[JOINT CONTRIBUTION FROM THE ILLINOIS INSTITUTE OF TECHNOLOGY AND ARGONNE NATIONAL LABORATORY]

The Influence of an Acidic Environment on the Spectra of Benzene and Some Methylbenzenes[1]

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The visible and ultraviolet absorption spectra of benzene, mesitylene and hexamethylbenzene have been studied in various solvents. In each case the effect of solvent acidity on the spectrum is evident. A qualitative explanation of these observations is given by relating environmental acid strength to π-electron attraction. In the moderately acid region, the predominant spectral change is the loss of fine structure. The absorption for the substituted benzenes becomes a single peak in the near ultraviolet. The extinction coefficient of the peak grows with increasing acidity. These spectral changes permit the establishment of an acidity scale based on electron mobility in a single species which is related to, although not identical with, the Hammett H_0 scale. In highly acidic media, both the methylbenzenes are proton acceptors and may be employed as H_0 indicators.

Introduction

The electronic absorption spectrum of benzene and the effect of substitution in this spectrum has been studied intensively in recent years and may be regarded as qualitatively well understood.[2] However, no existing theory appears to be quantitatively adequate.

Empirical observations on substituted benzenes are extensive.[3] Most substituents exert a mild bathochromic shift with some loss of fine structure and slight increase in intensity. (The use of oscillator strength rather than extinction coefficient to compare intensities is a refinement which regrettably is scarcely warranted in this investigation.) The loss of symmetry involved in all but hexa-substituted benzenes is usually reflected in the spectra. Nitro substituted aromatics are outstanding in their behavior and will be discussed below.

The effect of environment on the properties of aromatic solutes and their spectra has been studied, though in much less detail.[4] Bayliss, for example, finds trivial changes in wave length or intensity and only slight loss of structure in going from nonpolar inert solvents such as cyclohexane or isooctane to alcohol or water. While carbon tetrachloride or chloroform distort the spectra to a greater extent, the present investigation is not concerned with this type of solvent.

In general, many of the solvent effects may be interpreted in terms of classical optical interactions involving the refractive index of the solvent, or an absorption band which interacts strongly with the solute absorption. A residue remains to be interpreted in terms of the chemical forces between molecules or the parts of molecules.

One of the purposes of this investigation is to correlate spectral changes with those changes in the environment, associated with increasing acidity. Those environments which are regarded as acidic by criteria such as attack on metals or an effect on indicators, are characterized by having volume elements of low electron density either in the form of protons or vacant orbitals in the molecular periphery. It seems reasonable to suppose that such an environment will affect the π-electrons of the aromatic nucleus. It is, therefore, quite likely that the spectra of aromatic molecules will reflect the electron attracting power of the acid environment; in short, serve as an acid strength indicator.

If we employ such strongly acidic solvents that the aromatic molecule acts as a proton acceptor, we may anticipate an entirely new chemical species with a substantially different spectrum. Both hydrogen fluoride and sulfuric acid give solutions in which this process does take place. The equilibria for proton addition and subsequent ionization have been studied for a number of methylbenzenes.[5] There are scattered observations on benzene and substituted benzene spectra in $HF-BF_3$ mixtures,[6] and some studies of proton transfer in both acids using more complex aromatics.[7]

The present measurements have involved benzene and two substituted benzenes, mesitylene and hexamethylbenzene.

The characteristic spectra of benzene and substituted benzenes in the ultraviolet include a set of bands in the neighborhood of 2000 Å. and a much weaker set of bands in the neighborhood of 2600 Å. The latter region is accessible with more solvents and has been the region studied.

Hammett[8] has studied proton transfer indicators for very acid systems. He has defined an acidity scale which depends on the indicator charge type. The H_0 scale is used for proton transfer to a neutral base to give a cation acid, the H_- scale for protonation of an anion base to give a neutral acid, and the H_+ scale where the base form of the indicator is a cation. Each scale reduces to pH (defined as $\log 1/C_{(H_3O^+)}$ or $\log 1/A_{(H_3O^+)}$ in infinitely dilute aqueous solution. In each case a $pK_a{}^I$ is found for the indicator where the concentration of acid and basic forms are equal by intercomparison with a series of indicators in an increasingly acid en-

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[1] (a) Partially supported by the Petroleum Research Fund, American Chemical Society; (b) based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Sponer, *Revs. Modern Phys.*, **14**, 224 (1942); R. S. Mulliken, *Phys. Rev.*, **43**, 279 (1933), *J. Chem. Phys.*, **7**, 353 (1939); W. Moffitt, *ibid.*, **22**, 320 (1954).

[3] A.P.I.-NBS, Collection of ultraviolet spectrograms. R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York; L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1942); **71**, 2414 (1949); T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, *ibid.*, **69**, 880 (1943).

[4] N. S. Bayliss and L. Hulme, *Aust. J. Chem.*, **6**, 257 (1953); H. E. Ungnade, THIS JOURNAL, **75**, 432 (1953); N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[5] M. Kilpatrick and F. Luborsky, *ibid.*, **75**, 577 (1953).

[6] C. Reid, *ibid.*, **76**, 3264 (1954).

[7] (a) E. L. Mackor, G. Dallinga, J. H. Kruizinga and A. Hofstra, *Rec. trav. chim.*, **75**, 836 (1956); (b) V. Gold and F. I. Tye, *J. Chem. Soc.*, 2172 (1952).

[8] L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935); "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

vironment. Both mesitylene and hexamethylbenzene are potentially useful H_0 indicators. The acidity of an unknown environment is determined by adding the indicator and measuring the fraction protonated, assuming that the indicator constant is independent of the medium.

$$H_0 = pK_a^I - \log C_IH^+/C_I$$

The use of Hammett indicators and particularly the H_0 scale has been reviewed recently by Paul and Long.[9] They have revised slightly the indicator constants suggested by Hammett and their values have been used in this paper.

Experimental

Materials.—While preliminary scouting experiments showed that most of the substances of interest were commercially available as reagents whose spectra in inert solution showed no extraneous absorption, samples of the hydrocarbons taken off the shelf showed variety of absorptions in strong acid media which were not stable to purification of the sample. This led to some confusion in the early phases of this investigation. The data reported in this paper are only included for spectral peaks that are quantitatively reproducible on more than one sample of purified hydrocarbon. It is only fair to note, however, that a freshly opened sample of Fisher certified reagent grade benzene, Aldrich purissimum grade mesitylene, and Eastman Kodak purified hexamethylbenzene actually were of satisfactory purity to meet the criteria of this investigation. In each case, their spectra in acidic solvents were not significantly affected by distillation or recrystallization.

Eastman Kodak spectral grade 2,2,4-trimethylpentane (isoöctane) was used as received. The absolute ethanol employed was Commercial Solvents Gold Seal grade used as received.

Kahlbaum acetic acid was used as received and a sample of B and A reagent grade acetic acid was purified by fractional freezing. The highest m.p. found for this preparation was only 16.3°. A sample of quantitatively anhydrous acid was prepared by refluxing with acetic anhydride. However, solutions were made up in air, and the cells filled by pouring since small amounts of water were not found to affect the spectra of any solute.

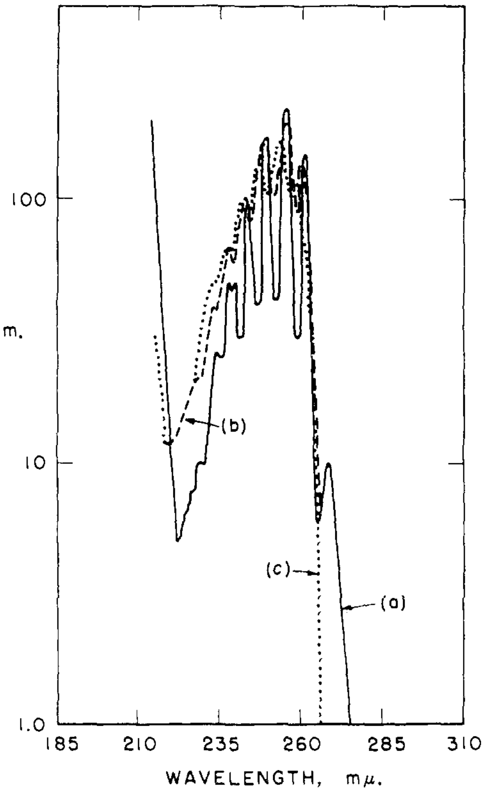

Fig. 1.—Absorption spectrum of benzene: (a) 2,2,4 TMP; (b) aq. concd. HF (50%); (c) 100% HF.

Kahlbaum formic acid was used as received. No difference in the observed spectra of mesitylene in this solvent was found when a portion was purified by fractional freezing. The highest m.p. found was 7.8°. A sample of Matheson, Coleman and Bell reagent grade 90% formic acid also was investigated. While the behavior of 90% acid was measurably different from the anhydrous acid, no attempt was made to prepare really dry material.

Minnesota Mining and Manufacturing trifluoroacetic acid was redistilled at atmospheric pressure collecting a middle fraction at 71–72°. Similar samples have been found to be quite pure by conductivity measurements, but, again, no attempts were made to obtain maximum freedom from water.

Sulfuric acid was B and A reagent grade material adjusted to concentration with reagent grade fuming acid or water.

Trichloroacetic acid was a Merck reagent grade chemical used as supplied.

Hydrogen fluoride was commercial material purified by fractional distillation in an efficient column. The product was collected and handled initially in poly-(chlorotrifluoroethylene) tubes connected to a vacuum line equipped with gold-lined fittings, thus avoiding contact with base metal. The quality of this material and acidity of hydrogen fluoride solutions have been discussed previously.[10]

Instruments.—Three spectrophotometers were employed at some time during this work, a manual Beckman DU, a Beckman DK-1 recording unit and a Cary Model 11 recording spectrophotometer. No inconsistencies were found were comparison runs were made. The DU was equipped with a cell compartment whose temperature could be readily adjusted. All measurements on trichloroacetic acid (at 40–50°) and some early measurements on hydrogen fluoride (at 15°) were made in the DU. Most other measurements were made on the DK recording instrument in a thermostatically controlled 25° room. Aside from the trichloroacetic acid observations, all the data reported were obtained with the Beckman DK-1. Conventional capped or stoppered fused silica cells were used for all measurements except those with hydrogen fluoride. Optical cells suitable for use with hydrogen fluoride solutions have been described previously by Hyman, Kilpatrick and Katz.[10,11] For the data reported in this paper both fixed and variable spacer cells with sapphire windows were employed. The fixed cells had poly-(chlorotrifluoroethylene) bodies; the variable spacer cells were made from nickel heavily gold plated.

Solution Preparation.—Benzene and mesitylene solutions were prepared volumetrically. Except for those containing hydrogen fluoride, solutions were prepared in air and poured into the cells with no protection from atmospheric contact. Hexamethylbenzene was weighed directly in most cases. Solutions in hydrogen fluoride had to be prepared in closed containers and hydrogen fluoride transferred by distillation rather than pouring. The hydrocarbon samples were weighed on a Fisher Gramatic microbalance in a small capsule fabricated from hand drawn poly-(chlorotrifluoroethylene) capillary tubing. Hydrogen fluoride was distilled into a poly-(chlorotrifluoroethylene) tube through a link of poly-(ethylene) tubing. The tubing was pinched shut, the capsule added to the length of tubing above the closure, and the cell capped. The pinchcock was then opened and the hydrogen fluoride mixed with the hydrocarbon. After thorough mixing the tubing could again be pinched shut, the tube connected to the cell, and the solution poured into the cell without exposure to any air other than the small volume left in the cell.

A number of alternative methods of solution preparation were tried. Of these, the one described above was found to be the simplest procedure giving adequate reliability in sample preparation and was actually employed for most of the HF solutions discussed below. Concentrations and molar extinction coefficients are probably good to ±2 and

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[9] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[10] H. H. Hyman, M. Kilpatrick and J. J. Katz, THIS JOURNAL, **79**, 3668 (1957).

[11] J. J. Katz and H. H. Hyman, *Rev. Sci. Instr.*, **24**, 1065 (1953).

±10%, respectively, although an insufficient number of duplicate runs are available to establish this accuracy.

Observations.—The benzene spectra are of relatively little interest. In most of the solvents employed the only noticeable change is loss of fine structure which is reflected in sharp increase in the height of the minima in benzene spectrum. The highest wave length maximum in benzene at 267 mμ disappears in a mildly acidic medium, but since the molar extinction coefficient of this peak in a hydrocarbon solvent is under 10, this observation is simply another aspect of the loss of resolution. Benzene, of course, is readily sulfonated in highly concentrated (>15 *M*) sulfuric acid solutions, so that the only highly acid system in which it was studied was anhydrous hydrogen fluoride. In this medium the benzene fine structure is virtually obliterated and the maximum shifted 2 mμ (300 cm.$^{-1}$) toward the violet.

The mesitylene spectra are much more varied in behavior as we go to strong and stronger acid solutions. Figures 2, 3 and 4 show three acid regions in which significant changes in spectra may be correlated with increasing acidity. The first of these lies in the region between water and acidity represented by anhydrous trifluoroacetic acid or a concentrated aqueous solution of hydrofluoric acid. In this region the elimination of fine structure is the primary spectral change.

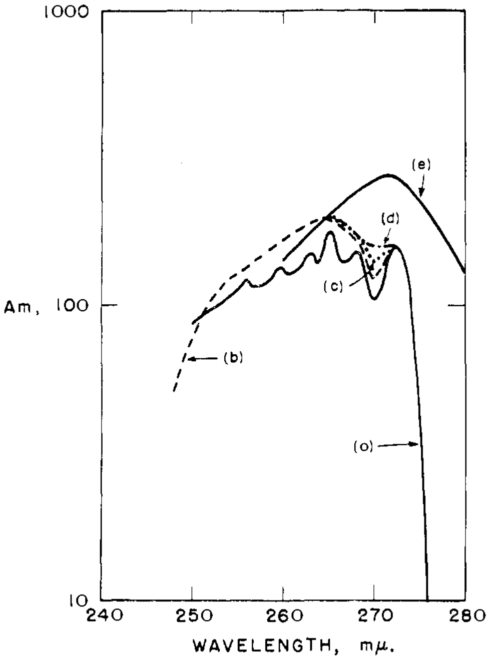

Fig. 2.—The ultraviolet spectrum of mesitylene in various solvents: (a) 2,2,4 TMP; (b) CH_3COOH; (c) HCOOH; (d) CF_3COOH; (e) (12.2 *M* HCl).

The most obvious quantitative indicator for this fine structure destruction is the difference in molar absorbancy between the minimum at 270 mμ and the nearby maximum at 272 mμ.

The second acidity region of interest is that associated with enhancement of the 260 mμ peak. This is observed, for example, in concentrated hydrochloric acid, hydrofluoric acid solutions above 50% HF, and it was also noted in trichloroacetic acid. The latter point, however, was measured at 50 rather than 25°.

The third region was observed only in hydrofluoric acid solutions containing more than 80% HF. Two peaks at 255 and 355 mμ were found, attributable to protonated mesitylene.

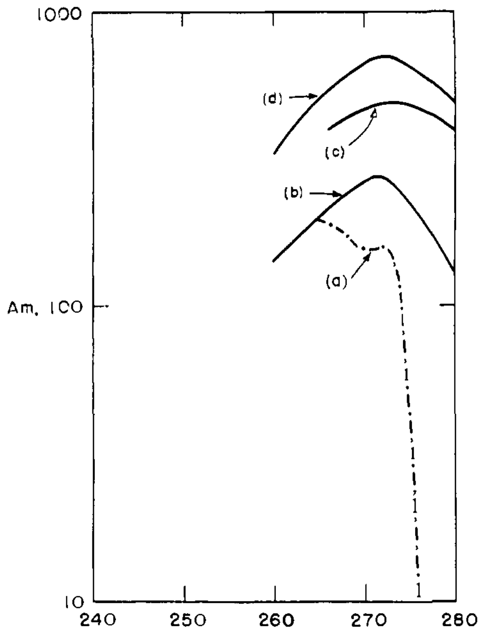

Fig. 3.—The ultraviolet spectrum of mesitylene in various solvents: (a) CF_3COOH; (b) 12.2 *M* HCl; (c) CCl_3COOH; (d) 10.7 *M* HCl, 2.0 *M* LiCl.

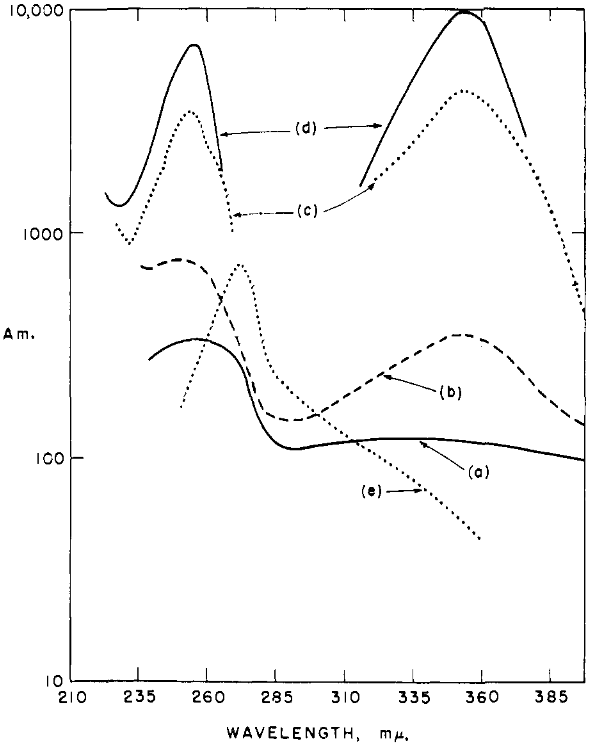

Fig. 4.—The ultraviolet spectrum of mesitylene in various solvents: (a) 80.0% HF; (b) 86.8% HF; (c) 97.2% HF; (d) 100.0% HF; (e) 10.7 *M* HCl; 2.0 *M* LiCl.

The observations with hexamethylbenzene in many ways parallel those with mesitylene. Since the fine structure of the hexamethylbenzene spectrum is not too prominent even in inert solvents, it is not practical to use the disappearance of fine structure as an acid strength indicator. However, the multiple peaks clearly separated by valleys in ethanol, are completely indistinguishable in anhydrous formic acid, although the position of the maximum and extinction coefficient at the maximum are virtually identical in these two solvents.

Hexamethylbenzene is not sufficiently soluble in aqueous hydrofluoric or sulfuric acid to study the growth of an absorption band with increasing acid concentration until we reach an acid concentration such that proton transfer is dominant. Gold and Tye[7] made an effort to study hydrocarbons in the less acid region by using solutions of sulfuric acid in acetic acid, but found that sulfuric acid in concentrations where protonation was not extensive, had a strong salting-out effect which made their observations inconclusive. Fortunately, we found that trifluoroacetic acid dissolves hexamethylbenzene quite nicely and may be diluted with sulfuric acid without decreasing the hexamethylbenzene solubility excessively. The growth of the 270 mμ band could be followed in sulfuric acid–trifluoroacetic acid solutions. This probably would be true of hydrofluoric acid–trifluoroacetic acid mixtures as well. Table I shows the growth of the 270 mμ peak which we believe was not due to protonation, and the growth of the 281 and 395 peaks corresponding to the protonated hydrocarbon absorption as observed in the mesitylene case.

TABLE I

ABSORPTION PEAKS FOR HEXAMETHYLBENZENE IN ACIDIC SOLVENTS

Solvent	H_0[a]	270[b]	A_m at 281[c]	395[c]	H_0[d]
HCOOH	−1.9	200			
CF_3COOH	−3.1	280			
0.62 *M* H_2SO_4 in CF_3COOH		360			
1.2 *M*		440		200	−6.7
1.7		530		375	−7.0
3.7		1250[e]		1610	−7.7
6.2			2100	3640	−8.3
9.3			3200	6660	−9.7
12.4			5500	9500	
CCl_3COOH[f]		700			
HF	110.2		4370	7350	
17.5 *M* H_2SO_4 in H_2O	−8.7		3300	5200	−8.7
18.0	−9.4		12,800	18,200	
18.65 *M* (100% H_2SO_4)	−11.0		22,000	35,000	

[a] The H_0 values based on the indicators suggested by Hammett. [b] A maximum at this wave length is associated with a neutral ground state. [c] Two maxima at these wave lengths are found in solutions where the hexamethylbenzene is presumed to be protonated. [d] The H_0 value calculated using hexamethylbenzene as an indicator with a pK_1 of −8.3. [e] The absorption maximum was at 275 mμ. [f] This spectrum was obtained at 50°.

The spectra observed were usualy unstable with respect to standing, the more acid solutions developing intense red colors in less than 1 hour. It usually was possible to obtain a spectral scan in a short enough time to avoid the necessity of plotting absorptions and extrapolating back to zero time.

Discussion

The foregoing observations suggest a number of items for discussion. Those taken up in this section include: 1, the effect of electron attraction in substitution or environment on the 260 mμ absorption band; 2, the minor influence of the environment on the observed benzene spectrum; 3, the determination of acid strength from spectral changes which do not involve proton transfer; 4, the dependence of acid strength on the entire system, rather than the concentration of an acid species; 5, proton transfer to substituted benzenes and their use as Hammett indicators.

The Effect of Electron Attracting Substituents or an Electron Deficient Environment on the 260 mμ Absorption Band.—The maximum molar extinction coefficients for benzene and most substituted benzenes in the 2600 Å. region are about 200. Nitrobenzene[12,13] is the most important exception, the extinction coefficient in this region being 40 times the benzene value. There is no separate band structure in the nitrobenzene spectrum.

While Doub and Vandenbelt[2] and later Wenzel interpreted the nitrobenzene spectrum in terms of a large bathochromic shift for the 200 mμ band, most modern workers support a somewhat different point of view: Nagakura and Tanaka, for example, have interpreted the observed spectrum in terms of the strong electron attracting nature of the nitro group which also accounts for its *meta*-directing influence in substitution.

This electron attraction results in a new low lying excited level and in effect a new absorption in this region rather than a modified benzene spectrum.

Mulliken, Orgel and their associates have discussed in considerable detail the formation of donor–acceptor complexes in which benzene or substituted benzene molecules serve as electron donors.[14,15] The optical characteristic of such complex formation is the charge-transfer absorption in which the ground state is similar to the uncomplexed donor ground state, but the excited state involves an orbital associated with the acceptor as well. The nitrobenzene spectrum is in one sense of this description, an internal charge-transfer spectrum.

We suggest that a sufficiently acid environment will yield a spectral pattern similar to that of nitrobenzene, *i.e.*, a more intense absorption with little structure in the 260 mμ region. While this effect was not observed in benzene, we believe it was observed in mesitylene.

Mesitylene and other hydrocarbons have been studied as solutes in anhydrous hydrogen fluoride. It is reasonably certain that mesitylene is protonated. The conductivity measurements of ref. 5 can be accounted for by an equilibrium involving one proton transfer per mesitylene. If we interpret the spectrum of mesitylene in anhydrous hydrogen fluoride as essentially that of a monoprotonated species, then the spectrum in 80% hydrogen fluoride cannot contain significant quantities of protonated material, and the enhanced absorption at 255 mμ must be interpreted in some other way. We suggest that the excited state involved in the optical absorption is one in which the π-electrons are attracted by the acidic environment much as they would be in nitrobenzene molecules.

The absorption band might be ascribed to a charge transfer spectrum in a complex containing mesitylene and some specific acidic group rather than mesitylene in an acidic environment. However, if we try to formulate a mass action equilibrium

$$\text{aromatic} + \text{acid species} \rightleftarrows \text{complex}$$

$$K = \frac{A_{\text{complex}}}{A_{\text{Ar}} \times A_{\text{acid}}}$$

and assume that the optical density at 255 mμ is

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(12) A. Wenzel, *J. Chem. Phys.*, **22**, 1623 (1954).

(13) S. Nagakura and J. Tanaka, *ibid.*, **22**, 236 (1954).

(14) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(15) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955); *Quart. Revs.*, **8**, 422 (1954).

proportional to the concentration of complex, we cannot use as the A_{acid}, an activity close to a reasonable value for the concentration of any of the known species that may be present, H_3O^+, H_2F^+, or even $(HF)_nH^+$. We must refer instead to the hypothetical species whose activity is described by the H_0 function. For a change of acid concentration from 80.0% HF to 86.8% HF corresponds to a greater than 2-fold change in extinction coefficient for the peak at 255 mμ. While the H_0 function changes by 2.5 (antilog 0.4) over this acidity range, no identifiable species present in significant concentration changes this much over this narrow range.

Obviously, the excited state associated with this absorption must differ from the excited state of an isolated mesitylene molecule. Therefore, an adequate quantum mechanical description of this state would involve a measurable contribution from at least one nearest neighbor solvent molecule, and the combination might well be described as a complex and most probably a π-bonded outer complex. Yet in view of the absence of any ground state interaction, and the transitory nature of the complex, it seems more convenient to treat this absorption in terms of an environmental interaction.

The Minor Influence of the Environment on the Observed Benzene Spectrum.—Benzene itself showed only a minor shift in wave length for the maximum absorption and some loss of fine structure in anhydrous hydrogen fluoride. In contrast to these observations, Reid[5] added benzene to $HF-BF_3$ mixtures at low temperatures and got an initial absorption at 284 mμ. On warming and standing, an intense absorption in the visible appeared which he attributed to the protonated benzene. During the course of the current investigation, the gradual and irreversible growth of colored solutions in hydrogen fluoride has been minimized though never entirely eliminated by purification of the reagents. It is very unlikely that such color changes are at all related to simple proton transfer. Disproportionation, isomerization and polymerization of a number of aromatic substances in this reagent are well known, though not for pure benzene. The conductivity observations show conclusively that in pure hydrogen fluoride and in solutions containing low concentrations of boron trifluoride in hydrogen fluoride, such as are obtainable under the conditions described in reference 6, a negligible fraction of the benzene is protonated.

Reid suggested that the absorption at 284 mμ might be due to a $C_6H_6-BF_3$ complex. He admitted, however, that this suggestion was not consistent with observations on the solubility of BF_3 in toluene pointed out to him by H. C. Brown.[6]

Reid did not investigate benzene in HF alone. If the absorption at 284 mμ is in fact due to a benzene solvent interaction, it is probably an interaction analogous to that for mesitylene in aqueous HF. $HF-BF_3$ might well be expected to be a stronger acid than HF alone. Benzene is much less basic than the methyl substituted derivative.

The Determination of Acid Strength from Spectral Changes which do not Involve Proton Transfer.—It is obvious that any measurable property which changes in regular fashion with acid concentration may be used to construct an acidity scale of sorts. Such a scale is valuable only if it can be used to correlate or predict subsequent behavior, as has been done with the Hammett acidity functions.

While the H_0 value is useful in comparing media as to their influence on reaction kinetics and solubility, at least one complicating factor in interpreting the data lies in the fact that the acidic and basic indicator species are different chemical entities. They have different charges and different structures, therefore, different chemical and physical properties. They may interact with the environment so specifically that generalizations as to the nature of the environment from equilibria are somewhat uncertain.

The use of spectra directly as a measure of acidity is not without uncertainties both in theory and practice. However, to the extent that there are a different set of variables involved, there may be advantages in supplementing H_0 measurements with an acidity scale based on changes in the spectrum of a single species rather than the equilibrium between two species.

In Fig. 2 a gradual disappearance of fine structure was noted in going from an inert solvent through acetic to formic and trifluoroacetic acid. A convenient measure of the fine structure is the difference between the peak at 272 mμ and the valley at 270 mμ. The elimination of this difference may be treated as an indicator reaction, *i.e.*, the maximum difference corresponds to the 100% basic form, and the fraction of this difference actually found may be used as the basic fraction in the Hammett expression. This may be used to designate an acidity scale H_S.

$$B = \text{fraction basic} = (A_{272} - A_{270})_{\text{soln}}/(A_{272} - A_{270})_{\text{inert solvent}}$$

$$H_S = H_S{}^I - \log\left[(1 - B)/B\right]$$

It is not practical at this time to determine an independent indicator constant for this spectral change. Instead, we may compare the change in H_S with the change in H_0 on varying the medium. For example, the H_0 value of anhydrous formic acid is -1.9. The H_S value for acetic acid is 0.7 unit less acidic and for trifluoroacetic acid 1.1 unit more acidic than the formic acid value.

We have measured the H_0 value for anhydrous trifluoroacetic acid as -3.1 using *p*-nitrodiphenylamine as indicator (in good agreement with a value extrapolated from the data of Randles and Tedder[16] for aqueous solutions of this acid). The change in H_0 in going from formic to trifluoroacetic acid is thus 1.2 units in good agreement with the H_S difference.

The H_0 value for glacial acetic acid is $+3.5$ and the H_S value would indicate this solvent is much more acidic, than the H_0 value would suggest. Hammett has pointed out that acetic acid shows a very much greater acid strength toward negative ions ($H_- < 0$) and its low dielectric constant is largely responsible for the weak ionization of neu-

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[16] J. E. B. Randles and J. M. Tedder, *J. Chem. Soc.*, 1218 (1955).

tral proton acceptors. This factor is much less important in the spectral effect, and H_S is much more negative. For very high dielectric solvents, H_S should approach the same value as H_0.

The disappearance of fine structure in hexamethylbenzene seems to occur at even lower acidities than mesitylene. However, even in inert solvents, this structure is not very pronounced and there seems to be no practical way to use the disappearance as an indicator.

Both mesitylene and hexamethylbenzene, however, show an enhanced peak at ~260 mμ which we have attributed to a non-protonated species in an acid environment. This can be used as an indicator, but in neither case has it been possible to show a good correlation with other acidity scales.

Since mesitylene is readily sulfonated by sulfuric acid, it was studied primarily in hydrogen fluoride. The indicator behavior of mesitylene is completely reversible. Indeed, most of the HF points were obtained by dilution of mesitylene solutions in anhydrous HF.

There are several complications in using the 255 mμ peak as a good acid indicator. The most important of these lies in the observation that in the strong acid region where mesitylene is protonated, an absorption peak at ~ 260 mμ appears which shows substantially higher absorption than that reached in the absence of measurable amounts of proton transfer. Compare Figs. 2 and 3.

As an additional complication the 255 mμ peak in hydrogen fluoride solutions is found near 270 mμ in the trichloroacetic acid and hydrochloric acid cases. Hammett, in noting a similar wave length shift in using proton transfer indicators, postulated that the shift in wave length was not a function of acidity, whereas, the extinction coefficient was. This implies that the energy difference associated with initial and final states differs with a different anionic species involved in the proton transfer, while the probability of transition depends solely on the concentration of protonated species. This postulate is probably equally valid in this case, if we assume that the excited state is a π-bonded complex rather than a cation anion pair.

On the basis of the observations summarized in Figs. 2 and 3, one may guess that the enhancement of the 260 peak for mesitylene would be one-half completed in the H_0 range approximating -8, and for hexamethylbenzene, the data in Table I lead to a range of 6–7 for the $-H_0$ value corresponding to the midway point in the growth of the 270 mμ peak. The latter, however, is in a trifluoroacetic acid–sulfuric acid system and the H_0 value is that using hexamethylbenzene itself as an H_0 indicator under unfavorable conditions. On this basis, anhydrous trifluoroacetic acid has an acidity closer to -5 than to -3, which as we have noted, is the acceptable H_0 value. Trifluoroacetic acid has a lower dielectric constant and would show stronger acid behavior with respect to its effect on spectra than an aqueous sulfuric acid system that had the same H_0 value. Furthermore, the addition of sulfuric to trifluoroacetic acid must have a profound medium effect on the activity coefficient of the un-ionized unprotonated hexamethylbenzene in solution. This effect, of course, is not taken account of in the usual H_0 calculations.

Additional experiments are planned on trifluoroacetic acid–sulfuric acid mixture and trifluoroacetic acid–hydrofluoric acid mixtures to help understand the difference between these acidity scales.

This type of failure of simple correlations of acidity scales should not be regarded as invalidating the use of such scales, but rather as pointing out their limitations and emphasizing the variety of chemical factors that actually go into determining any specific equilibrium or, for that matter, any optical absorption.

The Dependence of Acid Strength on the Entire System Rather than the Gross Concentration of an Acid Species.—One of the factors that suggests the value of treating acid strength as an environmental concept lies in the very great difference in acidity associated with the same concentration of added "acid" in different solvents.

It has long been recognized that the same concentration of sulfuric acid corresponded to a much higher acidity in acetic acid than in water.[8,9] The H_0 of 1 M H_2SO_4 in acetic acid is ~ -3 as against ~ 0 in H_2O. The data in Table I indicate that this acidity is even higher for similar concentrations of sulfuric acid in trifluoroacetic acid. (~ -6)

This is not surprising if we regard the acid substance in solution as the protonated solvent, and in the cases cited, the acid strength might be expected to run

$$HCF_3COOH^+ > HCH_3COOH^+ > H_3O^+$$

A less familiar medium effect is illustrated by the behavior of a lithium chloride, hydrochloric acid solution. The enhanced acidity of a hydrochloric acid solution due to lithium chloride was not unexpected.[17]

The difference between curves b (86.8% HF) and e (10.7 M HCl, 2.0 M LiCl) in Fig. 4 points up another discrepancy between H_0 values and an acidity scale based on enhancement of the 260 mμ peak. Both solutions give about the same enhancement of this peak, but the absorption at the 354 mμ peak corresponds to 3–4% protonation for the mesitylene in the HF solution and negligible protonation in the HCl–LiCl solution. There is no obvious explanation for this difference.

Proton Transfer to Methylbenzenes.—Both mesitylene and hexamethylbenzene are protonated in strong acids and should serve as Hammett indicators. The $pK_a{}^I$ for mesitylene as an H_0 indicator is approximately -8.8. The maximum extinction due to protonation is 10^4 at the 354 mμ peak. The optical extinction observed in the 260 mμ region approaches 10^3 for solutions with no proton transfer and 7.5×10^3 for the fully protonated species. Since there are specific solvent effects, the acidity indicated by the 260 mμ peak

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(17) This experiment was suggested by K. A. Kraus of Oak Ridge National Laboratory on the basis of similar observations with LiCl solution in elution from ion-exchange resins.

need not agree precisely with that indicated by the 354 mμ peak.

The two absorption peaks found for protonated mesitylene in HF at ~ 260 and ~ 360 mμ may correspond to those predicted by Muller, Pickett and Mulliken[18] for the benzenium ion (at 320 and 400 mμ), but the calculations are certainly too approximate to permit a clear distinction between the bonding suggested by the authors (a localized bonding stabilized by hyperconjugation) and the generalized π-bonding suggested by Dewar.[19]

The data for hexamethylbenzene are more difficult to interpret. The conductivity observations of ref. 5 would imply that hexamethylbenzene is completely ionized in anhydrous hydrogen fluoride. This would yield an absorption maximum at 395 mμ for singly protonated hexamethylbenzene of about 7400 and on the basis of the observed absorption in 17.5 *M* H_2SO_4 ($H_0 = -8.7$) the pK_a^I for hexamethylbenzene as a proton acceptor indicator would be −8.3. However, the optical absorption found in strong sulfuric acid corresponds to some additional process, either a rapid rearrangement followed by sulfonation or perhaps a second protonation. It is not immediately obvious why the latter should take place more readily in sulfuric than in hydrofluoric acid solutions showing comparable acid strength when measured with trinitroaniline. However, as was noted above, lack of exact correspondence in acidities in using two different types of indicators is unfortunately encountered in a number of similar situations.

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Some Physical Properties of Perfluoro-*n*-hexane

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A sample of perfluoro-*n*-hexane was refined by fractional crystallization and found to be 99.98 mole % pure by analysis of the freezing curves. The freezing point, heat of fusion, vapor pressures, densities of air saturated and degassed liquid between 15 and 45°, vapor densities at 30°, and critical temperature were determined.

Introduction

Although the characterization of fluorocarbons has been the object of intensive research since their discovery,[1] very little work has been done on highly purified samples. Impurities introduced during synthesis by existing methods are not easily removed by fractional distillation because a large number of substances, *e.g.*, fluorocarbons containing hydrogen,[2,3] nitrogen[3] or oxygen,[3] and even structural isomers[2,4,5] can boil at nearly the same temperature.

A sample of perfluoro-*n*-hexane, prepared by the Simons electrochemical process,[6] was obtained through the courtesy of the Minnesota Mining and Manufacturing Company. Purification methods investigated were fractional distillation, silica gel adsorption, treatment with cobalt trifluoride and fractional crystallization. Of these only the last was found to be capable of removing the impurities. A sample determined to be 99.98 mole % pure by analysis of the freezing curve was obtained.

Stiles and Cady[4] prepared a sample of perfluoro-*n*-hexane by fluorination of the pure hydrocarbon with cobalt trifluoride, treated it with alkaline permanganate and after fractional distillation obtained a product which they estimated to be 96.5 mole % pure. Their fluorocarbon boiled at 57.23°, 0.08° higher than ours. Our vapor pressures are approximately 1 mm. higher than theirs at 30° and 2 mm. higher at 60°. Although the liquid density of blended fractions from our distillation plateau was only slightly less than 1.6845 at 25° reported by the above workers, fractional crystallization produced a sample having considerably lower density. The density of our purified sample saturated with air at 25° is 1.66970 g./cm.³. The freezing point is −82.26°, 0.21° lower than the highest value obtained by Stiles and Cady.[5] The heat of fusion, calculated from the freezing point lowering produced by small amounts of perfluorotri-*n*-butylamine is 1580 ± 90 cal./mole. Stiles and Cady[5] report a value of 4300 cal./mole for this property.

The infrared spectrum of the refined sample is identical with that shown by Weiblen.[7] The only perceptible change in the infrared spectrum during purification was the removal of an absorption band at 830 cm.$^{-1}$.

Experimental

Purification.—The crude fluorocarbon was distilled in a fractionating column which when tested with hydrocarbons was found to have 90 theoretical plates. From 2.2 kg. of

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