

not isolated. B_6H_{10} reacts cleanly with $(CH_3)_2S$ to produce a white product.

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Robert E. Williams, F. James Gerhart

Space-General Corporation
El Monte, California

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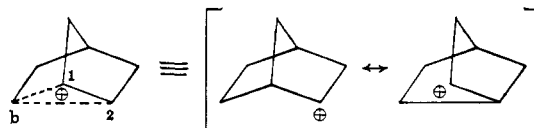
The Activation Volumes in the Solvolysis of *exo*- and *endo*-2-Norbornyl Brosylate

Sir:

It has been known for many years that ionization is accompanied by a net decrease in volume, typically of about 20 cm.³/mole, due to the very large forces exerted by the ions on surrounding molecules (electrostriction).¹ The magnitude of this volume change, ΔV , is dependent on the solvent, the temperature, the pressure, and the magnitude (and possibly the sign) of the charge; the same remarks apply to the activation volumes, ΔV^* , of reactions in which ionization represents the rate-controlling step. Drude and Nernst² showed that ΔV is furthermore affected by the degree of dispersion of the charge: for n charges of q it is twice as great as that for $2n$ charges of $1/2q$.³ It occurred to us that for this reason knowledge of ΔV^* might provide an added insight into the nature of the transition states leading to classical and nonclassical carbonium ions.

The carbonium ions formed from *endo*- and *exo*-2-norbornyl derivatives have been much discussed. The latter substrates generally are solvolyzed 10^{2-3} times faster than the former, and two schools of thought have developed to explain this difference. According to one of these,⁴ the cation formed from the *exo* compounds is stabilized by resonance, permitting relief of steric strain and involving delocalization of the positive charge to the C-1 carbon atom, and possibly the C-6 atom as well; this delocalization is presumed also to lower the free energy of the transition state preceding the ion. Such participation would not be possible in the *endo* transition state, since the developing p-orbital is not suitably oriented. The alternative point of view is that the *exo*-2-norbornyl derivatives solvolyze at normal rates and that their isomers are retarded by steric interference of the *endo* hydrogen atoms with ionization.⁵ Besides solvolysis rates, the criteria used to date have included product composition,⁶ stereo-

chemistry,⁴ the spectral properties of a number of stable carbonium ions,⁷ the effect of substituents on solvolysis rates,⁸ empirical calculations of the rate constants,⁹ and the rates of model compounds.¹⁰



A nonclassical transition state is by definition characterized by a diffuse charge, and hence its formation would presumably involve a smaller volume change than a normal, classical transition state. Since $\Delta V^* = -RT(\partial \ln k/\partial p)$, this means that solvolysis of *exo*-2-norbornyl brosylate should be accelerated by the application of pressure, but less so than that of cyclopentyl brosylate, the model compound used in this study. The magnitude of this difference may be estimated as follows. If it is assumed that half of the electrostriction is due to the cation, and that half of this is lost due to the distribution of the positive charge between (at least) two sites, $\Delta V^*_{exo} - \Delta V^*_{CyPe}$ is expected to be about 4 cm.³/mole (about $1/4\Delta V^*_{CyPe}$). In practice, the difference would be somewhat smaller as the two sites are not infinitely far apart and not yet completely equivalent, as assumed in the derivation by Drude and Nernst. No difference is expected between ΔV^*_{CyPe} and ΔV^*_{endo} . When the alternative point of view is examined, it is anticipated that the *endo* isomer, its ionization retarded because of steric hindrance, will be characterized by a volume diminution greater than that of cyclopentyl brosylate; in accordance with the Hammond postulate, the incipient ions should be more highly developed and thus have a greater effect on the surrounding solvent. No difference is now expected between ΔV^*_{CyPe} and ΔV^*_{exo} .

A difference of several cm.³ is a small one to look for. None of the additional factors that might affect the magnitude of the activation volumes (the temperature, the solvent, and the anion) were therefore varied in these experiments; the cations were the only variables. The rate constants were measured by means of the standard titrimetric method¹¹ with excellent precision (1-2%). The usual high-pressure apparatus was used¹² and the results obtained are well outside the limits imposed by the experimental technique (see Table I and Figure 1). The data show that at atmospheric pressure¹³ $\Delta V^*_{exo} - \Delta V^*_{CyPe} = 3.5 \pm 1$ ml., a value which is in accord with the view that the *exo* transition state is characterized by participation. The alternative prediction that $\Delta V^*_{CyPe} - \Delta V^*_{endo} > 0$ is not borne out. At atmospheric pressure the two are equal, and at higher pressures the activation volume

(1) See, e. g., S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, Chapters VIII and IX.

(2) P. Drude and W. Nernst, *Z. phys. Chem.*, **15**, 79 (1894).

(3) Experimental support for this contention is provided by inspection of a list of values of ΔV for the ionization of various acids (for a recent compilation, see L. G. Hepler, *J. Phys. Chem.*, **69**, 965 (1965)). Thus, for dibasic acids ΔV_2 is invariably greater by nearly 10 cm.³/mole than ΔV_1 ; for citric acid, $\Delta V_3 > \Delta V_2 > \Delta V_1$; $\Delta V_{H_2O} > \Delta V_{phenol} > \Delta V_{RCOOH}$; $\Delta V_{phenol} > \Delta V_{p-NO_2-phenol}$, etc. Similar but more limited observations apply to the ionization of amines.

(4) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 377 (1965).

(5) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 155; H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(6) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2423 (1963).

(7) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *ibid.*, **85**, 479 (1963).

(8) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964).

(9) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(10) H. C. Brown and F. J. Chloupek, *ibid.*, **85**, 2322 (1963).

(11) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952); H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(12) W. le Noble, *ibid.*, **85**, 1470 (1963).

(13) At higher pressures all activation volumes and the differences between them rapidly diminish; this curvature, commonly observed in such plots, shows that a relatively dense transition state is also relatively incompressible.

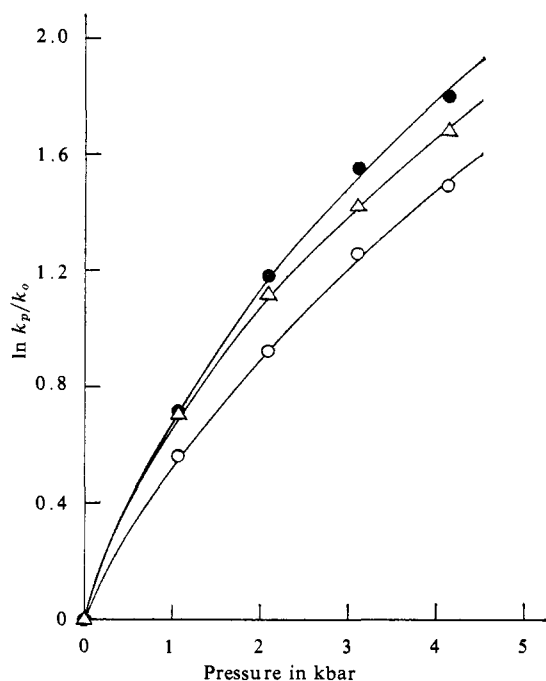


Figure 1. The effect of pressure on the hydrolysis rates of several brosylates: \circ = *exo*; Δ = *endo*; \bullet = cyclopentyl.

for the solvolysis of cyclopentyl brosylate is actually the *more* negative of the two.

Table I. The Effect of Pressure on the Rates of Solvolysis of *exo*- and *endo*-2-Norbornyl and -Cyclopentyl Brosylate in Aqueous Acetone^a at 40.0°

Pressure, kbar	<i>exo</i> ^b	10 ⁶ k ₁ , sec. ⁻¹	
		CyPe ^b	<i>endo</i> ^c
0.00	40.8	7.12	0.229
1.07	71.8	14.6	0.464
2.07	103	23.3	0.705
3.10	144	33.8	0.945
4.14	182	47.9	1.23
ΔV_0^* (cm. ³ /mole) ^d	14.3 ± 0.5	17.7 ± 0.5	17.8 ± 0.5

^a Containing 6% water by weight. ^b Each rate constant was calculated from five determinations; the reaction was followed to about 75%. ^c The rate constant was calculated from four determinations; the reaction was followed to about 30%. ^d Calculated by means of a second-order least-squares equation.

Our conclusion is open to the following questions. It may be argued that a low value for ΔV_0^* may be due to some peculiar packing feature which gives rise to a small partial molar volume of the *exo*-brosylate, a feature that does not occur with the other two substrates or with any of the three transition states.¹⁴ One may also argue that the same steric feature which presumably hinders ionization of the *endo* isomer also hinders solvation of the *exo* transition state, and that hindrance to ionization has a much greater effect on the free energy of activation than hindrance to solvation, but a much smaller effect on the volume of activation. Such arguments are difficult to meet except by

(14) One of the referees suggested that a second consequence of participation, the partial transannular bond, might tend to make the nonclassical *exo*-transition state somewhat more compact. If any correction were made for this effect, the conclusion would be that the result of charge dispersal alone is somewhat larger than 3.5 cm.³/mole.

means of further evidence, and we are therefore studying additional examples of solvolyses reputed to involve these controversial intermediates.

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W. J. le Noble, Brian L. Yates

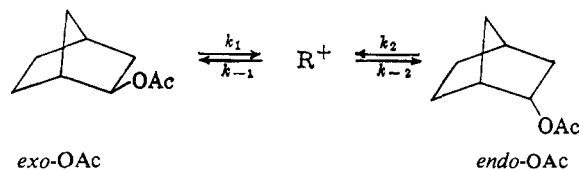
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York
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On the Stereoselectivity of Chemical Capture of the Norbornyl Cation¹

Sir:

Evidence for a symmetrical nonclassical carbonium ion in the norbornyl system includes: (1) stereoselective *exo* attack by solvent, (2) the symmetry properties of the cation, and (3) anchimerically accelerated rates of ionization of *exo* norbornyl derivatives.^{2,3} With regard to the stereoselectivity, *exo* attack predominates to the extent that *endo* isomers have not been detected in products resulting from irreversible solvent capture of the carbonium ion involved in solvolytic reactions.²⁻⁵ Recently, upper limits for the amount of *endo* isomer (*endo* attack) in solvolysis products have been lowered to 0.3^{4a}–0.5%^{6a} for acetolysis and 0.02%^{2a} for hydrolysis in 75% acetone.

We now report an investigation that provides a quantitative measure of the ratio of *exo* to *endo* attack (k_{-1}/k_{-2}) for solvent capture of the norbornyl cation in anhydrous acetic acid. The method involves comparison of rates of acid-catalyzed (HClO₄) loss of optical activity (reaction 1) of *exo*-norbornyl acetate (*exo*-OAc) and equilibration of the isomeric acetates (reaction 2). The rate of reaction 1 corresponds to that of formation of the carbonium ion (irreversible solvent capture gives completely racemic products)^{2a} and the forward rate of reaction 2 measures the rate of *endo* attack. The rate of acetate exchange (reaction 3) associated with these transformations was also determined. The data also provide relative rates of acid-promoted ionization (k_1/k_2) of the epimeric acetates.



(1) Research supported by the National Science Foundation, the National Institutes of Health, and the Wisconsin Alumni Research Foundation.

(2) S. Winstein, *et al.*: (a) *J. Am. Chem. Soc.*, **87**, 376 (1965); (b) *ibid.*, **87**, 381 (1965), and references therein.

(3) For references through early 1962 see J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(4) S. Winstein, *et al.*: (a) *J. Am. Chem. Soc.*, **84**, 4993 (1962); (b) *ibid.*, **74**, 1147, 1154 (1952).

(5) (a) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); R. G. Lawton, *ibid.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); E. J. Corey, *et al.*, *ibid.*, **85**, 169 (1963).