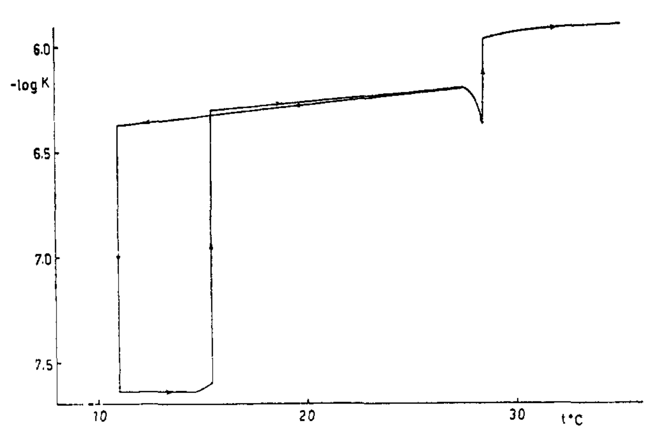


Figure 1. Plot of $-\log K$ *vs.* temperature for potassium perchlorate in sulfolane.

In Table I the conductance values at various temperatures for one run are given. From Table I the graph of Figure 1 has been constructed; in this diagram the arrows indicate the succession of temperature used.

Table I. Temperature Dependence of Log of the Conductivity for a $KClO_4$ in Sulfolane Solution[a]

Data obtained decreasing the temperature		Data obtained increasing the temperature	
Temp, °C	$-\log K$	Temp, °C	$-\log K$
26.00	6.210	11.00	7.638
23.00	6.245	12.00	7.638
21.00	6.269	13.00	7.638
17.00	6.306	14.00	7.638
16.00	6.319	15.00	7.620
15.90	6.319	15.10	7.615
15.70	6.321	15.30	7.602
15.50	6.323	15.42	7.595
15.40	6.324	15.45	6.305
15.30	6.325	15.53	6.303
15.25	6.326	15.73	6.301
15.00	6.329	16.35	6.294
14.50	6.333	24.95	6.213
14.00	6.339	27.50	6.192
13.50	6.344	27.70	6.211
13.00	6.350	27.81	6.214
12.00	6.361	28.00	6.238
11.00	6.371	28.10	6.256
		28.33	6.333
		28.40	6.338
		28.45	6.282
		28.50	5.961
		29.02	5.955
		30.00	5.930
		31.00	5.921
		33.00	5.900
		35.00	5.891

[a] $c = 1.2 \times 10^{-4}$ *M* at 30°.

Some interesting results can be deduced. Firstly, the sharp change of the conductivity at the transition point allows a precise determination of this temperature. The value is reproducible if obtained raising the temperature; when the temperature is decreased the system exceeds the transition point, and it may stay in a metastable state for several days. In this way a temperature of 15.45° was obtained which agrees very well with the value obtained from cryoscopic[1] and dielectric constant[7] measurements. Furthermore, the melting point agrees with the value obtained from cryoscopic determinations on pure sulfolane; therefore, owing to the high cryoscopic constant of this solvent (64), this accord is possible only when very dilute solutions are analyzed.

Figure 1 shows that in the temperature range 27.5–28.5° the conductivity of the solution at first decreases with increasing temperature and then rapidly increases near the melting point.

Figure 1 also shows that the mobility of the ions in the plastic phase of sulfolane is too high if compared with the mobility of the same ions in liquid sulfolane (the viscosity of the plastic sulfolane has not been measured, but it is probably very high).

To explain these facts we formulate the hypothesis that the ions are immersed in small liquid zones dispersed within the bulk of the solid solvent. Consequently, even if the measured resistance of the conductor between the two electrodes increases, the resistance of each liquid zone decreases as an effect of the increased electrolyte concentration. A similar hypothesis has been formulated to explain how certain chemical reactions are markedly accelerated when the solution is frozen.[8] The formation of liquid zones dispersed in the solid phase also seems consistent with the anomalous conductivity near the melting point; the broadening of the liquid zones can decrease the local concentration of the salt so that the conductivity decreases.

More definite conclusions on this problem will be made when conductivity data of several electrolytes at various concentration are obtained. Therefore, we are trying to obtain conductivity data in this phase of sulfolane which are reproducible within a few parts in a thousand.

---

(7) U. Lamanna, O. Sciacovelli, and L. Jannelli, *Gazz. Chim. Ital.*, **96**, 114 (1966).

(8) T. C. Bruice and A. R. Butler, *J. Am. Chem. Soc.*, **86**, 4104 (1964); R. E. Pincock and T. E. Kiovsky, *ibid.*, **87**, 2072 (1965); R. E. Pincock, *ibid.*, **87**, 1274 (1965); R. E. Pincock and T. E. Kiovsky, *ibid.*, **87**, 4100 (1965).

Mario Della Monica
Istituto Chimico, Università di Bari
Bari, Italy

Received November 5, 1968

The Stability of Ferrocenylcarbonium Ions[1]

Sir:

The high degree of stabilization of α-ferrocenylcarbonium ions is manifested in the unusual reactivity of ferrocene derivatives in a variety of reactions believed to proceed through such ions as intermediates.[2] This great stability has invited speculations about the structure of these carbonium ions and the nature of their stabilization. It was proposed some years ago on the basis of solvolysis results that a portion of the stabilization may arise from direct overlap of iron orbitals with the p orbital of the formally cationic carbon.[3] Recently, this interpretation has been questioned, and an alternative model involving "carbon–iron hypercon-

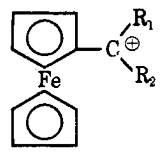
---

(1) Presented in part at the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968.

(2) For reviews, see M. Cais, *Record Chem. Progr.*, 27, 177 (1966); *Organometal. Chem. Rev.*, 1, 435 (1966).

(3) (a) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959); (b) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840, 4216 (1961); (c) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. **13**, 1 (1960).

Table I. Acidities and Spectra of α-Ferrocenylcarbonium Ions



R_1	R_2	λ_{max}, mμ (log ε)[a]	pK_R
H	H	256 (3.95)	−1.28[b]
CH_3	H	258 (4.04), *ca.* 375 (2.62)	−0.66[b]
C_6H_5	H	*Ca.* 227 (4.03), 252 (4.00), 280 (3.92), 329 (4.08), 405 (3.50)	+0.4,[b] +0.1[c]
C_6H_5	C_6H_5	258 (4.06), 365 (4.08), *ca.* 560 (3.37)	+0.75[c]

[a] In 58% H_2SO_4. [b] In aqueous H_2SO_4. [c] In ethanol–water–H_2SO_4 by comparison with trianisylmethyl cation.

jugation" was put forth.[4]

It seemed desirable to us to investigate the stability of ferrocenylcarbonium ions directly, rather than in the indirect manner allowed by kinetics. Accordingly, we report in Table I preliminary results of a Hammett–Deno type indicator acidity study[5] of several α-ferrocenylcarbonium ions. In all instances, the carbinols are converted in acidic solution to a new species which absorbs in the visible and ultraviolet regions. Reversibility of this conversion was confirmed by recovery experiments, and no further spectral changes were found to occur in more highly acidic solutions up to 96% sulfuric acid. The corresponding carbonium ion is the only reasonable possibility for the absorbing species. Dilute solutions of the carbinol and carbonium ion in acid were stable enough for straightforward spectroscopic studies, except in the case of the diphenylferrocenylcarbonium ion.[6]

The results in Table I demonstrate again the high stability of α-ferrocenylcarbonium ions. But furthermore, a closer examination of these results shows that *the thermodynamic stability of ferrocenylcarbonium ions is several powers of ten greater than kinetics studies indicate.* Several comparisons may be made. (1) Relative solvolysis rates of the acetates of ferrocenylmethanol, α-ferrocenylethanol, phenylferrocenylmethanol, and triphenylmethanol are 0.63:6.6:67:1.00.[3b] From the reported pK_R of triphenylcarbonium ion (−6.63)[5] and presuming twice the sensitivity to structure in ionization as in solvolyses, the ferrocenylcarbonium ions range from 3 to 6 pK units less acidic than predicted. (2) A pK_R value of −17.3 has been reported for 2,4,6-trimethylbenzyl cation.[8] Extrapolation[9] to the ferrocenylcarbonium ion using σ^+ − 1.55 for aryl=ferrocenyl[10] yields a predicted pK_R of −7.4. (3) From published pK_R values of mono- and disubstituted diarylcarbonium ions,[5] a ρ value of −5.2 may be derived. This correlation predicts pK_R for the phenylferrocenylcarbonium ion of −5.4 (*vs.* the observed value of +0.1 to 0.4). A multiple variation treatment of the type of Ritchie[11] raises the predicted value slightly (to *ca.* −4.0). A similar treatment[11] for the diphenylferrocenylcarbonium ion predicts a pK_R value only about 1.2 units more negative than the observed value.

The results above raise questions concerning the relevance of any kinetic evidence to the question of ferrocenylcarbonium ion structure. Customarily, the stabilities of carbonium ions may be correlated with their rates of formation in solvolysis reactions. The failure of such a correlation in the present instance suggests that the carbonium ion is substantially beyond the transition state along the reaction coordinate, and likely significantly different in geometry as well as energy. The high energy of the transition state (relative to carbonium ion) may reflect a large reorganization of bonding and structure in passing from carbinol to carbonium ion. The present results provide no basis for choice between the "metal participation" and "hyperconjugation" models for the ferrocenylcarbonium ion, since either might involve substantial changes in bonding. However, the remarkable stability of ferrocenylcarbonium ions and the slight additional stabilization achieved by methyl and phenyl substitution both argue for substantial change delocalization, most probably onto the iron. Further speculation does not appear to be warranted at this stage; a more extensive discussion of these results and other work currently in progress in our laboratory will be presented in a full publication.

[4] T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967). This paper also gives references to nmr data.

[5] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

[6] The diphenylferrocenylcarbonium ion decomposes to diphenylfulvene.[7] Spectral absorptions were extrapolated back to the time of mixing.

[7] A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, and N. A. Rodionova, *Dokl. Akad. Nauk SSSR*, **160**, 355 (1965).

[8] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

[9] A ρ value for monoarylcarbonium ions may be estimated as −10, as this approximates the total effect of substituents on di- and triarylcarbonium ions (see Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4979 (1958)), and an effective σ^+ value may be estimated for the *ortho*-methyl groups from *t*-cumyl chloride solvolyses (see H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *ibid.*, **79**, 1897 (1957)). The extrapolated value must be considered very rough because of uncertainties in studies of monoarylcarbonium ions.

[10] M. L. Gross, Ph.D. Thesis, University of Minnesota, 1966; based on solvolyses of a series of α-arylethyl acetates.

[11] C. D. Ritchie, W. F. Sager and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 2349 (1962).

[12] National Science Foundation Undergraduate Research Participant, Summer 1967.

E. Alexander Hill, Russell Wiesner[12]
Department of Chemistry, University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

Received September 13, 1968

The Identity of Benzyne from Various Precursors

Sir:

Does benzyne generated from various sources exhibit identical properties?[1] We wish to report that for a number of precursors the benzyne formed has identical properties, but that it may *appear* to be different due to the nature of the reactants and reaction conditions. We have also found 1,4-dimethoxyanthracene[2] to be an effective compound to use as a diagnostic tool to test for the equivalency of benzyne under various conditions.

Table I shows that, within the range of experimental error, only one of the benzyne precursors affords an *apparently* different benzyne in that the ratio of center- to end-ring adducts (B/A ratio) is significantly larger for

[1] R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).

[2] A. Etienne and Y. Lepage, *Compt. Rend.*, 240, 1233 (1955).