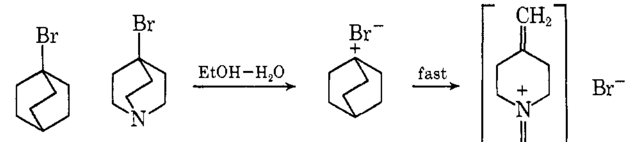
10^5 faster than that of 1-bromo[2.2.2]bicyclooctane (**10**).[57] It should be noted, however, that the rate of solvolysis of **11** is actually over 10 times *slower* than that of *tert*-butyl bromide.[58] It seems likely, then, that the faster rate for **11** as compared to **10** is caused primarily by circumvention of internal return from the ion pair initially formed from **11**, rather than by a driving force resulting from simultaneous bond formation and bond breaking.



10 $k = (1.0)$ **11** $k \cong 10^5$

circumvention of internal return by fragmentation

General Conclusions

Our general conclusions are that: (1) most base-initiated β eliminations which involve breaking of a bond of the type H–O, H–N, H–N=, H–C(EWG), or H–C(EWG)$_2$, where EWG = NO_2, CN, COR, SO_2R, or the like, proceed by anion mechanisms rather than a concerted mechanism; (2) although there is evidence for a driving force for C–Y bond cleavage from anions of the type $^-$O–C–Y, $^-$C–C–Y, and the like, there is no evidence for a driving force wherein O=C or C=C bond formation aids H–O or H–C bond breaking; (3) many examples of β eliminations heretofore classified as occurring by concerted E2 mechanisms probably occur by ion-pair E2 mechanisms; (4) when viewed as a whole, there are many more examples of two-stage than of one-stage β eliminations.[59]

One-stage β eliminations are probably uncommon for one or all of the following reasons: (a) torsional strain is introduced by eclipsing effects in the transition state; (b) an unfavorable entropy effect is introduced in the transition state by the freezing of rotations around three bonds of the substrate;[61] and (c) energy is required to lengthen and shorten bonds, and to change bond angles in the rehybridization process. Two-stage β eliminations in which ionic intermediates are formed presumably have the advantage that solvent and structural reorganization can occur in two stages rather than in one fell swoop.[62]

In view of the evident preference for the majority of β eliminations to follow two-stage mechanisms it appears appropriate to question many of the mechanistic assignments made in the literature, not only for β eliminations, but also for other reactions where as many as two bonds have been assumed to be formed and two bonds broken in concert.

I wish to thank the National Science Foundation (GP 29539X) and the Mobil Research Foundation for support of this work. I wish also to express my appreciation to Professors J. F. Bunnett, S. I. Miller, W. H. Saunders, Jr., and J. A. Zoltewicz for helpful comments. The contributions of my students were, of course, fundamental to the success of the work: their names are indicated in the references.

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(58) R. C. Fort and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 4194 (1964); *Chem. Rev.*, **64**, 277 (1964), report the solvolysis rate of **10** in 80% EtOH to be 10^6 slower than that of *t*-BuBr.

(59) The rarity of the heterolytic, one-stage β-elimination mechanism is not surprising when one considers that the microscopic reverse of this mechanistic type is rare; *i.e.*, most electrophilic and nucleophilic additions to C=C, C=O, C=N, etc., bonds occur by two-stage mechanisms. Miller has recently used this argument effectively in reaching the conclusion that iodide-initiated debrominations occur by two-stage rather than one-stage mechanisms.[60]

(60) C. S. T. Lee, I. M. Mathai, and S. I. Miller, *J. Amer. Chem. Soc.*, **92**, 4602 (1970).

(61) It is surprising to note in this regard that the entropies of activation for (presumably) concerted alkene-forming eliminations are generally much more positive than for accompanying S$_N$2 reactions (see, *e.g.*, ref 11, pp 46–48).

(62) This advantage, at least as a first approximation, can be considered to be an example of the application of the principle of least molecular deformation. For more critical analyses of this principle, however, see: J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966); S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969); O. S. Tee and K. Yates, *ibid.*, **94**, 3074 (1972).

Pressure Effects as Mechanistic Probes of Organic Radical Reactions

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Activation parameters are useful in understanding chemical reactions since they provide information about the nature of the activated complexes formed from the reactants. Enthalpies and entropies of activation (ΔH^* and ΔS^*) are routinely determined because they are easily obtained *via* the temperature dependence of rate constants. The volume change of activation (ΔV^*) is much less frequently reported, but in principle

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should provide equally valuable mechanistic information. It reflects the change in volume of the reacting system on passing from reactants to transition state. Its infrequent appearance in the literature is the result of experimental difficulties associated with its determination.

The activation volume is obtained from the pressure dependence of a reaction rate constant (eq 1), and its

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

magnitude determines how much the rate constant changes with pressure. While a change in reaction rate by a factor of 2 to 4 can be anticipated for a change in temperature of 10°, much greater pressure changes are required to bring about the same effect even for reactions with the relatively large activation volume of ±40 cm³/mole (Table I). The special equipment required to obtain the thousands of atmospheres of pressure needed has limited these studies to a few laboratories.

Table I
Pressure Required to Change a Reaction Rate by a Factor of 3

ΔV^*, cm³/mole	Pressure, atm
5	5800
10	2900
25	1200
40	700

Rapid development of mechanistic organic chemistry occurred at a time when pressure equipment was not readily available to workers in the field. As a result, pressure studies have largely played a confirmatory role with respect to major mechanistic discoveries. However, pressure effects on reactions have often permitted choices between mechanisms and have also enabled substantial refinement of mechanistic detail. This is illustrated by our pressure studies on free-radical initiator decompositions which are reviewed here.

Besides presenting specific details about radical reactions, we hope that this discussion will also provide the reader with a basis for the general understanding of pressure effects as probes of reaction mechanism. The following section contains a brief general review of pressure effects on organic reactions. Extensive reviews have been published.[1]

Background

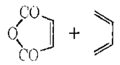
Pressure accelerates reactions which are characterized by a volume shrinkage in passing from reactants through transition state (negative ΔV^*) and retards those with a volume expansion (positive ΔV^*). These volume changes arise from two sources: (1) making and breaking of chemical bonds (molecular reorganization); and (2) interactions of the reactants and activated complex with the medium. They are illustrated by the volume changes associated with the *chemical equilibria* shown in Table II.[1] The first two entries are relatively free of solvent effects. The large volume change for dimerization of NO_2 reflects the expected decrease in volume of the system due to a decrease in the number of solute molecules. The small volume change for isomerization of 1,2-dichloroethylene is consistent with there being no major change in molecular structure and no change in the number of solute species. While the third and fourth reactions formally involve no change in numbers of solute species, the formation of ions and the resulting solvation lead to large volume decreases.

Table II
Volume Changes for Some Equilibria

Reaction	ΔV_0, cm³/mole
$c\text{-ClCH=CHCl} \rightleftarrows t\text{-ClCH=CHCl}$	+2
$NO_2 + NO_2 \rightleftarrows N_2O_4$	−23
$CH_3CO_2H + H_2O \rightleftarrows CH_3CO_2^- + H_3O^+$	−12
$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + OH^-$	−27

Observations on chemical equilibria provide a foundation for interpreting kinetic data. Some representative activation volumes are shown in Table III.[1] The first three reactions are nonionic and reflect changes in volume due to molecular reorganization in the transition states, the first involving volume expansion, and the second and third, volume contractions. The fourth reaction involves the creation of ions leading to increased solvation. The fifth and sixth reactions are both bimolecular displacements. The former involves no change in the number of charges, and solvation effects on ΔV^* are minimized, but the latter is characterized by charge neutralization in the transition state. The volume *expansion* in this last case clearly demonstrates the general trend that volume changes arising from creation or destruction of charge dominate those arising from molecular reorganization.

Table III
Activation Volumes for Some Reactions

Reaction	ΔV^*, cm³/mole
$PhCMe_2N{=}NCMe_2Ph \rightarrow$ homolytic scission	+5
 → dimerization	−40
$n\text{-}C_6H_{13}SH + DPPH^a \rightarrow$ hydrogen abstraction	−17
$t\text{-BuCl} + H_2O \rightarrow$ solvolysis	−15
$MeBr + OH^- \rightarrow$ displacement	−8
$Me_3S^+ + PhO^- \rightarrow$ displacement ($Me_2S + PhOMe$)	+12

[a] DPPH is diphenylpicrylhydrazyl.

Activation Volumes and Homolytic Scission Mechanism

When we began pressure studies of homolytic scission reactions we were struck by the relatively wide range of values of ΔV^*_{obsd} for these processes. Literature

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[1] Some reviews of pressure effects on chemical systems are: (a) S. D. Hamann in "High Pressure Physics and Chemistry," R. S. Bradley, Ed., Vol. II, Academic Press, New York, N. Y., 1963, Chapters 7ii and 8; (b) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93, (1964); (c) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967); (d) C. Eckert, *Annu. Rev. Phys. Chem.*, in press.

data available at that time are shown in Table IV,[2–4]

Table IV
Early Literature Data for Homolytic Scission Reactions[5]

Initiator	ΔV^*_{obsd}, cm³/mole
Benzoyl peroxide	+10
tert-Butyl peroxide	+5 to +13
Pentaphenylethane	+13
Azoisobutyronitrile (AIBN)	+4

and our first result was the very small value of about +1 cm³/mole (cumene, solvent) for decomposition of *tert*-butyl phenylperacetate (eq 2).[5,6]

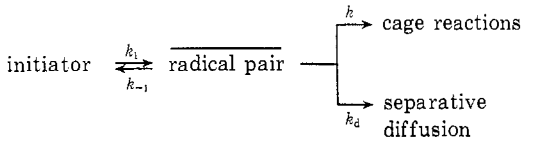
$$\text{PhCH}_2\text{CO}_2\text{OCMe}_3 \longrightarrow \text{PhCH}_2\cdot \quad \text{CO}_2 \quad \cdot\text{OCMe}_3 \qquad (2)$$

Consideration of these data led us to conclude that values of ΔV^*_{obsd} for decomposition of radical initiators do not necessarily reflect the volume change during homolytic scission. We proposed that values of ΔV^*_{obsd} for initiators which broke at least two bonds simultaneously in the primary decomposition process would reflect the characteristics of the homolytic scission step, but that this would not necessarily be true for those in which only one bond was broken (*e.g.*, decomposition of diacyl peroxides,[7] eq 3). In these latter

$$\text{RCO}_2\text{O}_2\text{CR} \rightleftarrows \text{RCO}_2\cdot \quad \cdot\text{O}_2\text{CR} \qquad (3)$$

cases recombination of the initial geminate radicals could lead to re-formation of starting material, a process unlikely in multiple bond scission systems (*e.g.*, eq 2).

From a general mechanism including "return" of the initial geminate radicals (eq 4) it can be seen that the



(4)

observed decomposition rate constant could depend not only on k_1 but also on k_{-1}, k_d, and k (eq 5). The

$$k_{\text{obsd}} = k_1\left[\frac{k_d + k}{k_{-1} + k_d + k}\right] \qquad (5)$$

pressure dependence of k_{obsd} would depend on that of this complex quantity, and observed activation volumes would be described by eq 6. We suggested that

$$\Delta V^*_{\text{obsd}} = \Delta V_1^* + RT\,\partial \ln\,[1 + k_{-1}/(k_d + k)]/\partial P \qquad (6)$$

ΔV^*_{obsd} would usually be greater than the actual volume change for scission (ΔV_1^*) because it seemed to us that the ratio $k_{-1}/(k_d + k)$ should generally increase with pressure; radical recombination (k_{-1}) would be pressure accelerated, while separative diffusion (k_d) would be retarded with increasing pressure.[6]

We have examined pressure effects on decomposition of a variety of two-bond scission initiators (Table V).[8–12] Their decomposition activation volumes of

Table V
Activation Volumes for Homolytic Scission of Two-Bond Initiators in Cumene

Initiator	ΔV^*_{obsd}, cm³/mole
$\text{Me}_2\text{C(CN)N}_2\text{C(CN)Me}_2$	+4
$\text{Me}_2\text{C(Ph)N}_2\text{C(Ph)Me}_2$	+5
$\text{Me}_2\text{C}(p\text{-MePh})\text{N}_2(p\text{-MePh})\text{Me}_2$	+4
$\text{Me}_3\text{CON}_2\text{OCMe}_3{}^a$	+4
$\text{C}_6\text{H}_{11}\text{CO}_2\text{OCMe}_3$	+4

[a] *n*-Octane.

+4 to +5 cm³/mole are substantially smaller than those for the one-bond scission initiators given in Table IV (note that azoisobutyronitrile, AIBN, decomposes *via* two-bond scission). In further agreement, the values of ΔV^*_{obsd} for *tert*-butyl perbenzoate decomposition, a one-bond scission process (eq 7), are relatively large (+11 cm³/mole; cumene, solvent).[9]

$$\text{C}_6\text{H}_5\text{CO}_2\text{OC(CH}_3)_3 \longrightarrow \text{C}_6\text{H}_5\text{CO}_2\cdot \quad \cdot\text{OC(CH}_3)_3 \qquad (7)$$

In the following sections more examples are presented which demonstrate that one-bond scission initiators give values of ΔV^*_{obsd} which are abnormally large. Data will also be presented which indicate that the *actual* volume change of activation for homolytic scission is generally +4 to +5 cm³/mole for single *or* multiple bond scission processes. For molar volumes between 150 to 250 cm³/mole, these values of ΔV^*_{obsd} indicate that homolytic scission transition states are on the order of 2 to 3% larger in volume than the ground-state initiators.

Polar Effects

Several two-bond scission peresters have given values of ΔV^*_{obsd} (cumene, solvent) substantially less than those obtained for other systems (Table V) and AIBN (Table IV). These include ring-substituted *tert*-butyl phenylperacetates ($\Delta V^*_{\text{obsd}} < 2$ cm³/mole)[13] and *tert*-butyl perpivalate (ΔV^*_{obsd} *ca.* +1 cm³/mole).[14] The former group has long been thought to decompose *via* polar transition states (eq 8),[5] and we believe that this

$$\text{ArCH}_2\text{CO}_2\text{OCMe}_3 \longrightarrow$$
$$\left[\text{Ar}\overset{\delta+}{\text{C}}\text{H}_2\text{---CO}_2\text{---}\overset{\delta-}{\text{O}}\text{CMe}_3\right]^{\ddagger} \longrightarrow \text{ArCH}_2\cdot \quad \text{CO}_2 \quad \cdot\text{OCMe}_3 \qquad (8)$$

is the explanation for the results. If ΔV^*_{obsd} reflects both molecular reorganization (ΔV^*_{bond}) and solvation (ΔV^*_{solv}) (eq 9), small negative values of the solvation

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[2] (a) A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97, 104 (1956).

[3] C. Walling and G. Metzger, *J. Amer. Chem. Soc.*, **81**, 5365 (1959).

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

[5] P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

[6] R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **89**, 4549 (1967).

[7] J. W. Taylor and J. C. Martin, *ibid.*, **88**, 3650 (1966).

[8] R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968).

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

[10] R. C. Neuman, Jr., *Intra-Sci. Chem. Rep.*, **3**, 269 (1969).

[11] R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970).

[12] R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972).

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

[14] R. C. Neuman, Jr., and R. P. Pankratz, unpublished results.

$$\Delta V^*_{\text{obsd}} = \Delta V^*_{\text{bond}} + \Delta V^*_{\text{solv}} \qquad (9)$$

term could effectively reduce a positive contribution of +4 to +5 cm^3/mole for ΔV^*_{bond} to the small positive values observed.[13]

Polar character in the decomposition transition state for *tert*-butyl perpivalate (eq 10; R = Me_3C) has been

$$RCO_2OCMe_3 \longrightarrow \left[\overset{\delta+}{R}\text{---}CO_2\text{---}\overset{\delta-}{O}CMe_3\right]^{\ddagger} \longrightarrow R\cdot \quad CO_2 \quad \cdot OCMe_3 \qquad (10)$$

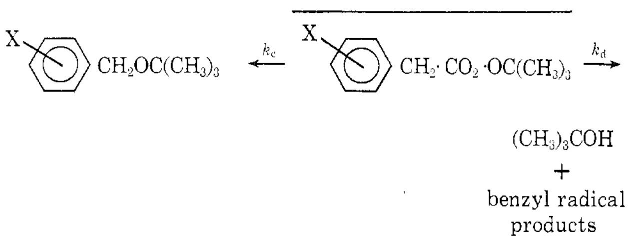
considered, but evidence has been weak.[15] In contrast to its low value of +1 cm^3/mole, ΔV^*_{obsd} for decomposition of *tert*-butyl perisobutyrate (R = Me_2CH) is +3 cm^3/mole, a value close to that expected when solvation effects are absent. All of the low values of ΔV^*_{obsd} are found for peresters whose R groups (eq 10) are particularly good at stabilizing electron deficiency.

Cage Reactions

The pressure dependence of product ratios from decomposition of several two-bond scission initiators has permitted us to probe the relative effects of pressure on the rapid competitive reactions available to geminate radical pairs. These processes most commonly include combination, disproportionation, and separative diffusion.

Two cases in which only combination and diffusion compete are those shown in Schemes I and II. Partitioning of the initial cages from ring-substituted *tert*-butyl phenylperacetate decomposition gives ethers *via* combination, and benzyl radical products and *tert*-butyl alcohol subsequent to diffusion (Scheme I).[16]

Scheme I



The pressure dependence of k_c/k_d can be determined from the ether/alcohol product ratio. Similarly, k_c/k_d for geminate *tert*-butoxy radicals from di-*tert*-butyl hyponitrite (DBH) (Scheme II) can be equated to the

Scheme II

$$(CH_3)_3CON{=}NOC(CH_3)_3$$

$$\downarrow$$

$$(CH_3)_3COOC(CH_3)_3 \xleftarrow{k_c} \overline{(CH_3)_3CO\cdot \quad N_2 \quad \cdot OC(CH_3)_3} \xrightarrow{k_d} 2(CH_3)_3COH$$

peroxide/alcohol ratio.[11,17-19] In both cases k_c/k_d increases with pressure (Figure 1).

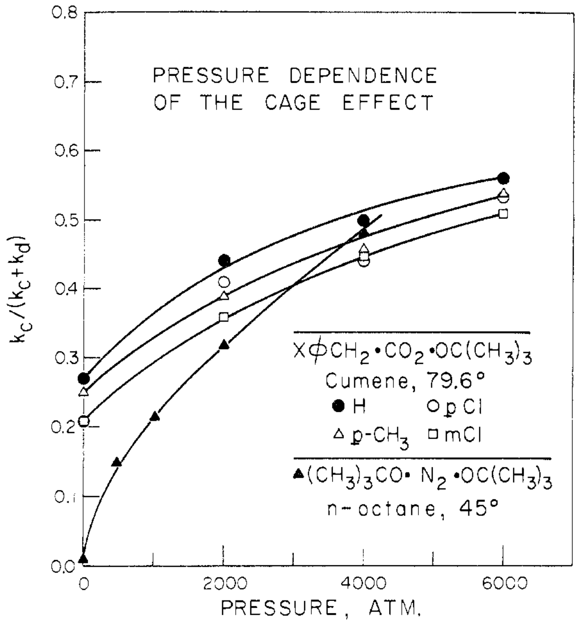


Figure 1.

We have suggested that radical combination should be pressure accelerated while diffusion is retarded. The qualitative trends in these results are thus consistent with expectation. However, in contrast we found that the "cage effect" from decomposition of azocumene (Scheme III) was relatively pressure insensitive, although it showed an initial increase (Figure 2).[20] In this case combination of the cumyl radicals to form bicumyl (k_c) *and* disproportionation to form cumene and styrene (k_a) are competitive with diffusion (k_d). These results prompted us to examine closely the available data, and we concluded that the pressure-induced increases in k_c/k_d for the phenylperacetates and DBH were smaller than might be expected *just* from the anticipated pressure retardation of k_d.[16] In other words, in all of these cases combination (and disproportionation) seemed to be somewhat *retarded* by pressure.

Scheme III

$$PhCMe_2N{=}NCMe_2Ph$$

$$\downarrow$$

$$\begin{matrix}\text{bicumyl} +\\ \text{cumene} +\\ \text{styrene}\end{matrix} \xleftarrow{k_c + k_a} \overline{Ph\dot{C}Me_2 \quad N_2 \quad \cdot CMe_2Ph} \xrightarrow{k_d} 2Ph\dot{C}Me_2$$

We have rationalized this by pointing out that bimolecular combination and disproportionation reactions require that the inert gas molecules (nitrogen or carbon dioxide) evacuate the region between the radicals (Scheme IV).[16] Such a process is akin to diffusion and might be expected to be pressure retarded. The effect is most dramatic for the azocumene system

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

(16) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 657 (1971).

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

(18) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968).

(19) See also R. C. Neuman, Jr., *J. Org. Chem.*, **37**, 495 (1972).

(20) M. Amrich, Ph.D. Dissertation, University of California, Riverside, 1971.

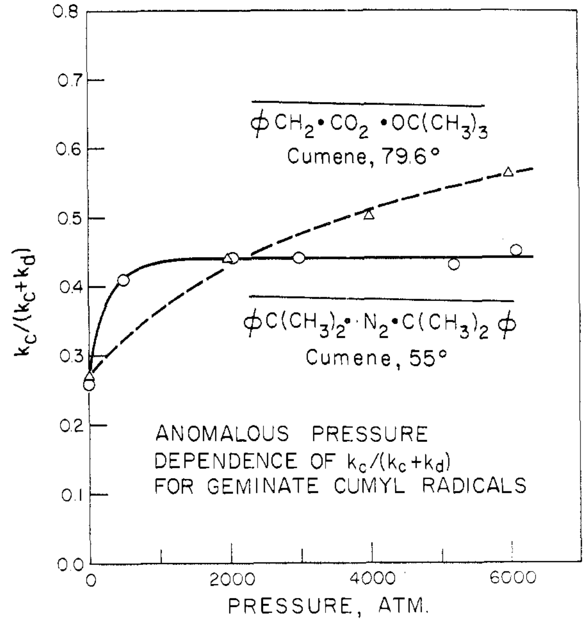
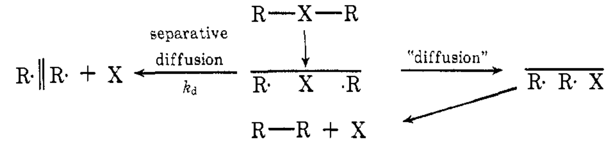


Figure 2.

Scheme IV

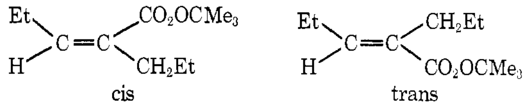


(Scheme III) where the radicals are particularly bulky and might make escape of nitrogen especially difficult. This analysis suggests that pressure effects on cage return for one-bond scission initiators (*e.g.*, $k_{-1}/(k + k_d)$; eq 4) could be substantially greater than had been predicted using the k_c/k_d data from two-bond scission initiators.

Increasing pressure seems to favor disproportionation of geminate radicals over combination. The disproportionation to combination ratio (k_a/k_c) for cumyl radicals from azocumene is derived from the relative yields of cumene and bicumyl. Our results indicate that k_a/k_c for these radical pairs increases from about 0.1 at atmospheric pressure to about 0.5 at 6000 atm.[20] Similar results have been observed for α-cyanocyclohexyl radical pairs from azocyanocyclohexane (see below).[21] It has been shown that the medium can have a dramatic effect on disproportionation/combination ratios,[22] and we ascribe these changes to pressure effects on the rotational motions of radicals within the solvent cage.[23]

Isomeric Vinyl Peresters

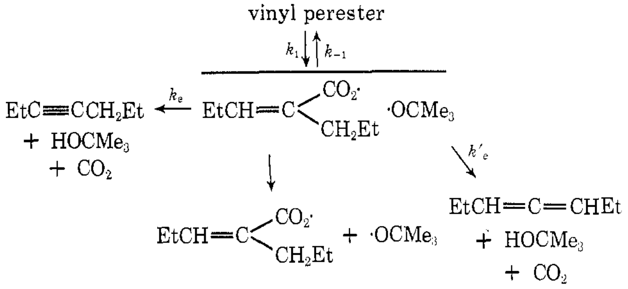
Most of our data for homolytic scission had been obtained from studies of two-bond scission initiators. To extend our knowledge of one-bond initiators we undertook a kinetic and product study of a pair of isomeric *tert*-butyl vinyl peresters.[24] The results of this



study are of particular interest because of the mechanistic information they provided.

The values of $\Delta V^*_{\mathrm{obsd}}$ for decomposition of the cis and trans peresters (cis, +6.8 ± 0.4 cm^3/mole; trans +9.0 ± 1.0 cm^3/mole) (cumene) were greater than those for two-bond scission initiators, thus supporting a one-bond scission mechanism with internal return (Scheme V).

Scheme V

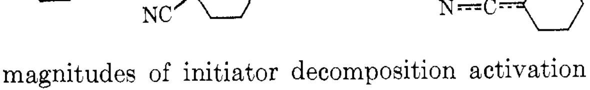


The remainder of Scheme V was supported by product data. In particular the data indicated that the acetylene and allene were formed only from the initial cage.

We were surprised that the values of $\Delta V^*_{\mathrm{obsd}}$ were smaller than those observed for other one-bond initiators and particularly that they were different for the two isomers. We concluded that this difference was due to a difference in reactivity of the first formed *isomeric vinyl carboxyl radicals.* All data suggested that the cis radical was more susceptible to cage bimolecular elimination of CO_2 to form the acetylene. A possible difference in k_{-1} could not be probed. The relatively low values of $\Delta V^*_{\mathrm{obsd}}$ indicated that k_e and k_e' (processes competing with k_{-1}) were pressure accelerated.

An Activation Volume for Homolytic Scission

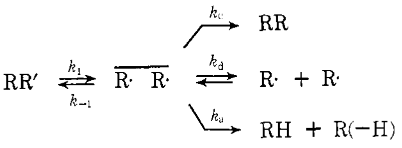
A study of the thermal decomposition of a ketenimine (eq 11) has provided evidence for our proposals about



(11)

magnitudes of initiator decomposition activation volumes. In the absence of radical scavengers, decomposition is described by the mechanism in Scheme VI where

Scheme VI



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[21] R. C. Neuman, Jr., and M. Amrich, *J. Amer. Chem. Soc.*, **94**, 2730 (1972).

[22] J. M. McBride, *ibid.*, **93**, 6302 (1971).

[23] Recently we learned that similar conclusions have been reached by V. M. Zhulin and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 331 (1972).

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

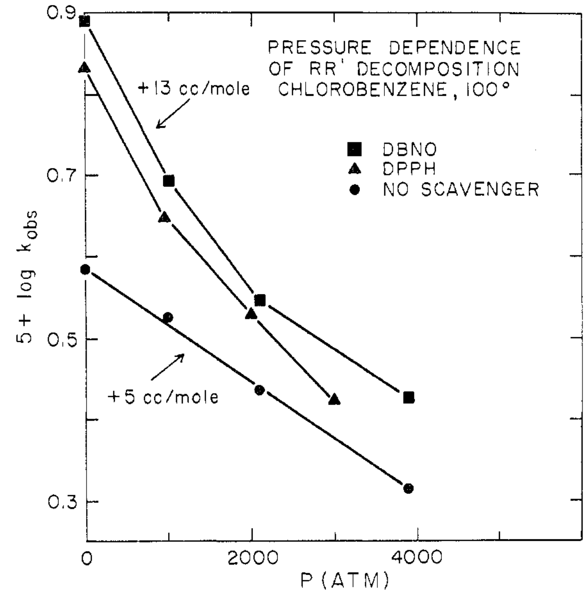
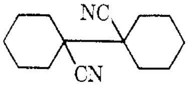
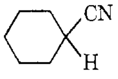
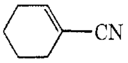


Figure 3.

RR′ is the ketenimine, RR is the symmetrical dinitrile coupling product, and RH and R(−H) are the disproportionation products, cyanocyclohexane and cyanocyclohexene, respectively.[25]


RR


RH


R(−H)

Because cyanoalkyl radicals are relatively stable, those which have separated by diffusion ultimately return to radical pairs. As a result, separative diffusion is not kinetically visible, and the observed rate of decomposition (and the observed decomposition activation volume) would *not* depend on separative diffusion (eq 12), behavior substantially different from that

$$k_{\mathrm{obsd}} = k_1\left[\frac{k_\mathrm{c} + k_\mathrm{a}}{k_{-1} + k_\mathrm{c} + k_\mathrm{a}}\right] \tag{12}$$

(eq 6) of other one-bond initiators previously discussed. However, in the presence of scavengers, diffusion would once again be a destructive process (eq 13) and k_d would

$$\overline{\mathrm{R\cdot\quad R\cdot}} \overset{k_\mathrm{d}}{\underset{\not\leftarrow}{\rightarrow}} \mathrm{R\cdot} + \mathrm{R\cdot} \xrightarrow{2\mathrm{S}} 2\mathrm{RS} \tag{13}$$

return to the kinetic expression (eq 6 and 14). The

$$k_{\mathrm{obsd}} = k_1\left[\frac{k_\mathrm{c} + k_\mathrm{a} + k_\mathrm{d}}{k_{-1} + k_\mathrm{c} + k_\mathrm{a} + k_\mathrm{d}}\right] \tag{14}$$

experimental results (Figure 3) indicated that the pressure dependence of k_d had a big effect on $\Delta V^*_{\mathrm{obsd}}$.[21] While this quantity in the absence of scavengers was on the order of +5 cm/mole, it increased to at least +13 cm^3/mole in the presence of either diphenylpicrylhydrazyl (DPPH) or di-*tert*-butyl nitroxide (DBNO).

In the absence of scavengers, product data suggested that the pressure dependence of the rate constant ratio $(k_\mathrm{c} + k_\mathrm{a})/(k_{-1} + k_\mathrm{c} + k_\mathrm{a})$ was very small. Thus, under the no-scavenger conditions the observed activation volume (+5 cm^3/mole) may be a good approximation to ΔV^*_1 (eq 15), the activation volume for

$$\Delta V^*_{\mathrm{obsd}} = \Delta V^*_1 + RT\,\partial \ln\,[1 + k_{-1}/(k_\mathrm{a} + k_\mathrm{c})]/\partial P \approx \Delta V^*_1 \tag{15}$$

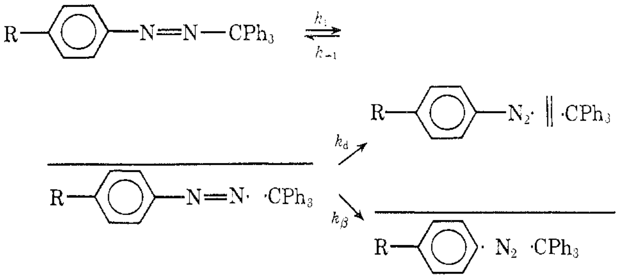
one-bond scission of the C–N bond in the ketenimine. Its approximate magnitude of +5 cm^3/mole is suggestively similar to many of those for two-bond scission which we have observed.

The Viscosity Test

Our studies and results have complemented a growing literature describing the use of atmospheric pressure variation of solvent viscosity to probe free-radical reaction mechanisms.[26] This "viscosity test" has proven to be valuable in demonstrating both the presence and extent of kinetically invisible cage return. Our conclusions have generally, but not always, been consistent with results of these studies.[13]

One of the first systems studied by the "viscosity test" was *p*-nitrophenylazotriphenylmethane (NAT) and its unsubstituted isomer phenylazotriphenylmethane (PAT). The decomposition rates of both decreased with increasing solvent viscosity, and it was proposed that they decomposed *via* one-bond scission (Scheme VII) with substantial return (k_{-1}). Before this study, little evidence was available supporting such a decomposition mode for azo systems. We have carried out pressure variation studies on both systems, and our data completely agree with these conclusions.[12] The observed activation volumes determined in several solvents fall within the range of +15 to +20 cm^3/mole, the largest reported values for homolytic scission to our knowledge. They seem to demand a substantial dependence of k_{obsd} on separative diffusion.

Scheme VII



Cyclic Systems

The viscosity test cannot be applied to studies of homolytic scission of cyclic systems which might produce diradicals (Scheme VIII). Since reactions of the diradical do not include separative diffusion, the observed decomposition rate constant should be viscosity insensitive whether or not return (k_{-1}) occurs in competition

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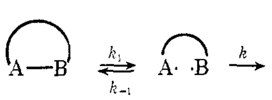
[25] H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1911 (1964).

[26] See, for example, W. A. Pryor and W. K. Smith, *ibid.*, **92**, 5403 (1970).

Scheme VIII

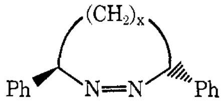


with the other reactions (k). However, the possibility that pressure effects on k_{obsd} might give clues concerning detailed mechanism (see eq 16) has led us to study a

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT\,\partial \ln (1 + k_{-1}/k)/\partial P \qquad (16)$$

series of cyclic azo compounds.

Kinetic and product studies of the six- through eight-membered ring systems shown below are in progress.[27]



$x = 2, 3, 4$

The values of ΔV^*_{obsd} for decomposition leading to expulsion of nitrogen for the six- and eight-membered ring systems are +5 and +7 cm^3/mole, respectively. Together with product data, the results suggest that mechanistic differences may be present which can be probed using pressure studies.

Summary

Effects of pressure on the decomposition rates and products of radical initiators have provided detailed mechanistic information about these systems. Decomposition activation volumes for homolytic scission appear to be *ca.* +4 to +5 cm^3/mole. Larger values indicate the presence of cage return regenerating the initiator, and smaller values can reflect polar effects in the decomposition transition state.

Cage reactions of radical pairs such as combination and disproportionation are generally favored over separative diffusion by increasing pressure. However, in spite of this, these cage bimolecular processes (combination and disproportionation) appear to be retarded by pressure because of its effect on the prerequisite rotational diffusion processes within the initial cages.

Pressure studies complement the use of solvent viscosity as a probe of initiator decomposition mechanism and provide information in cases where the latter technique cannot be used. Since diffusion rates can be altered by pressure without changes in temperature or medium, data derived from these studies may be of use in probing microscopic features of solvent structure and its interaction with solutes.

The work reported here was carried out by my able collaborators Drs. Michael Amrich, Joseph Behar, Robert Bussey, Gary Holmes, and Messrs. Ernest Ertley, George Lockyer, and Richard Pankratz. We thank the National Science Foundation for its continuing support of these studies. This account was written during the author's tenure as an NIH Special Research Fellow at Princeton University, 1971–1972.

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[27] R. C. Neuman, Jr., and E. W. Ertley, *Tetrahedron Lett.*, 1225 (1972).

Bimolecular Homolytic Substitution at a Metal Center

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Bimolecular heterolytic substitution reactions (SN2 and SE2) at a saturated center have been investigated intensively in recent years, principally by kinetic and stereochemical methods, and a great deal of information is now available on the way in which constitutional and environmental factors affect these processes.

Much less is known about bimolecular homolytic substitution (SH2), largely because there is as yet no firmly established example of this reaction taking place at a simple saturated carbon center. Such reactions occur usually at the peripheral monovalent hydrogen or halogen atoms in an organic compound (*e.g.*, eq 1 and 2),

$$(CH_3)_3CO\cdot + H\text{–}CH_2C_6H_5 \longrightarrow (CH_3)_3COH + \cdot CH_2C_6H_5 \qquad (1)$$

$$CH_3\cdot + Cl\text{–}CCl_3 \longrightarrow CH_3Cl + \cdot CCl_3 \qquad (2)$$

and infrequently at bivalent oxygen or sulfur. This severely limits the context within which the process can be studied and the techniques that can be employed.

Since 1966, however, it has become apparent that SH2 processes can occur, often extremely rapidly, at the metallic center of an organometallic compound (eq 3).[1]

$$X\cdot + MR_n \longrightarrow XMR_{n-1} + R\cdot \qquad (3)$$

This process provides a wide new context for studying the behavior of free radicals, and it supplies the key to the interpretation of many familiar organometallic reactions and the prediction of new ones. The kinetics of a number of these reactions have been studied, and

Alwyn Davies received his undergraduate training at University College London, and worked for his Ph.D. degree under the supervision of Professors E. D. Hughes and C. K. Ingold. From 1949 to 1953 he was a lecturer at Battersea Polytechnic under Joseph Kenyon, and then returned to the staff at University College. His research interests have moved from organic peroxides, through organometallic chemistry, to homolytic reactions.

Brian Roberts studied as an undergraduate at University College and obtained his Ph.D. degree in 1968 after working with Professor A. G. Davies on the mechanism of autoxidation of organometallic compounds. He is now Lecturer in Chemistry at University College.

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(1) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971.