High Pressure Studies. XV. Polar Effects in Aliphatic Perester Decomposition[1]

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Abstract: The activation volume for thermal decomposition of *tert*-butyl perpivalate in cumene ranges from *ca.* +0.3 to +1.9 ml/mol over a 5000 atm pressure range, while that for *tert*-butyl perisobutyrate in the same solvent changes from *ca.* +1.6 to +3.2 ml/mol over the same range. It is proposed that these results indicate that two-bond aliphatic perester thermolyses are characterized by polar contributions in their decomposition transition states.

Polar effects in free-radical reactions are a subject of continuing interest and debate. They have been proposed to account for rate correlations with the Hammett equation, particular selectivity patterns in competitive hydrogen abstractions, and solvent effects, among others. Classic examples have included the effect of substituents on hydrogen abstraction from substituted toluenes[3-5] and on the decomposition rates of *tert*-butyl phenylperacetates.[6-8]

The correlation of decomposition rates of the latter compounds with σ^+ led Bartlett and Rüchardt to propose that the two-bond scission transition state possessed polar character (**1**).[6] Modest solvent effects

$$\mathrm{Ph\dot{C}H_2\cdots CO_2\cdots \dot{O}CMe_3 \longleftrightarrow Ph\overset{+}{C}H_2\cdots CO_2\cdots \overset{-}{O}CMe_3}$$

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on rate consistent with this polar character have also been reported for these particular peroxyesters.[9]

Aliphatic peroxyesters (RCO_2OCMe_3) which decompose by two-bond scission have shown reactivity trends with structure and solvent which are compatible with polar character in the decomposition transition state (**2**), but no compelling evidence has been pre-

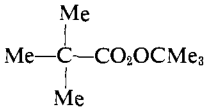
$$\mathrm{\overset{\delta+}{R}\cdots CO_2\cdots \overset{\delta-}{O}CMe_3}$$

2

sented. In particular, decomposition rates for a series of peroxyesters in which R includes simple aliphatic and alicyclic groups, as well as bridged systems, roughly parallel those expected for carbonium ion stability, but with differences greatly attenuated.[7b,10-13] Similarly, decomposition of several aliphatic peresters is accelerated in polar solvents, although again the effects are small.[14,15]

Recently, we showed that the dependence of the substituted *tert*-butyl phenylperacetate decomposition rates on pressure reflected the polar character originally proposed by Bartlett and Rüchardt.[16,17] The decomposition activation volumes while positive were unusually small compared to those for other homolytic scission reactions characterized by simultaneous two-bond scission. Such small values of ΔV^* apparently result from cancellation of a positive contribution due to bond stretching in the transition state by a negative component arising from solvation of the polar transition state. The data even reflect differences in polar character due to the different substituents and are supported by a "normal" value of ΔV^* for a perester ($C_6H_{11}CO_2CMe_3$) not expected to possess as much polar character.

The same low activation volumes have now been observed in a pressure study of *tert*-butyl perpivalate (**3**), a



$Me_3C{-}CO_2OCMe_3$

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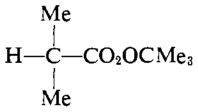

$Me_2CH{-}CO_2OCMe_3$

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perester with an aliphatic R group particularly favorable for polar contributions (**2**). In contrast, decomposition of *tert*-butyl perisobutyrate (**4**) shows significantly greater values of ΔV^* consistent with its lesser ability to be stabilized by carbonium ion contribution. Thus, polar character may be a general factor in two-bond scission decompositions of peroxyesters.

Results and Discussion

The difference in the pressure dependence of the decomposition rates (Tables I and II) of **3** and **4** can be seen (Figure 1) as qualitatively similar to the relative pressure effects on decomposition rates of *tert*-butyl phenylperacetate and $C_6H_{11}CO_2OCMe_3$ (Figure 2).[16,17] The slopes of these curves directly reflect the observed

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[1] (a) This work was kindly supported by a grant from the National Science Foundation. (b) Part XIII: R. C. Neuman, Jr., *Accounts Chem. Res.*, **5**, 381 (1972). (c) Part XIV: R. C. Neuman, Jr., W. Kauzmann, and A. Zipp, *J. Phys. Chem.*, 77, 2687 (1973).

[2] NDEA Fellow, 1968–1971.

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[5] (a) The literature has recently been reviewed and the need to invoke polar effects in toluene hydrogen abstractions has been questioned by Zavitsas.[5b] (b) A. Zavitsas and J. A. Pinto, *ibid.*, **94**, 7390 (1972). (c) But see W. A. Pyror, W. H. Davis, Jr., and J. P. Stanley, *ibid.*, **95**, 4754 (1973).

[6] P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

[7] (a) A recent discussion has been presented by Rüchardt.[7b] (b) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

[8] See also L. A. Singer in "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 285–288.

[9] R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

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[15] (a) *tert*-Butyl perpivalate: T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **89**, 2948 (1967). (b) *tert*-Butyl perisobutyrate: P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963).

[16] R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **91**, 6024 (1969).

[17] R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971).

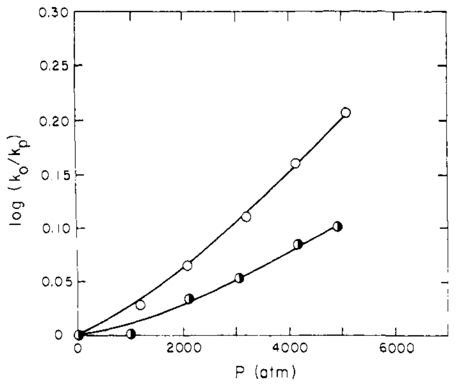

Figure 1. Pressure dependence of the decomposition rates of *tert*-butyl perpivalate (**3**; 65°) (◑) and *tert*-butyl perisobutyrate (**4**; 90°) (○) in the solvent cumene.

Table I. Rate Constants for Thermal Decomposition of *tert*-Butyl Perpivalate (**3**) in Cumene at 65° at Various Pressures[a,b]

Pressure, atm	$k \times 10^5$, sec^{-1}
1	6.44 ± 0.07
	6.52 ± 0.07
1020	6.38 ± 0.07
	6.53 ± 0.08
2110	6.06 ± 0.10
	5.90 ± 0.12
3060	5.77 ± 0.07
	5.69 ± 0.11
4180	5.31 ± 0.21
	5.35 ± 0.13
4930	5.11 ± 0.12
	5.16 ± 0.18

[a] Errors are standard deviations obtained from least-squares analysis of kinetic data. [b] Concentration 0.1 *M*.

Table II. Rate Constants for Thermal Decomposition of *tert*-Butyl Perisobutyrate (**4**) in Cumene at 90° at Various Pressures[a,b]

Pressure, atm	$k \times 10^5$, sec^{-1}
1	7.25 ± 0.10
	7.14 ± 0.07
1180	6.74 ± 0.15
2070	6.20 ± 0.11
3200	5.58 ± 0.07
4150	4.99 ± 0.06
5070	4.49 ± 0.08

[a] Errors are standard deviations obtained from least-squares analysis of kinetic data. [b] Concentration 0.1 *M*.

values of ΔV^* for decomposition ($\Delta V^* = (-RT/P) \ln (k_p/k_0)$) which are a combination of contributions from bond stretching and solvation (eq 1). Since the

$$\Delta V^*_{\text{obsd}} = \Delta V^*_{\text{bond}} + \Delta V^*_{\text{solv}} \qquad (1)$$

bond-stretching contribution seems to be relatively constant (+4 to +5 ml/mol) for a variety of free-radical systems,[1b] the low values of ΔV^*_{obsd} for *tert*-butyl phenylperacetate,[17] and now *tert*-butyl peripivalate, can be rationalized as arising from negative values of ΔV^*_{solv} due to carbonium ion character in the decomposition transition states.

The curvature in such plots has been ascribed to a decrease in solvent compressibility (and hence a decrease in ΔV^*_{solv}) with increasing pressure and this explanation remains consistent.[17] The apparent value of ΔV^* for **3** is less than +2 ml/mol up to 5000 atm while that for **4** becomes larger than +3 ml/mol between 2000 and 3000 atm (Table III). In both cases, these fall within the range expected for two-bond scission.[1b] Recently, Pryor has suggested that the "viscosity test" of initiator decomposition mechanism indicates that **4** might decompose to some extent *via* one-bond scission.[18] However, we do not find these data compelling.

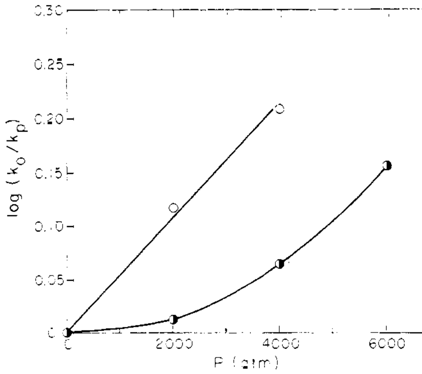

Figure 2. Pressure dependence of the decomposition rates of *tert*-butyl phenylperacetate (◑) and $C_6H_{11}CO_2OCMe_3$ (○) in the solvent cumene (79.6°).

Table III. Values of ΔV^* as a Function of Pressure for *tert*-Butyl Perpivalate (**3**) and *tert*-Butyl Perisobutyrate (**4**)[a]

	ΔV^*, ml/mol	
Pressure, atm	*tert*-Butyl perpivalate	*tert*-Butyl perisobutyrate
1000	0.3	1.6
2000	1.2	2.5
3000	1.6	3.2
4000	1.8	3.2
5000	1.9	3.2

[a] Values of ΔV^* shown for each pressure P_i were calculated from the relationship $\Delta V_{P_i}^* = (RT/(P_i - P_{i-1}))(\ln (k_0/k_{P_i}) - \ln (k_0/k_{P_{i-1}}))$ where $P_{i-1} = P_i - 1000$. Values of $\ln (k_0/k_P)$ were taken from the smooth curves (Figure 1).

The decomposition rate constants were determined using the solvent cumene under conditions where induced decomposition reactions are unlikely.[10,15] The first-order rate plots were linear throughout the 2–3 half-lives over which data were collected and the atmospheric pressure decomposition rate constants are in reasonable agreement with previous measurements (**3**,[10] 6.87×10^{-5} sec^{-1}, 64.6°; **4**,[12,15b] 6.7×10^{-5} sec^{-1}, 90.6°). Thus, we believe that these results reflect the varying polar character in the decomposition transition states which would be predicted from the analogous carbonium ion stabilities.[19]

The small variations in decomposition rates of *tert*-butyl peroxyesters with major structural changes in R, and solvent, require that such polar character be only a minor contributor to the transition state even in the

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(18) W. A. Pryor, E. V. Morkved, and H. T. Bickley, *J. Org. Chem.*, **37**, 1999 (1972).

(19) It might be aruged that *tert*-butyl perisobutyrate and $C_6H_{11}CO_2OCMe_3$ should show the same ΔV^* values and pressure dependence since both give secondary radicals. However, since the data for the latter perester were obtained in a much earlier study by a different worker[16,17] it is probably unwise to attempt any *quantitative* comparison between the results in Figure 1 and those in Figure 2.

most favorable cases.[6–15] This, however, is consistent with the results of the pressure studies. Since "normal" values of ΔV^* for homolytic bond scission are +4 to +5 ml/mol,[1b] the contributions from solvation are on the order of −2 to −3 ml/mol; in contrast, reactions leading to formation of ions (*e.g.*, solvolysis) not atypically show values of ΔV^* as "large" as −20 ml/mol.[1b,20]

While it could be argued that the differences in ΔV^* for these peresters reflect only differences in extent of bond stretching in the transition state *à la* the Hammond postulate,[7b] we consider this unlikely. Values of ΔV^* for decomposition of several symmetrical azo compounds not characterized by polar contributions, but of substantially different reactivity, are remarkably similar to each other (+4 to +5 ml/mol).[1b] Further, their rate–pressure plots do not show the curvature which we have associated with pressure dependence of solvent compressibility, a factor entering into reactions involving solvation.

Experimental Section[21]

Compounds. *tert*-**Butyl perpivalate** (K and K), obtained as a 75% solution in mineral spirits, was first purified by low temperature crystallization from pentane. It was subsequently recrystallized four times from pentane, taken up in pentane and dried over anhydrous magnesium sulfate, and recovered by evaporation of the solvent. The infrared spectrum showed a single carbonyl band at 1767 cm^{-1} and was free of any OH bands. The nmr spectrum in carbon tetrachloride solvent showed two equal intensity singlets at δ 1.21 and 1.27.

tert-**Butyl perisobutyrate** was synthesized from reaction of isobutyryl chloride with the sodium salt of *tert*-butyl hydroperoxide by conventional procedures.[8,21] The crude perester obtained by evaporation of the solvent pentane after filtration was purified by "bulb-to-bulb" distillation five times at low pressure (0.03 mm) and room temperature. The infrared spectrum of the purified material showed a single carbonyl band at 1775 cm^{-1}. The nmr spectrum in carbon tetrachloride solvent showed a doublet at δ 1.17, a singlet at 1.27, and a multiplet at 2.50; the combined area of the doublet and singlet was 15 times as great as the area of the multiplet.

Kinetic Studies. Thermal decomposition of 0.1 *M* solutions of the respective peresters in carefully purified cumene was monitored by infrared spectroscopy. The high pressure apparatus and procedures concerning its use in such kinetic studies have been described in detail.[16,17]

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(20) See W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

(21) For detailed experimental procedures, see R. P. Pankratz, Ph.D. Dissertation, University of California, Riverside, 1972.

Ring-Closure Reactions. I. Kinetics of Lactone Formation in the Range of Seven- to Twelve-Membered Rings

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Abstract: The kinetics of the formation of lactones from ω-bromoalkanoate ions in the range of 7- to 12-membered rings have been investigated in 99% aqueous DMSO solution at 50°. They were followed by a potentiometric technique allowing precise measurements at reactant concentrations as low as 1×10^{-4} *M*. Vpc product analyses were carried out in typical cases. The reaction proved to be first order in all cases at the lowest concentrations used. However, at higher concentrations, incursion of second-order kinetics which was attributed to a dimerization reaction was observed for the reaction of the 7-bromoheptanoate and 8-bromooctanoate ions. A kinetic analysis based on a mixed-order rate equation allowed the evaluation of the first- and second-order rate constants by a trial-and-error procedure. The reactivity pattern for ring closure shows a minimum at the eight- and nine-membered rings whose location is discussed in terms of conformational stability of the lactone as a function of ring size.

Bifunctional molecules can either undergo polymerization or ring formation, depending on their structure and reaction conditions. The scope of ring-formation reactions is not only broad in their own right but also includes neighboring group participation[1] and intramolecular catalysis,[2] as related topics in the general field of intramolecular reactions.

The factors affecting intramolecular reactivity[3] are several, but we cannot expect to make an even empirical assessment of their role, unless we obtain a substantial body of information of kinetic nature enabling us to understand the energetics of the processes. Most kinetic studies have concerned the formation of three- to six-membered rings[1,4] whereas little or no attention has been given to the seven-membered ring and to the so-called medium (8- to 11-membered) and large (12-membered and larger) rings.

Experimental difficulties of several kinds have contributed to limit some of the studies.[5] Since few and fragmentary data,[6–9a,10] whose reliability is even ques-

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(9) (a) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **17**, 1283 (1934); **18**, 1087 (1935). (b) The formation of dimeric lactones under the