

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.

Acknowledgment. Generous support by the National Science Foundation is gratefully acknowledged. Professors H. C. Brown and P. von R. Schleyer have kindly commented on this paper.

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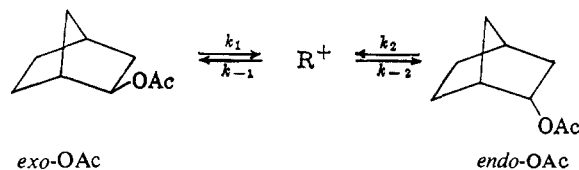
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Received May 13, 1965

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.



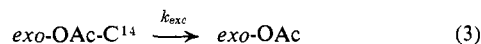
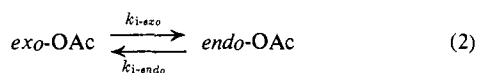
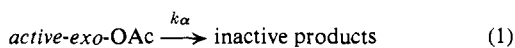
(1) Research supported by the National Science Foundation, the National Institutes of Health, and the Wisconsin Alumni Research Foundation.

(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).



Rate constants for reactions 1–3 are presented in Table I. All reactions are cleanly pseudo first order, and rates are proportional to acid concentration over the range 0.02–0.45 M. The constants in the table are second-order catalytic constants (i.e., $k/[\text{HClO}_4]$) and most are averages of several independent determinations for different acid concentrations. Reactions were followed by methods outlined earlier,⁶ and isomerization constants, k_{i-exo} and k_{i-endo} , were determined from the rate constant for irreversible equilibration ($k_{i-exo} + k_{i-endo}$) and the equilibrium constant for reaction 2; $K_{eq} = k_{i-exo}/k_{i-endo}$. The same values of K_{eq} and $k_{i-exo} + k_{i-endo}$ were obtained with both isomers. To maintain constant ionic strength and avoid other variations that might affect the rates, solvents for the various experiments were prepared from the same stock solutions of 0.45 M HClO_4 and 0.45 M LiClO_4 in anhydrous acetic acid.⁷

Table I. Catalytic Second-Order Constants for Acid-Catalyzed Transformations of Norbornyl Acetate in Acetic Acid^a

Temp., °C.	$10^3 k_\alpha$, ^b l. mole ⁻¹ min. ⁻¹	$10^3 k_{exc}$ l. mole ⁻¹ min. ⁻¹	$10^4 k_{i-exo}$ ^c l. mole ⁻¹ min. ⁻¹	$10^2 K_{eq}$ ^d
24.92	17.1 ± 0.1	13.1 ± 0.1		
36.61	85.7 ± 0.1			
48.90	411 ± 2	327 ± 4	0.81 ± 0.04	18.8 ± 0.6
78.46			40.5 ± 0.9	22.4 ± 0.9
99.41			440 ± 30	24.2 ± 0.3

^a $[\text{HClO}_4] = 0.02\text{--}0.45$ M; acid concentrations (25°) not corrected for thermal expansion of the solvent. ^b $E_a = 25.3 \pm 0.1$ kcal. mole⁻¹. ^c $E_a = 30 \pm 1$ kcal. mole⁻¹. ^d $\Delta H = 1.20 \pm 0.21$ kcal. mole⁻¹.

From the kinetic behavior it is apparent that these processes involve reversible protonation of the substrate followed by first-order transformations of the conjugate acids of the acetates. The observed constants are related to those in the scheme as follows.

$$k_\alpha = k_1 \quad (4)$$

$$k_{i-exo} = k_1 k_{-2} / (k_{-1} + k_{-2}) \quad (5)$$

$$k_{i-endo} = k_2 k_{-1} / (k_{-1} + k_{-2}) \quad (6)$$

Thus

$$k_\alpha / k_{i-exo} = (k_{-1} / k_{-2}) + 1 \quad (7)$$

and

$$K_{eq} = (k_1 / k_2) (k_{-2} / k_{-1}) \quad (8)$$

The partition (k_{-1}/k_{-2}) and reactivity ratios (k_1/k_2) determined from these relationships are presented in Table II. The necessary extrapolations of k_α to higher temperatures and k_{i-exo} and K_{eq} to lower temperatures

(6) H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **84**, 2779 (1962).

(7) Both stock solutions contained 0.6% acetic anhydride which has a negligible effect on the rates. Traces of water cause a remarkable decrease in rates; e.g., at an acid concentration of 0.2 M, rates are decreased 25 and >98% by 0.1 and 2% water, respectively.

Table II. Partition and Reactivity Ratios for Acid-Catalyzed Isomerization of Norbornyl Acetates in Acetic Acid

Temp., °C.	k_{-1}/k_{-2} ^a	k_1/k_2 ^a
24.92	9140 ± 880	1480 ± 190
36.61	6800 ± 470	1180 ± 100
48.90	5070 ± 290	953 ± 87
78.46	2810 ± 100	629 ± 49
99.41	1980 ± 190	479 ± 53

^a Uncertainties estimated from limiting values of the rate and equilibrium constants.

were made in the usual manner. In all cases the logarithmic plots were linear.

The k_{-1}/k_{-2} ratios correspond to 99.99 and 99.95% *exo* attack at 25 and 100°, respectively. As predicted by this ratio, acetolysis of *endo*-free *exo*-OTs in the presence of acetate ion at 100° (*exo*-OTs was added to the preheated solvent) gives *exo*-OAc containing 0.05 ± 0.02% *endo*-OAc. The *endo* isomer was barely, but reproducibly, detectable (ca. 0.01%) in the product resulting from acetolysis at 30°. Comparison of k_α and k_{exc} shows that ionization does not result in complete exchange. For reasons outlined elsewhere⁸ this is not unexpected.

The apparent activation energies (E_a) and ΔH in Figure 1 were determined in the usual manner; ΔE_a was determined from the temperature dependence of the

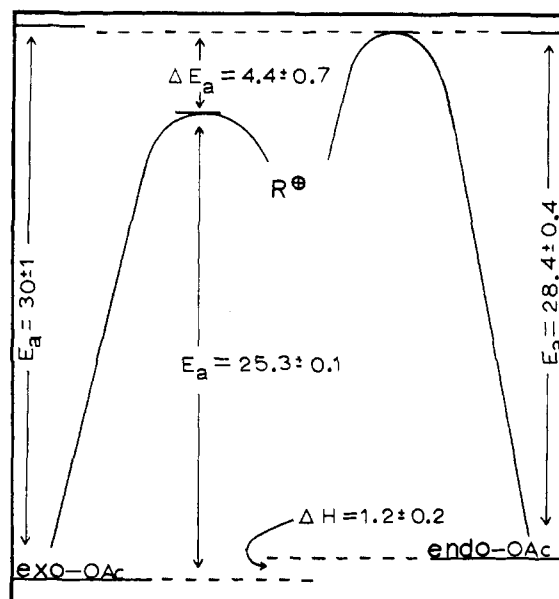


Figure 1. Apparent activation energies (E_a) for acid-catalyzed reactions of *exo*-OAc and *endo*-OAc and ΔH for equilibration.

k_α/k_{i-exo} ratio. The partition and reactivity ratios and ΔE_a are consistent with earlier estimates based on solvolytic studies.² As discussed elsewhere,^{2,4} the lower transition state energy for the *exo* than for the *endo* isomer is important evidence for the nonclassical structure for the carbonium ion; i.e., delocalization lowers the *exo* transition state energy about 4 kcal. mole⁻¹. The data do not provide information con-

(8) H. L. Goering and R. E. Dilgren, *J. Am. Chem. Soc.*, **82**, 5744 (1960).

cerning the mechanistic pathway connecting R^+ and the *endo* isomer. Presumably the classical ion is an intermediate in this step.²⁻⁵ It seems likely that the barrier for capture of the nonclassical ion is larger than that for capture of the less stable classical ion, in which case ΔE_a represents a lower limit for the energy difference of the classical and nonclassical ions.

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Received April 26, 1965

Alkali Fluoride Complexes of Tetravalent Protactinium

Sir:

We wish to report the first preparation of alkali fluoride complexes of *tetravalent protactinium*. The compounds were prepared by two methods: (1) vacuum heating of PaF_4 with alkali fluoride, and (2) hydrogen reduction of pentavalent protactinium compounds, which was the method yielding purer preparations. Compounds of tetravalent protactinium were obtained which are isostructural with known compounds of tetravalent uranium. In fluorine, the tetravalent protactinium compounds are oxidized to the starting compounds of pentavalent protactinium, identified by their own characteristic X-ray powder patterns. This hydrogen reduction-fluorine oxidation cycle can be repeated. Although a number of fluoride complexes of *pentavalent* protactinium are known, e.g., K_2PaF_7 ,² $MPaF_6$ ($M = NH_4, K, \text{ and } Rb$),³ and Na_3PaF_8 ,⁴ no fluoride complexes of *tetravalent* protactinium have been reported previously.

In our recent studies of MXF_6 compounds ($X = U \text{ or } Pa; M = \text{alkali}$)^{5,6} it was shown that $RbUF_6$ and $RbPaF_6$ are isostructural; more recent single crystal measurements have established their structure as orthorhombic.⁶ In the review of the alkali fluoride-uranium tetrafluoride systems by Thoma,⁷ it was shown that rhombohedral compounds of the type $7MF \cdot 6UF_4$ occur frequently, and a prediction of this structure for the then unknown compound $7RbF \cdot 6PaF_4$ was made. Thus, X-ray powder techniques offered an excellent method of establishing both the reduction of protactinium(V) fluoride complexes to protactinium(IV) compounds and also the reverse reaction.

The chemistry of the conversion was investigated as follows. Into a depression ground in a sapphire dish was placed a few milligrams of RbF and PaF_4 in the mole ratio $Rb:Pa = 7:6$. Into another sapphire dish was placed crystalline $RbF \cdot PaF_5$ prepared as previously described.³ Both materials were heated in a fluorine atmosphere (1-1.2 atm.) for ~ 2 hr. at 390° . X-Ray powder patterns established that $RbF \cdot PaF_5$ was the only phase detectable in each sample. Without

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) A. V. Grosse, *J. Am. Chem. Soc.*, **56**, 2501 (1934); *Proc. Roy. Soc. (London)*, **A150**, 363 (1935).

(3) L. B. Asprey and R. A. Penneman, *Science*, **145**, 924 (1964).

(4) D. Brown and J. E. Easey, *Nature*, **205**, 589 (1965).

(5) R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

(6) L. B. Asprey, F. H. Kruse, and R. A. Penneman, manuscript in preparation.

(7) R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

removal from the sapphire dishes, they were then exposed to very pure hydrogen (made from UH_3) for 4 hr. at 450° . The X-ray powder patterns of the reduction products showed that rhombohedral $7RbF \cdot 6PaF_4$ was the major phase in each case; it was isostructural with $7RbF \cdot 6UF_4$. Treatment with fluorine oxidized both samples to the original orthorhombic $RbPaF_6$ phase. Hydrogen reduction again formed the rhombohedral protactinium(IV) compound.

Identification of the tetravalent protactinium compound was accomplished by comparison with our X-ray data⁸ for rhombohedral $7NH_4F \cdot 6UF_4$ and with the $7RbF \cdot 6UF_4$ data listed by Brunton, *et al.*⁹ A partial list of the indexed X-ray powder pattern data for $7RbF \cdot 6PaF_4$ is given in Table I.

Table I.^a X-Ray Powder Pattern Data for $7RbF \cdot 6PaF_4$

<i>hkl</i>	<i>I/I</i> ₀	<i>d</i> _{obsd.} , Å.	<i>d</i> _{calcd.} , Å.
101	7	8.36	8.32
110	2	7.73	7.71
021	3	5.65	5.66
012	4	4.98	4.94
211	4	4.58	4.56
300	3	4.45	4.45
202	2	4.18	4.16
220	2	3.85	3.86
122	2	3.70	3.66
221	2	3.58	3.58 ^b
003	10	3.51	3.54
131			3.50

^a Cu K α radiation, Debye-Scherrer camera, 114.6 mm., Ilford "G" film; hexagonal indices, space group $R3-C_3$; ²; $a_0 = 15.43$, $c_0 = 10.63$ Å. (rhombohedral, $a_0 = 9.587$ Å., $\alpha = 107^\circ 9'$).

^b This line appears in typical patterns; not indexable in $R\bar{3}$.

Further work with the remaining alkali and ammonium fluorides is in progress.

(8) R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *ibid.*, **2**, 799 (1963).

(9) G. D. Brunton, H. Insley, T. M. McVay, and R. E. Thoma, ORNL-3761, Feb. 1965.

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Received May 8, 1965

σ -Overlap of p-Orbitals in Cyclic π -Electron Systems. *cis,cis,cis*-1,5,9-Cyclododecatriene

Sir:

Recently investigated^{1a-g} *cis,cis,cis*-1,4,7-cyclononatriene (I) is a cyclic six- π -electron system wherein σ -overlap of the p-orbitals could have been significant. Whether this overlap lowers the ground-state energy below that expected for the same cyclic system composed of "isolated" double bonds remains undecided in the case of I.^{1a,f,g} The important feature of this kind of system is not that the double bonds be homo-

(1) (a) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963); (b) K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963); (c) *J. Mol. Spectry.*, **14**, 156 (1964). For another synthesis and other properties see (d) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); (e) W. R. Roth, *Ann.*, **671**, 10 (1964); (f) W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *J. Am. Chem. Soc.*, **86**, 3178 (1964); (g) S. Winstein and F. P. Lossing, *ibid.*, **86**, 4485 (1964).