High Pressure Studies. IX. Activation Volumes and Solvent Internal Pressure[1,2]

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The effects of externally applied pressure on reaction rate constants for some free-radical reactions are compared with the solvent dependence of rate constants for these reactions at atmospheric pressure. In particular, there appears to be no correlation of the rate data with "internal pressure" of the solvents. A clarification of the relationship between internal pressure $(\partial E/\partial V)_T$ and cohesive energy density $(\Delta E_{\text{vap}}/V_T)$ is presented. The latter is commonly referred to as "internal pressure" but it differs markedly from $(\partial E/\partial V)_T$ for many common liquids.

Activation volumes for chemical reactions in solution are traditionally derived from the dependence of their rate constants on *externally* applied pressure (eq 1).[3,4] However, it has been suggested that values of

$$\Delta V^* = -RT(\partial \ln k/\partial P)_T \qquad (1)$$

ΔV^* might be obtained using a solvent property referred to as "internal pressure."[5,6]

During the course of our studies on solution phase reactions at elevated pressure, we have determined activation volumes for a variety of free-radical reactions.[4] For some of these, kinetic data are also available at atmospheric pressure in different solvents. We felt that a comparison of both sets of these data presented the possibility of examining whether internal and external pressure effects were correlated.

Results and Discussion

Activation volumes determined by external pressure variation for decomposition of a variety of free-radical initiators are given in Table I.[4,7] In all cases, the values of ΔV^* are positive, indicating that the decomposition rate constants decreased with increasing pressure. Such results are expected, since homolytic scission is characterized by a volume expansion, and also because cage return of radicals is pressure accelerated.[1,4]

If, as suggested by others,[5,6] values of ΔV^* can also be obtained using the solvent property internal pressure, these homolytic scission rate constants should decrease with increasing internal pressure at atmospheric pressure. Available data[8] are presented in Table II and it is immediately obvious that the predicted behavior is not observed. The data show either no correlation with "internal pressure" or an increase.[9]

TABLE I
EXTERNAL PRESSURE DEPENDENCE OF INITIATOR DECOMPOSITION RATES

Initiator	Conditions	ΔV,* cc/mol	Ref
Azocumene	Cumene, 55°	5	*a*
	Chlorobenzene, 55°	4	*a*
tert-Butyl phenylperacetate	Cumene, 80°	1	*b, c*
	Chlorobenzene, 80°	1	*b, c*
Di-*tert*-butyl hyponitrite	*n*-Octane, 55°	4	*d*
tert-Butyl peroxide	CCl_4, 120°	13	*e*
	Benzene, 120°	13	*e*
	Cyclohexene, 120°	7	*e*
	Toluene, 120°	5	*e*
Ketenimine[f]	Chlorobenzene	5	*a*
	tert-Butylbenzene	6	*a*

[a] Taken from the Ph.D. Dissertation of Michael Amrich, University of California, Riverside, Calif., Dec 1971. [b] References 4b and 4e. [c] These values of ΔV^* increase with increasing pressure to 3–4 cc/mol at 6000 atm. [d] Reference 4c. [e] Reference 7. [f] From azocyanocyclohexane; ketenimine = *N*-(1-cyanocyclohexyl)pentamethyleneketenimine; see, *e.g.*, H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1911 (1964).

In contrast to these negative correlations, we have noted that the effect of external pressure on the diffusion–combination ratios for *tert*-butoxy radicals[4c] does qualitatively parallel the variation of this ratio with solvent internal pressure[10] (Table III). The correspondence is not very good, however. Between the external pressures of 1 and 500 atm in *n*-octane at 45°, the value of $\Delta V_d^* - \Delta V_c^*$ is about 30 cc/mol, and it decreases with increasing pressure.[4c] The values of $\Delta V_d^* - \Delta V_c^*$ calculated from the solvent dependence data (Table III) are substantially larger and unrealistic.

One possible reason for the lack of correlation of these results may reside in the choice of values for "internal pressure." We have given two sets of values in Tables II and III, which have been taken from an extensive tabulation presented by Allen, Gee, and Wilson.[11] The first column gives values purported to correspond to $(\partial E/\partial V)_T$ for the various liquids. If so, these are correctly called *internal pressures*.[12] The

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[1] Part VIII: R. C. Neuman, Jr., and G. D. Holmes, *J. Amer. Chem. Soc.*, **93**, 4242 (1971).

[2] Support by the National Science Foundation (GP-23968) is gratefully acknowledged.

[3] For reviews see (a) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967); (b) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964); (c) S. D. Hamann in "High Pressure Physics and Chemistry," Vol. II, R. S. Bradley, Ed., Academic Press, New York, N. Y., 1963, Chapter 8.

[4] See also (a) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 657 (1971); (b) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **36**, 654 (1971); (c) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (d) R. C. Neuman, Jr., *Intra-Sci. Chem. Rep.*, **3**, 269 (1969); (e) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **91**, 6024 (1969).

[5] For a review of some of these proposals see W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 230 (1967).

[6] For a recent suggestion see R. J. Ouellette and S. H. Williams, *J. Amer. Chem. Soc.*, **93**, 466 (1971).

[7] C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959).

[8] (a) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966); (b) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *ibid.*, **83**, 3819 (1961); (c) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966); (d) E. S. Huyser and R. M. Van Scoy, *J. Org. Chem.*, **33**, 3524 (1968); (e) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

[9] (a) Two values of "internal pressure" are reported for most solvents. The quantity $(\partial E/\partial V)_T$ is *internal pressure* while $\Delta E_{\text{vap}}/V_T$ is *cohesive energy density*. Their relationship will be discussed later in the text. (b) Rate data in other solvents are available, but internal pressure values are lacking. (c) External pressure data are not available for diphenylazoethane, but it should have an activation volume comparable to that for azocumene.

[10] H. Kiefer and T. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).

[11] G. Allen, G. Gee, and G. J. Wilson, *Polymer*, **1**, 456 (1960).

[12] (a) W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928); (b) J. H. Hildebrand, *ibid.*, **34**, 649 (1929); (c) J. H. Hildebrand, *ibid.*, **34**, 984 (1929); (d) J. H. Hildebrand and J. M. Carter, *J. Amer. Chem. Soc.*, **54**, 3592 (1932); (e) see also J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold, New York, N. Y., 1950, Chapter 5; (f) for a recent review see A. F. M. Barton, *J. Chem. Educ.*, **48**, 156 (1971).

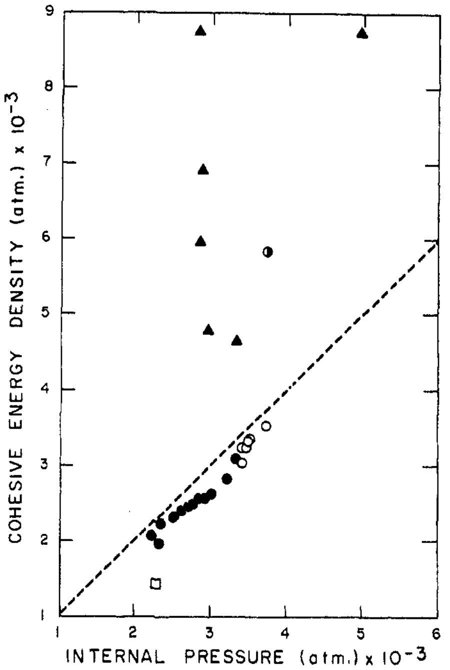

Figure 1.—Relationship between cohesive energy density ($\Delta E_{vap}/V_T$) and internal pressure ($(\partial E/\partial V)_T$ for simple alkanes (●), aromatic hydrocarbons (○), alcohols (▲), acetonitrile (◑), and perfluoromethylcyclohexane (□). The dashed line has a slope of one.

second set correspond to $\Delta E_{vap}/V_T$ where ΔE_{vap} is the energy of vaporization of a mole of the liquid occupying a volume V at the temperature T; these are called *cohesive energy densities.*[12]

Internal pressures of liquids may be determined according to eq 2, by measuring $(\partial P/\partial T)_V$ at different

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \qquad (2)$$

temperatures, but few such data are available. By and large, most authors attempting correlations with "internal pressure" *appear* to have utilized values of *cohesive energy densities*, perhaps assuming that these were reasonable approximations to $(\partial E/\partial V)_T$.[13] However, early work showed that these quantities differed rather substantially for certain liquids[14] and the apparent lack of correlation between them can be seen from the data plotted in Figure 1.[11]

In considering potential correlations between "internal pressure" and rate constants (Tables II and III) the temperature dependence of both $(\partial E/\partial V)_T$ and $\Delta E_{vap}/V_T$ has usually been ignored. In our comparison, the "internal pressures" correspond to 20°, while the rate constants were obtained at a variety of temperatures. It is known that $(\partial E/\partial V)_T$ is quite sensitive to temperature and this can be seen from work of Scott with CCl_4.[15] He found that $(\partial E/\partial V)_T$ decreased from 3346 atm at 25° to *ca.* 2044 atm at 70°.

TABLE II
KINETIC DATA FOR DECOMPOSITION OF INITIATORS IN VARIOUS SOLVENTS COMPARED TO THEIR INTERNAL PRESSURES

Solvent	"Internal Pressure"[a] $(\partial E/\partial V)_T$, atm	$\Delta E_{vap}/V_T$, atm	$k \times 10^5$, sec^{-1}		Ref
		Azocumene Decomposition (55°)			
Dodecane	2870	2564		(14.7)[b]	*c*
CCl_4	3402	3080	8.13		*d*
Cumene	3427	3039	8.10		*d*
Toluene	3501	3328	8.90	(18.0)[b]	*c*
Chlorobenzene		3730	8.50		*d*
		Diphenylazoethane Decomposition (97.30°)			
Dodecane	2870	2564	3.18		*e*
Diphenylmethane		3700	4.00		*e*
		tert-Butyl Phenylperacetate Decomposition (79.6°)			
Cumene	3427	3039	6.78		*f*
Chlorobenzene		3730	10.20		*f*
		Di-*tert*-butyl Hyponitrite Decomposition (65°)			
Isooctane	2325	1970	40.0		*g*
n-Butyl ether	(3000)		45.0		*g*
tert-Butyl alcohol	3344	4666	46.8		*g*
		tert-Butyl Peroxide Decomposition (120°)			
Cyclohexane	3212	2812	0.63		*h*
tert-Butyl alcohol	3344	4666	1.41		*h*
CCl_4	3402	3080		0.90	*i*
Toluene	3501	3328		1.34	*i*
Benzene	3737	3518	1.10	1.39	*h, i*
Acetonitrile	3737	5822	2.21		*h*
Tetrahydrofuran		3847	0.97		*h*
Nitrobenzene		4466	1.31		*h*
		Ketenimine Decomposition (100°)[j]			
n-Octane	2626	2391	1.63		*d*
tert-Butylbenzene		3000	2.38		*d*
Chlorobenzene		3730	3.85		*d*

[a] $(\partial E/\partial V)_T$ is *internal pressure* while $\Delta E_{vap}/V_T$ is *cohesive energy density;* these were taken from ref 11. [b] 60.2°. [c] Reference 8a. [d] Taken from the Ph.D. Dissertation of Michael Amrich, University of California, Riverside, Calif., Dec 1971. [e] Reference 8b. [f] References 4b and 4e. [g] Reference 8c. [h] Reference 8d. [i] Reference 8e. [j] See footnote *f* of Table I.

TABLE III
COMPARISON OF THE DIFFUSION–COMBINATION RATIOS FOR GEMINATE *tert*-BUTOXY RADICALS WITH INTERNAL PRESSURE OF SOLVENTS

Solvent	"Internal Pressure"[a] $(\partial E/\partial V)_T$, atm	$\Delta E_{vap}/V_T$, atm	k_d/k_c[b]	$\Delta\Delta V^*$,[c] cc/mol	Ref
n-Pentane	2241	2073	26.1		*d*
Isooctane	2325	1970	9.3	322	*d*
n-Hexane	2358	2221	15.1	120	*d*
n-Heptane	2527	2316	10.9	79	*d*
n-Octane	2626	2391	10.0	64	*d, e*
n-Nonane	2725	2457	7.7	66	*d, e*

[a] See footnote *a* of Table II. [b] 45°. [c] $\Delta V_d^* - \Delta V_c^*$; calculated using pentane as the reference system and $(\partial E/\partial V)_T$ values for "pressure." [d] Reference 10. [e] Reference 4c.

In summary, there appears to be no obvious correlation at this time between the effects of externally applied pressure and internal solvent pressure on free-radical decomposition rates. However, the utility of this latter parameter may not yet have been fully realized due to the lack of proper comparisons with kinetic data.

Registry No.—Azocumene, 33029-36-6; diphenylazoethane, 33029-37-7; *tert*-butyl phenylperacetate, 3377-89-7; di-*tert*-butyl hyponitrite, 14976-546; *tert*-butyl peroxide, 110-05-4; ketenimine, 32970-00-6; *tert*-butoxy, 3141-58-0.

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[13] For example see (a) A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968); (b) J. Halpern, G. W. Brody, and C. A. Winkler, *Can. J. Res.*, **28b**, 140 (1950); (c) reference 6.

[14] See (a) ref 12e, p 97; (b) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, pp 77–79.

[15] H. Benninga and R. L. Scott, *J. Chem. Phys.*, **23**, 1911 (1955).