404. *The Basicity of Hydrocarbons. Part III.* The Distribution of Some Conjugated Hydrocarbons between Acidic and Inert Solvents.*

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The distribution of 1 : 1-diphenylethylene, 1-α-naphthyl-1-phenylethylene, and triphenylethylene between *cyclo*hexane and sulphuric acid–water mixtures of different acidities has been studied. By making certain assumptions about the solubilities of the hydrocarbon bases in the acid layer, it is possible to arrange the hydrocarbons in the approximate order of their basicities and to deduce that the pK_a value for the conjugate acid of 1 : 1-diphenylethylene is -4 ± 2.

Having demonstrated that certain hydrocarbons behave as bases in strongly acid solvents, it is logical to enquire whether it is possible to determine this basicity quantitatively and to correlate basic strength with molecular structure. With most weak bases this is possible by means of the colorimetric and spectrophotometric methods described by Hammett and his collaborators ("Physical Organic Chemistry," New York, 1940, Chap. IX). Normally, measurements are carried out in solutions of an acidity such that acid and base forms are present in convenient concentrations of approximately the same order of magnitude. In this procedure it is essential that the base should remain in solution as the acidity of the solvent is reduced, a requirement which is not satisfied by the compounds and solvents employed by us. Furthermore, were it possible for both an olefin base and its conjugate acid to be present in reasonable concentrations, it is quite likely that considerable polymerization would take place.

Although these difficulties in the measurement of the basicity constants of hydrocarbons have not been overcome, it has been found possible—with certain assumptions—to compare approximately the basicities of 1 : 1-diphenylethylene, 1-α-naphthyl-1-phenylethylene, and triphenylethylene by partition experiments similar to those performed on azulenes by Plattner, Heilbronner, and Weber (*Helv. Chim. Acta*, 1949, **32**, 574).

Experimental

The preparation and purification of reagents and solvents have been described (Part I, *J.*, 1952, 2167).

Partition Experiments.—The distribution of olefin between *cyclo*hexane and aqueous sulphuric acids of different strengths was studied by introducing a weighed amount of olefin into the two layers, shaking, and then determining the concentration (C'_B) of olefin in the *cyclo*hexane layer from the intensity of ultra-violet light absorption at suitable wave-lengths. The concentration of olefin in the acid layer (C_{HB^+}) was obtained by subtraction. It was checked in a few cases that these values agree satisfactorily with values of C_{HB^+} obtained by direct spectrophotometry of the carbonium-ion concentration in the acid layer. In the subtraction method it is obviously essential to have comparable amounts of solute in the two phases. It was found that for 1 : 1-diphenylethylene $\log_{10} (C'_B/C_{HB^+})$ had reached a steady value after 10—15 minutes' shaking and, in order to minimize any errors due to secondary reactions, the values after 15 minutes were taken to be the equilibrium values. For the other two olefins the variations of $\log_{10} (C'_B/C_{HB^+})$ with time proved to be more serious, as shown in the example below:

Effect of duration of shaking on distribution.

(i) 1 : 1-Diphenylethylene (85·90% H_2SO_4 : λ 2510 Å used for measurement of concentration).

Time, min.	5	10	15	20	30	60
$\log_{10} (C'_B/C_{HB^+})$	−0·19	−0·26	−0·22	−0·23	−0·24	−0·31

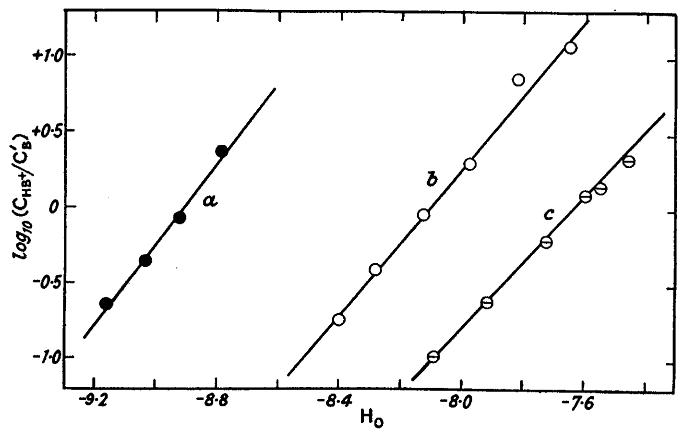
(ii) Triphenylethylene (85·90% H_2SO_4; λ 3020 Å used for measurement of concentration).

Time, mins.	5	27	48	66
$\log_{10} (C'_B/C_{HB^+})$	+0·361	+0·240	+0·141	+0·040

* Part II, preceding paper.

In order to get a rough comparison, the value of C'_B/C_{HB^+} was taken in each case as that obtained after 10 minutes (cf. Table 1, Part II). This is rather an arbitrary procedure and we do not claim high accuracy for the results which, moreover, suffer from the uncertainty that the time variation of the value may be different for different acidities of the acid layer.

Fortunately, the uncertainty involved, even on an extreme view of the inaccuracy [say 0·2 unit in $\log_{10}(C'_B/C_{HB^+})$], does not greatly affect the relative positions of the lines obtained on plotting $\log_{10}(C'_B/C_{HB^+})$ against H_0 (Fig.), where H_0 is Hammett's acidity function. The



a, Triphenylethylene (slope = 2·7).
b, 1-*α-Naphthyl-*1-*phenylethylene (slope* = 2·5).
c, 1 : 1-*Diphenylethylene (slope* = 2·2).

observation that the slopes of these lines do not differ much from that for the stable hydrocarbon 1 : 1-diphenylethylene also suggests that the time variations at different acidities may not be too dissimilar. The order of magnitude of the true distribution coefficients is therefore hardly in doubt.

Results of distribution experiments.

Hydrocarbon	H_2SO_4, %	H_0	$\log_{10}(C'_B/C_{HB^+})$	Hydrocarbon	H_2SO_4, %	H_0	$\log_{10}(C'_B/C_{HB^+})$
	83·88	−7·45	+0·32		85·90	−7·73	−0·22
$Ph_2C{:}CH_2$	84·55	−7·55	+0·15	$Ph_2C{:}CH_2$	87·47	−7·91	−0·62
	84·88	−7·59	+0·09		89·11	−8·09	−0·97
$Ph_2C{:}CHPh$ ...	95·50	−8·78	+0·38	$Ph_2C{:}CHPh$ ...	97·31	−9·03	−0·35
	96·62	−8·92	−0·06		97·83	−9·16	−0·63
	85·29	−7·65	+1·07		89·36	−8·12	−0·04
α-$C_{10}H_7$(Ph)$>C{:}CH_2$	86·56	−7·81	+0·84	α-$C_{10}H_7$(Ph)$>C{:}CH_2$	90·87	−8·28	−0·41
	88·04	−7·97	+0·30		91·99	−8·40	−0·74

Discussion

The equilibrium between a hydrocarbon base (B) and its conjugate acid (HB^+) in the acid layer is governed by the relation

$$H_0 = pK_{HB^+} - \log_{10}(C_{HB^+}/C_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_B and C_{HB^+} stand for the concentration in the acid layer of the species concerned, pK_{HB^+} is the acidity constant of HB^+, and H_0 is Hammett's acidity function (*op. cit.*). The distribution of B between the two immiscible phases can be formally expressed by

$$P = C_B/C'_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

if C'_B and C'_{HB^+} are the concentration of base and conjugate acid in the *cyclo*hexane; P is called the partition coefficient and is equal to the ratio of the solubilities of the base in the two layers. Experimentally we find that $C_{HB^+} \gg C_B$ and $C'_B \gg C'_{HB^+}$. We may combine equations (1) and (2) to obtain

$$H_0 = pK_{HB^+} + \log_{10} P - \log_{10}(C_{HB^+}/C'_B) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The experimental determination of the ratio C_{HB^+}/C'_B with acid layers of known values of H_0 therefore leads to a value of ($pK_{HB^+} + \log_{10} P$) but, without an accompanying measurement of P, it is impossible to derive from this an accurate value of pK_{HB^+}. A direct measurement of P would be very difficult in this case and has not been attempted. Plattner, Heilbronner, and Weber (*loc. cit.*), who have used a similar partition technique for the separation and characterization of the azulenes, another group of basic hydrocarbons, have suggested that the H_0 value at which the apparent partition coefficient (C_{HB^+}/C'_B) is unity (*i.e.*, $pK_{HB^+} + \log_{10} P$) could be regarded as a measure of relative basicity, called by them $H_0(K' = 1)$, but they were careful to point out that this treatment of the data was not rigorous.

A difficulty encountered with the application of equation (3) is the observation that ($pK_{HB} + \log_{10} P$) is experimentally not independent of H_0, but appears to be a linear function of H_0 of approximate slope -1. Stated alternatively, the plot of $\log_{10}$ (C_{HB^+}/C'_B) against H_0 is linear with a slope ~ -2. This has been found for the azulenes with either aqueous sulphuric or phosphoric acid in the acid layer (Plattner *et al.*, *loc. cit.*); we have also found it at considerably higher acidities with the three hydrocarbons now examined. We interpret these observations as arising out of a linear decrease of the logarithm of the solubility of base molecules in the acid with increasing values of H_0 (*i.e.*, an increase of solubility with increasing acidity). Such an effect has been reported for the basic form of organic oxygen compounds (Hammett and Chapman, *J. Amer. Chem. Soc.*, 1934, **56**, 1282), and therefore appears to be a fairly general one. This salting-in law for strongly acid solvents may alternatively be stated in the form

$$\log f_B = \alpha H_0 + \text{constant}$$

where α is ~ 1, and f_B is an activity coefficient of B relatively to any convenient standard state.

In order to arrive at a *comparative* estimate of the basicities of the three hydrocarbon bases examined, it is necessary to know how P depends on the base concerned (for a certain fixed acid composition). For three olefins of similar structure we would predict that the partition coefficients do not differ very widely and, therefore, the order of the values of ($pK_{HB^+} + \log_{10} P$) is probably also the order of their basicities, *i.e.*, $CPh_2{:}CH_2 \gg \alpha\text{-}C_{10}H_7{\cdot}CPh{:}CH_2 \gg Ph_2C{:}CHPh$, with the insoluble hydrocarbons stilbene and tetraphenylethylene much less basic still. In order to change the position of triphenylethylene in this sequence it would be necessary for P for the distribution of triphenylethylene between *cyclo*hexane and a particular solvent mixture to be more than 100 times smaller than P for 1-α-naphthyl-1-phenylethylene or more than 1000 times smaller than P for 1 : 1-diphenylethylene. A consideration of the ratio of the solubilities of related hydrocarbons in a paraffin solvent and water indicates that such an upset is improbable. It is not impossible, however, that differences in P may be responsible for the order of the first two compounds in the sequence; in this case the values of P would have to differ by a factor $\gg 10$ if the order were, in fact, the reverse of that stated.

The relative solubilities of aromatic hydrocarbons in *cyclo*hexane (paraffin solvents) and water are usually in the ratio $10^4 : 1$ to $10^5 : 1$. The solubility increase with acidity being borne in mind, the value of P is probably changed to 10^{-3} to 10^{-4} ($\log P = -3{\cdot}7$) (the data of Hammett and Chapman on nitrobenzene being taken as guidance on this point). For 1 : 1-diphenylethylene

$$pK_{Ph_2MeC^+} + \log_{10} P = -7{\cdot}63 \qquad \text{(see Fig.)}$$

therefore

$$pK_{Ph_2MeC^+} = -7{\cdot}63 + 3{\cdot}7 = -4 \pm 2$$

a generous estimate being taken of the uncertainties of various assumptions. This means that 1 : 1-diphenylethylene is at least as basic as acetophenone ($pK_{HB^+} \sim -6$) and, more probably, as strong a base as 2 : 4-dinitroaniline ($pK_{HB^+} = -4{\cdot}4$). It is certainly a stronger base than 2 : 4 : 6-trinitroaniline, anthraquinone, or nitro-hydrocarbons.

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