

pendences of dipolar splittings as well as in providing information about the ultrastructure and solvent-solute interactions of the solution.<sup>8</sup> A spectrum of a PBLG-CH<sub>2</sub>Cl<sub>2</sub> solution containing 5% of *p*-xylene is shown in Figure 2. The triplet arising from the dipolar interactions between the three protons of each rotating methyl group of *p*-xylene is cleanly resolved as is the doublet arising from interactions of the 2,3 and 5,6 protons of the phenyl ring. Quadrupolar splittings in the deuterium resonances of solutions consisting of PBLG-CD<sub>2</sub>Cl<sub>2</sub> have also been observed, an additional manifestation of solute and solvent ordering in these nematic systems.

These and other aspects of the structures of concentrated PBLG solutions will be detailed in a subsequent paper. The results of such studies appear to provide new insights of some generality into the structure of anisotropic solution phases.

(8) For related system see K. D. Lawson and T. J. Flautt, *J. Am. Chem. Soc.*, **89**, 5489 (1967).

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### Stable Carbonium Ions. LXXII.<sup>1</sup> Raman and Nuclear Magnetic Resonance Spectroscopic Study of the Nortricyclonium Ion (Protonated Tricyclo[2.2.1.0<sup>2,6</sup>]heptane) and Its Relationship to the 2-Norbornyl (Bicyclo[2.2.1]heptyl) Cation. Clarification of the Nature of the Stable, Long-Lived Norbornyl Cation in Strong Acid Solutions

Sir:

Recently the direct observation of the stable, long-lived norbornyl cation was achieved in SbF<sub>5</sub>-SO<sub>2</sub>, HF-SbF<sub>5</sub>-SO<sub>2</sub>,<sup>2</sup> FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>,<sup>3</sup> and GaBr<sub>3</sub>-SO<sub>2</sub><sup>4</sup> solutions and its nmr spectrum was reported. Owing to the slowness of the nmr method, no clear differentiation on the nmr time scale between a rapidly equilibrating pair of ions or a bridged symmetrical ion was possible. In order to be able to study the structure of the norbornyl cation without regard to possible rapid equilibration, instead of the slow nmr method, a fast physical method was needed. We selected Raman spectroscopy for our continued studies, assuming that vibrational transition rates are faster than hydride shifts or Wagner-Meerwein rearrangement.

In our studies a Cary Model 81 Raman spectrometer equipped with a helium-neon laser source was used. In order to avoid the observation of fluorescent spectra and to keep the solution of the ion colorless and stable, a low-temperature cell was constructed which allowed studies at temperatures as low as -100°.

Ionization of 2-*exo*-norbornyl chloride was carried out in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub> solution. The 100-MHz pmr resonance spectrum of ion I at -80° was similar to that observed previously for stable, long-lived 2-

(1) Part LXXI: G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, in press.

(2) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

(3) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

(4) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966).

norbornyl cation, showing resonances at  $\delta$  5.2, 3.1, and 2.1 with relative peak areas of 4:1:6. We also observed fine structure of the spectrum, similar to that reported by Jensen<sup>4</sup> at 60 MHz. The high-field resonance is split into what appears to be a broad sextet ( $J \sim 1.5$  Hz) coupled to both the four low-field protons and the lone methine bridgehead proton. The  $\delta$  3.1 resonance is very broad due to coupling to both the low- and high-field protons. The low-field resonance seems to be a broad septuplet, coupled to the six high-field methylene protons ( $J \sim 1.5$  Hz). The broadness of the peak likely arises from a further small coupling with the bridgehead methine proton. The couplings were experimentally verified by decoupling experiments.

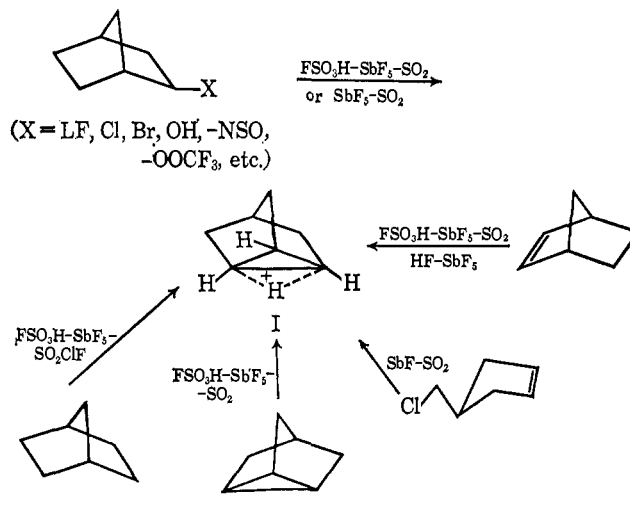
In order to be able to carry out the Raman spectroscopic studies, the acid solvent system was studied first and will be reported in detail separately.<sup>5</sup> This study allowed us to assign all Raman lines due to the solvent and gegenion. The Raman spectrum of ion I, obtained at -80°, is shown in Figure 1 with the absorption lines due to the solvent and gegenion deleted. In the C-C stretching frequency region there is only one strong line observed at 972 cm<sup>-1</sup> with a depolarization factor,  $\rho$ , of 0.35. The C-H stretching frequency region shows five lines, one of which is at 3110 cm<sup>-1</sup>.

Comparison of the Raman spectrum of ion I with the Raman spectra of nortricyclene (Figure 2) and 3-bromonortricyclene on the one hand and norbornane (Figure 3) and 2-*exo*-norbornyl halides on the other hand gives a clear indication of its structure.

The C-C stretching frequency region in nortricyclene and its derivatives shows only *one* strong absorption line, at around 950 cm<sup>-1</sup>, with a depolarization factor of 0.31. In contrast, norbornane and 2-norbornyl halides show *two* intense lines around 871 and 920 cm<sup>-1</sup> ( $\rho = 0.25$ ).

In the C-H stretching frequency region, norbornane and 2-*exo*-halonorbornanes show only three lines at frequencies below 3000 cm<sup>-1</sup>. In contrast, nortricyclene and 3-bromonortricyclene show five lines in this region, one of them at 3080 cm<sup>-1</sup>, characteristic of the cyclopropane ring.

When nortricyclene was protonated in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub> solution at -80°, the pmr and Raman spectra obtained were identical with those obtained for



(5) A. Commeyras and G. A. Olah, to be submitted for publication.

ion I from 2-norbornyl precursors. Norbornane, norbornylene, or  $\beta$ -(cyclopentenyl)ethyl halide derivatives ( $\pi$ -route precursors to the norbornyl cation) also gave the identical ion.

We feel that, based on the Raman spectroscopic studies, where the time scale of chemical shifts of equilibrations cannot affect the observed structure, ion I is not a rapidly equilibrating 2-norbornyl system but its structure is that of *protonated nortricyclene*.<sup>6</sup> If ion I would be a very rapidly equilibrating classical 2-norbornyl cation, its Raman spectrum should still be similar to that of 2-norbornyl derivatives. Also, fast equilibration should give rise to the doubling of some skeletal deformation bands, none of which was observed.

The skeletal vibrations of ion I suggest a structure similar to that of nortricyclene. The  $3110\text{-cm}^{-1}$  band is characteristic of the presence of a cyclopropane ring. A "face-protonated" structure would conform with the experimental facts and would have  $C_{3v}$  symmetry. This structure, however, is not expected, based on molecular orbital considerations and comparison with the related protonated cyclopropane system.<sup>7</sup> We suggest that protonated nortricyclene is an "edge-protonated" species. Such structure would not have  $C_{3v}$  symmetry but still would be in agreement with the Raman observations. The close similarity of the Raman spectra of nortricyclene and 3-bromonortricyclene, as well as that of norbornane with 2-*exo*-halonorbornenes, clearly indicates that skeletal similarities and not over-all point-group symmetries are reflected in the main spectral similarities, e.g., nortricyclyl and norbornyl derivatives, respectively, closely resembling each other.

The pmr spectrum is in accordance with the nortricyclonium ion structure. The  $\delta$  5.2 resonance represents the four equivalent protons associated with the "charged" cyclopropane ring. The  $\delta$  3.1 proton is the lone bridgehead proton, showing substantial deshielding which could be partially due to a "cage effect," sitting directly above the charged cyclopropane ring. The six methylene protons are at  $\delta$  2.1.

When nortricyclene was deuterated in excess  $\text{FSO}_3\text{D-SbF}_5\text{-SO}_2$  solution (95.1% deuterated) at  $-78^\circ$  the typical pmr spectrum of ion I was obtained, but instead of the relative peak areas of 4:1:6, respectively, we obtained relative areas of 3.1:1:6. Thus, only *one* deuterium atom per molecule is introduced, and no further intermolecular exchange takes place.

In order to explain the equivalence, on the nmr time scale, of the four protons associated with the cyclopropane ring, as well as the deuteration experiments, one could suggest that the protons scramble around all three edges through what amounts to be a "corner-protonated" transition state (with a plane of symmetry). Strong interaction, however, would keep the  $C_2\text{-C}_6$  distances similar to that in nortricyclene.

(6) J. D. Roberts and C. C. Lee (*J. Am. Chem. Soc.*, **73**, 5009 (1951); **76**, 450 (1954)) have originally suggested that the formation of the norbornyl cation precedes, or possibly is competitive with, the formation of a "nortricyclonium" ion. S. Winstein, *et al.* (*ibid.*, **87**, 376 (1965)) recently found that the proton elimination product in the acetylation of norbornyl *p*-bromobenzenesulfonate, which is only 4% of the overall reaction, was 98% nortricyclene and 2% norbornylene.

(7) NOTE ADDED IN PROOF. SCF calculations confirm our views. Personal communication from Professor O. Klopman, to be submitted for publication.

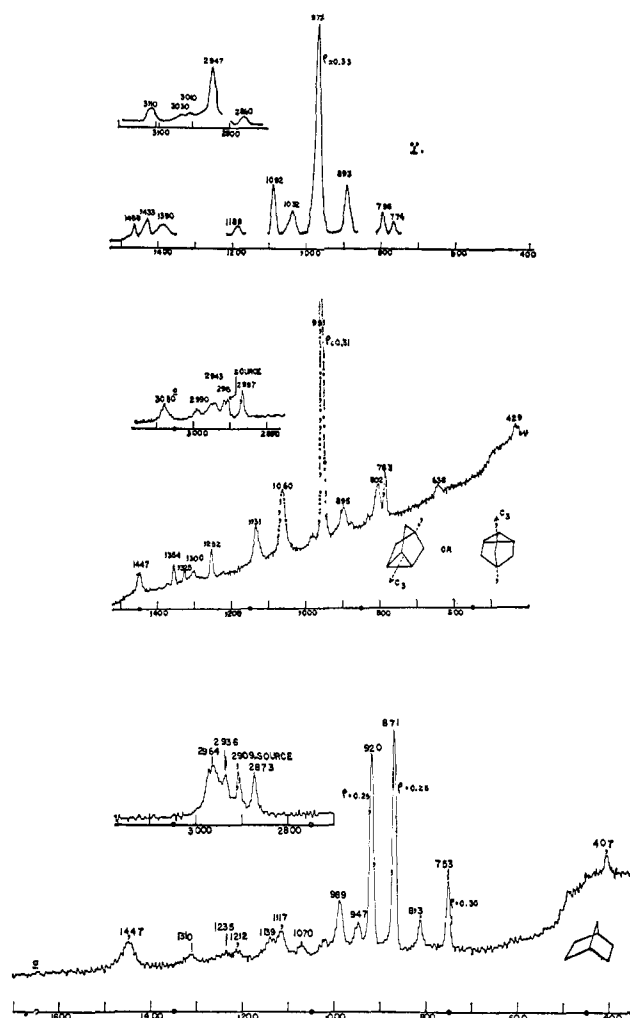


Figure 1 (top). Raman spectrum of ion I in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$  at  $-80^\circ$  (solvent and gegenion lines deleted).

Figure 2 (middle). Raman spectrum of nortricyclene.

Figure 3 (bottom). Raman spectrum of norbornane.

The quenching of the acid solutions of ion I in a tertiary base (pyridine) gave nortricyclene as 98% of all identifiable products with 1% norbornylene and norbornane found as major by-products. Thus, preferential proton elimination takes place in the absence of other nucleophiles. Hydrolysis or methanolysis under conditions where the solutions are not neutralized, on the other hand, give a practically quantitative yield of 2-*exo*-norbornyl quenching products, showing the great ease of the acid-catalyzed opening of the cyclopropane ring under solvolytic conditions. Methanol-base solutions gave mixtures of nortricyclene and 2-*exo*-norbornyl methyl ether, depending on the efficiency of neutralization.

Present observations and the well-investigated chemistry of the norbornyl cation can be satisfactorily accounted for on the basis that the nortricyclonium ion I is in equilibrium with the norbornyl cation II. In systems of low nucleophilicity, as in  $\text{FSO}_3\text{H-SbF}_5$ , I is favored, whereas with increasing nucleophilicity of the system going from strong acids to trifluoroacetic acid to formic acid to acetic acid, the importance of II increases. Due to the fact that in strongly acidic solvent systems preferentially the thermodynamically

most stable ion can be observed, protonated norbornyl cation must represent a lower energy level species than the norbornyl cation. Based on previous nmr studies, it was suggested that the 3,2-hydride shift in the norbornyl cation is relatively slow ( $\Delta F^\ddagger \sim 11$  kcal/mol in  $\text{SbF}_5\text{-SO}_2$ ) and can be frozen out in contrast with the exceedingly fast ( $\Delta F^\ddagger < 5.0$  kcal/mol) exchange of the 1, 2, and 6 hydrogen atoms. The observed barrier for the slow 3,2-hydride shift does not appear to be in agreement with other secondary-secondary hydride shifts. It is therefore reasonable to suggest that the activation energy barrier observed in the nmr spectra also includes the energy difference  $\text{I} \rightarrow \text{II}$ . Thus, the 3,2-hydride shift would take place in the norbornyl cation II, and not in ion I, where it is not favored. Rapid scrambling of hydrogens 1, 2, and 6, on the other hand, is possible in I.

Our study demonstrates the great power of laser-based Raman spectroscopy in the structural determination of carbonium ions, particularly when differentiation of potentially fast equilibrating systems from bridged ions is involved.

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### Oxygen Exchange between Tris(oxalato)rhodate(III) Ion and Solvent Water. Exchange of Outer and Inner Oxygens

Sir:

Acid-catalyzed oxygen exchange between complexes of the type  $\text{M}(\text{C}_2\text{O}_4)_n^{n-}$  and water has been examined previously<sup>1,2</sup> for  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ,  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ , and  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ . For each of these ions, all  $4n$  oxygens exchange, under fixed conditions, at apparently indistinguishable rates. Similar results were observed for oxalic acid.<sup>1-4</sup> In contrast, we find that  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  in acidic media exchanges one-half of its oxygens significantly more rapidly than the other half. The result is of particular interest because of possible relationships between racemization and oxygen exchange for this ion and related complexes.

Reaction solutions were prepared from solutions containing  $\text{Na}_3\text{Rh}(\text{C}_2\text{O}_4)_3$ ,<sup>5</sup>  $\text{HClO}_4$ ,  $\text{NaClO}_4$ , and  $\text{O}^{18}$  enriched water. Aliquots were quenched with cooled  $\text{AgNO}_3$ , and the precipitated  $\text{Ag}_3\text{Rh}(\text{C}_2\text{O}_4)_3$  was dried and thermally decomposed to Ag, Rh, and  $\text{CO}_2$ . The  $\text{CO}_2$  46/(44 + 45) ratios were measured with a Nuclide 6-60-RMS 2 mass spectrometer.

Linear first-order rate plots<sup>6</sup> for the early stages of

(1) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

(2) (a) J. E. Teggin and R. M. Milburn, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964 p 13-O; (b) *Inorg. Chem.*, 4, 793 (1965).

(3) R. M. Milburn and H. Taube, *J. Amer. Chem. Soc.*, 81, 3515 (1959).

(4) C. O'Connor and D. R. Llewellyn, *J. Chem. Soc.*, 2197 (1965).

(5) Prepared from  $\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3 \cdot 1.5\text{H}_2\text{O}$  kindly provided by Dr. Harriet Kruszyna.

(6) The rate equation may be written  $\log[(N_\infty - N_0)/(N_\infty - N_t)] = (k/2.303)t$ , where  $N$  = atom fraction of  $\text{O}^{18}$ .

reaction are obtained only if one uses for the infinity value the  $\text{O}^{18}$  enrichment expected if very close to one-half of the oxygens have equilibrated with solvent (Figure 1A).<sup>7</sup> Such plots provide pseudo-first-order rate constants which we associate with exchange of outer oxygens. After the outer oxygens have equilibrated with solvent, inner oxygen exchange can be followed. Linear first-order plots are obtained here if one takes as the initial time the point when one-half of all oxygens have equilibrated<sup>9</sup> (Figure 1B). A modified McKay equation for the case where one-half the atoms exchange at one rate and one-half at a different rate gives linearity for 90% of all oxygens.<sup>1,10</sup> For both inner and outer oxygens, exchange rates are first order in both complex and hydrogen ion concentrations. Arrhenius plots show good linearity for each kind of oxygen. At 25° outer oxygens exchange ~60 times more rapidly than inner oxygens; at 56° the difference is ~20-fold. Thus we have usually equilibrated the outer oxygens at 25° before following inner oxygen exchange at higher temperatures. That there are kinetically distinguishable oxygens in  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  and not in the Cr(III), Co(III), and Pt(II) analogs<sup>11</sup> is a reflection of the considerable inertness of the rhodium-oxygen bonds.<sup>13,14</sup> While slow, inner oxygen exchange in  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  is considerably more rapid under comparable conditions than aquation to give free oxalate.<sup>15,16</sup>

Table I summarizes our results<sup>17</sup> on oxygen exchange and available data on the racemization<sup>18</sup> and aquation<sup>15</sup> of the  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  ion. A comparison with our earlier results<sup>2</sup> is in Table II.

Based on studies of  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  and  $\text{HC}_2\text{O}_4^-$  it was predicted,<sup>2</sup> as a first approximation, that under comparable acidic conditions all nonlabile oxalato complexes of type  $\text{M}(\text{C}_2\text{O}_4)_n^{n-}$  will exchange oxygen at similar rates. Our results for  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  are in accord with this idea (Table II). Outer oxygen exchange in  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  is therefore considered to proceed by the previously suggested A2 mechanism.<sup>19</sup>

(7) If for  $N_\infty$  one assumes  $13/21$  of the oxygen has equilibrated, as might be suggested by the formulation of  $\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3 \cdot 4.5\text{H}_2\text{O}$  proposed by Porte, *et al.*,<sup>8</sup> the points lie closer to a straight line for slightly longer reaction times.

(8) A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, 34, 66 (1961).

(9) Thus  $N_0$  for inner oxygen exchange =  $N_\infty$  for outer oxygen exchange.

(10) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p 13.

(11) For the cationic complexes  $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{2+}$  and  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$ , however, kinetically distinct oxygens have been observed.<sup>12</sup>

(12) (a) R. B. Jordan, C. A. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, pp 381-394; (b) C. Andrade, R. B. Jordan, and H. Taube, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 13-M.

(13) R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2417 (1964).

(14) R. G. Pearson in "Some Aspects of Crystal Field Theory," T. M. Dunn, D. S. McClure, and R. G. Pearson, Ed., Harper and Row, New York, N. Y., 1965, p 106.

(15) (a) D. Barton and G. M. Harris, *Inorg. Chem.*, 1, 251 (1962); (b) K. V. Krishnamurty, *ibid.*, 1, 422 (1962).

(16) For 56° we estimate that the enrichment in the  $\text{CO}_2$  arising through exchange in freed oxalate can be no more than ~3% of that attributable to the inner oxygen exchange.

(17)  $k_2 = k_1/[\text{H}^+]$ .

(18) A. L. Odell, R. W. Olliff, and F. B. Seaton, *J. Chem. Soc.*, 2280 (1965).

(19) For oxygen exchange in  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ,  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ , and  $\text{H}_2\text{C}_2\text{O}_4$ , Bunton, *et al.*,<sup>1</sup> also observed similar kinetic parameters and proposed an A2 type mechanism. Their mechanism differs from ours in that it requires a ring opening before any oxygens can exchange. The quantitative results are difficult to include in the present comparison because of widely differing ionic strengths.