

402. *The Basicity of Hydrocarbons. Part I. Cryoscopy of Conjugated Hydrocarbon and Carbinol Solutes in Sulphuric Acid.*

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1:1-Diphenylethylene and 1- α -naphthyl-1-phenylethylene dissolve in 100% sulphuric acid giving a freezing-point depression twice as great as that produced by an ideal inert solute, in agreement with the hypothesis that these hydrocarbons behave as simple Brönsted bases. 1:1-Diphenylethanol gives a four-fold freezing-point depression, showing its ionisation as a secondary base. Triphenylethylene and 3:4-benzopyrene give rapidly time-variable depressions.

The application of thermistor thermometry in cryoscopic work is discussed.

THE attribution of basic properties to olefinic hydrocarbons has been a useful hypothesis in the explanation of acid-catalyzed hydrocarbons reactions. This idea, elaborated chiefly by Whitmore and his school (see, *e.g.*, Whitmore, *Ind. Eng. Chem.*, 1934, **26**, 94; *ibid.*, News Ed., 1948, **26**, 669; Schmerling and Ipatieff, "Advances in Catalysis," Vol. II, New York, 1950), has been particularly fruitful in the field of olefin polymerization. Carbonium ions are thought to be intermediates in numerous reactions of organic chemistry

and most of these can also be regarded as the conjugate acids (in the Brönsted-Lowry sense) of olefins; *e.g.*, the trimethylcarbonium ion (*tert.*-butyl cation)* is the conjugate acid of *isobutylene*.

The extension of this idea to the preparation of stable solutions of these conjugate acids and their characterization by some definite physical property has not been equally attractive, probably for the following reasons. First, the isolation of what are thought to be reactive intermediates would not appear to be promising and, secondly, it is a widespread notion that hydrocarbons will not dissolve in strong acids, except when dissolution is accompanied by some permanent chemical change in the compound (such as sulphonation); *e.g.*, Sidgwick ("The Chemical Elements and Their Compounds," Oxford, 1950, p. 913) remarks that sulphuric acid ". . . will not dissolve . . . aromatic and aliphatic hydrocarbons and their halides." This generalization is contradicted by only a few isolated examples in the literature and the evidence was perhaps thought to be capable of an alternative interpretation. In particular, perylene (Scholl, Seer, and Weitzenböck, *Ber.*, 1910, **43**, 2202), anthracene (Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2115), and 3:4-benzopyrene (Berenblum, *Nature*, 1945, **156**, 601) have been reported to dissolve without change in sulphuric acid. There are also observations on the solubility of aromatic hydrocarbons in hydrogen fluoride (Klatt, *Z. anorg. Chem.*, 1937, **234**, 189) and of the azulenes in various aqueous mineral acids (Sherndal, *J. Amer. Chem. Soc.*, 1915, **37**, 167, 1537; Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1949, **32**, 574).

It is the object of the present work to introduce a more quantitative examination of the basicity of hydrocarbons. In this paper cryoscopic measurements of hydrocarbon solutes in sulphuric acid are reported as evidence for the nature of the ionization. In Part II the ultra-violet absorption spectra of several of the conjugate acids are recorded, giving further evidence for the occurrence of basic ionization and permitting certain deductions about the structure of the conjugate acid. Part III relates to partition experiments with three hydrocarbons from which an order-of-magnitude assessment of their basicity constants is possible. In Part IV a theoretical discussion of basicity in conjugated hydrocarbons is given on the basis of simple molecular-orbital calculations.

In the search for suitable hydrocarbons, many were examined but only a few were satisfactory for our purpose. In many cases irreversible changes of some kind or other supervene, as is to be expected when a reaction medium of high chemical reactivity in several respects is used. Unfortunately, present techniques restrict cryoscopic measurements in strong acids to 100% sulphuric acid—and possibly methanesulphonic acid (Craig, Garrett, and Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 163)—as solvent. The occurrence of sulphonation was suspected in several cases from the detection of water-soluble products. Polymerization, esterification, and oxidation are other possible reactions. These complications were examined only insofar as was necessary to restrict or to correct for their occurrence; they have not as yet been studied in detail and for their own sake.

EXPERIMENTAL

Materials.—Sulphuric acid (100%) was prepared by dilution of SO₂-free oleum with 98% acid (*J.*, 1951, 2102).

1:1-Diphenylethylene and 1:1-diphenylethanol were prepared by Grignard reaction from bromobenzene and acetophenone (*Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 226). The hydrocarbon was purified by distillation under reduced pressure (b. p. 125°/5 mm.) before use; the carbinol was crystallized from light petroleum.

1- α -Naphthyl-1-phenylethylene was prepared by an adaptation of the above method, α -bromonaphthalene and acetophenone being used as starting materials.

Triphenylethylene (*Org. Synth.*, Coll. Vol. II, p. 606) and anthracene were purified synthetic specimens.

Tetraphenylethylene was prepared by reduction from benzophenone *via* benzpinacol and benzpinacolone (*op. cit.*, p. 73; Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 449). The compound is efficiently purified by extraction of impurities with concentrated sulphuric acid from an ice-

* The nomenclature for carbonium ions used here is an adaptation of the carbinol convention, *e.g.*, the ion derived from trimethylcarbinol by loss of a hydroxide ion is termed the trimethylcarbonium ion.

replaced by $n_1 C_p$, where C_p is the molar heat capacity of the solvent. With this substitution equation (1) reduces to the usual relation

$$\delta T = (C_p/\Delta H^f)\theta S$$

where the ratio $C_p/\Delta H^f$ has the value 0.012 deg.^{-1} for sulphuric acid (Gillespie, Hughes, and Ingold, *loc. cit.*). For the micro-apparatus this substitution is not permissible since the heat capacity of the cryoscope itself (C_0) makes an important contribution to C , *i.e.*,

$$C = C_p n_1 + C_0 \text{ or } \delta T = (C_0/\Delta H^f + 0.12)\theta S$$

Owing to the rapid temperature change during seeding, C_0 may not be the true heat capacity of the cryoscope but may contain heat-transfer terms. Its direct experimental determination

TABLE 1.

Molality	F. p. depn., obs.	T	S	θ	δT	ΔT^*	F. p. depn., corr.
1 : 1-Diphenylethylene.							
—	—	7.94°	2.05°	0.47°	0.012°	—	—
0.0080	0.096°	8.48	1.41	0.57	0.010	-0.004°	0.102°
0.0170	0.208	7.64	2.14	0.68	0.017	-0.008	0.211
—	—	7.78	2.28	0.48	0.013	—	—
0.0039	0.054	7.84	2.09	0.54	0.014	-0.002	0.055
0.0126	0.146	7.85	1.99	0.63	0.015	-0.006	0.150
1 : 1-Diphenylethanol.							
—	—	7.65	2.33	0.48	0.013	—	—
0.0048	0.113	8.14	1.72	0.59	0.012	-0.005	0.119
0.0096	0.241	7.49	2.25	0.72	0.019	-0.010	0.245
0.0140	0.325	8.54	1.11	0.81	0.011	-0.016	0.343
0.0189	0.422	7.60	1.96	0.91	0.021	-0.020	0.434

* Correction for incomplete suppression of self-dissociation of sulphuric acid (computed from values of constants given by Gillespie, *J.*, 1950, 2493, 2516).

TABLE 2. *Time variation of freezing-point depression by 1- α -naphthyl-1-phenylethylene (0.0090 molal).*

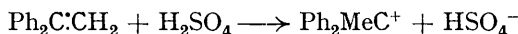
Time (min.)	F. p. depn., obs.	T_f	S	θ	δT	F. p. depn., corr.*	" i " Factor
—	—	7.79°	2.41°	0.26°	0.008°	—	—
20	0.153°	7.74	2.30	0.42	0.012	0.149°	2.77
50	0.191	7.61	2.40	0.45	0.013	0.186	3.45
83	0.212	7.80	2.18	0.48	0.013	0.207	3.85
120	0.238	7.34	2.62	0.50	0.016	0.230	4.27
155	0.240	8.01	1.95	0.50	0.012	0.236	4.38
1200	0.349	6.94	2.91	0.61	0.021	0.336	6.24

* Owing to the uncertainty of the nature of the secondary process the correction ΔT has not been applied in this case. For a 0.0090-molal solution of a simple base this correction would amount to -0.007° (increasing the magnitude of the freezing-point depression). A correction of this order of magnitude does not affect our conclusions.

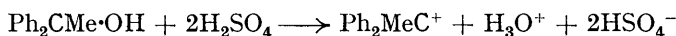
or theoretical evaluation was therefore not considered to be promising and its value was obtained empirically by carrying out measurements on a solute of known freezing-point depression (potassium sulphate).

DISCUSSION

1 : 1-Diphenylethylene gives a two-fold freezing-point depression in sulphuric acid and 1 : 1-diphenylethanol a four-fold one. The simplest explanation compatible with these findings is that diphenylethylene ionizes as a simple base



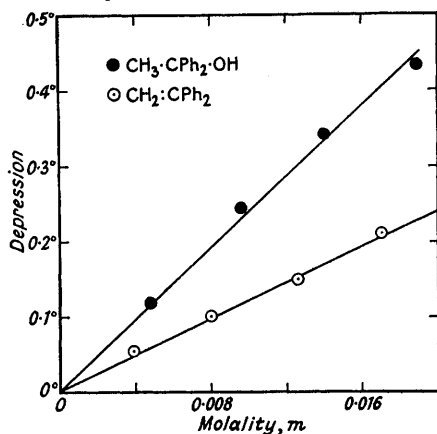
and the carbinol as a secondary base (Gold and Hawes, *J.*, 1951, 2102)



The cryoscopic data do not, of course, furnish information about the structure of the carbonium ion in solution; this will be discussed on the basis of more relevant experimental data in Part II. The above formulation of the ion anticipates the result of this discussion.

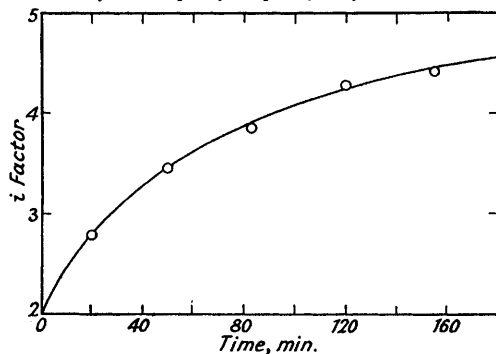
A. G. Evans (*J. Appl. Chem.*, 1951, 1, 240) has recently published the results of similar experiments on 1:1-diphenylethylene and has come to the same conclusion. His results were, however, calculated on the basis of obsolete cryoscopic constants for sulphuric acid, and their recalculation by using the most reliable value of the cryoscopic constant available, *viz.*, 5.98 moles⁻¹ deg. (Gillespie, Hughes, and Ingold, *loc. cit.*), leads to a value of

FIG. 1. Freezing-point depressions of 1:1-diphenylethylene and 1:1-diphenylethanol in sulphuric acid.



(Lines are drawn with theoretical slopes corresponding to $i = 2$ and $i = 4$.)

FIG. 2. Time variation of freezing-point depression of 1- α -naphthyl-1-phenylethylene.



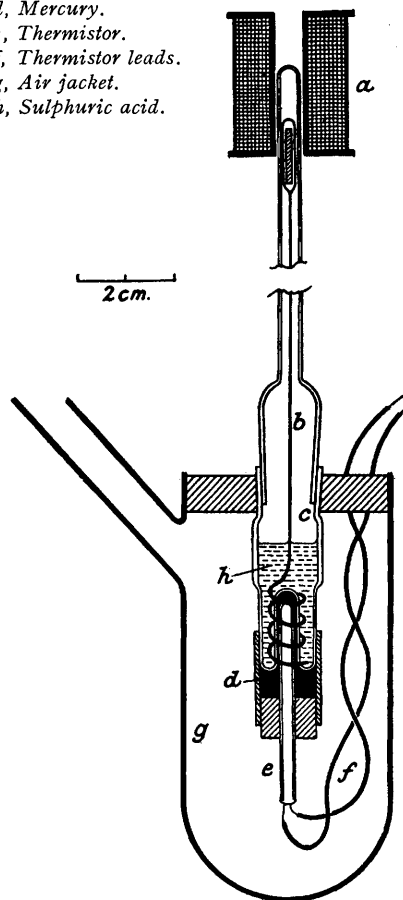
~ 2.6 for the i -factor. Our results are therefore not in very good agreement and we are uncertain about the cause of this.

The result for 1- α -naphthyl-1-phenylethylene appears less simple than that for 1:1-diphenylethylene since the freezing-point depression is found to show a progressive increase with time (Fig. 2). Extrapolation of the curve back to zero time makes it very probable that the initial value of the i -factor is 2, as in the case of 1:1-diphenylethylene. The high values obtained after longer time intervals are consistent with the occurrence of sulphonation.

Triphenylethylene and 3:4-benzopyrene also gave i -values greater than 2, but the time variation was rather too rapid for a reliable back-extrapolation to zero time. In five experiments with 3:4-benzopyrene the first freezing point, taken 15–20 minutes after introduction of the solute, corresponded to an i -value of 3.7 ± 0.2 , and extrapolation

FIG. 3.

- a, Solenoid.
- b, Magnetically operated stirrer.
- c, B.14 standard cone and socket.
- d, Mercury.
- e, Thermistor.
- f, Thermistor leads.
- g, Air jacket.
- h, Sulphuric acid.



to zero time led to a value of 3.5 approx. The precise significance of this result is not readily obvious, but it is likely that rapid sulphonation occurs in 100% sulphuric acid at $\sim 15^\circ$. This may not occur so readily during the extraction of the hydrocarbon with 98% acid at a lower temperature (cf. Berenblum, *loc. cit.*).

Stilbene and tetraphenylethylene were insoluble in sulphuric acid.

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