Activation Volumes for Combination and Diffusion of Geminate *t*-Butoxy Radicals[1,2]

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Abstract: Geminate *t*-butoxy radicals were generated by decomposition of di-*t*-butyl hyponitrite (DBH) in *n*-octane solution at pressures ranging from 1 to 6000 atm. The difference between the activation volumes for separative diffusion and combination of the *t*-butoxy radicals ($\Delta V_d^* - \Delta V_c^*$), determined from the pressure dependence of the *t*-butyl peroxide:*t*-butyl alcohol product ratio at 45°, was found to be pressure dependent ranging from $> +30$ cc/mol (1 atm) to $+7.0$ cc/mol (4000 atm). A comparison of these data with those from a viscosity variation study at atmospheric pressure indicates that ΔV_c^* is about -5 cc/mol over this pressure range. At 55° the observed activation volume for decomposition of DBH is about $+4.3$ cc/mol over a 6000-atm pressure range. This value is compared with those for other homolytic scission reactions and is shown to support a simultaneous two-bond scission mechanism for DBH decomposition.

In order to understand better the mechanisms of organic reactions and how they might be affected by pressure variation, we have been studying the pressure dependence of the rates and product distributions of simple free radical reactions in solution. The pressure dependence of a rate constant for a single step reaction yields the activation volume (ΔV^*) (eq 1)

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

which represents the difference in the partial molar volumes of transition state and reactant(s).[4] While ΔV^* includes contributions from changes in bond lengths, geometry, and solvation during the activation process, it is often difficult to determine quantitatively the relative contribution of each of these. For this reason, it is important to study simple systems for which one can, to a first approximation, assign the observed values of ΔV^* to a predominant effect.

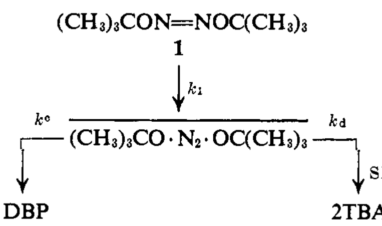
Solvation effects, while not totally absent in free radical reactions, would be expected to contribute less to values of ΔV^* for such processes than for polar reactions. Hence, values of ΔV^* for the former usually can be assigned mainly to bond length and geometry changes.

This article embodies the results of a variable pressure study on the free radical thermal decomposition of di-*t*-butyl hyponitrite (**1**) in *n*-alkane solvents.

Traylor and Kiefer[5] demonstrated that the products *t*-butyl peroxide (DBP) and *t*-butyl alcohol (TBA) quantitatively account for the starting azo compound (**1**) and have proposed the decomposition and product forming mechanism outlined in Scheme I.

This system was chosen by us for study in part because the pressure dependence of the rate of decomposition of **1** (*i.e.*, the magnitude of the decomposition activation volume ΔV_{obsd}^*) would provide a test for the generality of our proposals concerning the differences in activation volumes for one- and two-bond scission *t*-butyl peresters.[1a,6] Of primary interest, however, was the pressure dependence of the product distribution (DBP):(TBA) which would be directly related to that of the rate constant ratio k_c/k_d.

Scheme I



Traylor determined the viscosity dependence of this rate constant ratio in a series of hydrocarbon solvents at atmospheric pressure and interpreted his results solely in terms of a viscosity dependence of k_d.[5] Reasoning that the pressure dependence of k_d might be interpretable as a viscosity effect quantitatively the same as that observed at atmospheric pressure by Traylor, it seemed possible that the latter data could be combined with the pressure dependence of k_c/k_d to yield indirectly the absolute pressure dependence of k_c. This would allow the determination of a quantity notably absent from the literature, an activation volume for radical coupling (ΔV_c^*).

Based on the transition-state theory derivation of activation volumes,[4] the overall reaction volume for a single step reaction (ΔV) should be equal to the difference between the activation volumes for the forward and reverse reactions ($\Delta V_f^* - \Delta V_r^*$). It is conceivable, however, that transition states may in some cases be sufficiently short lived so that they do not reach equilibrium with the surrounding medium. In such cases ΔV might not equal $\Delta V_f^* - \Delta V_r^*$.[7] A comparison of a typical value of ΔV_c^* with activation volumes for

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(1) (a) High Pressure Studies. V. Part IV: R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969); (b) support by the National Science Foundation (GP-7349 and GP-8670) is gratefully acknowledged.

(2) (a) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968); (b) R. J. Bussey, Ph.D. Thesis, University of California, Riverside, Calif., 1969.

(3) University Predoctoral Fellow, 1965–1966.

(4) A detailed list of reviews on this subject can be found in the previous paper in this series.[1a]

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

(6) (a) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **89**, 4549 (1967); (b) R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968).

(7) This general problem associated with all activation parameters is briefly discussed in J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 72–73.

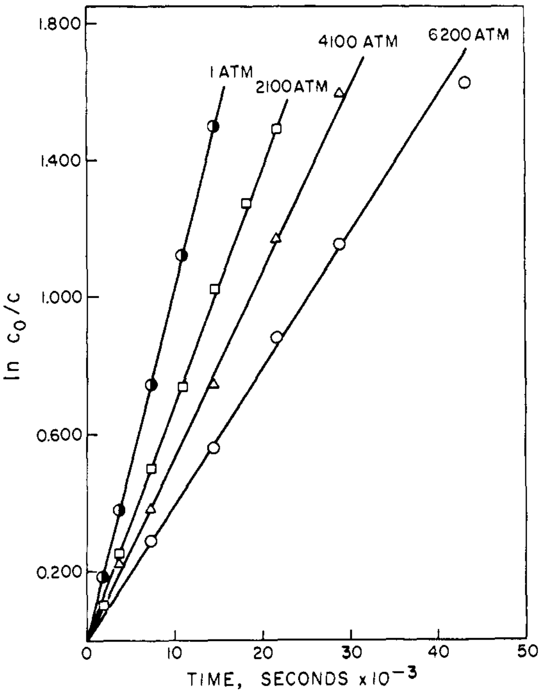

Figure 1. First-order rate plots for the decomposition of 0.01 *M* DBH in *n*-octane at 55.07° and various pressures.

homolytic scission[1a,6] and overall reaction volumes for radical formation[4] could permit a test of these proposals.

Results and Discussion

Activation Volume for Homolytic Scission, The rate of thermal decomposition of di-*t*-butyl hyponitrite (DBH) in *n*-octane solution at various external pressures was determined by monitoring the decrease in an intense band at 995 cm^{-1} in the infrared.[5,8] Kinetic data obtained using 0.01 *M* solutions of DBH at 55.07° are reported in Table I and representative kinetic plots are reproduced in Figure 1. Additionally, an atmospheric pressure rate constant was obtained at 45.00° using a 0.01 *M* DBH sample and its value was 0.252 × 10^{-4} sec^{-1}. This latter value and the atmospheric pressure rate constant at 55.07° (1.03 ± 0.01 × 10^{-4} sec^{-1}) are in reasonable agreement with comparable data obtained by Traylor[5] using 10^{-4} *M* solutions of DBH in isooctane: 45°, 0.272 × 10^{-4} sec^{-1}; 55°, 1.07 × 10^{-4} sec^{-1}.[9]

Table I. Rate Constants for the Thermal Decomposition of Di-*t*-butyl Hyponitrite in *n*-Octane (55.07°) at Various Pressures

Pressure, atm	$k_1 \times 10^4$, sec^{-1}
1	1.013
1	1.039
2100	0.713
2100	0.709
4100	0.527
4100	0.541
6200	0.374
6200	0.401

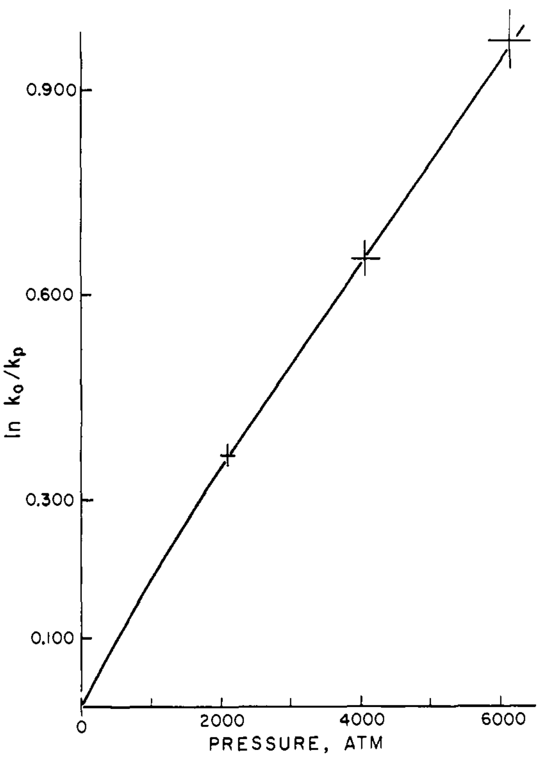

Figure 2. Pressure dependence of the rate constants for decomposition of 0.01 *M* DBH in *n*-octane at 55.07°.

Pressure decreases the rate of decomposition of DBH and this can be clearly seen in the log *k* *vs.* *P* plot (Figure 2). While the data approach a linear dependence of log *k* on *P* there appears to be some curvature in the low-pressure region similar to that observed in many pressure studies.[4] The slope of the line between 1 and 2100 atm yields a ΔV^* of +4.7 ± 0.5 cc/mol while the best line between 2100 and 6200 atm gives a value of +4.0 cc/mol. The best straight line through all of the data yields a value of +4.3 cc/mol.

Previously, we have discussed the relationship between the magnitude of activation volumes for homolytic scission reactions and the mechanism of homolytic scission.[1a,6] For the general scheme shown below the rate constant for initiator decomposition (k_{obsd})

$$\text{initiator} \underset{k_c'}{\overset{k_1}{\rightleftarrows}} \underset{\text{pair}}{\text{geminate}} \xrightarrow{k_d'} \underset{\text{radicals}}{\text{free}}$$

is given in eq 2. When k_c' is equal to zero (initiator is

$$k_{\text{obsd}} = k_1/(1 + k_c'/k_d') \qquad (2)$$

not regenerated from the initial geminate radical pair) k_{obsd} is equal to k_1 and ΔV_{obsd}^* is equal to that for homolytic scission (ΔV_1^*). However, when k_c' is greater than zero, ΔV_{obsd}^* depends not only on the pressure dependence of k_1 but also on that of the ratio k_c'/k_d'. We have shown for *t*-butyl peresters that in the former case values of ΔV_{obsd}^* (*i.e.*, ΔV_1^*) are about +4 cc/mol, while in the latter case values of ΔV_{obsd}^* tend to be in the region of +10 cc/mol or larger.[1a,6]

The activation volume for DBH decomposition in *n*-octane is thus in agreement with that expected for a two-bond scission mechanism as shown in Scheme I.[10]

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(8) H. Kiefer and T. Traylor, *Tetrahedron Lett.*, 6163 (1966).

(9) Traylor showed that the decomposition rate constant for DBH was somewhat solvent dependent but that induced decomposition was unimportant.[8,5]

(10) (a) The activation volume for decomposition of azobisiso-

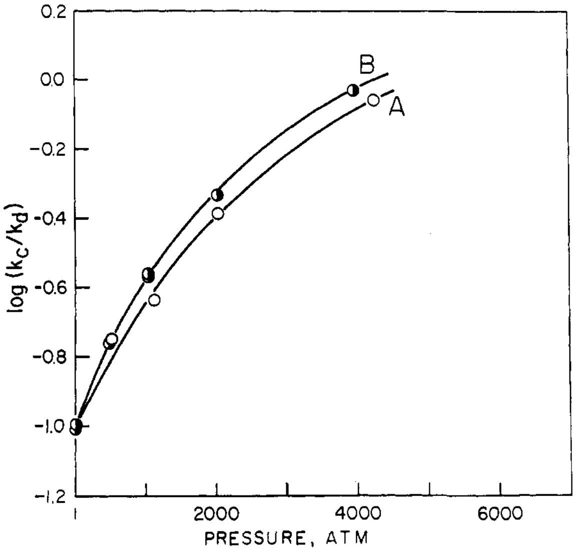

Figure 3. Pressure dependence of the relative rate constants for combination (k_c) and separative diffusion (k_d) of geminate *t*-butoxy radicals from decomposition of 0.1 *M* DBH in *n*-octane at 45.00°. The open and half-solid circles designate separate studies (see text).

The absence of an inverse dependence of decomposition rate on viscosity at atmospheric pressure[5,8] and the values of the activation energy and entropy for DBH decomposition in isooctane[8] offer independent support[11] for this mechanism. Thus, we are encouraged to generalize our conclusions[1a,6] concerning the relationship between the magnitude of activation volumes for homolytic scission reactions and their mechanisms and offer the prediction that concerted two-bond scission reactions without significant polar contributions will give values of ΔV_{obsd}^* in the region of +4 to +5 cc/mol.

Activation Volumes for Combination and Diffusion of Geminate Radicals. The pressure dependence at 45° of the molar product ratio (DBP):(TBA) was determined from glpc analyses of completely reacted samples initially 0.1 *M* DBH in *n*-octane. The absence of unreacted DBH was verified by infrared analysis (*vide supra*).[12] Traylor and Kiefer have demonstrated that decomposition of DBH in hydrocarbon solvents leads to quantitative formation of DBP and TBA and that DBP arises only from the initially formed geminate aggregates.[5] Thus, the rate constant ratio k_c/k_d (Scheme I) is directly related to the molar product ratio (eq 3). The pressure dependence of the ratio

$$k_c/k_d = 2(\text{DBP})/(\text{TBA}) \qquad (3)$$

k_c/k_d gives the difference in activation volumes for separative diffusion (ΔV_d^*) and combination (ΔV_c^*) of the *t*-butoxy radicals (eq 4).

$$\partial \log (k_c/k_d)/\partial P = (\Delta V_d^* - \Delta V_c^*)/2.3RT \qquad (4)$$

The rate constant ratios are given in Table II along with the viscosities[13] of pure *n*-octane at 45° for the several pressures studied.[14] The values of log (k_c/k_d) are plotted *vs.* pressure in Figure 3. The open circles represent data reported in our preliminary communication.[2] The half-solid circles are data points obtained in a subsequent study in which greater care was taken in sample handling and preparation of standard solutions for glpc analysis. While both sets of data are shown we have more confidence in the accuracy of the half-solid points and these are used in the subsequent discussion.

Table II. Pressure Variation of the Ratio k_c/k_d in the Solvent *n*-Octane (45°)

P, atm	η, cP[a]	k_c/k_d[b]
1	0.420	0.098 ± 0.008
1	0.420	0.101 ± 0.007
475	0.629	0.175 ± 0.005
510	0.641	0.179 ± 0.007
1020	0.943	0.274 ± 0.015
1020	0.943	0.275 ± 0.012
1120	1.010	0.233 ± 0.015
2010	1.802	0.466 ± 0.028
2040	1.825	0.413 ± 0.018
3950	5.051	0.936 ± 0.052
4220	5.682	0.883 ± 0.067

[a] Values of η at pressures greater than 1 atm determined from interpolation of data obtained by Bridgeman.[13] [b] Calculated from the (DBP):(TBA) product ratios obtained by glpc analyses; see text.

Analysis of curve B (half-solid circles) gives the values of $\Delta V_d^* - \Delta V_c^*$ in Table III. Values from curve A are essentially identical with those from curve B at pressures above 1000 atm.[15,16] The obvious

Table III. Values of $\Delta V_d^* - \Delta V_c^*$ as a Function of Pressure from Curve B of Figure 3[a]

Pressure, atm	$\Delta V_d^* - \Delta V_c^*$, cc/mol
1	
500	+30.0
1000	+21.4
1500	+16.5
2000	+13.8
2500	+11.7
3000	+9.6
3500	+8.3
4000	+7.0

[a] Values of $\Delta V_d^* - \Delta V_c^*$ shown for each pressure P_i were calculated from the relationship $(\Delta V_d^* - \Delta V_c^*)_{P_i} = [2.3RT/(P_i - P_{i-1})]$ [log $(k_c/k_d)_{P_i}$ − log $(k_c/k_d)_{P_{i-1}}$] where $P_{i-1} = P_i - 500$. Values of log (k_c/k_d) were taken from the smooth curve B through the data points.

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butyronitrile, a two-bond initiator, was determined many years ago to be *ca.* +4 cc/mol (toluene, 70°).[10b] (b) A. H. Ewald, *Discussions Faraday Soc.*, 22, 138 (1956).

(11) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967).

(12) Unreacted DBH in *n*-octane solution decomposes in the injection block of the gas chromatograph yielding mainly TBA.

(13) P. W. Bridgeman, "Collected Experimental Papers," Vol. IV, Harvard University Press, Cambridge, Mass., 1964, p 2043.

(14) (a) An attempt was made to obtain product data at 5800 atm; however, after reaction times >10 half-lives based on a decomposition activation volume of +4.5 cc/mol 28% unreacted DBH was observed in two separate samples. Preliminary kinetic runs at 45° gave the expected rates (ΔV^* *ca.* +4.5 cc/mol) for both 0.01 *M* and 0.1 *M* DBH solutions at 4100 atm, and for a 0.01 *M* solution at 6000 atm; however, that for a 0.1 *M* DBH solution at 6000 atm was abnormally slow (apparent ΔV^* *ca.* +8 cc/mol). All of these results suggest that the solubility limit for DBH in *n*-octane at 45° becomes less than 0.1 *M* at some pressure between 4200 and 5800 atm and that solid DBH decomposes more slowly[14b] than that in solution. (b) Di-*t*-butylperoxyoxalate also decomposes more slowly in the solid state than in solution; R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3768 (1965).

(15) It is interesting to compare these data with the results of a much more limited study of the coupling *vs.* diffusion reactions of *t*-butoxy-carbon radical pairs.[1a] Two-point values of $\Delta V_d^* - \Delta V_c^*$ between 1 and 4000 atm for a benzyl-*t*-butoxy radical pair and for a

pressure dependence of the quantity $\Delta V_d^* - \Delta V_c^*$ could reside in either or both of the two separate activation volumes. On the basis of discussion to follow we propose that it primarily arises from an inverse pressure dependence of ΔV_d^*.

Data obtained in these laboratories indicate that true activation volumes for homolytic scission are not significantly pressure dependent when polar effects are absent (*e.g.*, see the results for DBH in the preceding section of this paper).[1a,6] While these observations do not require that values of ΔV_c^* (the reverse process) be pressure insensitive, they are suggestive of this. Further, the magnitude of the variation in $\Delta V_d^* - \Delta V_c^*$ (+30 cc/mol to +7.0 cc/mol) cannot reasonably be accommodated entirely or even primarily in ΔV_c^*. This proposal is further supported by limited data on the pressure dependence of diffusion constants in organic liquids.[17,18] The positive activation volumes for self-diffusion (ΔV_D^*) show a large inverse pressure dependence in those cases investigated.[17b,19]

While the activation volume for diffusion (ΔV_d^*) is a convenient way of expressing the pressure dependence of diffusion rate constants (k_d), an alternate approach might be to consider the known dependence of solvent viscosity on pressure[13] and attribute the variation in values of k_d to the viscosity variation. If such an analysis was correct and if appropriate data for the dependence of k_d on viscosity were available, it would be possible to extract the pressure dependence of k_c and thus determine an absolute activation volume for radical combination (ΔV_c^*).

In fact, Traylor and Kiefer have determined the viscosity variation of the rate constant ratio k_c/k_d for DBH decomposition at atmospheric pressure.[5] The results of this study using 0.1 *M* DBH solutions at a decomposition temperature of 45° in a series of hydrocarbon solvents are shown using the open and solid circles in Figure 4. We have repeated their experiments at atmospheric pressure using the solvents *n*-hexane and isooctane and extended the range of solvents by including *n*-nonane. These results are shown using the open triangles. All of the atmospheric pressure data are given in Table IV and their viscosity dependence is represented by curve A (Figure 4).

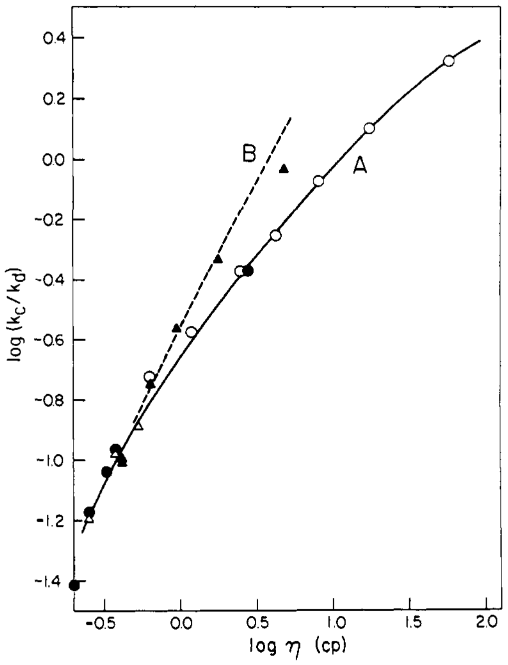

Figure 4. Viscosity dependence of the relative rate constants for combination (k_c) and separative diffusion (k_d) of geminate *t*-butoxy radicals from decomposition at 45° of 0.1 *M* DBH in various solvents (see text) at atmospheric pressure (●, ○, △) and in *n*-octane at various pressures (▲).

The values of log (k_c/k_d) from our high-pressure study using *n*-octane (45°) are also included in this figure (solid triangles). It can be seen that they lie above curve A. If it is assumed that the viscosity dependence of k_d is identical in both studies, this indicates that k_c is increased by increasing pressure and thus the activation volume for radical coupling (ΔV_c^*) is a negative quantity. This is in agreement with prediction.[4,20] If ΔV_c^* is −5 cc/mol and pressure in-

Table IV. Solvent Dependence of the Ratio k_c/k_d at Atmospheric Pressure (45°)[a]

Solvent[b]	η, cp[c]	k_c/k_d
n-Pentane	0.200	26.06
n-Hexane	0.250	14.89
		15.56[e]
n-Heptane	0.326	10.91
Isooctane	0.386[d]	9.204
		9.290[e]
n-Octane	0.420	9.886[e]
		10.23[e]
n-Nonane	0.527	7.674[e]
n-Octadecane	2.774	2.333
20% Nujol	0.626[d]	5.248
40% Nujol	1.161[d]	3.758
60% Nujol	2.512[d]	2.333
70% Nujol	4.280[d]	1.778
80% Nujol	7.989[d]	1.175
90% Nujol	17.59[d]	0.785
100% Nujol	46.50[d]	0.471

[a] All rate constant ratios except those indicated were determined by Traylor and Kiefer.[5] [b] All solutions 0.1 *M* DBH. [c] Viscosity of pure solvent at 45°. [d] These viscosity values are different than those originally reported[5] and represent revised data determined by Traylor; T. Traylor, personal communication. [e] Determined in this study.

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cyclohexyl-*t*-butoxy radical pair are +10 and +11 cc/mol, respectively. Analogous two-point values (1–4000 atm) for curves A and B are +14 and +15 cc/mol, respectively.

(16) (a) Lamb and Pacifici determined a value of $\Delta V_d^* - \Delta V_c^*$ for phenyl radical–trityl radical pairs formed from decomposition of phenylazotriphenylmethane in methylcyclohexane.[16b] They reported a "low-pressure" value of +51 cc/mol. It seems likely that this quantity could be subject to large error since the values of k_c/k_d were extremely small; (b) R. C. Lamb and J. G. Pacifici, *J. Phys. Chem.*, 70, 314 (1966).

(17) (a) D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Chem. Phys.*, **31**, 1555 (1959); (b) some of the values of activation volumes for self-diffusion (ΔV_D^*) determined at 28° and at pressures below 700 atm by McCall, *et al.*[17a] are: nitromethane, +13.6 cc/mol (1 atm), +6.5 cc/mol (500 atm); acetone, +13.0 cc/mol; benzene, +20.0 cc/mol; cyclohexane, +28 cc/mol; isopentane, +34 cc/mol (1 atm), +16 cc/mol (500 atm).

(18) See W. A. Steele and W. Webb in "High Pressure Physics and Chemistry," Vol. I, R. S. Bradley, Academic Press, New York, N. Y., 1963, pp 163–176.

(19) (a) The pressure dependence of a diffusion constant ($\partial \ln D/\partial P = -\Delta V_D^*/RT$) is not equal to that of the diffusion rate constant ($\partial \ln k_d/\partial P) = -\Delta V_d^*/RT$ since k_d is equal to a function containing not only the first power of D, but also the reciprocal of the two-thirds power of the molar (molecular) volume ($V^{2/3}$).[19b] The latter decreases with pressure leading to the result that values of ΔV_d^* for hydrocarbons are less than values of ΔV_D^* by about 2 cc/mol or less; (b) I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 59–64.

(20) No directly measured activation volumes for radical combination are available. Attempts have been made to obtain activation vol-

dependent, and curve A quantitatively reflects the viscosity dependence of k_d in the pressure study, the dashed curve B describes the theoretical relationship between log (k_c/k_d) and log η for the pressure study.[22] The deviation of the highest pressure point may indicate that ΔV_c^* is pressure dependent; however, the reasonable fit of the majority of the data to curve B indicates that the large observed pressure dependence of $\Delta V_d^* - \Delta V_c^*$ (Table IV) resides mainly in ΔV_d^* as proposed above.

It is interesting that the value of ΔV_c^* (−5 cc/mol) is approximately of the same magnitude as those obtained in several systems for the reverse homolytic scission process (+4 to +5 cc/mol). This suggests that overall reaction volumes for radical formation are on the order of +10 cc/mol (see introductory statement). While this differs greatly from the one such value measured (N_2O_4 dissociation; +20 cc/mol)[23] it is not clear that the comparison is significant.

The quantitative aspects of the analysis yielding ΔV_c^* depend in part on the placement of curve A and its significance. The data used to construct this curve were obtained in a variety of solvents at atmospheric pressure using the same DBH concentration and reaction temperature. The reproducibility between individual laboratories is indicated by a comparison of the data for *n*-hexane and isooctane. A basic assumption is that k_c is independent of the specific solvent composition. This is most certainly not true in view of the wide range of solvent variation from simple alkanes (solid circles, open triangles) to isooctane–Nujol mixtures ranging from 20 to 100% Nujol (open circles).[5] However, the magnitude of the variation is probably relatively small in comparison to the viscosity variation of k_d. Also, the functional dependence of k_d on viscosity may not be continuous throughout the series. It should be noted that the atmospheric pressure points for *n*-octane and isooctane show a distinct discontinuity, and one can envision separate curves for the low molecular weight hydrocarbons ($C_5 - C_9$) and the isooctane–Nujol mixtures.[24]

In view of these potential complications and the possibility of a third functional dependence of k_d on viscosity in the pressure study, the quantitative aspects of the comparison are tentative. The data do, however, support a negative value for ΔV_c^* and they encourage us to pursue these studies. The results may be improved by comparing pressure data with atmospheric pressure studies using pure *n*-alkane solvents rather than Nujol mixtures, and pressure data in different solvents should also be compared.

Experimental Section

Preparation of Di-*t*-butyl Hyponitrite, (a) Sodium Amalgam (0.64%). Clean mercury (2500 g, 184 ml) was allowed to react with clean sodium (16 g) following a modification of a published procedure.[25] *Only a very few drops of mercury were placed in contact with sodium to initiate the reaction.* Attempts to follow the procedure as published led to a violent reaction and explosion of the reaction flask.

(b) Silver Hyponitrite.[26] A 1-l. three-necked flask equipped with a mechanical stirrer, addition funnel, and a low-temperature thermometer was charged with an aqueous solution prepared by dissolving 20 g of sodium nitrite and 10 g of sodium hydroxide in 100 ml of water. The flask was cooled using a −25° Dry Ice-2-propanol bath. All of the sodium amalgam (*vide supra*) was added to the rapidly stirring solution at such a rate (1.5 hr addition time) that the temperature of the mixture did not rise above 0°. A white foam which formed during addition persisted when addition was complete. Sufficient cold water was added to dissolve the foam and the clear liquid was siphoned under a positive nitrogen pressure into a 2-l. erlenmeyer flask which had been precooled to −5°.

This solution was neutralized to pH 7.5–8 (Hydrion paper) using a solution prepared by mixing 85 ml of HNO_3 and 415 ml of H_2O. The temperature was not allowed to rise above 0° during neutralization. Mercuric oxide (5 g) was added, stirred for a few minutes, filtered through Celite, and the solution precisely neutralized with the nitric acid solution. A solution of 50 g of $AgNO_3$ in 100 ml of H_2O was then added rapidly. The resulting yellow precipitate was filtered, washed with hot water, and dried in the absence of light over P_2O_5 *in vacuo*. The surface of the solid, yellow silver hyponitrite sometimes turned green during drying. The yield was 4 g.

(c) Di-*t*-butyl Hyponitrite. This azo compound was prepared from silver hyponitrite (2 g) as described by Kiefer and Traylor.[8] The resulting red-brown mass was recrystallized three times from anhydrous methanol at −78° using an apparatus which allowed the operation to be carried out in the absence of moisture. The white needles were dried at room temperature by blowing dry nitrogen through them for 30 min. The yield was 400 mg; 43%.

As reported by Traylor, this compound showed infrared absorption bands at 2959, 1368, 1184, and 995 cm^{-1}. The compound was stored in the freezer until needed.

Solvents. Research grade *n*-heptane and pure grade *n*-hexane, *n*-octane, and *n*-nonane were obtained from the Phillips Petroleum Co.; isooctane (2,2,4-trimethylpentane) was obtained from Eastman Organic Chemicals. All solvents were used without further purification.

High Pressure Apparatus. The apparatus, sample cells, technique of operation, and specific details associated with its use in kinetic studies have been previously discussed.[1a] Pressure measurements using the bulk modulus cell were checked against those using a recently acquired manganin cell. The two cells gave identical pressure readings in the region of 4000 atm while the bulk modulus cell gave pressure readings about 4% higher than those from the manganin cell at pressures in the region of 6000 atm. These deviations are insignificant and do not affect the conclusions. Data from the bulk modulus cell are reported.

Kinetic Studies. All kinetic runs with the exception of two runs at 45° (see text and Table II) were carried out using samples of master solution prepared to be 0.01 *M* DBH in *n*-octane. The rate of decomposition of DBH was determined in all cases by monitoring its intense band in the infrared at 995 cm^{-1} using 1.0-mm sodium chloride cells in conjunction with a Perkin-Elmer 621 spec-

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umes for the termination step in radical polymerization (ΔV_t^*) from the overall pressure dependence of polymerization rates; however, the required assumptions and approximations leave the results very tenuous. Values of ΔV_t^* for the polymerization of styrene[21a] and vinyl acetate,[21b] respectively, were determined to be +18 and −5 cc/mol. In any case, termination activation volumes (ΔV_t^*) could reflect not only the volume change for coupling of geminate radicals (expected to be negative), but also that associated with the prerequisite diffusion-controlled encounter (expected to be positive). Hence values of ΔV_t^* may be quite different from typical values of ΔV_c^*.

(21) (a) A. E. Nicholson and G. W. Norrish, *Discussions Faraday Soc.*, 22, 104 (1956); (b) V. M. Zhulin, M. G. Gonikberg, and R. I. Baikova, *Bull. Acad. Sci., USSR, Div. Chem. Soc. (Eng. Transl.)*, 418 (1965).

(22) The dashed curve B was obtained by assuming that curve A describes the viscosity dependence of k_d in the pressure study. The value of −5 cc/mol was then used to calculate values of ln (k_c^P/k_c^0) at various pressures. These values of ln (k_c^P/k_c^0) were added to curve A using the relationship between pressure and viscosity of *n*-octane at 45° and curve B is the result.

(23) See W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 290 (1967).

(24) (a) It has been suggested[24b] that values of k_d may be proportional to $(1/\eta)^{1/2}$. Such a correlation is found for the k_c/k_d ratios determined using isooctane–Nujol mixtures,[24b] but the dependence of the k_c/k_d ratios using the pure low molecular solvents is closer to $1/\eta$ as predicted by the Stokes–Einstein and other relationships.[24c] No improvement in any of these correlations (including the data from the pressure study) was obtained by including additional dependences on density and/or molar volume variations; (b) T. Koenig, *J. Amer. Chem. Soc.*, **91**, 2558 (1969); (c) G. Houghton, *J. Chem. Phys.*, 40, 1628 (1964).

(25) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 1030.

(26) G. Brauer, "Handbook for Preparative Inorganic Chemistry," Vol. I, Academic Press, New York, N. Y., 1963, p 493.

trometer. Atmospheric pressure rate constants were obtained from analysis of samples of bulk solution (45°) and individual samples in sealed tubes (55°). Pressure samples were placed in Teflon tubes and handled as previously described.[1a] The infrared spectral data were treated essentially the same way as those for *t*-butyl phenylperacetate in order to obtain decomposition rate constants.[1a]

Product Ratio Studies. All product studies were carried out using samples of master solutions prepared to be 0.1 *M* DBH in the various solvents. Samples were decomposed at 45.00 ± 0.01° for greater than seven half-lives either in sealed tubes (atmospheric pressure) or in Teflon tubes (high pressure). The ratio of DBP to TBA was determined from glpc analyses using standard solutions containing both components. Area ratios were determined using a Disc integrator in conjunction with an L and N Model H recorder. Error limits were calculated using the extreme values of area ratios for standard and reaction solutions. Absolute product yields confirmed the quantitative formation of DBP and TBA.

Analyses of *n*-octane solutions were carried out using either a 24 ft × $^1/_8$ in. stainless steel column packed with 20% Apiezon L on 60–80 firebrick AW at an oven temperature of 105° (30 ml/min He flow) in conjunction with an F & M Model 700 gas chromatograph, or a 15 ft × $^1/_8$ in. stainless steel column packed with 20% Apiezon L and 0.15% polypropylene glycol on 60–80 Chromosorb P AW-DMCS at an oven temperature of 105° (20 ml/min N_2 flow) in conjunction with an Aerograph Hi-Fi Model 600 C flame ionization gas chromatograph. Solutions in all other hydrocarbons were analyzed using a 35 ft × $^1/_8$ in. copper column packed with 20% Carbowax 20M on 60–80 firebrick AW at an oven temperature of 75° (20 ml/min N_2 flow) in conjunction with the flame ionization gas chromatograph.

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Cyclopropanes. XXV. The Cyclopropyl Anion[1]

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Abstract: The rate of hydrogen–deuterium exchange and rate of racemization of 2,2-diphenylcyclopropylnitrile (**1**) and its acyclic analog 2-methyl-3,3-diphenylpropionitrile (**2**) have been investigated. The cyclic nitrile exhibits a very high degree of retention of configuration in methanol, *t*-butyl alcohol, and methanol–dimethyl sulfoxide (10:90) using sodium alkoxide as the base. In contrast, extensive racemization was observed for the acyclic nitrile. Small kinetic isotope effects ($K_H/K_D \approx 2$) were observed with both nitriles. These observations in conjunction with results of ancillary studies are interpreted by us to show that proton abstraction by base is *not rate determining* in both the exchange and racemization reaction of 2,2-diphenylcyclopropylnitrile (**1**).

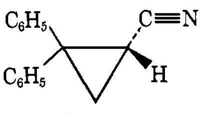
The general subject of carbanion chemistry has been reviewed recently by Cram in his excellent monograph.[2] We have, over the years, been interested in the stereochemical fate of the cyclopropyl anion and have reported that in aprotic solvents the 1-lithium[3] and 1-sodium[4] derivatives of 1-methyl-2,2-diphenylcyclopropane are capable of maintaining their configuration to a large degree. On the other hand, when the 1-methyl group is replaced by a cyano group the 1-lithium derivative was incapable of maintaining its configuration.[5]

In contrast to the results found in aprotic solvents, the 2,2-diphenylcyclopropylnitrile (**1**) was shown to be capable of retaining its configuration in protonic solvents.[6] In this article we wish to present our data on the rates of racemization and hydrogen–deuterium exchange of **1** and its acyclic analog, 2-methyl-3,3-diphenylpropionitrile (**2**). Data will also be given which will demonstrate that proton abstraction by base is not the rate-determining step in the exchange and racemization reaction of **1**.

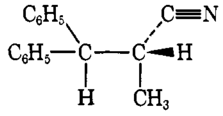
Results and Discussion

The synthesis of **1** has previously been described[5] but the 1-deuterio and 1-tritio derivative of **1** as well as the synthesis of **2** have not and they may be found in the Experimental Section. The absolute configurations given for **1** and **2** are based on the previously determined absolute configurations of their precursor carboxylic acids.[7]

Exchange and Racemization Rates. The kinetic methods used are discussed in the Experimental Section. The second-order rate constants were determined by dividing the pseudo-first-order rate constants by the base concentration. The first-order rate plots yielded straight lines in all cases studied.



(−)-(*R*)-**1**



(+)-(*R*)-**2**

Racemization of (−)-(*R*)-2,2-Diphenylcyclopropylnitrile (1). The above data (Tables I–III) show that the reaction of **1** with metal alkoxides in polar protic solvents occurs with a very high degree of retention of configuration. Asymmetric solvation, as defined by Cram, must be unimportant in this instance since the highest degree of retention of configuration is observed in methyl alcohol, a "racemization" solvent.[8] A high

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[1] The support of this work by grants from the National Science Foundation and Public Service Research Grant No. CA 04065 from the National Cancer Institute is gratefully acknowledged.

[2] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

[3] H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964).

[4] J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968).

[5] H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, **77**, 6026 (1955).

[6] H. M. Walborsky, A. A. Youssef, and J. M. Motes, *ibid.*, **84**, 2465 (1962).

[7] H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).