonyl band (1783 cm^{-1}) in the infrared. Most of the data were gathered at 79.6°; however, the rapid decomposition rate precluded high pressure studies of **1e** at this temperature and these data were obtained at 60.0°.[10]

The pressure dependences of log *k* for each of the peresters (Figures 1 and 2) are somewhat different from each other, and all give low-pressure activation volumes significantly less than +4 cc/mol (see Table II). Error bars are shown in Figure 1 for the top curve (*m*-Cl) and for the bottom curve (*p*-CH_3). While these are rather large, it is clear that the pressure dependence plots of the decomposition rate constants for the *m*-Cl- and *p*-CH_3-substituted peresters are different; the former is relatively linear while the latter shows distinct curvature. These two substituents possess the extreme val-

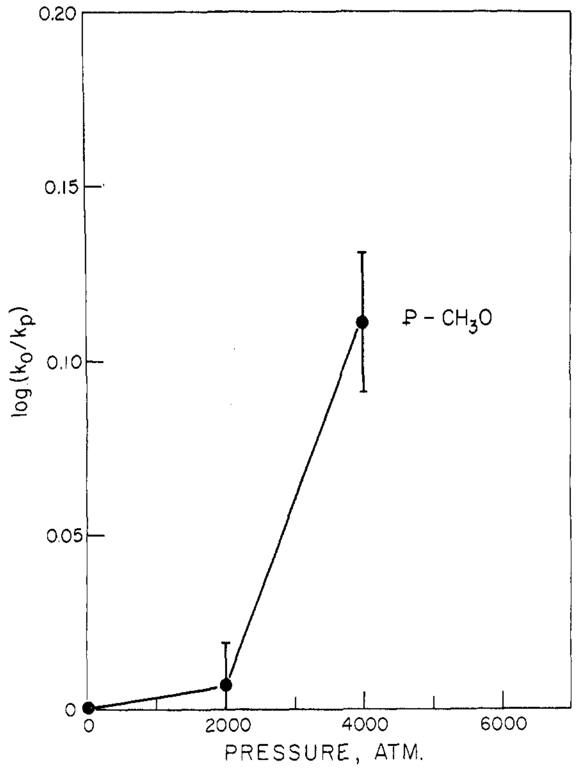

Figure 2.—Pressure dependence of the decomposition rate constant for *tert*-butyl *p*-methoxyphenylperacetate (cumene, 60.0°).

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF SUBSTITUTED *tert*-BUTYL PHENYLPERACETATES AS A FUNCTION OF PRESSURE (CUMENE, 79.6°)

Perester[a]	σ^{+b}	Pressure, atm	$k \times 10^4$, sec^{-1}	ΔV^{*},[c] cc/mol
1a, *m*-Cl	+0.399	1	0.298 ± 0.001	
		2000	0.266 ± 0.001	1.6
		4000	0.235 ± 0.002	1.8
		6000	0.199 ± 0.003	2.4
1b, *p*-Cl	+0.114	1	0.654 ± 0.010	
		2000	0.601 ± 0.006	1.2
		4000	0.527 ± 0.008	1.9
		6000	0.445 ± 0.007	2.5
1c, H	0.0	1	0.677 ± 0.004	
		2000	0.657 ± 0.002	0.4
		4000	0.584 ± 0.006	1.7
		6000	0.474 ± 0.004	3.0
1d, *p*-CH_3	−0.311	1	1.649 ± 0.022	
		2000	1.622 ± 0.019	0.2
		4000	1.469 ± 0.015	1.4
		6000	1.180 ± 0.008	3.2
1e, *p*-OMe	−0.778	1	5.942 ± 0.039	
		1	0.685 ± 0.010[d]	
		2000	0.675 ± 0.007[d]	0.2
		4000	0.531 ± 0.017[d]	3.5

[a] 0.1 *M* in cumene. [b] σ^+ substituent constants for the ring substituents; see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 204. [c] Obtained from the slope of the line connecting the data points at pressures *P* and *P* + 2000. [d] 60.0°.

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[10] (a) It is unlikely that these rate constants contain contributions from induced decomposition. While Bartlett noted that a small amount of induced decomposition may have been present in studies of the peresters **1** at relatively high concentration in chlorobenzene, the use of cumene[10b] and the lower concentration used in these studies should have precluded such problems. Decomposition rates for **1c** are higher in chlorobenzene than in cumene; however, the apparent decomposition activation volumes are very similar.[3b,5b] A previous pressure study in which induced decomposition was proposed showed a dramatic rate increase at high pressures, a result quite contrary to those found here.[10c] (b) See P. D. Bartlett and J. M. McBride, *J. Amer. Chem. Soc.*, **87**, 1727 (1965). (c) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, Jr., *ibid.*, **87**, 518 (1965).

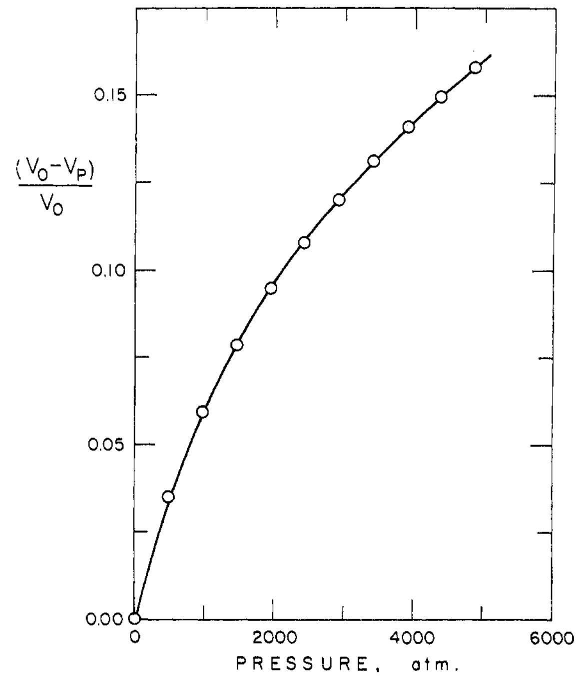

Figure 3.—Effect of pressure on the volume of cumene at "room temperature" (see text).

ues of σ^+ (Table II) *among those represented in Figure 1,* and the evident trends in these plots are an increase in curvature and a decrease in initial slope as σ^+ decreases.

The observed decomposition activation volumes can be thought of as the resultant of separate contributions for bond stretching (ΔV^*_{bond}) and solvation changes (ΔV^*_{solv}) (eq 3).[9b] If it is assumed that ΔV^*_{bond}

$$\Delta V^*_{obsd} = \Delta V^*_{bond} + \Delta V^*_{solv} \qquad (3)$$

can be approximated by the observed decomposition activation volumes in Table I, *e.g.*, +4 cc/mol, the low pressure values for ΔV^*_{solv} (units of cc/mol) would be −2.4 (*m*-Cl), −2.8 (*p*-Cl), −3.6 (H), and −3.8 (*p*-CH_3).[11,12] The negative signs of these numbers support a transition state **2** more polar than the reactant, and their magnitudes increase as the electron-donating ability (as measured by σ^+) of the substituent group increases.[13] This trend suggests that the amount of polar character in the transition state increases as the substituents become better able to stabilize electron deficiency on the benzylic carbon (see **2**).

The activation volumes for those systems in Table I used as models for ΔV^*_{bond} are pressure independent.[1a,3b,5,6] The increasing slopes of the log *k* *vs.* *P* plots (*i.e.*, increasing values of ΔV^*_{obsd}) for the *tert*-butyl phenylperacetates (Figures 1 and 2) thus suggest that the magnitudes of the quantities ΔV^*_{solv} decrease with increasing pressure. The solvation activation volumes (ΔV^*_{solv}) reflect the solvent's response to a change in polarity between the reactant and transition state. This response should depend on the solvent's compressibility (χ_T) (eq 4),[14] and it seems reasonable

$$\chi_T = (-1/V_o)(\partial V/\partial P)_T \qquad (4)$$

that a decrease in χ_T would lead to a smaller value of ΔV^*_{solv}. The compressibility of cumene at "room temperature" is given by the slope of the plot in Figure 3.[15] Its decrease with pressure thus provides a rationale for the observed decreases in the magnitudes of ΔV^*_{solv} with pressure.

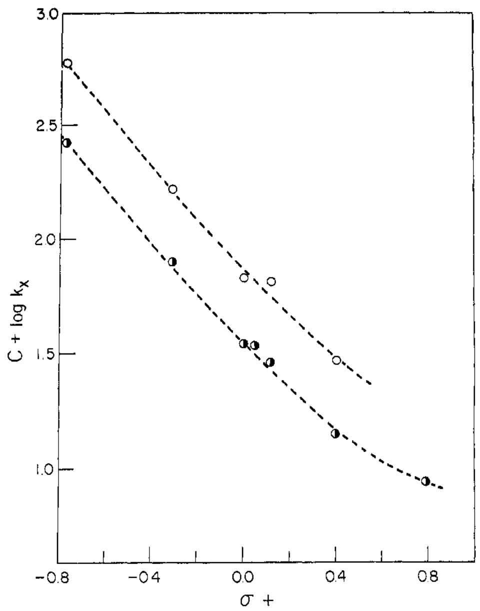

Figure 4.—Plot of log k_x at atmospheric pressure *vs.* σ^+ for the variously substituted *tert*-butyl phenylperacetates in cumene at 79.6° (C = 6) (○) and chlorobenzene (Bartlett, see text) at 90.7° (C = 5) (◑).

The variation in ΔV^*_{solv} with pressure should be most noticeable in those systems with the greatest transition state polarity. In agreement, the pressure dependence of ΔV^*_{obsd} is greatest for *tert*-butyl *p*-methoxyphenylperacetate (**1e**) (Figure 2).[16] However, the low pressure value of ΔV^*_{obsd} for this system rather than being lower is about the same as that for *tert*-butyl *p*-methylphenylperacetate (**1d**) (Table II). This discrepancy may be due to the 20° temperature differential between the decomposition temperatures for **1d** and **1e**. Compressibility decreases as temperature is decreased and the values of χ_T at each pressure for cumene at 60° would be lower than at 79.6°. These differences in compressibility are in the correct direction to explain the larger values of ΔV^*_{obsd} (smaller values of ΔV^*_{solv}) for **1e** than expected.

Plots of the decomposition rates at atmospheric pressure *vs.* σ^+ are shown in Figure 4. The data using chlorobenzene (90.7°) are those of Bartlett[7b] and those using cumene (79.6°) are taken from Table II. In calculating an apparent ρ value of *ca.* −1.1, Bartlett excluded the data point for the *p*-nitro-substituted perester, and our data also give essentially the same apparent ρ value.

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[11] The assumption that ΔV^*_{bond} can be approximated by the values in Table I is based on the presumed absence of transition state polarity for those compounds and the similarity of their values of ΔV^*_{obsd} in spite of their structual differences.

[12] The "low pressure" values of ΔV^*_{solv} were obtained using the equation $\Delta V^*_{solv} = \Delta V^*_{0,2000} - \Delta V^*_{bond}$ (see Table II).

[13] Negative activation volumes indicate a contraction of the system on proceeding from reactants to the transition state.

[14] See W. A. Steele and W. Webb, "High Pressure Physics and Chemistry," Vol. 1, R. S. Bradley, Ed., Academic Press, New York, N. Y., Chapter 4i.

[15] P. W. Bridgman, "Collected Experimental Papers," Vol. VI, Harvard University Press, Cambridge, Mass., 1964, pp 3915–3931.

[16] A determination of the decomposition rate for **1e** at 6000 atm (60°) was in progress when the high pressure apparatus failed. The apparatus had to be dismantled and overhauled precluding further studies on these systems by Dr. Behar.

However, in view of the proposals made to explain the variable pressure results (*vide supra*), the Hammett relationship should not rigorously apply to any of these data. If this constraint is removed, the p-nitro point need not be interpreted as an abnormally fast rate for this substituted perester.[7b] Rather, the upward curvature in the plot of Bartlett's data *including the latter point* can be interpreted as a reflection of both the increasing polar character and solvation of the transition state with an increase in electron-donating ability of the substituent (*vide supra*).

Based on our limited high pressure data at 79.6° (cumene solvent) for the p-CH_3, H, p-Cl, and m-Cl peresters, the *apparent* ρ value is pressure insensitive (*ca.* -1.1). This is not surprising in view of the small variation in the rate constants with pressure and the narrow range of σ^+ covered by these substituents. However, this result does indicate that no *major* mechanism variations occurred at high pressure.[17]

A small inverse viscosity dependence of the decomposition rate for **1c** at atmospheric pressure had led to the suggestion that its decomposition mechanism involves both one-bond (O–O) and concerted two-bond (C–C and O–O, eq 2) scission processes.[18] The rates of decomposition of **1d** and **1e** were viscosity invariant.[18] However, observed activation volumes of +7 to +10 cc/mol for authentic one-bond scission peresters[19] indicate that those of the peresters **1** are too small to be consistent with such a mechanism.[3b] Additionally, the similarity in the plots for **1c** and **1d** (Figure 1) precludes the gross mechanistic variation implied by the comparative viscosity results. All other observations support the two-bond scission mechanisms.[20]

Experimental Section

Perester Syntheses.—The substituted *tert*-butyl phenylperacetates were synthesized from the corresponding phenylacetyl chlorides and *tert*-butyl hydroperoxide.[3b,7b] The acid chlorides and *tert*-butyl hydroperoxide were distilled prior to their use. All peresters showed a carbonyl absorption in the infrared at 1783 cm^{-1}.

Attempts at iodometric titration of the peresters gave widely varying results on portions of the same sample. Samples were rechromatographed until their infrared spectra were free of extraneous carbonyl bands as well as any OH absorption. In addition, infrared spectra of completely decomposed samples (infinite time samples) in cumene exhibited only solvent absorption bands in the carbonyl stretching frequency region, indicating the absence of any contaminating carbonyl containing species among the decomposition products. The peresters were crystalline solids and decomposition rate constants did not vary for different samples of the same perester. All peresters were stored at low temperature.

High Pressure Apparatus and Kinetic Studies.—A complete description of the apparatus and experimental techniques has been presented.[3b] Kinetic runs and the data analysis were carried out following the procedures reported for unsubstituted *tert*-butyl phenylperacetate.[3b] Each kinetic point represented a separate pressure experiment.[3b]

Registry No.—**1a,** 27396-17-4; **1b,** 27396-18-5; **1c,** 3377-89-7; **1d,** 27396-20-9; **1e,** 27396-21-0.

[17] (a) The reaction products from decomposition of the substituted peresters are analogous to those formed from *tert*-butyl phenylperacetate,[3b] and their relative yields show the expected dependence on pressure.[17b] (b) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 657 (1971), accompanying paper.

[18] (a) W. A. Pryor and K. Smith, *Intra-Sci. Chem. Rep.*, **3**, 255 (1969); (b) *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[19] (a) These data were obtained from a study of *tert*-butyl perbenzoate in cumene[3b] and from a study of the cis and trans isomers of *tert*-butyl 2-propyl-2-peroxypentenoate in cumene.[19b] (b) R. C. Neuman, Jr., and G. D. Holmes, unpublished results.

[20] (a) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2574 (1969); (b) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

High Pressure Studies. VII. The Pressure Dependence of Cage Effects. Products from Substituted *tert*-Butyl Phenylperacetates[1,2]

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Thermal decompositions of ring-substituted *tert*-butyl phenylperacetates in cumene (79.6°) give the corresponding *tert*-butyl benzyl ethers, toluenes, bibenzyls, benzylcumyls, bicumyl, and *tert*-butyl alcohol as reaction products. The pressure dependences of the ether/*tert*-butyl alcohol ratios give the pressure dependence of the cage effect (combination *vs.* diffusion) for the initially generated geminate benzyl and *tert*-butoxy radicals. The cage effects increase with pressure but not so rapidly as might be expected. An analysis of the trends involving the potential role of the intervening carbon dioxide molecule is outlined. The remaining products reflect the distribution of diffused benzyl radicals, and the pressure dependences of yields indicate that a major source of the toluenes involves hydrogen abstraction by the benzyl radicals from the solvent cumene.

We have been investigating the effects of pressure on the rates of free-radical reactions in solution. Studies of homolytic scission reactions have shown that care must be used in interpreting the significance of the observed activation volume (ΔV^*_{obsd}) for decomposition of radical initiators.[1a,3] If the initially formed geminate radicals (eq 1) can return to starting material

$$\text{A–B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{\text{A}\cdot\text{B}\cdot} \xrightarrow{k} \qquad (1)$$

(k_{-1}), ΔV^*_{obsd} is not simply related to the activation volume for homolytic scission (ΔV^*_1) but depends as well on the competition between recombination (k_{-1}) and other processes (k) available to the caged pair (eq 2).

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT\partial \ln (1 + k_{-1}/k)/\partial P \qquad (2)$$

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[1] (a) Part VI: R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971), accompanying paper. (b) Support by the National Science Foundation through Grants GP-4287, 7349, and 8670 is gratefully acknowledged.

[2] Taken from the Ph.D. Dissertation of J. V. Behar, University of California, Riverside, 1969.

[3] R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).