Table I. Primary Hydration Number of Trimethylplatinum(IV)[a]

$[(CH_3)_3Pt^+]$, *m*	$[Dy^{+3}]$, *m*	$[H^+]$, *m*	δ_{H_2O},[b] ppm	$\delta_{H_2O}{}^b/[Dy^{+3}]$, ppm m^{-1}	δ_{H_2O},[c] ppm	$\delta_{H_2O}{}^c/[Dy^{+3}]$, ppm m^{-1}
2.167	0.434	0.520	212 ± 2	488		
1.969	0.802	0.486	397 ± 2	495	449 ± 1	560
1.758	1.197	0.451	585 ± 2	489	661 ± 2	552
0	0.406	0.051	188 ± 2	463		
0	0.829	0.033	380 ± 2	458	413 ± 1	498
0	1.194	0.043	547 ± 2	458	599 ± 1	502

[a] Resonance measured at 7.66 Mc/sec; solutions enriched to 4.5 atom % ^{17}O. [b] At 29°. [c] At 5°.

hedral platinum(IV) and d^6 complexes, in general,[6] illustrates the labilizing effect on the other ligands caused by alkyl groups in the first coordination sphere. This has been recognized previously for platinum(II) complexes.[7] It seems likely that the coordinated water molecule in aquocobalamin (vitamin B_{12a}) which is *trans* to a carbanion ligand in this d^6 cobalt complex has at least as high an exchange rate, and this is in agreement with the observation that substitution reactions proceed rapidly at this site.[8–10]

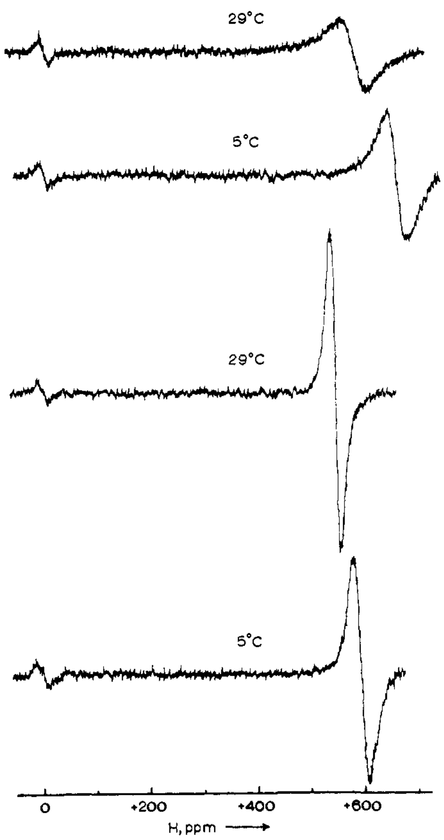


Figure 2. Bulk-water resonance with respect to an external water sample. Solution composition: (top spectra) 1.758 *m* $(CH_3)_3PtClO_4$, 1.197 *m* $Dy(ClO_4)_3$, 0.451 *m* $HClO_4$; (bottom spectra) 1.194 *m* $Dy(ClO_4)_3$, 0.043 *m* $HClO_4$.

Since the suggestion by Jackson, Lemons, and Taube that oxygen-17 nmr might be used to count the number of water molecules in the first coordination sphere of metal ions,[4] hydration numbers have been determined only for Be^{+2} (4.2 ± 0.1,[11] 3.8 ± 0.1[3]), Al^{+3} (5.9 ± 0.1[3,11]), and Ga^{+3} (6.28 ± 0.26, 5.89 ± 0.20;[12] 5.9 ± 0.1[13]).

---

[6] For example, the half-life for exchange of $Rh(OH_2)_6{}^{+3}$ is *ca.* 33 hr at 64.4°: W. Plumb and G. Harris, *Inorg. Chem.*, **3**, 542 (1964).

[7] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[8] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *Chem. Commun.*, 400 (1967).

[9] J. M. Pratt and R. G. Thorp, *J. Chem. Soc., Sect. A*, 187 (1966).

[10] G. C. Hayward, H. A. O. Hill, J. M. Pratt, N. J. Vanston, and R. J. P. Williams, *J. Chem. Soc.*, 6485 (1965).

[11] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1749 (1963).

[12] D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).

[13] T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *ibid.*, **46**, 40 (1967).

[14] NASA Trainee, 1964–1967.

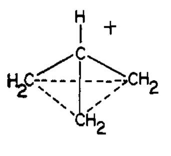
Gary E. Glass,[14] R. Stuart Tobias
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received August 24, 1967

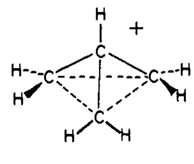
Stability and Symmetry of the 8,9-Dehydro-2-adamantyl Cation

Sir:

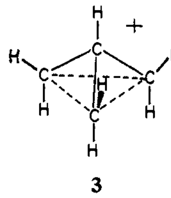
A nonclassical tricyclobutonium ion intermediate with C_{3v} symmetry (**1**) was initially proposed[1,2] to rationalize the unexpectedly high reactivity of cyclopropylcarbinyl halides[3] and benzenesulfonate[2] and the remarkable degree of equivalence achieved by the three methylene groups during the nitrous acid deamination of cyclopropylcarbinylamine-α-C^{14}.[1] It has subsequently gained disfavor as an intermediate, but retained prominence as a possible transition-state species connecting other less symmetrical ions.[4,5] Of the two geometries for a tricyclobutonium ion, **2** and **3**, the former has seemed favored by molecular orbital calculations[6] and the latter by geometrical considerations.[4]



1



2



3

We now report that the solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (**4**), a system potentially capable of generating a carbonium ion of C_{3v} symmetry geometrically analogous to **3** but unable to adopt a form similar to the alternative conformation **2**, occurs with the marked rate acceleration characteristic of cyclopro-

---

[1] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

[2] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[3] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

[4] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[5] P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966), and references therein.

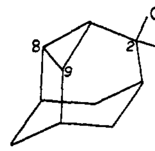
[6] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963).

Table I. Deuterium and Tritium Labeling Results for Solvolyses of 2-Deuterio- and 2-Tritio-8,9-dehydro-2-adamantyl 3,5-Dinitrobenzoate in 60% Aqueous Acetone

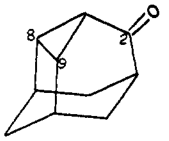
				Ketone **5** act., %		
Run	Starting alcohol (**6**) act., %[a]	Product alcohol act., %	Added 2,4,6-collidine, equiv	From starting alcohol	From equild[b] starting alcohol	From product alcohol
1, 2-*d*	102	100	0	1	25	65
2, 2-*t*	107	100	1.4	3	16	60
3, 2-*d*	104	100	4	6	8	59
4, Theoretical for C_{3v} symmetric ion		100				66.7

[a] The absolute activities of the starting alcohols were 90% d_1, 10% d_0; 11.9 μcuries/mmole; 94% d_1, 6% d_0. [b] From equilibration of the starting alcohol under the solvolysis conditions with 1 equiv of added 3,5-dinitrobenzoic acid and oxidation to the ketone with chromium trioxide.

pylcarbinyl systems,[7–9] and during the solvolysis the original 2, 8, and 9 positions achieve nearly complete equivalence.



4, R = $C_7H_3N_2O_5$
6, R = H



5

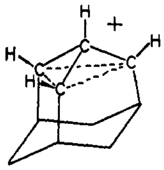
Reduction of 8,9-dehydro-2-adamantanone (**5**),[10] $\bar{\nu}_{max}$ (CCl_4) 1705 cm^{-1}, with sodium borohydride gave the alcohol **6**, mp 211–213°,[11] which was converted to its 3,5-dinitrobenzoate, mp 121.5–122.5°. Solvolytic rate constants in 60% aqueous acetone for this 3,5-dinitrobenzoate were 7.78×10^{-6} sec^{-1} at 45.02°, 4.73×10^{-5} sec^{-1} at 59.97°, and 2.37×10^{-4} sec^{-1} at 74.30°. From these rate constants, $\Delta H^{\ddagger} = 25.6$ kcal/mole and $\Delta S^{\ddagger}$ (25°) = −1.6 eu. These solvolyses afforded a 95% yield of 8,9-dehydro-2-adamantanol (**6**).

The 2-deuterio and 2-tritio analogs of alcohol **6** were prepared with labeled borohydrides. Oxidation of these alcohols with chromium trioxide and dry pyridine gave the corresponding ketone **5** with loss of almost all of the activity. Solvolyses of the derived 3,5-dinitrobenzoates (**4**, position 2 labeled) led to nearly complete scrambling of the label in the recovered alcohol. Subjection of the labeled alcohols to the solvolytic reaction conditions in the presence of 1 equiv of 3,5-dinitrobenzoic acid gave partial scrambling of the label. The results are summarized in Table I.

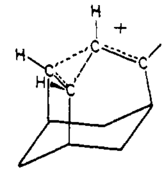
Using a factor of 500 for converting solvolysis rates for 3,5-dinitrobenzoates in 60% aqueous acetone at 100° to solvolysis rates for tosylates in acetic acid at 25°,[5,12,13] one may estimate 15×10^{-1} sec^{-1} for the rate of acetolysis of 8,9-dehydro-2-adamantyl tosylate at 25°.[14] The rate acceleration above what would be expected if a classical ion were formed is some 10^5–10^6.[15,16]

The deuterium contents were determined with an Atlas CH4 mass spectrometer using a variable-temperature vacuum-lock inlet system; the tritium activities were determined by liquid scintillation counting. The sources of error in the two methods are dissimilar, and one may have confidence in their common result: the 2, 8, and 9 positions of the dehydroadamantyl system attain a high degree of equivalence during the solvolysis reaction. Thus, access to the tricyclobutonium ion geometry of **2** is not mandatory for positional equilibrations in potentially C_{3v} symmetric systems.

Any rationalization of the kinetic and isotopic labeling results through the C_{3v} symmetric nonclassical cationic intermediate **7** would be censured on theoretical grounds.[5,6]



7



8

The geometrical framework of the dehydroadamantyl system affords ready access to the symmetrical "bisected" ion **8**,[5] thus accounting for the kinetic data. The labeling experiments, and the theoretically based strictures against tricyclobutonium ions as intermediates or transition states, lead us to postulate a rapid equilibration of "bisected" ions through a transition state having a plane but no higher element of symmetry.

Acknowledgments. We wish to thank Dr. R. F. Nystrom for his help with the tritium analyses and Mr. J. Wrona for running the mass spectra.

J. E. Baldwin,[17] **W. D. Foglesong**[18]
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois 61801

Received July 10, 1967

---

(7) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(8) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1856 (1964).

(9) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

(10) J. E. Baldwin and W. D. Foglesong, *Tetrahedron Letters*, 4089 (1966).

(11) This and all other new compounds described had analytical and spectral properties consistent with expectations.

(12) K. B. Wiberg and A. J. Ashe III, *Tetrahedron Letters*, 1553 (1965).

(13) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

(14) The rate of acetolysis of 2-adamantyl tosylate at 25° is 3×10^{-9} sec^{-1}: P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

(15) C. S. Foote, *ibid.*, **86**, 1853 (1964).

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

(17) Alfred P. Sloan Research Fellow.

(18) National Institutes of Health Predoctoral Fellow, 1966–1967.