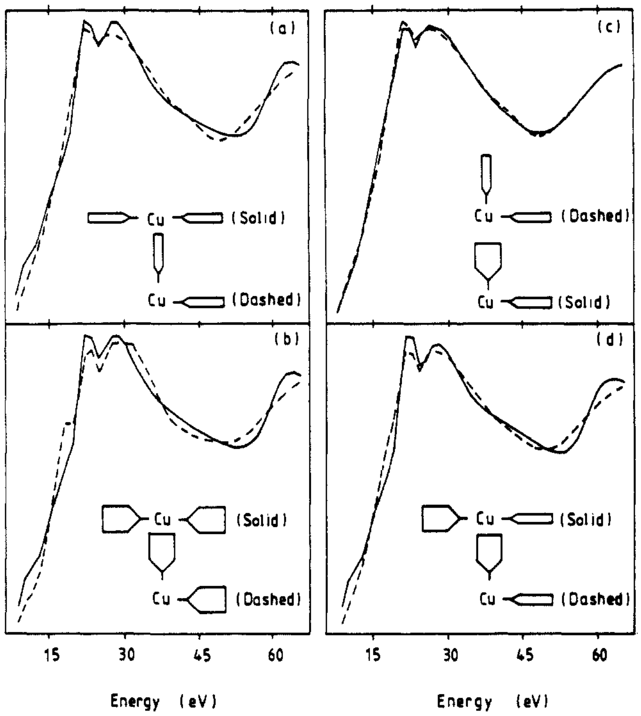


Figure 5. This shows a series of calculations involving only two imidazole rings. The relative orientation of the rings is varied as indicated in the figure.

calculations (Figure 5c) is at the position marked by an arrow, which corresponds to the region we have labeled D and E in the experimental data (Figure 1). This difference is enhanced when all four rings are present, as shown in Figure 4a, and the evidence suggests that it is due to "inter-ring" scattering. In other words, the electron is scattered between adjacent ring atoms before being backscattered to the copper atom, thus suggesting a type of "cage effect" at the low electron energies associated with the XANES region.

These calculations, and those shown in Figure 4a, show that the XANES spectra are sensitive to the relative orientation of the imidazole rings. This insight offers the possibility that the relative orientation of different residues around a metal site can be investigated by using high-resolution XANES spectra, particularly when strong multiple scattering may occur from the atoms of such ligands. Figure 4a shows reasonable agreement with the experimental data (Figure 4b) for most of the features with respect to their relative position; however, the relative amplitudes of these features are not as well reproduced. This problem is known to be associated with the general one of calculating accurate phase shifts for the low-energy scattering regime. Thus, it is likely that a more accurate method of calculating phase shifts is required if the recent advance in XANES theory is to be fully exploited. Self-consistent field methods of calculating atomic potentials may prove useful in this respect. On the other hand, genuine many-electron excitations may also be occurring; in general, such effects lie beyond a single-particle scattering approach. In this instance, the strength of many-electron effects seems to be quite small but may complicate the quantitative details of the analysis. We also note that such detailed understanding is only feasible if the nature and position of ligands are well-defined from other methods, such as crystallography and EXAFS. It is also important that XANES profiles are compared within a related family of compounds, as similar features may be observed from chemically unrelated systems due to similar backscattering paths.

Conclusion

A detailed investigation of the XANES of a family of Cu(II) imidazole complexes has shown that the spectral features observed for this class of compounds can be understood in terms of electron-scattering theory. The potential for extracting useful stereochemical information from the XANES has been demonstrated.

Acknowledgment. We thank the Science and Engineering Council for their support of this work. We are also thankful to several of our colleagues, particularly to Drs. N. J. Blackburn and C. D. Collison and Professor C. D. Garner for their support and useful discussions. Dr. Blackburn and Professor Garner also supplied the protein and chemical compounds, respectively.

Rotational Reorientation of the 1-Adamantyl Cation: A Sensitive Probe of Carbocation–Medium Interactions

David P. Kelly* and D. Ralph Leslie[†]

Contribution from the Department of Organic Chemistry, The University of Melbourne, Parkville, Victoria, Australia 3052.

Received October 10, 1989

Abstract: Rotational reorientation of the 1-adamantyl cation has been determined over a range of temperatures (−90 to −40 °C) and concentrations (0.21–0.69 M), of the cation generated from different precursors (ROH, RCl) in different superacids (SbF_5, FSO_3H/SbF_5) with different solvents (SO_2, SO_2ClF). The anisotropy of reorientation, as measured by the ratio of the diffusion constants ($\sigma = D_\parallel/D_\perp$), was independent of precursor, temperature, and concentration, but not the solvent. In SO_2 solution the cation reorients isotropically ($\sigma = 1$) but anisotropically ($\sigma = 2.5$) in SO_2ClF. This anisotropy is considered to arise from weak electrostatic interactions of the cationic center with a diffuse anionic "cloud" in the medium and not from ion pair formation. These results are in contrast to those from thermochemical studies.

The study of carbocations as stable, long-lived species was made possible by the discovery of the liquid superacids, in particular SbF_5, FSO_3H, and "Magic Acid".[1] The very existence of stable carbocations in these acids attests to the very low nucleophilicity of the acids, their conjugate bases, and the counterions generated during cation formation. While there is now a large body of literature dealing with the structure of the carbocations in superacid media,[1-3] there has been relatively little investigation of

---

[†] Current address: Materials Research Laboratory, DSTO P.O. Box 50, Ascot Vale, Victoria, Australia 3052.

(1) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley Interscience: New York, 1985.

0002-7863/90/1512-4268$02.50/0

the interactions of these cations with the medium.

Consideration of the low dielectric constant of SbF_5 and the requirement for an excess of this Lewis acid for the formation of stable alkyl carbocations in it led Olah and co-workers in 1964 to propose that alkyl carbocations existed as solvated tight ion pairs in this medium.[4] However, as the study of carbocations as stable species in superacid solutions was pursued, mainly by NMR spectroscopy, it was concluded that anion and solvent interaction with the cations was nonspecific.[5] Consistent values of NMR parameters (chemical shifts and coupling constants) for cations generated from different precursors in a range of superacids and solvents were cited as evidence for nonspecific interactions.

In their NMR study of C1 to C5 alkyl fluorides and chlorides, Olah and Donovan showed that the ^{13}C shifts of tertiary cations varied little (<0.6 ppm) between SbF_5/SO_2 and SbF_5/SO_2ClF, the lower shifts of the cationic centers in SO_2 possibly attributed to a biased equilibrium between the free cation and traces of alkylated SO_2.[6] However, in the case of non-tertiary systems, methyl, ethyl, and isopropyl fluorides in SbF_5/SO_2 gave rise to alkylated SO_2 ($ROSO^+$) as the only observable species. In SbF_5/SO_2ClF, the isopropyl cation is formed together with a low concentration of isopropylated SO_2, the SO_2 being present as an impurity in SO_2ClF. In SO_2F_2, however, the free isopropyl cation is formed cleanly.[6]

The concept of carbocations being "free", that is, without specific interactions with the counterions or medium, was supported initially by comparison of thermochemical data from the condensed and gas phases. The thermochemistry of carbocations in superacids has been extensively studied by Arnett and coworkers.[7-12] Early work on alkyl and cycloalkyl cations generated from chloride precursors showed that the enthalpy for rearrangement of the *sec*-butyl to *tert*-butyl cation was 15 kcal/mol in SbF_5/SO_2ClF,[7-9] which compared favorably with that determined in the gas phase, 15–17 kcal/mol.[13] Similarly, the heats of formation of a range of secondary and tertiary cyclic and acyclic carbocations in SbF_5/SO_2ClF relative to that of the *tert*-butyl cation were in good agreement with those in the gas phase.[10] Although molecular orbital calculations on carbocations in the gas phase predicted relative stabilities and energy barriers comparable with those determined experimentally in the condensed phase,[14] theoretical studies of carbocation solvation by HCl or HF predicted that solvent stabilization of carbocations would increase with increasing charge localization.[15] However, the magnitude of preferential solvation of more charge localized cations was anticipated to be attenuated in solvents of very low nucleophilicity such as those used to support stable carbocations.

Later work by Arnett and Hofelich demonstrated that carbocation generation was dependent upon the precursor. Thus the enthalpies of ionization of acyclic and alicyclic alcohols in SbF_5/SO_2 or $SbF_5/FSO_3H/SO_2$ exhibited a greater variation with structure than the corresponding halides in either SO_2 or SO_2ClF solutions of SbF_5, and of alcohols in SbF_5/SO_2ClF.[11] They thus concluded that there were strong structure-dependent interactions between carbocations and counterions for $ROH/SbF_5/SO_2$ systems that were not detectable from the NMR spectra. In summarizing, Arnett stated "The present results call for examination of the role of ion pairing and anion structure in solutions of carbocation salts in different superacid media",[11] and later "Unfortunately, the degree of ion pairing remains unknown for all these systems and we have shown that it may be a very significant thermochemical factor in some cases".[12]

Comparison of Arnett's heats of ionization (ΔH_i) of RCl in SO_2ClF with their gas phase, chloride ion transfer reactions ($R_o + RCl = R_oCl + R^+$) led Kebarle and co-workers to conclude that the significant differences that they observed between the two sets of results were best explained in terms of differential nonspecific solvation, rather than differential nucleophilic solvation (e.g., to form transient species such as R^+SO_2ClF) or differential ion pair formation.[16] In the case of the 1-adamantyl cation, the difference between the chloride ion affinities ($\delta\Delta H_2$) in the gas and condensed phases was estimated as 9.3 kcal/mol compared with that for *tert*-butyl ($\delta\Delta H_2 = 0$). This was twice that estimated for 2-methyl-2-norbornyl (4.9 kcal/mol) and was rationalized in terms of reduced nonspecific solvation due to exclusion of solvent from the cationic site by the large hydrocarbon cage.[16]

In recent ^{13}C NMR and theoretical studies on 2,4-dimethyl- and 2,5,5-trimethyl-2-adamantyl cations generated in a range of superacid media and studied over a range of temperatures, Sorensen and co-workers showed that the (nonequivalent) β carbon shifts were anomalous. They proposed that equilibration occurs (also in 2-methyl-2-adamantyl) between two "partially pyramidalized carbocations preferentially solvated on the open face". While this description of a localized interaction at the cationic site involves the solvent "which probably also includes the counterion", tight ion pairs were not considered to be involved.[17,18]

From the above, albeit brief, summary, it is obvious that the extent to which carbocations in superacid media experience specific interactions with counterions and the supporting medium is poorly understood.

We have reasoned that specific interactions between a carbocation and other species in solution should be manifest in its molecular dynamics, particularly the anisotropy of its rotational reorientation.[19] This is not without precedent; association of pyridine with hydrogen bonding solvents provides one example.[20] Assuming axial symmetry of the pyridine–solvent complexes, the ratio of the diffusion coefficient for rotation about the major axis passing through the nitrogen and C4 nuclei to that of the perpendicular axes ranged from 2.0 to 3.4 compared to unity when not associated. Similarly, a value of 28 is found for the ratio of diffusion coefficients in the axially symmetric dimer of adamantyl carboxylic acid compared to values of 3 or less for 1-bromoadamantane, which is monomeric in solution.[21]

A theoretical basis for extracting rotational diffusion coefficients from NMR relaxation time data has been developed by Woessner.[22] Following earlier work on the *tert*-butyl and 2-methyl-

---

(2) Olah, G. A. *Top. Curr. Chem.* **1980**, *80*, 19–88.

(3) For earlier reviews, see: *Carbonium Ions*; Olah, G. A., Schleyer P. v. R., Eds.; Wiley Interscience: New York; Vol. 1, 1968; Vol. II, 1970; Vol III, 1972; Vol. IV, 1973; Vol. V, 1976.

(4) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360–1373.

(5) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53–59.

(6) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5163–5169.

(7) Bittner, E. W.; Arnett, E. M.; Saunders, M. *J. Am. Chem. Soc.* **1976**, *98*, 3734–3735.

(8) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402–5407.

(9) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408–5416.

(10) Arnett, E. M.; Pienta, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 3329–3334.

(11) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522–3524.

(12) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.

(13) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179–240. Franklin, J. L. *Carbonium Ions*; Vol. I, 1968, see ref 3. Lessing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955–965. Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* **1975**, *97*, 2625–2628.

(14) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 302–304. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294–1301. Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935–5945. Jorgensen, W. L. *Tetrahedron Lett.* **1976**, 3033–3036.

(15) Jorgensen, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 280–283, 4272–4276. Jorgensen, W. L.; Monroe, J. E. *Tetrahedron Lett.* **1977**, 581–584.

(16) Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3755–3757.

(17) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7816–7823.

(18) The 2-methyl-2-adamantyl cation was also considered to be a partially pyramidalized cation in which the distortion from trigonal symmetry could be up to ±20°. Application of the ΔJ criterion to this cation supports this proposal since $\Delta J_{C_\alpha H} = J_{C_\alpha H}(\text{cation}) - J_{C_\alpha H}(\text{ketone}) = 147 - 137 = 10$ Hz, thus $\Theta \simeq 35°$. Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106–3111.

(19) Kelly, D. P.; Leslie, D. R.; Craig, R. A. *J. Magn. Reson.* **1983**, *52*, 480–491.

(20) Campbell, I. D.; Freeman, R.; Turner, D. L. *J. Magn. Reson.* **1975**, *20*, 172–176.

(21) Beierbeck, H.; Martino, R.; Saunders, J. K. *Can. J. Chem.* **1979**, *57*, 1224–1228.

(22) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647–654.

Table I. Relaxation and Rotational Diffusion Data for the 1-Adamantyl Cation at -90 °C[a]

carbon	T_1, s	nOe	T_1^{DD}, s	T_1^{DD}(calc), s	$D_\perp$, 10^8 s^{-1}	σ
α	0.44 ± 0.02	1.91 ± 0.07	0.46 ± 0.03	0.434		
β	0.71 ± 0.02	1.80 ± 0.09	0.78 ± 0.05	0.819	18.0 ± 0.6	2.6 ± 0.2
γ	0.32 ± 0.01	1.89 ± 0.07	0.34 ± 0.03	0.339		

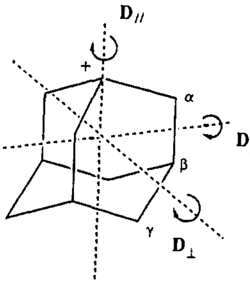
[a] Cation (0.69 M) generated from 1-chloroadamantane in 5.2 M SbF_5/SO_2ClF.

Table II. Rotational Anisotropy of the 1-Adamantyl Cation at −90 °C

entry	concn, M	superacid	solvent	precursor[a]	σ
1	0.69	5.2 M SbF_5	SO_2ClF	Cl	2.6 ± 0.2[b]
2	0.67	5.1 M SbF_5	SO_2ClF	OH	2.2 ± 0.1[c]
3	0.29	1.3 M SbF_5	SO_2	Cl	1.1 ± 0.1[d,e]
4	0.29	1.2 M SbF_5	SO_2	OH	0.9 ± 0.1[d,f]
5	0.25	1.2 M SbF_5	SO_2ClF	OH	2.1 ± 0.2[g]
6	0.44	46% v/v SbF_5/FSO_3H (1:1)	SO_2ClF	Cl	1.9 ± 0.2
7	0.47	50% v/v SbF_5/FSO_3H (1:1)	SO_2ClF	OH	2.3 ± 0.2
8	0.44	46% v/v SbF_5/FSO_3H (1:1)	SO_2	Cl	2.0 ± 0.2
9	0.47	50% v/v SbF_5/FSO_3H (1:1)	SO_2	OH	1.9 ± 0.1
10	0.21	25% v/v SbF_5/FSO_3H (1:1)	SO_2ClF	OH	2.0 ± 0.1
11	0.21	25% v/v SbF_5/FSO_3H (1:1)	SO_2	OH	1.0 ± 0.1

[a] Cation generated from 2-adamantanol (OH) or 1-choroadamantane (Cl). [b] Additional values of σ at −85, −75, and −65 °C were all 2.4 ± 0.2. [c] Additional values at −75, −63, and −47 °C were 2.4 ± 0.2, 1.9 ± 0.1, and 1.9 ± 0.1, respectively. [d] Obtained at −70 °C, as precipitation (SbF_5:SO_2 complex)[24] occurred at lower temperatures. [e] Additional values at −60 and −40 °C were both 1.0 ± 0.1. [f] Additional values at −60 and 40 °C were 1.0 ± 0.1 and 1.3 ± 0.1, respectively. [g] Additional values at −40, −80, −70, −60, and −40 °C were all 1.7 ± 0.1.

2-adamantyl cations,[19] we have determined ^{13}C spin–lattice relaxation times and nuclear Overhauser enhancements of the three resonances arising from the protonated carbon nuclei in the 1-adamantyl cation.[23,24] The dipole–dipole relaxation times (T_1^{DD}) calculated from these parameters have been analyzed by application of Woessner's equations, assuming the cation reorients as an axially symmetric ellipsoid. From this we have obtained the diffusion coefficient for rotational reorientation about the two equivalent minor axes of the ellipsoid ($D_\perp$) and also σ, the ratio $D_\parallel/D_\perp$ ($D_\parallel$ being the diffusion coefficient for rotation about the symmetry axis). In this report we relate the anisotropy (σ) in the rotational behavior of the 1-adamantyl cation to interactions between it and the surrounding medium.



Results and Discussion

Extraction of diffusion coefficients from T_1^{DD} data requires knowledge of the structural geometry of the reorienting species (i.e., bond lengths and angles). The reported structure of the 1-adamantyl cation, calculated by theoretical methods (STO-3G),[25] has been used with the C_{3v} axis assumed to be the major axis for rotation. All intramolecular ^{13}C–^1H interactions were included in the calculation of the rotational diffusion parameters as it has been suggested that neglect of the contribution to relaxation of ^{13}C nuclei by nonbonded ^1H nuclei could lead to large errors.[26] Even so, the estimates of $D_\perp$ rely largely on the dipolar interaction of directly bonded ^{13}C–^1H pairs. Given the sixth power dependence of this interaction on the C–H bond length, the suitability of the STO-3G values requires consideration.

For adamantane, the ratio of the optimized STO-3G estimates of carbon–hydrogen bond lengths and the experimental values is 0.982.[25,27] Assuming this ratio is maintained for the cation, the estimates of $D_\perp$ using the theoretical structure are too large and a correction factor of $(0.982)^6$ should be applied. In this work the emphasis is on the anisotropy in reorientation, rather than the magnitude of the diffusion coefficients. Provided the relative magnitude of the C–H bond lengths reflect the true ratios, errors in the absolute values will have little effect on the estimates of σ. Nevertheless, the values of $D_\perp$ in Tables I and III are those obtained after application of the above correction.[28]

The procedure we have used to extract rotational diffusion parameter from T_1^{DD} values closely matches that described by Gerhards et al.[29] A computer program was devised that used initial estimates of $D_\perp$ and σ and the coordinates of the protonated carbons and ^1H nuclei of the 1-adamantyl cation to calculate the ^{13}C T_1^{DD} values of each protonated carbon in the cation. The values of $D_\perp$ and σ were then systematically adjusted until the calculated T_1^{DD} values most closely matched the experimental data. A typical set of experimental T_1^{DD} values are given in Table I. Included are the optimized $D_\perp$ and σ values, which give the set of calculated values shown.

The rotational anisotropy of the 1-adamantyl cation, prepared from either 1- or 2-adamantanol or 1-chloroadamantane, has been determined as a function of temperature, superacid, precursor, solvent, and concentration (Table II). The variation observed in σ over the range of 0.9 to 2.6 is evidence that there is also variation in the interactions between the cation and the supporting medium.

Effect of Precursor. The differences in ΔH_i for ionization of ROH in SO_2-containing superacid media compared with those in SO_2ClF (or of RCl in either system) were postulated to arise from strong interactions between the carbocations and the complex antimony anions produced upon ionization.[11] Implicit in this argument is the assumption that the counterions formed by ion-

---

(23) (a) Schleyer, P. v. R.; Fort, R. C.; Watts, W. E.; Comisarow, M. G.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 4195–4197. (b) Olah, G. A.; Lucas, J. *J. Am. Chem. Soc.* **1968**, *90*, 933–938. (c) Olah, G. A.; Surya Prakash, G. K.; Ship, J. G.; Krishnamurthy, V. V.; Mateescu, Gh. D.; Liang G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764–2772.

(24) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957–965.

(25) Sunko, D. E.; Hirsl-Starcevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163–6170.

(26) Stilbs, P.; Mosely, M. E. *J. Magn. Reson.* **1979**, *33*, 209–210.

(27) Harris, R. K.; Newman, R. H. *Mol. Phys.* **1981**, *43*, 1069–1081.

(28) It should be noted that in the case of solid 3,5,7-trimethyl-1-adamantyl cation, the crystal structure reveals significant differences from the idealized adamantyl structure, with the cationic center flattened and very small (99°) C–C–C bond angles around C2,C8,C9. It is of interest that no interaction between cation and anion was found in the crystal lattice: Laube, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 349–350.

(29) Gerhards, R.; Dietrich, W.; Bergmann, G. J.; Duddeck, H. *J. Magn. Reson.* **1979**, *36*, 189–197.

ization of alcohols and chlorides in superacids are different. However, this is not supported by Gillespie's studies of antimony anions.[30] Investigations of halide and other ligand exchange between SbF_5X^- anions and SbF_5 provide strong evidence that when alkyl halides are ionized in the presence of excess SbF_5, the anions initially formed undergo further reactions to ultimately yield anions such as $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$.[30] Structural information regarding the anions formed from the ionization of alcohols in excess SbF_5 is limited. However, the ^{121}Sb NMR spectrum obtained for a solution of SbF_5 in dry ethanol revealed that the predominant antimony species was SbF_6^-.[31] In the presence of excess SbF_5 this anion forms $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$, the very same anions formed by the reaction of alkyl chlorides with SbF_5.[30,32] This evidence suggests there is little difference in the anions formed upon ionization of alcohols or chlorides in excess SbF_5.

Entries 1,2; 3,4; 6,7; and 8,9 of Table II make up four pairs of solutions of the cation; one solution of each pair was prepared from the chloride and the other from the alcohol. Within each pair the solution composition and cation concentrations were kept approximately constant. Although σ varied between solutions of different composition, the nature of the precursor had little effect on the rotational behavior. *Thus interactions of this cation with counterions are largely independent of precursor.* These data are also consistent with, but not unequivocal evidence for counterions being the same, irrespective of precursor. An alternative interpretation of the thermochemical data is therefore now required.

It was observed in the present work that attempted preparation of the 1-adamantyl cation from 1-adamantanol in SbF_5/SO_2 at -90 °C gave a solution for which the ^{13}C spectrum differed significantly from that reported for the cation.[23,24] When measured at -70 °C the major feature of the spectrum was a very broad resonance at about δ 52 ppm with sharp resonances of much less intensity at δ 67.6, 35.1, and 28.2 ppm. No signal corresponding to the cationic carbon was observed. After warming the solution to -30 °C its spectrum was remeasured at -70 °C and contained only those resonances reported for the 1-adamantyl cation.[23,24] Thus ionization of the alcohol or dissociation of the ion pair was incomplete prior to warming and was readily detected from the ^{13}C spectrum.[33] Under these same conditions 1-chloroadamantane ionized cleanly to the 1-adamantyl cation as determined by the ^{13}C spectrum of the solution. Dissolution of 1-adamantanol (0.21 M) in 25% v/v $[SbF_5/FSO_3H\ (1{:}1)]/SO_2$ also required warming of the solution before cation formation was observed.[34] This is the same combination of precursor/acid/solvent as used by Arnett in the thermochemical studies, yet ionization was considered to be complete in their case, as ^{1}H spectra corresponding to the appropriate cations were obtained for the alcohol/superacid solutions.[11] The possibility that ionization/dissociation was completed during transfer of the solutions to NMR tubes cannot be ignored. Rearrangement of the *sec*-butyl to the *tert*-butyl cation did occur under the same conditions.[8]

It may be significant that the heats of ionization (ΔH_i) from which the presence of specific cation–counterion interactions were inferred were not directly measurable but were calculated as the difference between the molar heat of solution and ionization of the precursor R–X in a solution of excess superacid in the solvent indicated, $-\Delta H_{\mathrm{rxn(superacid/solvent)}}$, and that of RX in pure solvent under the same conditions, $-\Delta H_{\mathrm{s(solvent)}}$.

$$\Delta H_{\mathrm{i(superacid/solvent)}} = \Delta H_{\mathrm{rxn(superacid/solvent)}} - \Delta H_{\mathrm{s(solvent)}} \qquad (1)$$

Strictly, the $-\Delta H_{\mathrm{s(solvent)}}$ term should be replaced by $-\Delta H_{\mathrm{s(superacid/solvent)}}$, that is, the molar heat of solution of the substrate in the superacid/solvent system without the occurrence of ionization. This term is not accessible experimentally, hence the use of $-\Delta H_{\mathrm{s(solvent)}}$. It is possible that the greater structural dependence of ΔH_i for alcohols with SO_2 as solvent compared to other precursor/solvent combinations arises from a structural dependence of $\Delta H_{\mathrm{s(superacid/SO_2)}}$ for the alcohols. The important point is that the thermochemical data derived from the ionization of a precursor to form a cation are dependent on interactions other than those between the cation produced (observed directly by NMR) and its supporting medium. Contrasting this, the rotational anisotropy of the 1-adamantyl cation can only be influenced by interactions in which the cation is directly involved.

The unusual thermochemical behavior for the ionization of alcohols in SO_2 solutions containing SbF_5 therefore remains unexplained.[35] However, the results from this study reveal it is not a consequence of differences in the interactions between cations and counterions that are dependent on the cation precursor.

Effect of Solvent. Although the anisotropy in the reorientation of the 1-adamantyl cation is independent of the cation precursor, it is dependent on solvent (Table II). Thus the cation reorients isotropically in 1.2 M SbF_5 or 25% v/v Magic Acid when the solvent is SO_2 but reorients anisotropically when the solvent is SO_2ClF (compare entries 3 and 4 with 5, and 10 with 11). Clearly the interactions between the cation and its supporting medium vary, implying that the external stabilization thereby afforded to the cation also varies with the solvent. The ability of the solvent to influence the stabilization of the cation in Magic Acid solutions diminishes as the concentration of acid increases (compare entries 6 to 9 with 10 and 11) (vide infra). Thermochemical studies have been equivocal in determining the effect of solvent on the stabilization of carbocations in superacid solutions. Even though ΔH_i for the reaction of *tert*-butyl chloride with SbF_5 in SO_2, SO_2ClF, or SO_2F_2 varies by 17 kcal/mol, this value is matched exactly and oppositely by the heat of solution of SbF_5 in the solvents.[9] This was interpreted to indicate that virtually all the solvent effect on the ionization of *tert*-butyl chloride arose from the heat required to transfer SbF_5 from its solvated neutral state to a solvated ionic state, while solvation changes for the *tert*-butyl cation are negligible. Comparison of $[\Delta H_{i(\mathrm{SbF/solvent})}]$ for other alkyl halides with that of *tert*-butyl chloride indicated that solvent effects on the stabilities of other cations are also small.

However, addition of increments of SO_2 to solutions of *sec*-butyl cation in SO_2ClF was observed to cause 8–10-fold rate enhancements of the rearrangement to *tert*-butyl cation.[11] Also, Olah and co-workers observed a similar effect in the case of the 5,6-trimethylene-2-norbornyl cation, which is stable in SO_2ClF but rearranges rapidly to the 1-adamantyl cation in SO_2.[23c] This supports the idea that greater external stabilization is afforded to the cations in SO_2ClF than in SO_2–superacid media.

The significant variation in values of σ obtained for the 1-adamantyl cation caused by changing solvent (Table II) reveals that the *anisotropy in rotational reorientation of the cation is sensitive to differences in interactions with the supporting media that are too small to be identified by currently available thermochemical methods.*

The approximately spherical symmetry of the 1-adamantyl cation suggests that it should reorient isotropically in the absence of any specific interactions with other species in solution. Since any such interactions would involve the cationic site in the ion, rotation about the axes perpendicular to the C_{3v} symmetry axis (minor axis) defined by the vacant orbital of the cationic carbon will be inhibited as it requires reorientation of the cationic site. Rotation about the major axis need not be greatly affected by such interactions as the orientation of the interacting site is unchanged

---

(30) Bacon, J.; Dean, P. A. W.; Gillespie, R. J. *Can. J. Chem.* **1969**, *47*, 1655–1659; **1971**, *49*, 1277–1283.

(31) Hatton, J. V.; Saito, Y.; Schneider, W. G. *Can. J. Chem.* **1965**, *43*, 47–56.

(32) Dean, P. A. W.; Gillespie, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 7264–7269.

(33) Dissolution of 2-adamantanol in FSO_3H/SO_2, FSO_3H/SO_2ClF, or neat FSO_3H yields solutions, the NMR spectra of which are not consistent with either 2-adamantyl species or stable, long-lived 1-adamantyl cations. However, the temperature-sensitive, ^{13}C spectra are consistent with equilibria involving mainly covalently bound substituents at C1 such as $-OH_2^+$ and/or $-OSO_2F$.

(34) Prior to heating, the solution at -90 °C gave a ^{13}C spectrum that contained only a very broad resonance at about δ 55 and 88 and a ^{1}H spectrum with one sharp line at δ 4.94 and a broader line at δ 3.0 ppm. The 1-adamantyl cation gives ^{1}H resonances at δ 2.30, 4.19, and 5.19 ppm, see ref 23c.

(35) The enthalpy for complexation of tetrahydrofuran with $SbCl_5$ in 1,2-dichloroethane is ca. 20 kcal/mol (see ref 8). The reaction of SbF_5 with alcohols in SO_2 and other solvents may well include an enthalphy for complexation, the magnitude of which varies with structure of the substrate.

Table III. Rotational Diffusion Coefficients for the 1-Adamantyl Cation

concn, M	superacid	solvent	temp, °C	$D_\perp$, 10^8 s^{-1}	σ	$D_\parallel$, 10^8 s^{-1}
0.29	1.2 M SbF_5	SO_2	−70	176 ± 6	0.9 ± 0.1	160 ± 16
			−60	235 ± 8	1.0 ± 0.1	240 ± 25
			−50	340 ± 16	0.8 ± 0.1	280 ± 36
0.25	1.2 M SbF_5	SO_2ClF	−70	80 ± 2	1.7 ± 0.1	137 ± 10
			−60	109 ± 3	1.7 ± 0.1	180 ± 14
			−50	132 ± 3	1.6 ± 0.1	217 ± 16
0.21	25% v/v SbF_5/FSO_3H (1:1)	SO_2	−90	120 ± 3	1.0 ± 0.1	122 ± 8
0.21	25% v/v SbF_5/FSO_3H (1:1)	SO_2ClF	−90	51 ± 1	2.0 ± 0.1	103 ± 7

by such motion. Thus the rotational diffusion constants obtained in this work provide clear evidence that the *1-adamantyl cation interacts more strongly with its supporting medium (thereby experiencing greater stabilization) when SO_2ClF is the solvent (σ always >1) than when SO_2 is the solvent.*

Confirmation of this interpretation is found in the diffusion coefficients (Table III). Comparison of $D_\perp$ and $D_\parallel$ for the cation between solutions that differ only in solvent indicates that rotation about the symmetry axis is only slightly more restricted (i.e., smaller $D_\parallel$) with SO_2ClF as solvent rather than SO_2. In contrast, rotation about the minor axis is significantly reduced. While the detection of anisotropy in the rotation of the 1-adamantyl cation provides a sensitive measure of the *extent* of interaction, it gives little information regarding the nature of the interacting species, although tight ion pairs can be excluded according to the following argument.

The rotational anisotropy for the 1-adamantyl cation, should it form an ion pair, may be estimated from the values of σ found for several 1-substituted adamantanes in organic solvents.[21] In deuteriomethanol solutions the values for 1-adamantanecarboxylic acid, 1-adamantanol, and 1-aminoadamantane were determined to be 28, 9.8, and 3.0, respectively. The relative order of the σ values was attributed to the size of the barriers to rotation about the adamantyl C_1-substituent bond, which are approximately 8, 17, and 42 kcal/mol for C–COOH, C–OH, and C–NH_2, respectively. Thus the lowest barrier corresponds to the greatest value of σ.

If the 1-adamantyl cation were part of an ion pair, the internal barrier to rotation about the C_3 axis of the 1-adamantyl moiety would be expected to be low for the following reasons. First, the distance between the cationic carbon and the nearest nuclei in the counterion will be large compared to a covalent bond between the same nuclei, thereby minimizing resistance to rotation. Second, the magnitudes of rotational barriers generally decrease with increasing symmetry.[36] The C_3 symmetry of the cation requires that internal rotation be governed by at least a 3-fold barrier and axial symmetry of the counterion would increase the multiplicity of this barrier. Ion pair formation would not therefore greatly affect rotational diffusion about the C_3 axis of the cation. Rotation about the minor axes of the cation would be restricted as this motion also requires reorientation of the counterion if the ion pair were to remain associated. This rotation would require severe disturbance of solvent molecules. Thus ion pair formation should result in large values of σ for the 1-adamantyl cation in an ion pair, similar to those of 1-adamantane carboxylic acid or 1-adamantanol in methanol solution.

The modest values of σ (0.8–2.6) obtained for the 1-adamantyl cation provide convincing evidence that *this cation does not reorient as an ion pair.* We believe the anisotropy results from relatively weak electrostatic interactions between the cationic site and diffuse negative charge cloud[37] of the anionic species present, SbF_6^-, $Sb_2F_{11}^-$, $Sb_2F_{16}^-$ in SbF_5 solutions and $[SbF_5{\cdot}FSO_3]^-$, $[SbF_5{\cdot}FSO_3{\cdot}SbF_5]^-$, $[SbF_4(FSO_3)_2]^-$, and $Sb_2F_{11}^-$ in solutions of Magic Acid. Such interactions are inversely proportional to the dielectric constant (ϵ) of the supporting medium, suggesting that ϵ is smaller for SO_2ClF than SO_2. Although a value for ϵ for SO_2ClF has not been reported, ϵ for the structurally similar sulfuryl halide SO_2F_2 is smaller than that of SO_2 at the same temperature.[38] This interpretation is supported by the fact that σ increases with increasing concentration of the charged species in SO_2.

Conclusions

The rotational anisotropy of the 1-adamantyl cation is very sensitive to interactions between its cationic site (C1) and the supporting medium. In solutions of SbF_5 or Magic Acid these interactions are independent of the cation precursor but vary with solvent. The stronger interactions detected for cations in superacid solutions with SO_2ClF, rather than SO_2 as solvent, indicate that external stabilization of the charge is greater in SO_2ClF. The magnitude of the σ values determined for the rotation of the 1-adamantyl cation suggests that electrostatic interactions are responsible for the anisotropy in its rotational reorientation and that the cation does not reorient as an ion pair. These studies suggest that any carbocations with less charge localization at the cationic center than adamantyl will also not reorient as part of a long-lived ion pair.[39]

Experimental Section

Preparation of Cation Solutions. Antimony pentafluoride (Ozark-Mahoning Co.) and fluorosulfonic acid (Columbia Organic Chemicals Co.) were redistilled before use and stored in PTFE containers. Sulfuryl chloride fluoride (Columbia Organic Chemicals Co.) was distilled from SbF_5 to remove SO_2 which may have been present as an impurity.[8] The 1-adamantyl cation was prepared by adding the precursor (1-adamantanol, 2-adamantanol, or 1-chloroadamantane) in small amounts as a finely divided solid to precooled solutions of the appropriate acid and solvent at −90 or −78 °C in graduated reaction vessels and stirred vigorously under dry nitrogen. The solutions were transferred to 10-mm NMR tubes via a cooled double-ended syringe needle.[24]

NMR Measurements. NMR spectra were recorded on a JEOL FX-100 spectrometer with a $\pi/2$ pulse time of 24.5 μs. Ion solutions were restricted to a height of 17 mm to enable a true null to be obtained with a π pulse. Internal field stabilization was provided by a 3 mm o.d. capillary of acetone-d_6 containing $(CH_3)_4Si$. The temperature in the probe was measured before and after T_1 measurements with a calibrated, digital, platinum resistance thermometer. No significant heating due to proton decoupling was observed when the temperature was measured by this thermometer in an ion solution. All T_1 values were determined by the fast inversion–recovery method[40] and the intensity data were fitted by an iterative procedure[41] to eq 2, where I is the inhomogeneity (in B_1)

$$S_\tau = S_\infty[1 - (1 + I)e^{-\tau/T_1} + Ie^{-(\tau+\mathrm{PD})/T_1}] \qquad (2)$$

parameter, PD is the pulse delay, and other symbols have their usual

---

(36) Alger, T. D.; Grant, D. M.; Harris, R. K. *J. Phys. Chem.* **1972**, *76*, 281–283. Ladner, K. H.; Dalling, D. K.; Grant, D. M. *J. Phys. Chem.* **1976**, *80*, 1783–1786.

(37) Sorensen visualized such a cloud in the case of 2-adamantyl cations, see ref 17.

(38) Weast, R. D. Ed. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1982–83.

(39) In as much as the ^{13}C chemical shifts are a reasonable guide to charge localization, then only a few alkyl and cycloalkyl carbocations have higher positive charge density than 1-adamantyl; e.g., δC^+ 299 1-adamantyl,[23c,24] 336 *tert*-butyl, 337 1-methyl-1-cyclopentyl, 322 2-methyl-2-adamantyl;[24] see also: Servis, K. L.; Shere, F.-F. *J. Am. Chem. Soc.* **1980**, *102*, 7233–7240. With use of Olah's "total chemical shift difference" criterion, 1-adamantyl has one of the largest differences of any carbocation, $\Delta\delta C = \sum\delta C(\text{cation}) - \sum\delta C(\text{hydrocarbon}) = 515$ ppm. However, it is generally agreed that a significant contribution arises from substantial deshielding of the β-carbons caused by C–C hyperconjugation: Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

(40) Canet, D.; Levy, G. C.; Peat, I. R. *J. Magn. Reson.* **1975**, *18*, 199–204.

(41) Wolberg, J. R. *Prediction Analysis*; D. Van Nostrand: Princeton, NJ, 1967.

meaning. Nuclear Overhauser enhancements were measured by comparison of noise-decoupled and gated decoupled spectra in the normal manner, with pulse delays of $5T_1$ (noise) and $10T_1$ (gated).

Acknowledgment. This work was supported by the Australian Research Grants Committee and by a Commonwealth Postgraduate Award to D.R.L. We are grateful to Dr. R. A. Craig for reading the manuscript.

Registry No. Adamantyl cation, 12558-95-1.

Variations in the Heterogeneity of the Decay of the Fluorescence in Six Procyanidin Dimers

Donghwan Cho,[†] Rujiang Tian,[‡] Lawrence J. Porter,[§] Richard W. Hemingway,[⊥] and Wayne L. Mattice*,[†]

Contribution from the Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, Chemistry Division, Department of Scientific and Industrial Research, Petone, New Zealand, and Southern Forest Experiment Station, Pineville, Louisiana 71360. *Received October 10, 1989*

Abstract: The decay of the fluorescence has been measured in 1,4-dioxane for six dimers of (2*R*,3*R*)-(−)-epicatechin and (2*R*,3*S*)-(+)-catechin, hereafter denoted simply epicatechin and catechin. The dimers are epicatechin-(4β→8)-catechin, epicatechin-(4β→8)-epicatechin, catechin-(4α→8)-catechin, catechin-(4α→8)-epicatechin, epicatechin-(4β→6)-epicatechin, and epicatechin-(4β→8;2β→O→7)-epicatechin. The monomers and the bridged dimer have a fluorescence that decays as a single exponential. The remaining five dimers have a heterogeneous decay that can be described by the sum of two exponentials. The heterogeneity is most apparent in the two dimers with 4α→8 interflavan bonds. In view of the molecular origin of the heterogeneous decay in the presence of two rotational isomers at the interflavan bond, polymeric procyanidins with predominantly α stereochemistry for the interflavan bond at C(4) should be more disordered and more compact than those with predominantly β stereochemistry.

The most common naturally occurring polymeric procyanidins are polymers of two 2,3-flavan-3-ols, (2*R*,3*R*)-(−)-epicatechin and (2*R*,3*S*)-(+)-catechin, hereafter referred to simply as epicatechin and catechin. These polymers are found in the leaves, fruits, and barks of many woody and herbaceous plants.[1] Interest in these polymers is increasing because of their potential as a renewable source of useful chemicals,[1] their probable use by plants as a defense mechanism,[2] and their formation of complexes with a variety of naturally occurring and synthetic polymers.[3–7]

An interflavan bond from C(4) of one monomer unit to C(8) of its neighbor is the most common linkage between monomer units in the naturally occurring polymers.[8] Interflavan bonds from C(4) to C(6) also occur. Figure 1 depicts the covalent structures of six dimers of catechin and/or epicatechin. The trivial nomenclature of the six unbridged dimers is procyanidin B1, B2, B3, B4, B5, and B7. The full nomenclature described by Hemingway et al.[9] is epicatechin-(4β→8)-catechin, epicatechin-(4β→8)-epicatechin, catechin-(4α→8)-catechin, catechin-(4α→8)-epicatechin, epicatechin-(4β→6)-epicatechin, and epicatechin-(4β→6)-catechin, respectively. These names are based on the constituent monomer units and the location and stereochemistry of the interflavan bond between monomer units. Figure 2 depicts the covalent structure of two bridged dimers, procyanidin A1 and A2. Their longer names are epicatechin-(4β→8;2β→O→7)-catechin and epicatechin-(4β→8;2β→O→7)-epicatechin, respectively. The bridges from C(2) to C(7) in procyanidin A1 and A2 prevent internal rotation about the interflavan bond.

Since it was first reported a few years ago,[10,11] the fluorescence of the oligomeric procyanidins has played an important role in the development of an understanding of the conformations of the higher polymers. Upon excitation near 280 nm in dilute solution in 1,4-dioxane, both monomers show a single emission band at 320–324 nm.[11,12] The decay of the intensity of the fluorescence, $I(t)$, can be described by a single exponential.

$$I(t) = \alpha \exp(-t/\tau) \tag{1}$$

The fluorescence lifetimes, τ, for the two monomers are indistinguishable.[11] Higher oligomers exhibit an emission maximum in the same spectral region, but with a lower fluorescence quantum yield, Q, than that obtained with the monomers.[11,12] Although a constrained dimer, procyanidin A1, exhibits a fluorescence decay that can be described by eq 1, two unconstrained dimers, procyanidins B1 and B7, exhibit a heterogeneous decay that requires the sum of two exponentials for an adequate description.[11]

$$I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \tag{2}$$

[†] The University of Akron.
[‡] Bowling Green State University.
[§] Department of Scientific and Industrial Research.
[⊥] Southern Forest Experiment Station.

(1) Hemingway, R. W., Karchesy, J. J., Eds. *Chemistry and Significance of Condensed Tannins*; Plenum Press: New York, 1989.

(2) Haslam, E. *Biochem. J.* **1974**, *139*, 285.

(3) Oh, H. I.; Hoff, J. E.; Armstrong, G. S.; Hoff, L. A. *J. Agric. Food Chem.* **1980**, *28*, 394.

(4) Hagerman, A. E.; Butler, L. G. *J. Biol. Chem.* **1981**, *256*, 4494.

(5) Bergmann, W. R.; Mattice, W. L. *ACS Symp. Ser.* **1987**, *No. 358*, 162.

(6) Tilstra, L. F.; Maeda, H.; Mattice, W. L. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1613.

(7) Tilstra, L. F.; Cho, D.; Bergmann, W. R.; Mattice, W. L. In *Chemistry and Significance of Condensed Tannins*; Hemingway, R. W., Karchesy, J. J., Eds.; Plenum Press: New York, 1989; p 335.

(8) Thompson, R. S.; Jacques, D.; Haslam, E.; Tanner, R. J. N. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1387.

(9) Hemingway, R. W.; Foo, L. Y.; Porter, L. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1209.

(10) Bergmann, W. R.; Barkley, M. D.; Mattice, W. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27* (2), 320.

(11) Bergmann, W. R.; Barkley, M. D.; Hemingway, R. W.; Mattice, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 6614.

(12) Cho, D.; Porter, L. J.; Hemingway, R. W.; Mattice, W. L. *Polymer* **1989**, *30*, 1955.

0002-7863/90/1512-4273$02.50/0