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 $1-\alpha$ -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 *iso*butylene.

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 though 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 SO_2 -free oleum with 98% acid (*J.*, 1951, 2102).

l : 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. $125^{\circ}/5$ mm.) before use; the carbinol was crystallized from light petroleum.

 $1-\alpha$ -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.

cold solution in benzene until the acid layer no longer develops a violet colour; it was crystallized from benzene-ethanol.

A purified specimen of 3:4-benzopyrene (200 mg.) was generously given to us by Dr. R. Schoental.

Apparatus and Procedure.—The design and operation of the ordinary cryoscope were based on descriptions of previous work (Hammett and Deyrup, J. Amer. Chem. Soc., 1933, 55, 1900; Treffers and Hammett, *ibid.*, 1937, 59, 1788; Gillespie, Thesis, London, 1949; Gillespie, Hughes, and Ingold, J., 1950, 2473). The recommended precautions of these authors were followed in all essential details.

We have modified the method by employing a thermistor, Type 2311/300, supplied by the Standard Telephone Company, as thermometer device. The resistance of the thermistor $(2500 \omega \text{ approx.})$ was measured by means of a Wheatstone bridge which was sensitive to differences of 0.1 ohm, corresponding to temperature differences of 0.001° approx. The thermistor was calibrated against a standard thermometer (accuracy of N.P.L. calibration $\pm 0.02^{\circ}$) by taking simultaneous readings of the temperature (t) of a bath and of the corresponding resistance (R_i) of an immersed thermistor at 0.1° intervals in the range $6.5-11.5^{\circ}$. The results were fitted to an empirical equation log $R_t = mt + c$ (m and c being constants) which was found to be closely obeyed over the short temperature range studied. The use of the theoretically more accurate relation log R = m'/T + c' is excessively laborious. The following points concerning thermistor thermometry need emphasizing. Whereas, in platinum-resistance thermometers the temperature rise caused by the measuring current in the instrument is very small, yet it can be seen from the maker's specifications that this is not true with this type of thermistor if a 2-v accumulator as source of e.m.f. and a Wheatstone bridge of approximately equal arms are used. It follows that the resistance observed will depend on the rate of dissipation of the thermal energy generated, i.e., on the medium surrounding the resistance element. The difficulty seems to be eliminated by surrounding the thermistor with a thin glass sheath fitted with spacers to hold the thermistor in position and filled with mercury. Although it greatly increases the heat capacity of the thermometer, this sheath should be employed when the thermistor calibration and measurements with it relate to different media. A reliably steady source of e.m.f. and a constant setting of the bridge ratio arms must be used. By using this procedure the temperature of the thermistor tip will not be the same as that of the calibration thermometer but slightly higher. However, this is immaterial if the same conditions obtain during calibration and use of the thermistor. All these difficulties could alternatively be overcome by the use of a minute measuring current.

The calibration has to be repeated periodically, since thermistors appear to age. The effect is not so serious if small temperature *differences* only are measured. The ageing alters mainly the value of c; m is not so markedly affected. This behaviour was found with seven thermistors of this type.

A cryoscope of normal size (capacity, 50 ml. approx.) was used for all material available in reasonable amount. Some of the results are given in Tables 1 and 2 and Figs. 1 and 2). For the measurements on 3:4-benzopyrene a micro-modification of the apparatus was constructed (Fig. 3) with which it was possible to measure freezing-point depressions on as little as $1\cdot5$ ml. of solution and of the order of 5 mg. of solute. The general technique of measurement, bridge assembly, and calibration were the same as before, but certain new features accompanied the reduction in scale. Absorption of moisture from the atmosphere during the introduction of the solute became appreciable. The depression caused by opening the apparatus to the atmosphere for a definite time was noted and a proportionate correction applied for each addition of solute according to the time required for the operation.

The inducement of seeding by touching the inner container with a piece of solid carbon dioxide caused a considerable reduction in the temperature of the solvent before crystallisation occurred. Thus the temperature had to be followed throughout the seeding process and the lowest temperature recorded was taken as the super-cooling temperature (T_s) . It follows from thermodynamic considerations (Gillespie, Hughes, and Ingold, *loc. cit.*) that the supercooling correction (δT) is given by

where C is the thermal capacity of the cryoscope and contents, θ the observed depression from the freezing point of the pure solvent, S the amount of supercooling, n_1 the number of moles of solvent in the solution, and ΔH^j the molar heat of fusion of the solvent. For an apparatus of ordinary scale, C depends almost entirely upon the solvent present in the cryoscope and may be replaced by n_1C_p , where C_p is the molar heat capacity of the solvent. With this substitution equation (1) reduces to the usual relation

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

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

			IADL	C I.								
Molality	F. p. depn., obs.	Т	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	-0.005	0.055					
0.0126	0.146	7.85	1.99	0.63	0.012	0.006	0.120					
			1: 1-Diphe	nylethanol.								
		7.65	2.33	0.48	0.013							
0.0048	0.113	8.14	1.72	0.59	0.012	-0.002	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	-0.050	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 $1-\alpha$ -naphthyl-1-phenylethylene (0.0090 molal).

Time	F. p. depn.,					F. p. depn.,	'' i ''
(min.)	obs.	T_{\bullet}	S	θ	δT	corr.*	Factor
		7·79°	$2 \cdot 41^{\circ}$	0.26°	0.008°		
20	0.153°	7.74	$2 \cdot 30$	0.42	0.012	0·149°	2.77
50	0.191	7.61	$2 \cdot 40$	0.45	0.013	0.186	3.45
83	0.212	7.80	2.18	0.48	0.013	0.502	3.85
120	0.238	7.34	$2 \cdot 62$	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

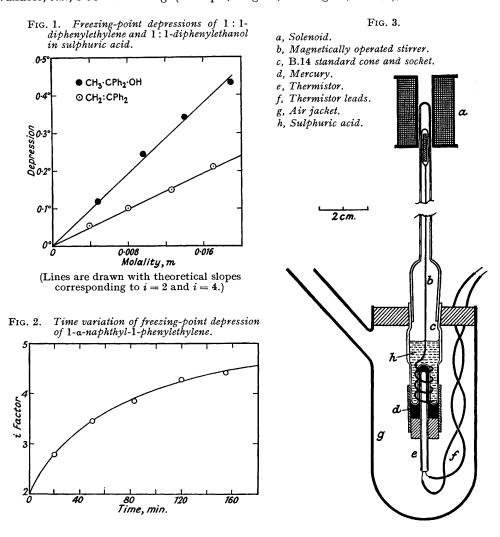
$$Ph_2C:CH_2 + H_2SO_4 \longrightarrow Ph_2MeC^+ + HSO_4^-$$

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

$$Ph_2CMe \cdot OH + 2H_2SO_4 \longrightarrow Ph_2MeC^+ + H_3O^+ + 2HSO_4^-$$

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



 ~ 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 $1-\alpha$ -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

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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