approach[14] can be used in connection with many photochemical problems such as the effect of substituents on the mechanism and stereochemistry of photochemical pericyclic reactions.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Registry No.—Butadiene, 106-99-0; ethylene, 74-85-1; anthracene, 120-12-7; 2,3-dimethyl-2-butene, 563-79-1; 2,4-hexadienediol, 3249-28-3; 1,2-ethenediol, 1571-60-4; 1,3-butadiene-1,4-diol, 42466-41-1; malealdehyde, 3675-13-6; 9,10-dicyanoanthracene, 1217-45-4.

References and Notes

(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(2) N. D. Epiotis, *J. Amer. Chem. Soc.* **94**, 1941, 1946 (1972). Similar ideas have been expressed by Herndon, *et al.*, in connection with the problems of carbonyl photocycloadditions: W. C. Herndon, *Tetrahedron Lett.* 125 (1971); W. C. Herndon and W. B. Giles, *Mol. Photochem.*, **2**, 277 (1970); *Chem. Commun.*, 497 (1969); W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

(3) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

(4) T. Forster, *Pure Appl. Chem.*, **34**, 225 (1973).

(5) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972).

(6) M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973).

(7) N. D. Epiotis, in press.

(8) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 1405 (1972); N. C. Yang, J. Libman, L. Barrett, Jr., M. H. Hui, and R. L. Loeschen, *J. Amer. Chem. Soc.*, **94**, 1406 (1972).

(9) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **92**, 1086 (1970).

(10) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(11) H. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960).

(12) J. P. Simons, *Trans. Faraday Soc.*, **56**, 391 (1960).

(13) However, the [4 + 2] photoadditions of the esters of maleic and fumaric acids to anthracene appears to proceed *via* diradical intermediates rather than a stereoselective [4s + 2s] fashion: G. Kaupp, *Chimia*, **25**, 230 (1971). This may be due to the fact that these olefins are much inferior acceptors compared to maleic anhydride, for example.

(14) The correlation diagrams for semipolar and polar [4 + 2] photocycloadditions are constructed by reference to symmetrical reactants. However, the same conclusions are valid for unsymmetrical reactants, since the local symmetry of the ethylenic and butadienic MO's is the important factor.

The Activation Volume for Single-Bond Homolysis From Empirical Internal Solvent Pressure

J. Owens* and T. Koenig

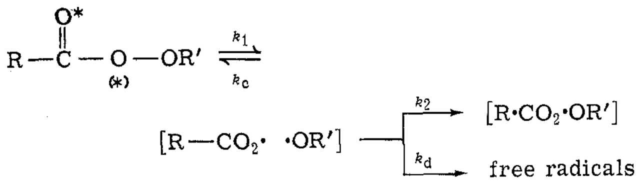
Department of Chemistry, University of Oregon,
Eugene, Oregon 97403

Received April 22, 1974

Neuman and coworkers[1] have measured apparent activation volumes for a number of free-radical initiators. These parameters (ΔV_e^*) were small for peresters previously proposed[2] to undergo concerted (C–C and O–O) decomposition and large for *tert*-butyl perbenzoate. The activation volumes were thus considered an additional criterion of mechanism. We,[3] as well as others,[4] have examined viscosity effects on overall rates of decomposition of peroxides. We have used Scheme I as a general one in analyzing the results quantitatively. Equations 1 and 2 (where k_o and k_s are observables) give the predictions of this scheme for overall disappearance of initiators.

Assuming k_d is the only viscosity-sensitive (interpretive) rate constant and *knowing* the value of k_1 allows the analysis of the k_o–fluidity dependence in terms of fraction recombination. Pryor and coworkers[4] have used essentially the same scheme and proposed extrapolation of $1/k_o$ *vs.* η^α to zero viscosity as a means of estimating the value of $1/k_1$. An alternative is to measure the rate constant for scrambling of carbonyl-^{18}O (k_s). Under the assumption above, the sum of $k_o + k_s$ (k_1) should be constant.

Scheme I



$$\frac{1}{(k_1/k_o) - 1} = \frac{k_2}{k_c} + \frac{k_d}{k_c} = \left(\frac{1}{f_{\text{recombination}}} - 1\right) = \frac{k_o}{k_s} \qquad (1)$$

$$k_1 = k_o + k_s \qquad (2)$$

These sums were not constant for either of the two cases which we investigated[3] (Table I, Scheme I; R = Ph, CH_3; R′ = *t*-Bu). We wish to point out that the positive activation volumes determined by the external pressure variation[1] imply that k_1 could only *fortuitously* be constant over the range of solvents investigated because of differences in internal solvent pressure.[5]

It is possible to circumvent the problems of calculating internal pressures by defining an empirical set of differential solvent pressures (DSP) from a reaction of known activation volume. This is analogous to the definition of Hammett[10] substituent constants from an arbitrary reaction. The apparent activation volume for *tert*-butyl perbenzoate is reported[11] to be +10.4 cc/mol in cumene and +12.9 cc/mol in chlorobenzene. Assuming that the activation volume in the hydrocarbon solvents which we have used is similar[12] and that the differential solvation energy is zero, the relative rates (Table I) can be used to determine the differential solvent pressures for the solvent series at 130° (Figure 1, Table I). A plot of ln ($k_o + k_s$) for the peracetate, also at 130°, *vs.* the DSP values is linear, giving an activation volume of +5 cc/mol (Figure 1), which is in agreement with

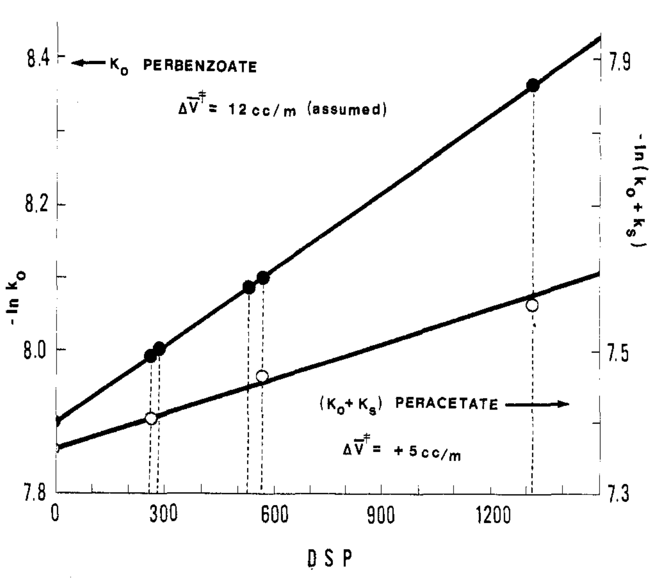


Figure 1. Activation volumes from empirical differential solvent pressures.

Table I
Rate Constants[a] for Decomposition and ^{18}O Scrambling at 130°
RCO_3-*t*-Bu

Solvent	k_o (R = CH_3)	k_s (R = CH_3)	$k_o + k_s$ (R = CH_3)	k_o (R = Ph)	k_s (R = Ph)	$k_o + k_s$ (R = Ph)	DSP,[b] atm
Hexane	50.8	13.1	63.9	3.72	0.16	3.88	0
Isooctane				3.36	0.20	3.56	288
Dodecane				3.08	(0.24)	3.42	534
60% hexane oil	44.3	16.6	60.9	3.39	(0.28)	3.67	263
30% hexane oil	38.0	19.3	57.1	3.04	(0.36)	3.40	571
Paraffin oil	31.3	20.8	52.1	2.33	(0.50)	2.83	1320

[a] × 10^5 sec^{-1}; values in parentheses are interpolated from Figure 1, ref 3b. [b] Empirical differential solvent pressures from Figure 1 of this work.

Table II
Activation Volumes from DSP for RCO_3-*t*-Bu

R	Rate constant	ΔV^*_{DSP}, cc/mol[a]	ΔV^*_{ext}, cc/mol[b]	Registry no.
C_6H_5	k_o[3b]	(+12.00)	+10.4, +12.9[11]	614-45-9
C_6H_5	$k_o + k_s$[3b]	+8.0		
CH_3	$k_o + k_s$[3a]	+5.0	(+5)[1,c]	107-71-1
$CH_3OC_6H_4CH_2$	k_o[13]	+3.0	+3.1[16]	27396-21-0
$C_6H_5CH_2$	k_o[13]	−2.0	+1.7[11]	3377-89-7
$(CH_3)_2CH$	k_o[14]	−1.0	+1.6[15]	109-13-7

[a] Using the empirical differential solvent pressures derived here. [b] Using external pressure variation. [c] The value for a simple one-bond process.

expectations from the external pressure studies of Neuman.[1]

It is possible to estimate the k_s values for the perbenzoate by comparison with the corresponding hyponitrite (ref 3b, Figure 1). These values, summed with the appropriate k_o, give an activation volume of +8 cc/mol for the O–O bond homolysis of the perbenzoate. Table II contains the activation volumes for all the compounds for which we have data. The agreement with external pressure measurements is quite good if the sign inversions for the phenylacetyl[11,13] and isobutyryl[14] compounds are attributed to differential solvation. Solvation effects have similarly been invoked to explain the nonlinearity of the external pressure plots for these systems.[15]

Finally, we note that the apparent activation volume for the *tert*-butyl *p*-nitrophenylperacetate, as estimated from cohesive energy densities of the hydrocarbon solvents and the rate data of Pryor and Smith,[4a] is very large (+15 cc/mol). This reinforces their suggestion that this compound may be in part a one-bond initiator. A large value of ΔV^* is an indication of reversibility and not of intrinsic differences in transition state structures for the one-bond compared to two-bond process. The k_o/k_s method of estimating fraction return is not subject to the complications of variable k_1. Ruling out 1,3-sigmatropism,[14,16] they give the best estimate of reversibility in peroxide decomposition.

References and Notes

(1) R. C. Neuman, Jr., *Accounts Chem. Res.*, **5**, 381 (1972).

(2) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(3) (a) T. Koenig, J. Huntington, and R. Cruthoff, *J. Amer. Chem. Soc.*, **92**, 5413 (1970); (b) T. Koenig, M. Deinzer, and J. A. Hoobler, *ibid.*, **93**, 938 (1971).

(4) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); (b) W. A. Pryor, E. Morkved, and H. Bickley, *J. Org. Chem.*, **37**, 1999 (1972).

(5) Neuman[6] has recently criticized studies of activation volumes through internal pressure on two grounds. The first was that the experimental data were compared with cohesive energy density rather than internal pressure. He showed that these two were not always correlated. Second, he showed negative correlations of some perester rates in solvents of rather different characteristics. He failed to point out the striking agreement of the difference in activation volumes for disproportionation and combination of ethyl radicals, observed by external pressure methods,[7] with that predicted previously from cohesive energy density correlations.[8,9] He also did not point out that a differential solvation energy of only 250 cal/mol completely swamps the effect of a differential internal pressure of 1000 atm for a reaction with an activation volume of 10 cc/mol. The latter comment applies to viscosity effects as well and our solvent series was chosen to minimize the differential solvation problem. Also, Figure 1 of ref 6 shows that internal pressure and cohesive energy density are related for hydrocarbons. In the original version of this work, correlations with calculated cohesive energy density were used. These gave essentially identical activation volumes, including the 12 cc/mol for the k_o values of the perbenzoate.

(6) R. C. Neuman, Jr., *J. Org. Chem.*, **37**, 495 (1972).

(7) C. M. Backman, S. Claesson, and M. Szwarc, *Trans. Faraday Soc.*, **66**, 3061 (1970).

(8) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 2551 (1963).

(9) A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968); *J. Phys. Chem.*, **73**, 1257 (1969).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

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

(12) We assumed the value to be 12.000 cc/mol, the rounded average of the two reported values.

(13) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2574 (1969).

(14) T. Koenig and J. G. Huntington, *J. Amer. Chem. Soc.*, **96**, 592 (1974).

(15) R. C. Neuman and R. P. Pankratz, *J. Amer. Chem. Soc.*, **95**, 8372 (1973).

(16) M. Goldstein and H. Judson, *J. Amer. Chem. Soc.*, **92**, 4220 (1970).

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

Structural Effects on Intramolecular Carbene Reactions. Δ^3-Cyclopentenylmethylcarbene

Alfred Viola,* Shyamala Madhavan, and Robert J. Proberb

Department of Chemistry, Northeastern University,
Boston, Massachusetts 02115

Received January 9, 1974

Intramolecular carbene insertions and cycloaddition reactions constitute a favorite route to small-ring polycyclic