

nitrogen. Thus, Swift and Lo³⁴ find the primary solvation number of magnesium nitrate or perchlorate in liquid ammonia to be 5.0. In chlorophyll, magnesium is coordinated to four nitrogen atoms, which should reduce the Lewis acid character of the magnesium with respect to further coordination. This view appears to be consistent with the calculations of Zerner and Gouterman³⁵ on the positive charge of metals in metalloporphyrins. The large difference between K_1 and K_2 in our experiments, which strongly implies a preference for penta-coordination of the magnesium, is thus consistent with other evidence.

The fact that K_1 is changed by a factor of 4 when the added alcohol was changed from methanol to *t*-butyl alcohol suggests that there is a definite steric requirement for coordination of nucleophiles with the central magnesium of chlorophyll. Steric interaction would favor coordination of the low molecular weight alcohols, enol phosphates, or amines with chlorophyll as compared to the bulkier phospho- or sulfolipids or sugar phosphates. Preliminary measurements show plant sulfolipid to be a weak coordinating agent for chlorophyll *a* in CCl_4 solution.³⁶

The calculations of ligand-chlorophyll interaction geometries and theoretical chemical shifts for the $\text{Chl}(\text{ROH})$ complexes show surprisingly close agreement in both directions. This close agreement can be taken as support of the assumptions in the calculations, as it is difficult to see how a broadly self-consistent pattern would emerge from these calculations if the assumptions were very much out of line. The Mg-O bond distance

(34) T. J. Swift and H. H. Lo, *J. Amer. Chem. Soc.*, **89**, 3988 (1967).

(35) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).

(36) J. J. Katz, *Progr. Appl. Spectry.*, in press.

required by our calculations (3.1 Å) is somewhat longer than would have been anticipated for a strong Mg-O coordination bond. The chlorin π -electron cloud, which has a half-width of 2.5 Å, probably presents a substantial steric barrier to a shorter Mg-O distance.

Conclusion

We believe the experiments described here provide direct evidence for chlorophyll-ligand interactions in halocarbon solvents. The nmr method in conjunction with deuteriochlorophylls makes possible the direct examination of all of the macro species involved in the equilibria, for not only are the nmr spectra simplified, but the C-10 proton, which is now clearly visible, can be used simultaneously to follow the state of aggregation of the chlorophyll itself. The principal species in the equilibrium between aggregated chlorophyll and alcohol are the chlorophyll dimer and the chlorophyll monomer monosolvate. The equilibrium constants for disaggregation of chlorophyll dimer by 2 mol of alcohol to form chlorophyll monosolvate appear to be of the order of 60 l. mol⁻¹. Both chlorophyll dimer and monosolvate contain penta-coordinate magnesium(II). Chlorophyll disolvate species, in which magnesium is hexacoordinate, appear much less important in the solvent systems we have used. The procedure described here appears to be broadly applicable, and other classes of ligands are under investigation.

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Communications to the Editor

Stabilities of Carbonium Ions in Solution. I. Calorimetric Heats of Formation in Fluorosulfonic Acid-Antimony Pentafluoride Mixtures at -60° ¹

Sir:

We report herein a method for calorimetric estimation of the heats of formation, ΔH_{C^+} , of simple carbonium ions in solution. Until recently the evidence for aliphatic and alicyclic carbonium ions rested mainly on strong inference from kinetic data and analogy to the well-characterized triarylcarbonium salts. Lately, Olah,^{2,3} Deno,⁴ and Gillespie⁵ have demonstrated that

(1) We gratefully acknowledge support of this work by National Science Foundation Grant GP-6550X.

(2) G. A. Olah and C. U. Pittman, Jr., *Advan. Phys. Org. Chem.*, **4**, 305 (1966).

(3) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

(4) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(5) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

many kinds of aliphatic and alicyclic compounds are converted quickly and completely to stable, well-characterized ions in very strong acid solutions. The carbonium ions are most stable and formed most cleanly in fluorosulfonic acid-antimony pentafluoride mixtures ($\text{SbF}_5\text{-HSO}_3\text{F}$) at low (-40 to -90°) temperatures where their structures are demonstrated by nmr. With good evidence in hand for their existence in super acid, there is a strong incentive to determine the energy changes for formation of the ions. In this report we describe a calorimeter capable of measuring the heat resulting from rapid formation of 10^{-3} M carbonium ion at temperatures down to -65° with solvents as viscous as 15 mole % SbF_5 in HSO_3F .

The instrument is basically that described earlier.⁶ Ethanol replaces mineral oil as the liquid in the heater. The thermistor (Teflon coated, 2000 ohms at -60°) was

(6) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

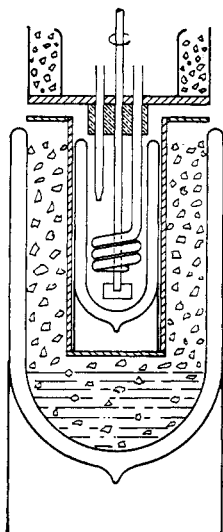


Figure 1. Assembly diagram of low-temperature calorimeter.

made to order by Keystone Carbon Co., St. Marys, Pa. The dewar calorimeter vessel (Figure 1) is placed in an O-ring sealed brass can suspended in a Dry Ice-acetone bath. The Teflon head is machined to fit the dewar tightly at 25° and is mounted on a brass plate which can be bolted to the supporting flange on the can. The head assembly is drilled to accept the heater, thermistor, stirrer, and the sample-introduction device⁶ (not shown in Figure 1). Powdered Dry Ice within the peripheral annular space is used to chill the brass top. Due to careful balancing of the heat of stirring against heat leaks, the apparatus holds a temperature of -60° for at least 8 hr with no significant temperature drift when the solvent is 11.5 ± 0.5 mole % SbF₅-HSO₃F, the medium in which almost all of our measurements were made. Within experimental error, Δ*H*_{obsd} is independent of the SbF₅ concentration over the range of 6 to 13 mole % SbF₅ in HSO₃F for several trial systems.

The relationship of measured heat terms to (Δ*H*)_{C⁺-60}, the heat of forming the carbonium ion from a complexed precursor, is shown in Figure 2. For a variety of reasons, solubility being the most important, the reference state for our measurements is high dilution in carbon tetrachloride at 25°. Independent experiments demonstrated that, if corrections for phase changes are made, the partial molal heats of solution (Δ*H*_s) for a number of typical solutes in carbon tetrachloride are essentially independent of temperature over a 50° range. Therefore (allowing for heat of fusion, if necessary) (Δ*H*_s)²⁵(CCl₄) ≈ (Δ*H*_s)⁻⁶⁰(CCl₄). Thus the hypothetical heat of transfer from infinite dilution in carbon tetrachloride to infinite dilution in SbF₅-HSO₃F at -60°, (Δ*H*)⁻⁶⁰(trans), is equivalent to Δ*H*_{obsd}, the difference between the two measured values (Δ*H*)⁻⁶⁰(react.) and (Δ*H*_s)²⁵(CCl₄). Furthermore, it is known that (Δ*H*)⁻⁶⁰(complex), the heat of complexing without formation of a carbonium ion (e.g., for π complexes), is not sensitive to changes in molecular structure.⁷⁻⁹ It therefore follows that large

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(8) C. F. Douty, Ph.D. Thesis, University of Pittsburgh, 1965.

(9) E. M. Arnett and J. W. Larsen in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., John Wiley and Sons, Inc., New York, N. Y., in press.

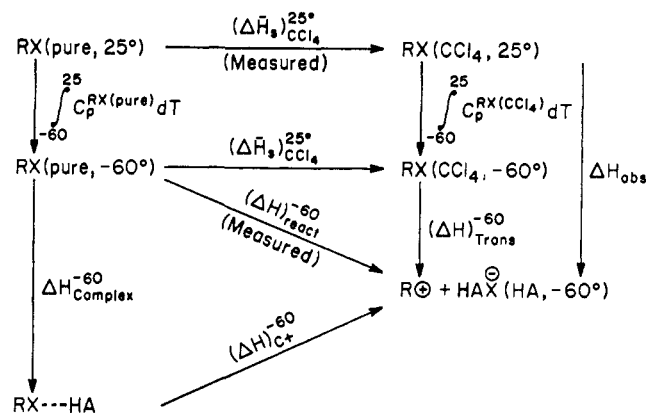


Figure 2. Cycle relating measured enthalpies to Δ*H*_{C⁺}.

changes in Δ*H*_{obsd} within a series of related compounds reflect primarily the influence of structure on (Δ*H*)_{C⁺-60}, the enthalpy of carbonium ion formation.

In addition to absolute calibration of every measurement by electrical heating⁶ there are several checks of our over-all method. Firstly, Δ*H*_{obsd} for mesitylene (mp -52°) was measured at -60° from a supercooled liquid and as a solid. The difference between the values is 3.0 ± 1.2 kcal/mole and is within experimental error of the heat of fusion.¹⁰ Secondly, for cyclohexene and methylcyclopentene, both of which go cleanly to the methylcyclopentyl cation¹¹ in SbF₅-HSO₃F at -60°, Δ*H*_{obsd} values are -16.8 ± 0.8 and -18.3 ± 0.5 kcal/mole, respectively. The difference, 1.5 ± 0.9 kcal/mole, corresponds closely to the difference in their heats of formation, 1.4 kcal/mole, obtained from combustion¹² or estimation by group equivalents.¹³

Carbon tetrachloride, which is probably not protonated even in acid of this strength,¹⁴ gave a Δ*H*_{obsd} of -1.28 ± 0.57 kcal/mole. Further details on technique and more demonstrations of thermodynamic consistency will be included in later reports.

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(13) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

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Stabilities of Carbonium Ions in Solution. II.¹ Benzenonium Ions in Antimony Pentafluoride-Fluorosulfonic Acid at -60°

Sir:

Reported here are calorimetric measurements² of the heats of formation for a variety of carbonium ions ob-

(1) Supported by National Science Foundation Grant GP-6550X.

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