403. *The Basicity of Hydrocarbons. Part II.* Ultra-violet Absorption Spectra of Conjugated Hydrocarbons in Sulphuric Acid Solution.*

By V. GOLD and F. L. TYE.

The ultra-violet absorption spectra of the conjugate acids of 1 : 1-diphenylethylene, triphenylethylene, anthracene, and 1-α-naphthyl-1-phenylethylene have been obtained from measurements on the hydrocarbons in sulphuric acid solution. The spectra are very different from those of the parent hydrocarbons but show certain similarities among themselves, and it is concluded that proton addition to the first three compunds mentioned occurs in such a way that the conjugate acids possess substituted diphenylcarbonium-ion structures.

It is shown that the hydrocarbon base is re-formed when the acidity of the medium is reduced.

Some light-absorption measurements on acid solutions of 3 : 4-benzopyrene are also reported.

MOST organic bases have been found to have ultra-violet absorption spectra which are very different from those of their conjugate acids and this has been extensively utilized in colorimetric and spectrophotometric determinations of dissociation constants. It would similarly be expected that the conjugate acid of a hydrocarbon—whatever its structure—would have a light absorption which is detectably different from that of the hydrocarbon itself. Colour reactions of conjugated hydrocarbons with sulphuric acid are well known and have been used to characterize the compounds (see, *e.g.*, Pfeiffer, " Organische Molekülverbindungen," 2nd edn., Stuttgart, 1927, p. 205; Clar, " Aromatische Kohlenwasserstoffe," Berlin, 1941 ; Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 451 ; Radulescu, *Ber.*, 1931, **64**, 2243). However, these colour formations are usually associated with irreversible changes and the hydrocarbon cannot be recovered from the acid solution by dilution.

We have examined the absorption spectra of the acid solutions of those hydrocarbons which, on the basis of cryoscopic work (Part I *), are believed to accept a proton in 100% sulphuric acid. In agreement with this view, the spectra were found to be quite different from those of the hydrocarbon bases in less acidic solvents in a manner which cannot be attributed simply to a " solvent effect " on the electronic transition. Solvent effects on the absorption spectra of organic bases in acid solvents have been examined by several workers with the conclusion that a slight wave-length displacement of the spectrum may occur but that the shape and intensity of the absorption curve are not detectably altered (Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103; Brand, *J.*, 1950, 997). Moreover, some of the spectra of the acid solutions show certain striking similarities among themselves (although those of the hydrocarbons in non-acidic solvents do not) and we believe that this permits conclusions to be drawn about the position of proton attachment in the conjugated hydrocarbon.

It was hoped to apply the difference of the absorption spectra to a determination of the basicity constants of the hydrocarbons, by examining the spectra of hydrocarbons in sulphuric acid–acetic acid mixtures of different acidities, following the method of Flexser, Hammett, and Dingwall ((*loc. cit.*). However, it was found that, whereas the hydrocarbons are soluble in acetic acid, giving the spectrum of the base, and soluble in sulphuric acid, giving

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* Part I, preceding paper.

the spectrum of the conjugate acid, the solubilities are too low in mixtures of these solvents which are not sufficiently acidic to convert all the solute into its conjugate acid form but contain too much sulphuric acid—a very poor solvent for un-ionized hydrocarbons—to dissolve the base form.

EXPERIMENTAL

Materials.—The preparation of 100% sulphuric acid and of the conjugated hydrocarbons examined has been described in Part I. The " concentrated " sulphuric acid used was 98% " AnalaR " acid.

The *cyclo*hexane used in those experiments in which it did not come into contact with sulphuric acid was a B.D.H. " Spectroscopic " sample; for the other experiments it was purified by successively shaking it for 24 hours each with oleum (15% free SO_3), concentrated sulphuric acid, sodium hydroxide solution (10%), and 1N-potassium permanganate solution first in 10% sodium hydroxide solution and then in 10% sulphuric acid solution. Between and after these extractions it was repeatedly washed with water and finally dried ($CaCl_2$), distilled, and again dried (Na wire).

Spectroscopic Measurements.—Many of the absorption spectra of the acidic solutions examined varied with time owing to occurrence of irreversible chemical changes. In these cases the spectrum of the initial solution was obtained by the following procedure. As soon as possible after preparation of the solution the light absorption was recorded photographically, a Hilger medium quartz spectrograph being used in conjunction with a Spekker photometer and an iron-spark source. From the plate obtained, 15—20 characteristic wave-lengths of the spectrum were selected, such as positions of maxima, minima, and points of inflection. The solution was then prepared again (zero time) and the optical densities at the selected wave-lengths recorded by use of a Hilger Uvispek Spectrophotometer, together with the time at which each measurement was made. When all the optical densities had been measured once, they were determined a second time and so on until it was possible, at every selected wave-length, to draw a smooth curve connecting optical density with time. The curves were extrapolated to zero time to obtain points on the initial spectrum. The whole process was repeated for other wave-lengths until there were sufficient data to draw the detailed absorption curve at zero time, or, by interpolating between readings, after various definite time intervals after zero time. Usually about 30 such extrapolations were carried out for each spectrum in sulphuric acid. The extrapolation procedure is illustrated by a few examples in Fig. 1. The absorption spectra of stable solutions were directly measured with the " Uvispek " spectrophotometer. In some of the cases (triphenylethylene and anthracene) the dissolution of solid hydrocarbon is inconveniently slow compared with the speed of the secondary reaction. To overcome this difficulty, these hydrocarbons were first dissolved in 0·5 ml. of *cyclo*hexane, and then 100 ml. of concentrated sulphuric acid were added. The partitioning of the solute takes place very rapidly under these conditions and the amount of hydrocarbon remaining in the *cyclo*hexane layer is negligible. In some cases the solution in sulphuric acid was made by dilution of a more concentrated solution in acetic acid with sulphuric acid.

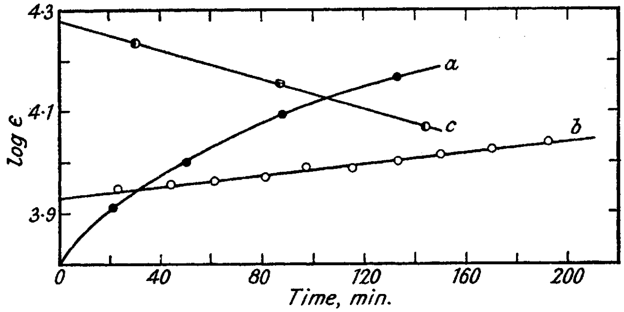


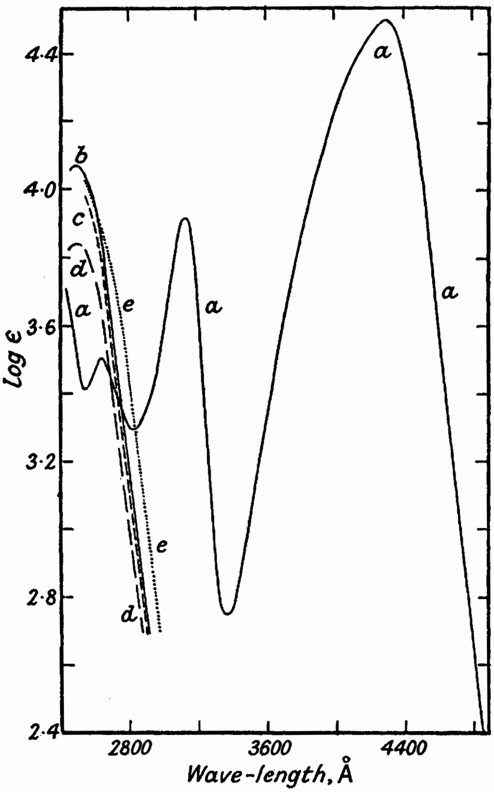
FIG. 1. *Illustration of extrapolation method for obtaining initial spectra of solutes in sulphuric acid.*

a, Triphenylethylene, λ 3100 Å.
b, 3 : 4-*Benzopyrene,* λ 3960 Å.
c, 1-α-*Naphthyl*-1-*phenylethylene,* λ 5450 Å.

Dilution Experiments.—In order to test the reversibility of the primary change undergone by the hydrocarbon in solution in sulphuric acid, the acidity of the solution was reduced by one of two methods, and the spectrum of the resulting species measured. In the first procedure (*A*) 5 ml. of the solution of the hydrocarbon in sulphuric acid were added dropwise and with shaking to approx. 95 ml. of acetic acid.* The second method (*B*) was to add 5 ml. of the acidic solution to 250 ml. of water and 100 ml. of *cyclo*hexane and then to shake the two layers. The recovered hydrocarbon was extracted into the *cyclo*hexane layer.

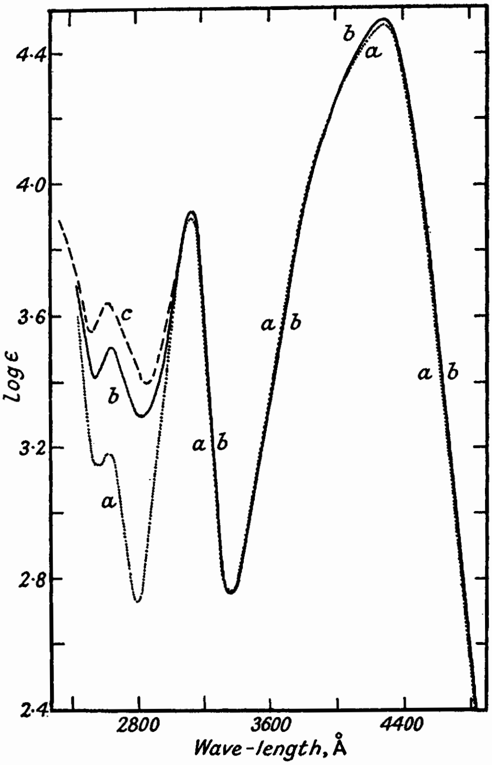
Results.—1 : 1-Diphenylethylene gives a stable absorption curve in concentrated sulphuric acid which is the same whether the solution is prepared by dissolving the hydrocarbon in sulphuric acid or by diluting a concentrated stock solution in acetic acid with concentrated sulphuric acid. The spectrum is quite different from that in the non-acidic solvents *cyclo*hexane and acetic acid. Dilution of the yellow acidic solution by either procedure (*A*) or (*B*) caused the disappearance of the characteristic bands of the conjugate acid form. The spectra of the dilute colourless solutions showed certain small discrepancies from those of the hydrocarbon dissolved directly in the non-acidic solvent (Fig. 2). These may perhaps be attributed to a partial dimerization or further polymerization which may occur in solutions of intermediate acidity formed during the slow dilution when *both* the species $Ph_2C{:}CH_2$ and Ph_2MeC^+ are present, *i.e.*,

FIG. 2. *Absorption spectra of* 1 : 1-*diphenylethylene.*



a, In concentrated sulphuric acid. b, In cyclo*hexane. c, In acetic acid. d, In* cyclo*hexane [by dilution method* (B)]. *e, In acetic acid [by dilution method* (A)].

FIG. 3. *Absorption spectrum of* 1 : 1-*diphenylethanol, etc., in sulphuric acid.*



a, 1 : 1-*Diphenylethanol. b*, 1 : 1-*Diphenylethylene (freshly distilled). c*, 1 : 1-*Diphenylethylene (ordinary purification).*

$$Ph_2C{:}CH_2 + Ph_2MeC^+ \longrightarrow {}^+CPh_2{\cdot}CH_2{\cdot}CPh_2Me \longrightarrow Ph_2C{:}CH{\cdot}CPh_2Me + H^+$$

This reaction does not take place in concentrated sulphuric acid where only the conjugate acid form of the hydrocarbon is stable (cf. Schlenk and Bergmann, *Annalen*, 1928, **463**, 239; Lebedev, Andreeskii, and Matruskina, *Ber.*, 1923, **56**, 2349).

The spectrum of 1 : 1-diphenylethanol in sulphuric acid was almost identical with that of 1 : 1-diphenylethylene. There is an intensity discrepancy below 3000 Å but this is probably due

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* Acetic acid is too weakly acidic to convert the hydrocarbons studied here into their conjugate acids, and may be regarded in this connection as a non-acidic solvent.

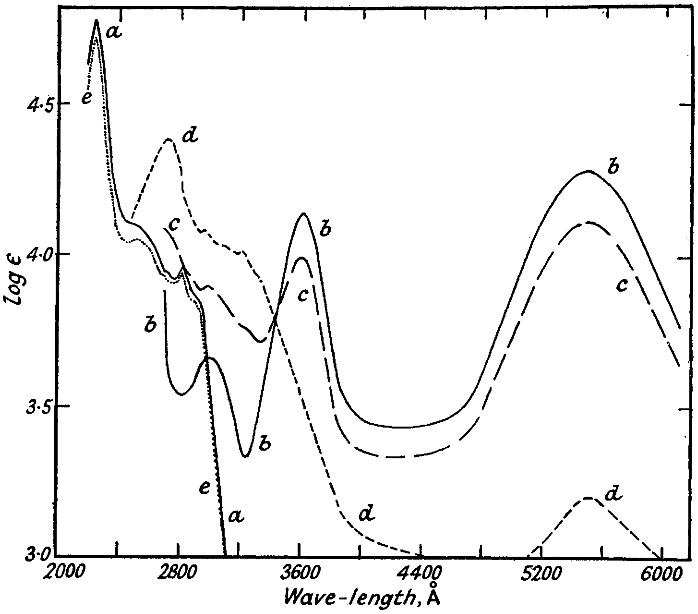
to the presence in the olefin of a small amount of impurity with an absorption maximum in this region, since the discrepancy could be reduced by redistilling the olefin. However, the last traces of impurity seem to be difficult to remove, whereas the solid carbinol may be purified more readily (Fig. 3).

The absorption spectrum of 1 : 1-diphenylethylene in concentrated sulphuric acid recently reported by A. G. Evans (*J. Appl. Chem.*, 1951, **1**, 240) agrees with ours in the position of the maxima but differs in the intensities in the region of low absorption, particularly below 3000 Å. The intensities recorded by Evans in this region are considerably higher than ours, and we would hazard the guess that this may be due to the presence of the same impurity which causes the discrepancy between our 1 : 1-diphenylethylene and 1 : 1-diphenylethanol.

Solutions of 1-α-naphthyl-1-phenylethylene in sulphuric acid and in non-acidic solvents also had totally different absorption spectra. In the acidic solutions a slow irreversible reaction occurred (Fig. 4). Since the changing spectra pass through an isosbestic point, this reaction is probably a simple one of the type A $\longrightarrow$ B. Dilution experiments by method (*B*) restored the light absorption to that characteristic of the olefin in non-acidic solvents. The amounts of olefin which could be recovered by this procedure after certain lengths of time, as estimated from the absorption spectra of the *cyclo*hexane layers, were compared with the amount of primary solute remaining in the sulphuric acid solution, as estimated from the curves in Fig. 4. It was found that the two sets of values agreed closely (see Table) and it follows that the total amount of olefin present in sulphuric acid in the form of its conjugate acid was recovered by dilution. The complication of dimerization or polymerization encountered in the dilution experiments with 1 : 1-diphenylethylene therefore did not arise in this case. The following facts have a bearing on deciding the probable fate of the irrecoverable secondary reaction product. The absorption spectrum of the secondary product must approximate to curve *d* in Fig. 4, which is similar to that of the olefin in *cyclo*hexane. This spectrum did not occur superimposed in the spectrum of the 8% extracted olefin in dilution experiment 3 (see Table), which shows that the secondary product is much more soluble in water than in *cyclo*hexane. These observations point to the

FIG. 4. *Absorption spectra of* 1-*α-naphthyl*-1-*phenylethylene.*

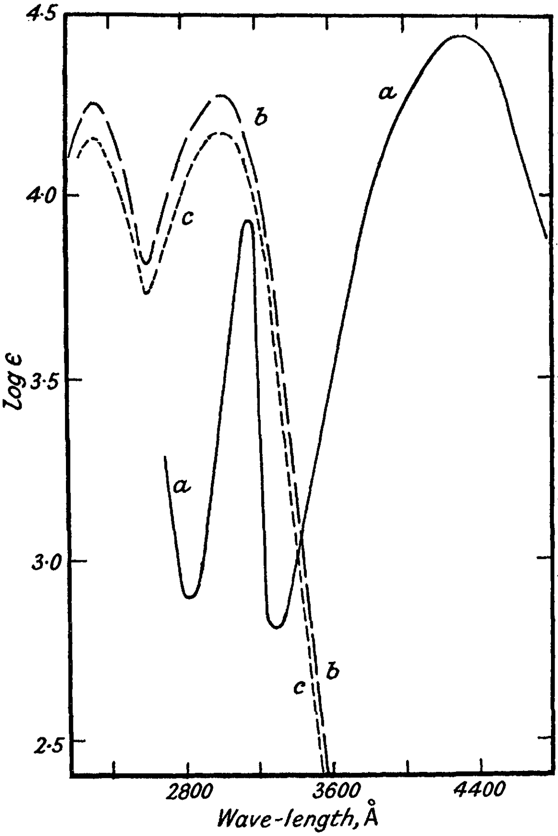
a, In cyclo*hexane. b, c, d, In concentrated sulphuric acid; (b, zero-time extrapolation; c, after* 120 *min.; d, after* 20 *hours*). *e, In* cyclo*hexane [dilution* (B) *after* 11 *min. in concentrated sulphuric acid; Expt.* 1, *see Table*].



Expt.	Hydrocarbon	Time (min.)	% Absorbing species remaining in solution	% Hydrocarbon recoverable by dilution
1	$\begin{matrix}\alpha\text{-}C_{10}H_7\\ Ph\end{matrix}>C{:}CH_2$	11	97	95
2		83	77	77
3		1440	8	8
4	$Ph_2C{:}CHPh$	10	92	79
5		111	34	34

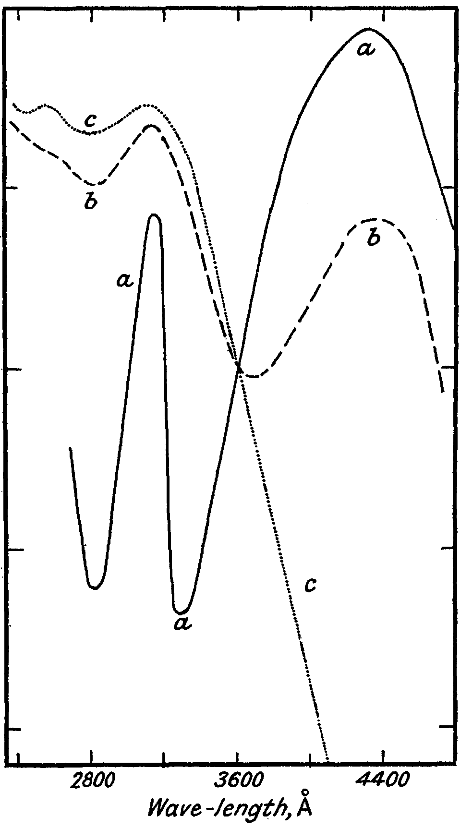
occurrence of monosulphonation as the secondary reaction. By analogy with the case of α-phenylnaphthalene, sulphonation is expected to occur in the 4-position of the naphthyl group (Braun and Anton, *Ber.*, 1934, **67**, 1051), although our data furnish no evidence on this and do not exclude the formation of a mixture of isomeric monosulphonic acids. This interpretation need not conflict with the cryoscopic observation (preceding paper) that the *i*-factor for this compound rises above the value of 3 which corresponds to monosulphonation, since further sulphonation may occur in the more concentrated medium to which the cryoscopic measurements refer.

FIG. 5*a*. *Absorption spectra of triphenylethylene.*



In concentrated sulphuric acid: a, zero-time extrapolation. b, In cyclo*hexane. c, In* cyclo*hexane [dilution* (B) *after* 10 *min. in concentrated sulphuric acid; Expt.* 4].

FIG. 5*b*. *Absorption spectra of triphenylethylene.*



In concentrated sulphuric acid: a, zero-time extrapolation; b, after 120 *mins.; c, after* 20 *hours.*

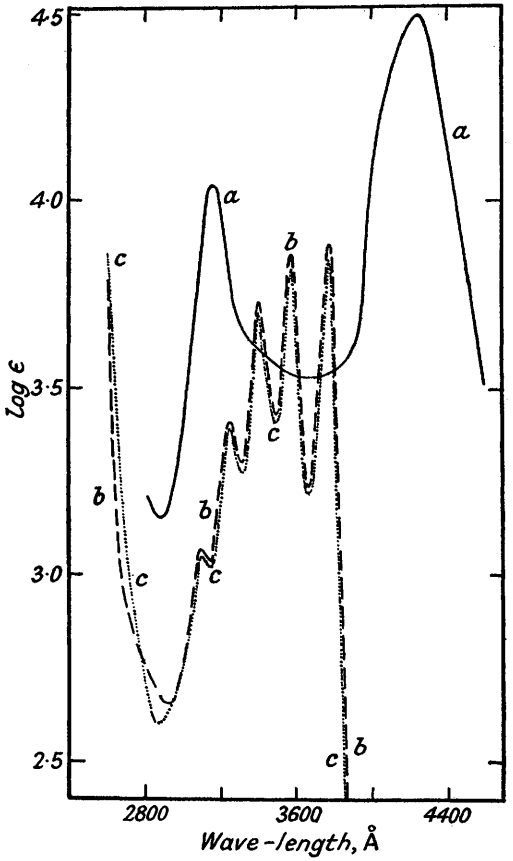
The solutions of a crude specimen of methyl-α-naphthylphenylcarbinol in concentrated sulphuric acid showed the same purple colour as the solution of the olefin in the same solvent, with main absorption maxima at 3620 and 5500 Å, in addition to some less intense bands which were ascribable to impurities.

The absorption spectrum of triphenylethylene in sulphuric acid (Fig. 5*b*) was even more rapidly variable with time than that of 1-α-naphthyl-1-phenylethylene. The decrease of the typical absorption bands was again compared with the olefin recovery attainable by procedure (*B*), the somewhat poorer agreement in this case being probably due to the greater speed of the secondary reaction (see Table). The existence of the isosbestic point in the family of curves again points to the occurrence of a single reaction. After more than 20 hours, dilution procedure (*B*) showed no extraction of absorbing species by *cyclo*hexane. The secondary reaction product was therefore probably again a monosulphonic acid or a mixture of several isomers.

The spectra of triphenylethylene in acidic and non-acidic solvents and the spectrum of the product recovered by dilution procedure (*B*) after 10 minutes in concentrated sulphuric acid are shown in Fig. 5*a*.

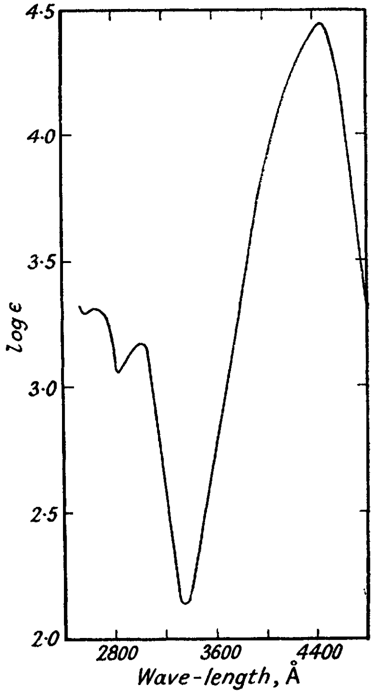
Anthracene can be extracted from *cyclo*hexane solution by 98% sulphuric acid to give a yellow solution. Dissolution of the solid itself in sulphuric acid is slow and less clean. The absorption spectrum was again time-variable (and the recorded intensities are therefore probably not precise), but dilution procedure (*B*) carried out 10 minutes after the hydrocarbon had been dissolved in the acid led to 90% recovery of anthracene (Fig. 6).

FIG. 6. *Anthracene.*



a, In concentrated sulphuric acid. b, In cyclo*hexane. c, In* cyclo*hexane [dilution* (B) *after* 10 *min. in concentrated sulphuric acid].*

FIG. 7. *Diphenylmethanol.*



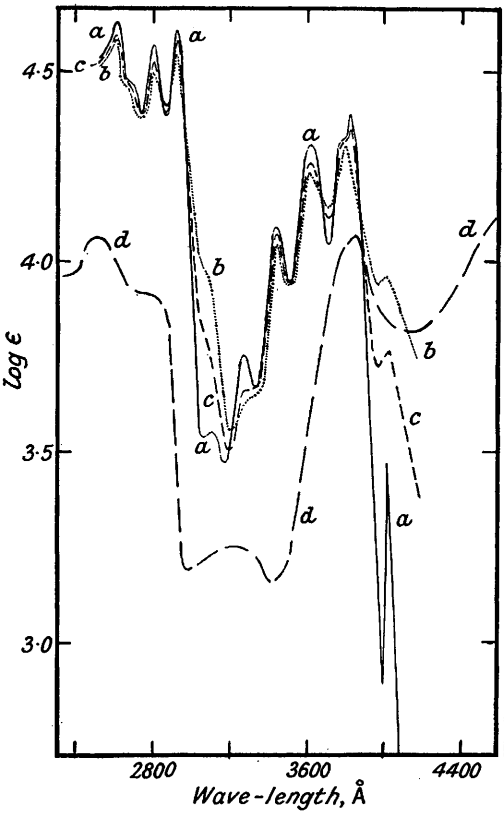
The absorption spectrum of diphenylmethanol in concentrated sulphuric acid (extrapolated to zero time) is shown in Fig. 7.

3 : 4-Benzopyrene and its solutions were stored and handled in the dark or by the light of a red safety lamp to avoid possible complications through photo-oxidation. The variation of the absorption spectrum with time was followed for both 98% and 100% sulphuric acid. The light-absorption curve obtained by extrapolation back to zero-time was different from the spectrum of the hydrocarbon in non-acidic solvents (Fig. 8*a*). Dilution by procedure (*A*) from acidic solutions, kept at 0° to retard the secondary change, led to substantial recovery of the hydrocarbon. Such differences as were found between the absorption spectrum in acetic acid and that obtained after dilution with acetic acid increased both with the time of storage before dilution and with the concentration of the acid from which the dilution was made. The fluorescence colour of 3 : 4-benzopyrene solutions is blue in acetic acid, yellow-green in sulphuric acid, and is restored to blue by dilution method (*A*).

DISCUSSION

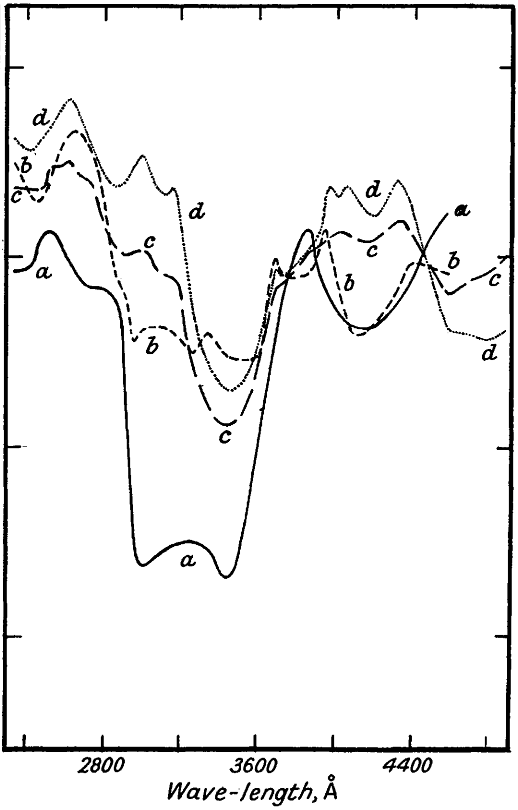
The results just presented show that the solutions in sulphuric acid of several conjugated hydrocarbons have absorption spectra which are very different from those of the hydrocarbons in non-acidic solvents, and that the original compounds can be recovered from the solutions by reducing their acidity. In conjunction with the cryoscopic measurements on two of the compounds (1 : 1-diphenylethylene and 1-α-naphthyl-1-phenylethylene, preceding paper) this constitutes strong evidence that we are in all these cases dealing with a simple acid–base equilibrium, the hydrocarbon accepting a proton from the acid solvent to go over into the conjugate acid cation. The absorption spectra of the solutions in sulphuric acid (if appropriately extrapolated to zero time where necessary) are therefore those of the conjugate acids.

FIG. 8*a*. 3 : 4-*Benzopyrene.*



a *In acetic acid.* *b, In acetic acid* [*dilution* (B) *after* 12·5 *min. in ice-cold* 100% *sulphuric acid*]. *c, In acetic acid* [*dilution* (B) *after* 16 *min. in ice-cold* 98% *sulphuric acid*]. *d, In* 98% *sulphuric acid* (*zero-time extrapolation*).

FIG. 8*b*. 3 : 4-*Benzopyrene in sulphuric acid.*



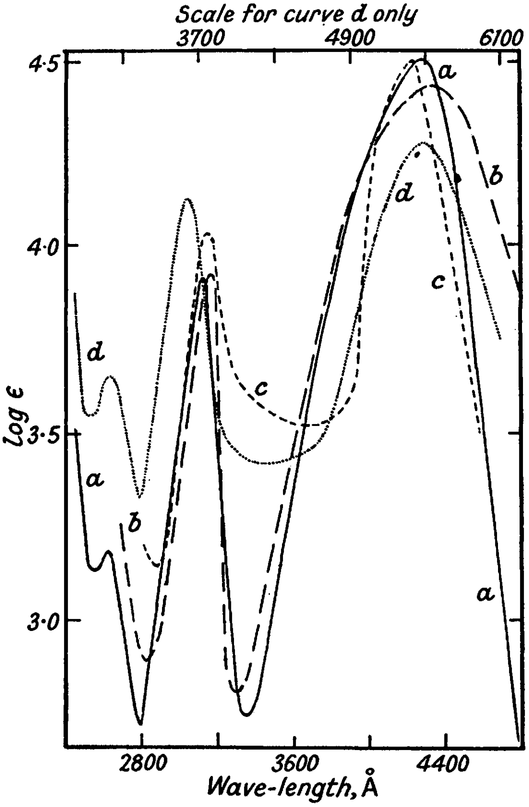
a, In 98% *acid* (*zero-time extrapolation*). *b, In* 98% *acid* (*after* 210 *min.*). *c, In* 100% *acid* (*after* 60 *min.*). *d, In* 100% *acid* (*after* 210 *min.*).

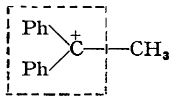
In the case of anthracene the number of primary solute particles present in sulphuric acid solution could not be established by cryoscopy, and therefore we must briefly consider whether other rapid and reversible reactions could afford an explanation of the spectra. In particular, sulphonation has in some cases been reported to be reversible by treatment of the sulphonic acid with dilute sulphuric acid, *i.e.*, under conditions similar to those under which our dilution experiments (procedure *B*) were shown to lead to the recovery of anthracene (cf. Minaev and Fedorov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 143; Berkenheim and Snamenskaya, *J. Gen. Chem. U.S.S.R.*, 1934, **4**, 31; Marschalk, *Bull. Soc. chim.*, 1935, 2, 1809). However, an explanation based on sulphonation and its reversal is unlikely, since absorption spectra of sulphonic acids have been reported to be similar to those of the parent hydrocarbons and this is not true in our case. There is, furthermore, a suggestive similarity between the spectrum of anthracene in concentrated sulphuric acid and those of 1 : 1-diphenylethylene and triphenylethylene (Fig. 9).

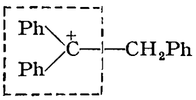
This similarity of the absorption spectra is a striking feature of this work and points to a similarity of the three conjugate acid cations, formed from the hydrocarbons. Since light absorption in the near ultra-violet and the visible region of the spectrum is associated with electronic transitions within the π-electron shell of the molecule, it is suggested that the conjugated system present in these three species is the same, a requirement which may be satisfied if the proton attachment occurs so as to form in each case the conjugated system of a substituted diphenylcarbonium ion, *viz.*

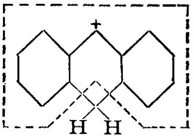
FIG. 9. *Absorption spectra in concentrated sulphuric acid.*

a, 1 : 1-*Diphenylethylene. b, Triphenylethylene (zero-time extrapolation). c, Anthracene (zero-time extrapolation). d,* 1 - *Phenyl* - 1 - *α* - *naphthylethylene (zero-time extrapolation).*









In each case the extent of the largest conjugated system in the ion is shown by the broken line. In Part IV it will be shown that theoretical considerations would, in fact, lead us to predict the proton attachment to occur in these positions, provided we start with the assumption that the added proton is held to a certain carbon atom and not to a bond or molecular π-electron cloud as envisaged by Dewar ("The Electronic Theory of Organic Chemistry," Oxford, 1949).

It would be expected that the diphenylcarbonium ion, formed from the ionization of diphenylmethanol as a secondary base in sulphuric acid (Welch and Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 4748) :

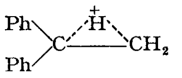
$$Ph_2CH{\cdot}OH + 2H_2SO_4 \longrightarrow Ph_2HC^+ + H_3O^+ + 2HSO_4^-$$

should have the same conjugated system as the above ions and therefore a similar absorption spectrum. This prediction is largely substantiated (Fig. 7). The differences that exist between the various spectra of what are believed to be substituted and unsubstituted diphenylcarbonium ions do not seem to be greater than one would expect from the substitutions. The chief variation that occurs is in the intensity of the second absorption band. Since this band is considerably weaker than the first one in all the spectra examined, it may probably be ascribed to a forbidden transition, and the variations in intensity with different substituents may perhaps be associated with a varying degree of breakdown of a selection rule depending, for instance, on the extent to which the benzene rings are tilted with respect to the plane of the carbonium ion valencies. Thus the transition may be more forbidden in Ph_2HC^+ than in $^+CPh_2{\cdot}CH_2Ph$ or Ph_2MeC^+ where coplanarity may be more difficult to achieve.

The absorption spectrum of the conjugate acid of 1-α-naphthyl-1-phenylethylene is similar to those of the diphenylcarbonium ions except that the spectrum has been shifted towards the red, as is usual when a phenyl group is replaced by an α-naphthyl group.

It has been pointed out (A. G. Evans, *loc. cit.*) that the spectrum of triphenylmethanol in sulphuric acid resembles that of 1 : 1-diphenylethylene in the same solvent. In particular, the double-peaked first absorption band of the triphenylcarbonium ion—although it is much broader—also occurs around λ 4200 Å. However, we do not believe that this has any simple explanation, since the conjugation in the triphenylcarbonium ion is diminished by the difficulty or impossibility of forming a coplanar structure (cf. Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 42).

Although it is possible to explain the similarity between the absorption spectra of different hydrocarbons in sulphuric acid by the hypothesis that proton attachment to a particular carbon atom occurs, yet this is not true if we assume the carbonium ions to possess a " non-classical " structure, formulated as



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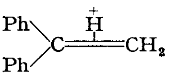
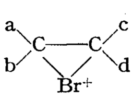


Dewar considers that attachment to the π-electrons of a double bond may occur without interrupting the conjugation through the bond (*ibid.*, p. 50). The conjugated systems in the conjugate acids of 1 : 1-diphenylethylene and triphenylethylene should then differ from each other by as much as those of the parent hydrocarbons, and we might expect the same bathochromic shift on going from the first compound to the second both in the case of the conjugate acids and in that of the hydrocarbon bases. Even without accepting this view on the uninterrupted conjugation through a bond which has accepted a proton, it would still be difficult to see why the π-electron systems of the conjugate acids of 1 : 1-diphenylethylene and anthracene should resemble each other if the proton attachment occurs to a bond (or a pair of atoms) rather than to a single carbon atom. If such " non-classical " structures are accepted, the spectral similarities pointed out appear to be curiously fortuitous.

It would be interesting to examine the heterolytic addition of hydrogen halides to double bonds in the light of these considerations. Formation of *trans*-addition products in the thermal addition of bromine to a double bond has been given as evidence for a triangular structure of the intermediate (Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947) (see inset). The bonding envisaged by the authors is different from the type postulated by Dewar and should no longer be possible when a proton replaces the bromine cation. The steric course of the hydrogen halide addition should show whether the postulation of a triangular structure is also required for the intermediate conjugate acids of the olefins which, from this work, we conclude to have " classical " structures.



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[*Received, December 17th*, 1951.]