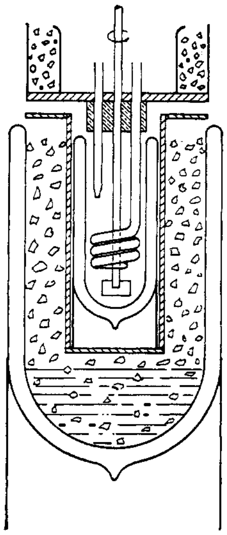

Figure 1. Assembly diagram of low-temperature calorimeter.

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 device[6] (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 % SbF_5–HSO_3F, the medium in which almost all of our measurements were made. Within experimental error, ΔH_{obsd} is independent of the SbF_5 concentration over the range of 6 to 13 mole % SbF_5 in HSO_3F for several trial systems.

The relationship of measured heat terms to $(\Delta H)_{\mathrm{C}^+}{}^{-60}$, 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 $(\Delta\bar{H}_s)$ 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) $(\Delta\bar{H}_s)^{25}(\mathrm{CCl_4}) \simeq (\Delta\bar{H}_s)^{-60}(\mathrm{CCl_4})$. Thus the hypothetical heat of transfer from infinite dilution in carbon tetrachloride to infinite dilution in SbF_5–HSO_3F at −60°, $(\Delta H)^{-60}$(trans), is equivalent to ΔH_{obsd}, the difference between the two measured values $(\Delta H)^{-60}$(react.) and $(\Delta\bar{H}_s)^{25}(\mathrm{CCl_4})$. Furthermore, it is known that $(\Delta H)^{-60}$(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 changes in ΔH_{obsd} within a series of related compounds reflect primarily the influence of structure on $(\Delta H)_{\mathrm{C}^+}{}^{-60}$, the enthalpy of carbonium ion formation.

$$\begin{tikzcd}
\mathrm{RX(pure, 25^\circ)} \arrow[r, "(\Delta\bar{H}_s)^{25^\circ}_{\mathrm{CCl_4}}", "\mathrm{(Measured)}"'] \arrow[d, "\int_{-60}^{25} C_p^{\mathrm{RX(pure)}}\,dT"] & \mathrm{RX(CCl_4, 25^\circ)} \arrow[d, "\int_{-60}^{25} C_p^{\mathrm{RX(CCl_4)}}\,dT"] \arrow[dd, bend left, "\Delta H_{\mathrm{obs}}"] \\
\mathrm{RX(pure, -60^\circ)} \arrow[r, "(\Delta\bar{H}_s)^{25^\circ}_{\mathrm{CCl_4}}"] \arrow[dr, "(\Delta H)^{-60}_{\mathrm{react}}", "\mathrm{(Measured)}"'] \arrow[dd, "\Delta H^{-60}_{\mathrm{Complex}}"] & \mathrm{RX(CCl_4, -60^\circ)} \arrow[d, "(\Delta H)^{-60}_{\mathrm{Trans}}"] \\
 & \mathrm{R^{\oplus} + HA\overset{\ominus}{X}\,(HA, -60^\circ)} \\
\mathrm{RX{-}{-}{-}HA} \arrow[ur, "(\Delta H)^{-60}_{\mathrm{C^+}}"] &
\end{tikzcd}$$

Figure 2. Cycle relating measured enthalpies to ΔH_{C^+}.

In addition to absolute calibration of every measurement by electrical heating[6] there are several checks of our over-all method. Firstly, ΔH_{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 cation[11] in SbF_5–HSO_3F at −60°, ΔH_{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 combustion[12] or estimation by group equivalents.[13]

Carbon tetrachloride, which is probably not protonated even in acid of this strength,[14] gave a ΔH_{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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(7) H. C. Brown and J. J. Melchiore, *J. Am. Chem. Soc.*, **87**, 5269 (1965).

(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.

(10) R. D. Taylor and J. E. Kilpatrick, *J. Chem. Phys.*, **23**, 1232 (1955).

(11) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2692 (1967).

(12) "Combustion Tables," American Petroleum Institute, Pittsburgh, Pa., 1960, p 719.

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

(14) G. Olah, personal communication.

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Stabilities of Carbonium Ions in Solution. II.[1] Benzenonium Ions in Antimony Pentafluoride–Flurosulfonic Acid at −60°

Sir:

Reported here are calorimetric measurements[2] of the heats of formation for a variety of carbonium ions ob-

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

(2) E. M. Arnett and J. W. Larsen, *J. Am. Chem. Soc.*, **90**, 791 (1968).

tained by protonation at −60° of aromatic hydrocarbons in 11.5 ± 0.5 mole % SbF_5-HSO_3F. These correlate closely with similar values obtained by Mackor and coworkers[3] in liquid hydrogen fluoride at 0°. Hence thermodynamic properties for arenonium ion formation in our system are quite relevant to processes leading to these ions under very different conditions of medium and temperature.

There are a number of reasons why benzenonium ions were selected as the point of departure for a systematic study of the relationship between the structure and stability of carbonium ions. A wealth of nmr and other spectral data have established their clean, rapid formation in systems such as ours at low temperatures.[4,5] The necessary compounds are readily available in high purity, and there are no complications due to a leaving group. Brown and Melchiore[6] have shown that there is virtually no variation in the energy of π-complex formation for a series of polyalkylbenzenes, assuring us thereby that structural effects on ΔH_{obsd} reflect primarily changes in carbonium ion stability.

Figure 1 compares our calorimetric heats of carbonium ion formation (ΔH_{obsd}) in SbF_5-HSO_3F at −60° with those determined by Mackor[3] in HF-BF_3 at 0° using an ice calorimeter. Both sets of enthalpy data are plotted against ΔG_{C^+}, the free energy of arenonium ion formation in liquid HF-BF_3.[7] Linear relationships between free energies of protonation and rates of electrophilic substitution reactions are well documented.[4,10] Both plots in Figure 1 are good straight lines whose least-squares slopes agree within experimental error (1.0 ± 0.1 and 1.16 ± 0.08,[11] respectively, for Mackor's results and our data). Therefore, temperature and solvent effects on *relative* ΔH_{C^+} values within this series of benzenonium ions are probably negligible.[12] Other examples of broad correlations between heats of ionization in one medium and free energies of ionization in another have been observed previously.[13]

All calorimetric measurements were repeated at least six times in a given batch of acid and many of the results include runs in different batches on different days. Relative errors (standard deviations) were 5% or less except for azulene (point 12) for which $\Delta H_{\text{obsd}} = -32.3 \pm 3.0$ kcal/mole. Thus, all points are within their individual experimental errors of the correlation line with the exception of 8, hexamethylbenzene. It is probably significant that this is the only ion in the series with an alkyl group at the point of protonation.

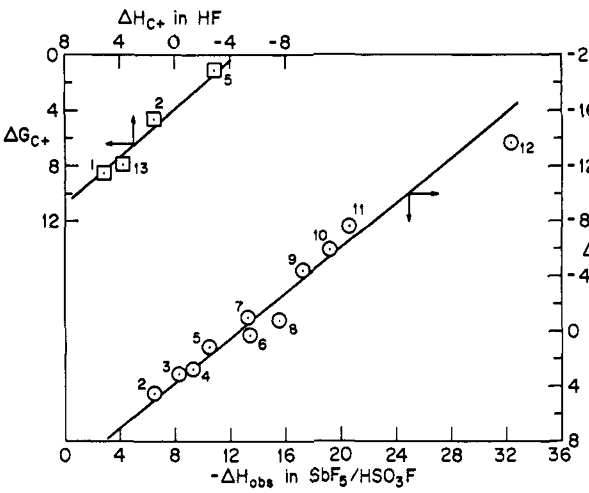

Figure 1. Correlation of heats of carbonium ion formation in SbF_5-HSO_3F at −60° and in HF-BF_3 at 0° with free energy of ionization in HF-BF_3 at 0°. Points correspond to ions derived from the following compounds: (1) toluene; (2) *m*-xylene; (3) 1,2,4,5-tetramethylbenzene; (4) 1,2,3,4-tetramethylbenzene; (5) 1,3,5-trimethylbenzene; (6) 1,2,3,5-tetramethylbenzene; (7) pentamethylbenzene; (8) hexamethylbenzene; (9) anthracene; (10) 2-methylanthracene; (11) 9,10-dimethylanthracene; (12) azulene; and (13) *p*-xylene.

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[3] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

[4] Reviewed by H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 195 (1966).

[5] Reviewed by G. A. Olah and M. W. Meyer in "Friedel Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 623 ff.

[6] H. C. Brown and J. J. Melchiore, *J. Am. Chem. Soc.*, **87**, 5269 (1965).

[7] These values were calculated from p*K* data corrected for symmetry factors.[4] With the exception of azulene (point 12), measured in aqueous perchloric acid[8] and extrapolated to HF by acidity functions, all p*K* values were determined in liquid HF-BF_3.[9]

[8] F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **86**, 327 (1964).

[9] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

[10] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[11] Point 12 (azulene) was not included in the determination of the slope.

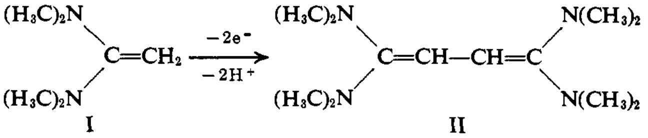
[12] Obviously there are large *absolute* differences between ΔH_{C^+} in the two systems.

[13] E. M. Arnett and J. J. Burke, *J. Am. Chem. Soc.*, **88**, 4308 (1966).

Electrolytic Oxidations of Organics. I. Oxidative Coupling of Vinylidenebisdimethylamine to 1,1,4,4-Tetrakis(dimethylamino)butadiene[1]

Sir:

Interest has sharply increased in electrochemical oxidations of organics, primarily aromatics.[2] This interest has long been delayed because of the complexity of reactions subsequent to initial charge transfers. In the present paper we wish to report the observation of a major product, a butadiene, in the electrooxidation of a somewhat simple organic, an ethylene. We have observed that vinylidenebisdimethylamine[3] (I) can be oxidized elecrolytically to 1,1,4,4-tetrakis(di-



$$((H_3C)_2N)_2C{=}CH_2 \xrightarrow[-2H^+]{-2e^-} ((H_3C)_2N)_2C{=}CH{-}CH{=}C(N(CH_3)_2)_2$$

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[1] Presented at the 1967 Midwest Regional American Chemical Society Meeting, University of Missouri, Columbia, Mo., Nov 2-3, 1967.

[2] For example: (a) M. E. Peover in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1967; (b) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967); (c) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967); (d) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967); (e) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *ibid.*, **88**, 3498 (1966); (f) L. Eberson and K. Nyberg, *ibid.*, **88**, 1686 (1966); and (g) L. L. Miller and A. K. Hoffman, *ibid.*, **89**, 593 (1967).