radiation of shorter wave lengths or to competition between (10) and (14). If it is assumed that there is no stray radiation an estimate can be made of k_{14}/k_9. This gives 323 and 316 for the two runs. Thus if every collision of an activated molecule with oxygen is effective in preventing formation of methylene radicals, the steric factor for the deactivation by ketene must be not greater than 0.003. This would make $a_{10} = 3 \times 10^7$ sec.$^{-1}$, rather than 10^{10} as given above.

A second method may be used to estimate k_{14}/k_9. From the data in Table II it is found that 2.8 oxygen molecules are consumed for each ethylene molecule formed at 2700 Å. The remaining oxygen must be consumed by reaction 14 and the reactions which follow it. If it is assumed that only one oxygen molecule is used as a result of (14) one can obtain k_{14}/k_{10} and combine this with k_9/k_{10} to obtain k_{14}/k_9. The two runs give 77 and 54, respectively. Of the two methods the second seems to be based on the more doubtful assumptions.

One may take a_{10} to be not more than 10^8 sec.$^{-1}$ so that $k_{10} < 10^8 \exp(-4500/RT)$. At 107° $k_{11}/k_{10} \sim 8$ (Fig. 2) and $E_{10} - E_{11} \sim 3500$ cal./mole. Hence $a_{11} < 10^7$ sec.$^{-1}$ and the mean life will be greater than 10^{-7} sec. A calculation of the mean life based on the integrated absorption coefficient gives 3×10^{-6} sec.[22] The approximate agreement between the mean lifetimes obtained by the two methods may be fortuitous but does suggest the desirability of a more careful investigation of the spectrum and possible fluorescence of ketene vapor. These mean lifetimes would be compatible with existence of rotational structure in the ketene spectrum.

More detailed work will be necessary to establish the nature of the reaction of excited ketene molecules with oxygen but it may be said with considerable certainty that such a reaction does occur.

The results presented in this paper do not establish conclusively the detailed mechanism of the reactions of methylene radicals with oxygen largely because the lack of variation of the results with experimental conditions prevents use of the customary methods of competitive reactions. It may be concluded that in the case of ketene, and probably also for other molecules, it is necessary to exercise considerable care in experimental procedure and in interpretation to be sure that reactions of active molecules with oxygen are not confused with reactions of radicals.

ROCHESTER, NEW YORK

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[22] We are indebted to Mr. H. K. Dice and Dr. O. V. Luke of the Celanese Corporation of America, Clarkwood, Texas, for permission to use absorption coefficients obtained in their research laboratory by Messrs. J. S. Hill and R. C. Wilkerson. The calculation of the mean life was made by Mr. Richard Holroyd at the suggestion of Professor A. B. F. Duncan.

[CONTRIBUTION FROM LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

The Aromatic Carbonium Ions[1]

BY C. REID[2]

RECEIVED FEBRUARY 1, 1954

The spectra of a number of aromatic hydrocarbons dissolved in liquid hydrogen fluoride containing boron trifluoride have been examined. Two kinds of absorption bands have been observed and are attributed (1) to the aromatic carbonium ions RH^+ and (2) to the complexes $R:BF_3$. The carbonium ions are subdivided into two groups with spectra centered at about 4,000 and 4,800 Å., respectively, and a tentative explanation for these is put forward. Photochemical changes have also been observed on irradiation of some of the polycyclic carbonium ions and are discussed.

Introduction

The fact that the more basic, polynuclear hydrocarbons dissolve in strong sulfuric acid, and that even the less basic ones, benzene, toluene, etc., will dissolve in anhydrous hydrofluoric acid, in the presence of boron trifluoride, is well-known.[3a,b] Differences in basicity have been used as a mode of separation of these hydrocarbons.[3]

Nevertheless, data on the "carbonium ions" which are formed, it is thought by the addition of a proton to the hydrocarbon—which thus acts as a base—are very scanty, although some spectra of sulfuric acid solutions of the more basic hydrocarbons have been published.[4] The experimental work here described shows that in fact the phenomena occurring in HF–BF_3 solutions are quite involved, addition compounds of BF_3 and hydrocarbon sometimes forming as well as the carbonium ion, which may itself react to form further products.

Experimental

Absorption.—Anhydrous HF (Mathieson C.P.) and dry boron trifluoride (from the same source) were distilled through Teflon tubes directly into the absorption cell which was kept at −80° during the distillation and subsequently. In some of the earlier runs the HF was distilled from a small copper cell and the middle fraction only used. However, no difference in transmission could be detected between this material and that distilled directly from the supply cylinder. It showed no trace of the absorption band at 2800 characteristic of SO_2, and was assumed substantially free of that material. BF_3 was distilled into the cell through a cold trap kept at −100° by a pentane-bath. It was assumed

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[1] This work was assisted by the Office of Ordnance Research under Project TB2-0001 (505) of Contract DA-11-022-ORD-1002 with the University of Chicago.

[2] On leave of absence from the University of British Columbia, Vancouver, B. C., Canada, which is presently the correct address.

[3] (a) M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953), and references given there; (b) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[4] V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952), and references therein.

that any traces of moisture in the HF would be removed by the BF_3. Small amounts of boric acid thus formed should not invalidate the observations reported. For quantitative measurements a 1-cm. Teflon cell with thin quartz windows was used in a specially constructed dewar vessel (Fig. 1). The cell consisted of a half-inch long section of Teflon tube 1 inch external and $^{1}/_{2}$ inch external diameter, into which was screwed a length of $^{1}/_{4}$ inch external Teflon tube onto which a thread had been cut. The quartz windows rested in $^{5}/_{8}$ inch diameter recesses cut in the ends of the tube, and secured in position by brass washers flanged to fit the quartz circles, and screwed into the body of the Teflon cell. The dewar vessel was provided with holes into which "double window" cells were cemented with Araldite cement. The windows fitted closely against those of the cell proper to avoid coolant transmission difficulties. The cell could be closed by means of a small Teflon plug. At the temperatures used (−80°) in this phase of the work quartz is not attacked appreciably by the acid mixture, and windows may be used 15–20 times before clouding becomes noticeable. Attempts to use thin Teflon windows were not successful. With this arrangement, a Beckman model DU spectrophotometer was used, and quite reproducible results could be obtained, except for some anomalies in the far red region of the spectrum which will be mentioned later.

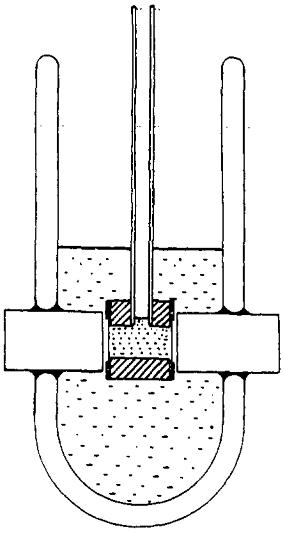


Fig. 1.—Low-temperature absorption apparatus. The shaded body of the cell is made of Teflon. The space between the double windows is evacuated.

For some phases of the investigation, the point-by-point spectrophotometer was unsuitable, and instead a Hilger E_2 spectrograph was used. The advantages were: (1) photographs could be taken only a few seconds after adding the hydrocarbon to the $HF–BF_3$ mixture; (2) in cases where higher temperatures were required (*e.g.*, for benzene, which at −80° crystallizes almost completely from the $BF_3–HF$ solution), the absorption cell could be kept several feet from the optical system to avoid attack by hydrogen fluoride vapor. Accurate absorption coefficients were not obtained by this method, however. Although (1) some of the polynuclear hydrocarbons are sufficiently basic for solution in HF alone, this is not true of the less basic monocyclic compounds or of naphthalene which were found not sufficiently soluble to obtain absorption spectra in the system described. In view of this fact, no systematic observations were made on the systems hydrocarbon + HF alone.

Emission.—Low-temperature emission spectra were taken of frozen systems at −180°. These systems were not the usual solid glasses used in emission work but crystalline masses of HF containing the carbonium ions as impurities. Since solid HF is a molecular rather than an ionic crystal, however, with absorption only at much higher energies than in the range studied, it is not surprising that the absorption spectra observed are in general obviously those of the same species which absorbs in the liquid systems. Most of the emission spectra were of short-lived species. In a few cases a mechanical phosphoroscope was used to separate a short-lived from a long-lived component. Loss of light by scattering in the crystalline mass was considerable, but emitted light intensities were still high enough for photographs to be taken in one to five minutes, using a 1,500-watt high pressure mercury arc as illuminating source.

NOTE ADDED IN PROOF.—The author is indebted to Professor H. C. Brown of Purdue University for an account of recent unpublished work on the solubility of BF_3 in toluene (see also THIS JOURNAL, **74**, 3750 (1952)). The low solubility of BF_3 in the molecular aromatics is interpreted as evidence that the complexes $ArH{\cdot}BF_3$, if they exist, must be very unstable. Accordingly the suggestion made in this paper that the "low temperature" ultraviolet absorption is due to such complexes may be incorrect.

Results and Discussions

Curves showing some typical spectra are given in Figs. 2–9. The outstanding features are the following.

(1) The ions examined divide themselves clearly into two groups: (a) those whose "long-wave" absorption is close to 4,000 Å.; this group includes all the monocyclic hydrocarbons, naphthalene and

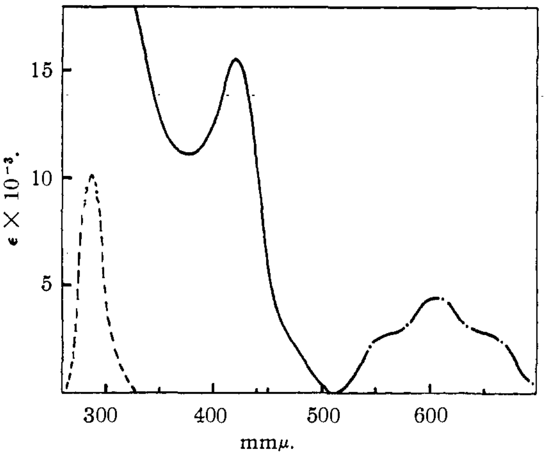


Fig. 2.—Spectrum of the benzene–$HF–BF_3$ system: -----, $C_6H_6{\cdot}BF_3$ complex absorption; ——, $C_6H_7^+$ absorption; -·-·-, $C_6H_7^+$ fluorescence emission.

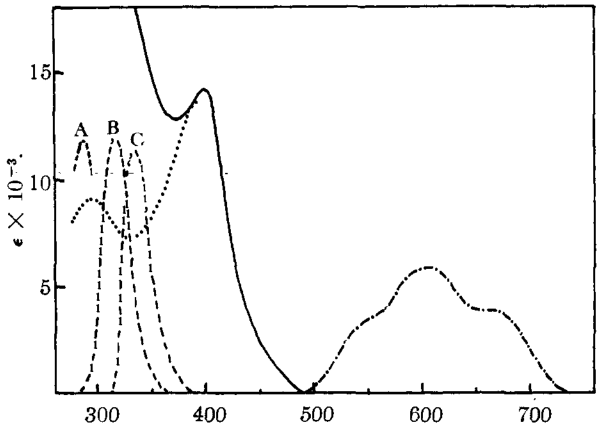


Fig. 3.—Spectrum of the toluene–$HF–BF_3$ system: -----, curve B, $C_7H_8{\cdot}BF_3$ complex absorption; curve A, $C_6H_6{\cdot}BF_3$; curve C, *o*-xylene·BF_3, for comparison; ——, absorption curve after 5 minutes at −20° showing the $C_7H_9^+$ peak; ...., absorption curve after 30 minutes at −20°; -·-·-, fluorescence emission spectrum of final solution

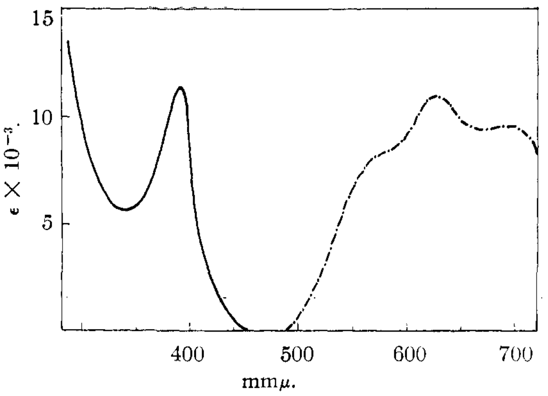


Fig. 4.—Spectrum of the naphthalene–HF–BF$_3$ system: ——, $C_{10}H_9^+$ absorption; -·-·-, $C_{10}H_9^+$ fluorescence emission.

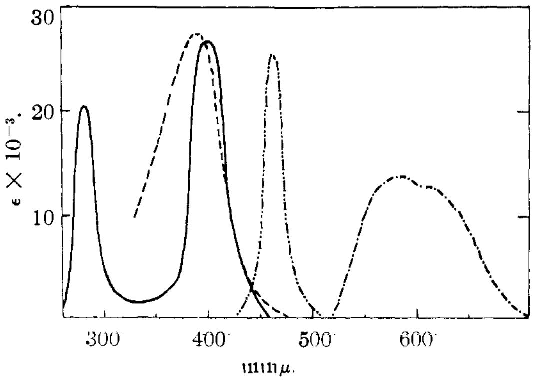


Fig. 5.—Comparison of the mesitylene and hexaethylbenzene spectra in HF–BF$_3$, the left-hand ordinate is for hexaethylbenzene, that on the right for mesitylene: – – – –, mesitylene·H$^+$ absorption; -·-·-, mesitylene·H$^+$ fluorescence emission; ——, hexaethylbenzene·H$^+$ absorption; -·-·-·-, hexaethylbenzene·H$^+$ fluorescence emission.

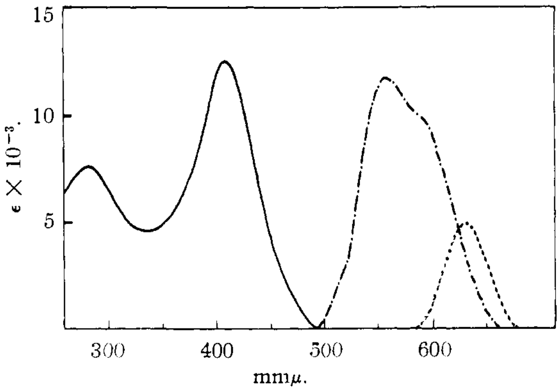


Fig. 6.—Spectrum of the anthracene–HF–BF$_3$ system: ——, $C_{14}H_{11}^+$ ion absorption; -·-·-·-, fluorescence emission (short-lived); – – – – – – phosphorescence emission (long-lived).

anthracene; (b) those whose long-wave absorption is at considerably lower energies, usually in the neighborhood of 4,800–5,000 Å., but not quite so sharply delineated as group (a); this group includes phenanthrene, naphthacene, pyrene, fluoranthene, etc.

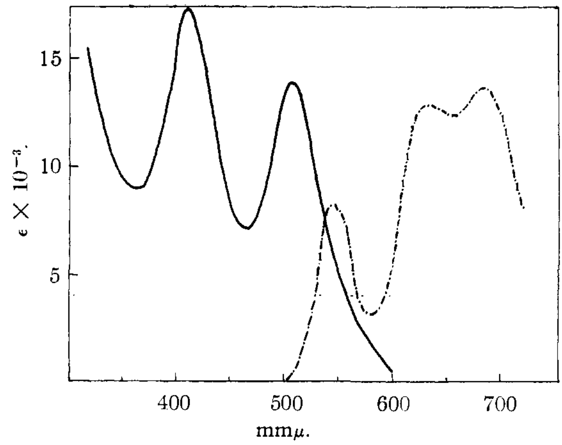


Fig. 7.—Spectrum of the phenanthrene–HF–BF$_3$ system: ——, $C_{14}H_{11}^+$ ion absorption; -·-·-, $C_{14}H_{11}^+$ ion fluorescence emission.

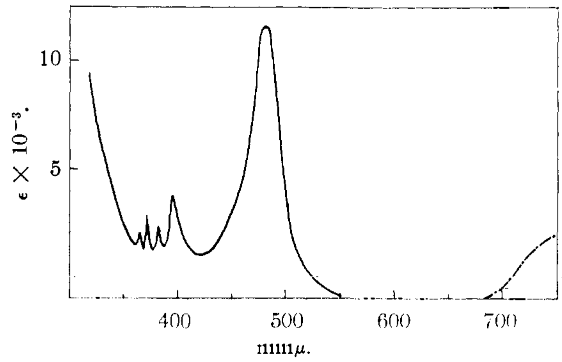


Fig. 8.—Spectrum of the naphthacene–HF–BF$_3$ system: ——, $C_{16}H_{13}^+$ ion absorption; -·-·-, fluorescence emission of system.

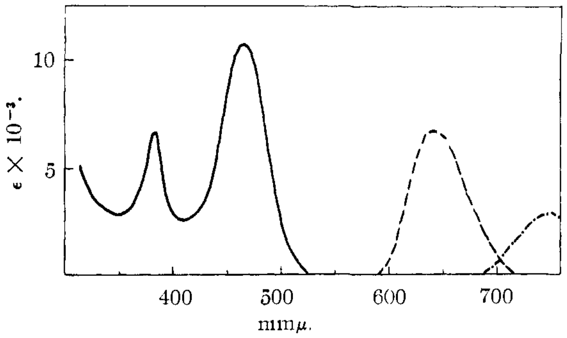
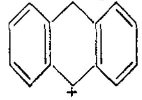


Fig. 9.—Spectrum of the pyrene–HF–BF$_3$ system: ——, $C_{16}H_{11}^+$ ion initial absorption: -·-·-, fluorescence emission spectrum of system; – – – – –, new absorption band appearing after irradiation.

It must be emphasized that the position of the "carbonium ion" band is not directly related to the position of the absorption spectrum of the parent hydrocarbon. Thus we find phenanthrene, itself absorbing at slightly shorter wave lengths than anthracene, with a carbonium ion absorption at much longer wave lengths. Similarly, naphthacene, chrysene and pyrene all have carbonium ion absorption in approximately the same region, although, of the parent hydrocarbons, naphthacene absorbs at considerably longer wave lengths than do the other two.

There is no very obvious relationship between the structure of the parent molecule and the position of the absorption maximum of the carbonium ion. If we adopt the usually accepted geometrical structure for the carbonium ion, in which the proton forms a normal CH_2 group (which then "hyperconjugates" with the rest of the ring[5]), the most likely explanation seems to be that the 4,000 Å. group of carbonium ions are those for which only one ring of the hydrocarbon is strongly involved, while in the 4,800–5,000 Å. group more than one ring is strongly involved.

This idea for instance explains very well why the anthracene long-wave length carbonium ion absorption is almost identical with that of benzene. (Here also see Gold and Tye,[4] whose spectrum of the anthracene carbonium ion in strong sulfuric acid is similar to that obtained here in hydrofluoric acid). The 9–19-positions of anthracene are so much more susceptible to attack by electropositive reagents that we may safely assume that the carbonium ion has the structure  (as also assumed by Gold and Tye). This means that the anthracene bonds are to some extent "frozen" into a particular structure much in the way that they were visualized as frozen in quinonoid compounds by Evans,[6] and the probability of the positive charge migrating into the end rings is low, *i.e.*, the "carbonium ion" structure is essentially confined to the middle ring. The fact that for naphthalene and anthracene the positive charge remains largely localized in the ring first attacked is substantiated by the substitution reactions of these molecules. Thus for monosubstituted naphthalenes, when the substituent is one attracting electrons, we find that a second (electrophilic) substituent goes into the second ring, and at a rate similar to that of monosubstitution in benzene. It follows that the *deactivation* is localized in the ring first attacked, and that the positive charge can therefore be considered as largely localized on this ring.

In the case of the benzene carbonium ion, the observed spectrum (Fig. 2) is in fairly satisfactory agreement with the theoretical prediction[5] that this ion should show two strong peaks near 4,000 and 3,200 Å., respectively, with the latter about 2.5 times as strong as the former.

To explain the long wave length absorption of the phenanthrene carbonium ion, we must assume that in it—and in all the larger polycyclics—strong migration of positive charge into rings other than that attacked by the proton must occur.

Neglecting hyperconjugation effects, this means that the conjugated system increases from 5 centers + 4 electrons to 9 centers + 8 electrons or 13 centers + 12 electrons, according to whether two or three rings are involved. A simple free-electron calculation suggests that the observed shifts fit the two-ring much better than the three-ring picture.

(2) In the case of the weakest bases (benzene, toluene, etc.), at the low temperatures used, the appearance of the characteristic carbonium ion peak at 4,000 Å. is not the first observation. Instead, the solution at first remains colorless, but examination of the absorption spectrum shows an intense peak in the ultraviolet at 3,180 Å. for toluene and at 2,840 Å. for benzene. These peaks are certainly not simply due to a solvent shift of the hydrocarbon bands, which themselves may be seen weakly at shorter wave lengths. It seems certain that these new bands are charge-transfer spectra[7] due to the presence of molecular complexes such as $C_6H_6:BF_3$ and $C_7H_8:BF_3$. Highly allowed optical transitions lying in approximately the region where these bands were observed are then expected, to states approximately described as $C_6H_6^+\cdot BF_3^-$ and $C_7H_8^+\cdot BF_3^-$. The differences in position of the benzene, toluene and xylene bands (about 3,000 cm.$^{-1}$) are in good agreement with what would be expected from their differences in ionization potential.[8] Warming of the colorless solutions to above about $-20°$ results in the rapid development of color due to the appearance of the characteristic carbonium ion absorption at 4,000 Å. Even at $-70°$ in the case of xylene the appearance of color takes only a minute or two.

(3) Most of the systems investigated are not stable for an indefinite period even after the carbonium ion has formed. Quite early in the investigation it was found that absorption bands appeared erratically in the red and infrared and bore no consistent relationship to the main absorption around 4,000 Å. Some insight into what such phenomena may involve is provided by the case of pyrene (Fig. 9).

Solution of pyrene in $HF–BF_3$ leads to the immediate production of a yellow-orange solution with a sharp absorption band just below 5,000 Å. It is found, however, that the *emission* is far to the red of this, and further that irradiation leads to a change in color, the solution rapidly becoming a clear green and remaining thus when irradiation is discontinued. Reinvestigation of the absorption spectrum after irradiation shows a new absorption band with obvious mirror relationship to the emission.

It appears therefore that the first formed carbonium ion after excitation undergoes tautomerism or perhaps chemical reaction in the excited state, the new species then emitting and persisting in the ground state.

Schematically such a process can be visualized on the basis of the potential curves shown in Fig. 10. Curves A and B then represent the ground- and excited-state potential curves of the originally formed carbonium ion, and C and D those of the new species, tautomerism being effected by a radiationless transition from curve B to curve C. Since the green end-product does not revert to the original carbonium ion again there must be a considerable barrier between states A and D. A similar wide

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[5] L. W. Pickett, N. Muller and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953); THIS JOURNAL, **76**, in press (1954).

[6] M. G. Evans, *Trans. Faraday Soc.*, **42**, 101 (1946).

[7] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[8] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953); S. M. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953).

separation between absorption and emission, and ready photodecomposition is found for the naphthacene carbonium ions.

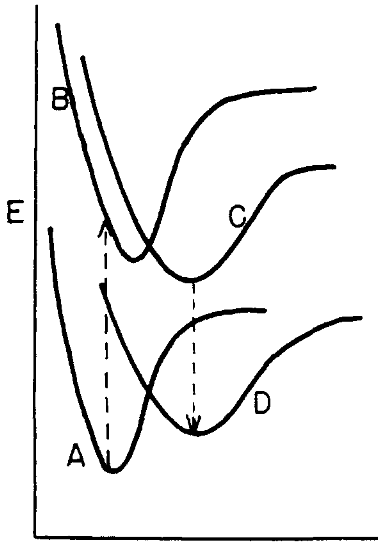

Fig. 10.—Possible potential curves for pyrene carbonium ion system: A, initial carbonium ion; B, excited state of same; C, curve onto which system moves in upper-state tautomerism; D, ground state of photoproduct.

(4) Some ambiguity is present in the case of hexaethylbenzene. The BF_3–hydrocarbon complex and the carbonium ion may in this case be expected to absorb in approximately the same region of the spectrum. The observed absorption peak is very sharp, and so is the corresponding emission. The bands are certainly different in appearance from the usual "carbonium ion" bands, and it is tentatively suggested that they are in fact charge-transfer bands. If this is so, the non-appearance of the "carbonium" band must be attributed to a greater stability of the charge-transfer complex, which perhaps is itself not a good enough donor to form a carbonium ion. This different behavior may be due to the steric effect of the bulky ethyl groups which probably result in some buckling of the aromatic ring.

(5) Finally it is noteworthy that of all the hydrocarbon carbonium ions examined, only that of anthracene showed a long-lived (presumably triplet) phosphorescence spectrum. Although perhaps coincidental, it is remarkable that anthracene is the one hydrocarbon which itself shows so little phosphorescence that the position of its lowest triplet level is in debate.[9]

If it is granted as reasonable that the triplet levels like the singlets will shift to the red in the carbonium ion, the position of the carbonium ion triplet (5,800 Å.) is evidence in favor of the assignment of the anthracene triplet[8] at 5,200 Å. rather than at 6,900 Å.

Acknowledgments.—The author wishes to take this opportunity to thank Professor R. S. Mulliken for the invitation to Chicago which made this work possible and for many helpful discussions. Thanks are also due to the University of British Columbia for granting special leave of absence and to many members of the Chicago group for hospitality and stimulating conversations.

[9] C. Reid, *J. Chem. Phys.*, **20**, 1214 (1952).

VANCOUVER, CANADA

[CONTRIBUTION FROM WM. H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

The Effect of Water on the Vapor Phase Dissociation of Acetic Acid

BY BORIS LEVY AND THOMAS W. DAVIS

RECEIVED JANUARY 18, 1954

A study of the effect of added water on the vapor phase dissociation of acetic acid shows that dissociation to anhydride and water offers at most a small contribution to the over-all equilibrium at temperatures around 100°. The *PVT* data in the temperature range 90–120° suggest a reversible interaction of water and acid vapor.

The 1:1 compound of water and acetic anhydride has long been known to dissociate in the vapor phase.[1] The density of the "compound" falls with increasing temperature or with decreasing pressure from approximately the sum of the densities of water and acetic anhydride to half this value. It is usual to attribute the variable density to an equilibrium between monomer and dimer, *viz.*

$$(CH_3COOH)_2 \rightleftarrows 2CH_3COOH \qquad (I)$$

The data are equally consistent with an equilibrium between water, acetic anhydride and acetic acid dimer, *viz.*

$$(CH_3COOH)_2 \rightleftarrows (CH_3CO)_2O + H_2O \qquad (II)$$

A similar ambiguity concerning the nature of the dissociation products, Ricci has pointed out,[2] applies to any monohydroxy acid, for example HNO_3, HClO, or the like. A resolution of the ambiguity can be achieved in the case of acetic acid by determination of the way added water affects the density of acetic acid vapor. We have made such determinations.

Experimental

We have used a tensiometer of the type described by Sanderson.[3] The acetic acid (C.P.) was recrystallized eleven times according to the method of Ritter and Simons.[4] The acid, however, showed premelting to an extent correspond-

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[1] W. Ramsay and S. Young, *J. Chem. Soc.*, **49**, 790 (1886).

[2] J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 121.

[3] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 83.

[4] O. H. Ritter and J. H. Simons, THIS JOURNAL, **67**, 757 (1945).