$(C_6H_5CH_2)_2SI_2$ in benzene at 5°. Considering the differences in the organic groups, the temperature and the solvent, this is consistent with the value found for $(CH_3)_2SI_2$ in the present study.

Additional work on the dissociation constants of compounds of the type R_2SI_2, R_2SeI_2 and R_2TeI_2 is planned.

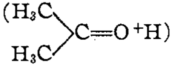
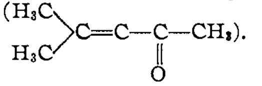
LOS ANGELES, CAL.

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

Spectrophotometric Studies on the Interaction between Acetone and Sulfuric Acid[1]

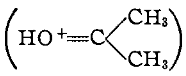
BY S. NAGAKURA,[2] A. MINEGISHI[2] AND K. STANFIELD

RECEIVED OCTOBER 25, 1956

One of the problems treated in the present paper is the mechanism of the blue shift of the $\pi^* \leftarrow n$ transition band of acetone in sulfuric acid. As the result of careful measurements of this absorption band in various concentrations of sulfuric acid, it is shown that the blue shift in the acid should principally be due to the formation of the onium ion of acetone  $(\mathrm{(H_3C)_2C{=}O^+H})$ and moreover that the basic strength of acetone can be discussed quantitatively by the use of spectrophotometric methods. Another problem is the mechanism of coloration of acetone, that is, the remarkable change of absorption spectrum observed on mixing it with concentrated sulfuric acid. This mechanism seemed to be complicated, but finally it was concluded that the change could be explained by the formation of condensation products of acetone, especially mesityl oxide  $(\mathrm{(H_3C)_2C{=}C{-}C({=}O){-}CH_3})$. Furthermore, the mechanism of the anomalously large red shift of the 231 mμ band of mesityl oxide in *n*-heptane to 284 mμ in concentrated sulfuric acid is discussed on the basis of the conception of intramolecular charge transfer absorption.

Introduction

In this paper, two phenomena which are observed with acetone in sulfuric acid are studied by the use of the spectrophotometric method. One of them is the effect of the acid on the weak absorption due to the $\pi^* \leftarrow n$ transition of acetone. It is well known that this type of absorption generally shifts to shorter wave lengths with increasing dielectric constant of solvent and that this wave length shift is especially large in acid media. This blue shift is regarded as one of the typical properties by which the $\pi^* \leftarrow n$ transition can be distinguished from the ordinary $\pi^* \leftarrow \pi$ transition.[3-5] As to the mechanism of the large blue shift in acid, Kasha suggested that it may be caused by the attachment of a proton to the atom containing non-bonding electrons, for instance, the oxygen atom of acetone. As far as the authors know, however, no substantiating experimental evidence has been published for the system of acetone and sulfuric acid. Furthermore, this interaction seems to be interesting from the standpoint of organic chemistry, too, because the formation of acetonium cation $[\mathrm{HO^+{=}C(CH_3)_2}]$ is predicted as the intermediate state for some reactions of acetone in acid media.[6] In order to obtain some experimental knowledge on these problems, we have measured the near ultraviolet absorption of acetone in various concentrations of sulfuric acid. Consequently, we were led to the conclusion that the blue shift of the $\pi^* \leftarrow n$ transition band of acetone in acid is actually due to specific interaction between these two species, namely, to the formation of acetonium cation



$$\left(\mathrm{HO^+{=}C(CH_3)_2}\right)$$

Moreover, on the basis of this interpretation of the blue shift, we have succeeded in obtaining a somewhat quantitative knowledge about the basic strength of acetone.

The blue shift phenomenon is observed in relatively dilute sulfuric acid. On the other hand, in concentrated sulfuric acid (93%), acetone becomes colored yellow or brown, and the ultraviolet absorption spectrum changes remarkably compared with that in the dilute acid or an organic solvent. This coloration, which may be regarded as one of the most typical examples of halochromy, is another problem considered in the present paper. Although the mechanism of this coloration already has been studied by Poggi and others,[7] no final conclusion has ever been obtained. We undertook to study this phenomenon, because we thought it might be intimately related with the intermolecular charge transfer absorption which has frequently been observed in the case of molecular complex formation between an electron donor and acceptor and whose mechanism had already been studied by Mulliken.[8] The results obtained actually were more complicated than our initial expectation, but

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(1) (a) This work was assisted in part by the Office of Ordnance Research under Project TB2-0001(505) of Contract DA-11-022-ORD-1002 with the University of Chicago. (b) Some parts of this work were done in the Institute of Science and Technology, Tokyo University.

(2) Institute of Science and Technology, Tokyo University, Meguro-ku, Tokyo, Japan.

(3) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

(4) (a) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951); (b) H. McConnell, *ibid.*, **20**, 700 (1952).

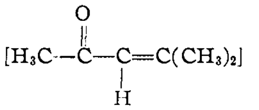
(5) S. Nagakura and A. Kuboyama, THIS JOURNAL, **76**, 1003 (1954).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

(7) A. Paul Poggi, G. Serchi, G. Adembri and A. Monaci, *Gazz. chim. ital.*, **79**, 80 (1949).

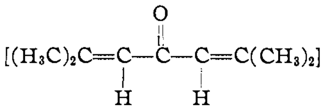
(8) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

they could finally be explained on the basis of the interaction of sulfuric acid with mesityl oxide



$$[H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{C}=C(CH_3)_2]$$

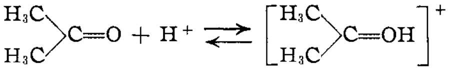
and with phorone



$$[(H_3C)_2C=\underset{\underset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{C}=C(CH_3)_2]$$

both of which can be formed by the condensation of acetone.[9]

The Effect of Sulfuric Acid on the $\pi^* \leftarrow$ n Transition of Acetone.—In order to get some knowledge on the mechanism of the blue shift, we measured the $\pi^* \leftarrow$ n transition band of acetone in various concentrations of sulfuric acid. This band of acetone, which appears at 285 and 265 mμ in heptane and water, respectively, shifts to shorter wave lengths in acid.[10] The experimental results are given in Fig. 1, which shows that the extinction at 265 mμ becomes lower with increase in the concentration of the acid, and the absorption maximum shifts to shorter wave lengths. Moreover, an isosbestic point where five absorption curves for different concentrations cross is seen. Thus it seems to be shown conclusively that acetone is a base here and there exists an equilibrium between acetone and sulfuric acid or more probably hydrogen ion. This equilibrium can be represented by the following equation, by analogy with the cases of acetophenone, etc., whose basic properties were studied by Hammett, *et al.*[11]



acetonium cation

However, it seems to be impossible to neglect completely the effect of the properties of acid as a whole (for instance, the dielectric constant) on the blue shift phenomenon, since the absorption curves observed at somewhat higher concentrations of the acid do not cross at the isosbestic point (see curve 6 in Fig. 1). Magnitudes of deflections of these curves from the isosbestic point probably depend on the concentration of sulfuric acid and are not very large for the solutions used in the present experiment whose sulfuric acid concentrations are below 14 *N*. So it may be concluded safely that the formation of acetonium cation, whose absorption appears at shorter wave lengths than that of acetone itself, is an important reason for the blue shift phenomenon, at least under the present experimental conditions.

On the basis of the above-mentioned interpretation of the blue shift phenomenon for acetone, we can determine somewhat quantitatively the basic strength of acetone. The combination of the equation used for the determination of the equilibrium constant of a hydrogen bonded system by one of the authors[12] with Hammett's acidity function[6,11] gives the equation

$$K_B = (AH^+)/(A)(H^+) = \{(\epsilon_\lambda' - \epsilon_\lambda)p'' - (\epsilon_\lambda'' - \epsilon_\lambda)p'\}/(\epsilon_\lambda'' - \epsilon_\lambda')p'p''$$

where ϵ_λ, ϵ_λ' and ϵ_λ'' are the molar extinction coefficients observed at the wave length λ[13] with the aqueous solution of acetone and its solutions in sulfuric acid whose acidity functions are H_O' and H_O'', respectively, and p' and p'' are the abbreviation of $10^{-H_O'}$ and of $10^{-H_O''}$, respectively. The relation between the acidity function and the concentration of sulfuric acid is given by Hammett.[6] Then by the aid of this equation, which can be derived under the assumption that the concentration of acetonium cation is negligibly small compared with that of the acid, the basicity constant of acetone pK_B ($-\log K_B$) can easily be evaluated by measuring absorbance values of three solutions with a fixed concentration of acetone and with different concentrations of sulfuric acid. The results obtained for various wave lengths and for two different combinations of H_O' and H_O'' values are shown in Table I.

TABLE I

pK_B VALUE OF ACETONE OBTAINED BY THE SPECTROPHOTOMETRIC METHOD

$10^{-H_O'}$	$10^{-H_O''}$	pK_B (280 mμ)	pK_B (270 mμ)	pK_B (250 mμ)	pK_B (242 mμ)
25.5	211	1.54	1.71	1.63	1.72
25.3	86	1.39	1.52	1.52	1.59

pK_B (av.) = 1.58

The fact that the pK_B values obtained at various wave lengths, especially at both sides of the isosbestic point, are almost constant seems to support the above interpretation that the change of the absorption band of acetone in various concentrations of sulfuric acid is principally due to the formation of acetonium cation.

Next, we will consider the reason why the $\pi^* \leftarrow$ n transition band of the acetonium cation should appear at shorter wave lengths than that of acetone. Although the attachment of a proton to the oxygen atom may probably be accompanied by a remarkable change in the electronic structure of acetone, we assume in the first step of consideration that its effect can be expressed by the change of coulomb integral of the atom. The attachment of a proton to it will cause an increase of absolute value of its coulomb integral. According to simple calculation made by one of the authors,[14] whose result is given in Table II, the energy difference corresponding to the $\pi^* \leftarrow$ n transition (ΔE) apparently increases with the absolute value of the coulomb integral (α_O). So we can explain qualitatively the observed blue shift by the change of the coulomb integral.

The Absorption Spectrum of Acetone in Concentrated Sulfuric Acid.—In concentrated sulfuric

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[9] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1950, p. 570.

[10] McConnell showed in Fig. 1 of ref. 4(b) that the 265 mμ band of acetone shifts toward longer wave lengths in acid. This apparently is in error.

[11] L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935); L. A. Flexser and L. P. Hammett, *ibid.*, **60**, 885 (1938); L. Zucker and L. P. Hammett, *ibid.*, **61**, 2785 (1939).

[12] S. Nagakura, *ibid.*, **76**, 3070 (1954).

[13] These values can be replaced by the absorbance when the concentrations of acetone in the three solutions are equal.

[14] S Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952).

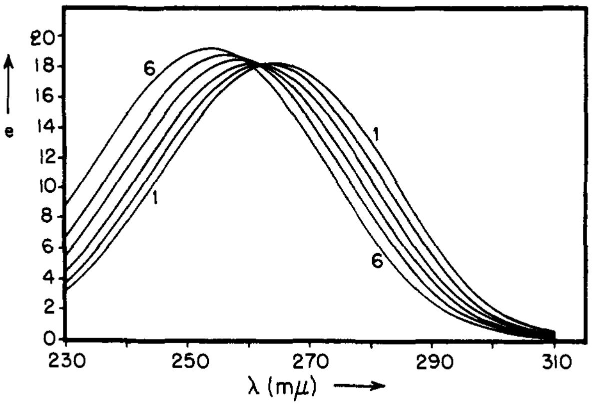


Fig. 1.—Absorption spectra of acetone in various concentrations of sulfuric acid: 0, 3.96, 6.84, 9.12, 10.80 and 14.00 *N* for curves 1, 2, 3, 4, 5 and 6, respectively.

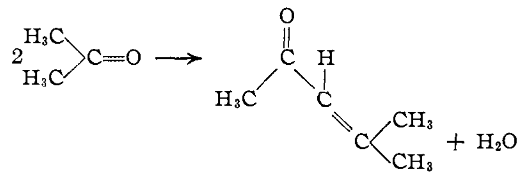
acid (about 93%), acetone shows some coloration which largely depends on the procedure used in mixing them. Under the moderate condition, where concentrated sulfuric acid is added slowly to a rather small quantity of acetone (<2 cc.) with cooling by water, the mixed solution becomes pale yellow. We have tried to clarify the mechanism of such a coloration. First of all, we measured absorption spectra of some colored solutions. One typical example of the results is shown in Fig. 2. This absorption curve is for a solution which was made by slowly adding concentrated sulfuric acid to 2 cc. of acetone until the total volume became 10 cc. The absorption of this solution changed with time. The curve in Fig. 2 was measured after the result became almost constant (about 20 hours after mixing). This absorption curve is very different from that in water or dilute acid, shown in Fig. 1. The most remarkable characteristic of the former is that there appears a very strong band at 284 mμ. As the first step to explain the mechanism of coloration, we thought it necessary to identify this absorption. This problem was solved by taking note of the fact that mesityl oxide can be formed from acetone and concentrated sulfuric acid by the condensation reaction

TABLE II

THE RELATION BETWEEN THE COULOMB INTEGRAL OF OXYGEN (α_0) AND THE TRANSITION ENERGY CORRESPONDING TO THE $\pi^* \leftarrow$ n TRANSITION (ΔE)[a]

α_0	4.92β	5.41β	5.74β	6.07β	6.56β
ΔE	-1.34β	-1.72β	-1.99β	-2.28β	-2.72β

[a] In this table, the energy values are represented in units of β (the exchange integral between two adjacent atomic orbitals).



That is to say, we considered that the strong absorption band at 284 mμ observed with acetone–concentrated sulfuric acid system may be due to the interaction between mesityl oxide and sulfuric acid. In order to get experimental evidence for this, we measured the absorption spectrum of pure mesityl oxide in concentrated sulfuric acid. The result is also shown in Fig. 2. We find that the absorption spectrum of acetone in concentrated sulfuric acid is similar in its position and shape to that of mesityl oxide in the same condition. From this experimental result we are led to the conclusion that the absorption of acetone under consideration should be due to the formation of mesityl oxide.

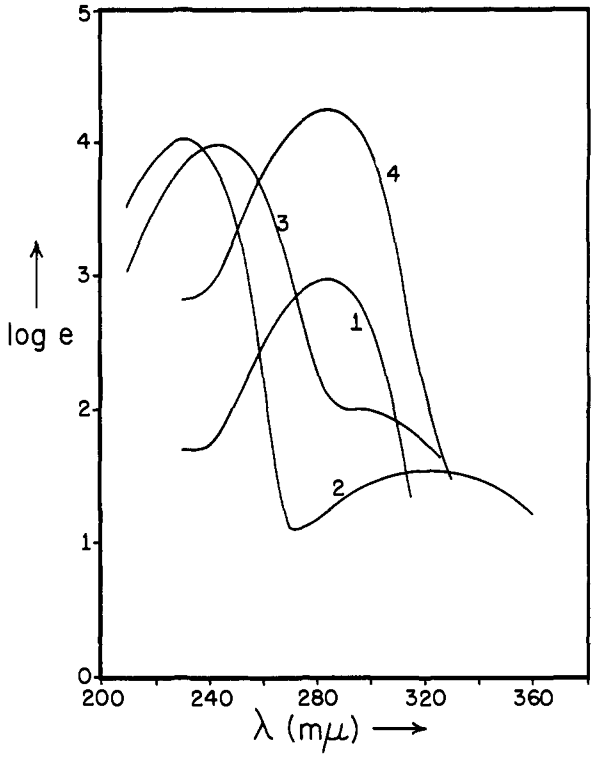
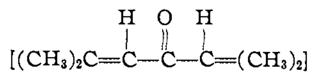


Fig. 2.—Absorption spectra of acetone and mesityl oxide in various conditions: curve 1, acetone in concentrated sulfuric acid; curve 2, mesityl oxide in *n*-heptane; curve 3, mesityl oxide in water; curve 4, mesityl oxide in concentrated sulfuric acid.

In this connection one more point should be considered. It is well known that in the case of the condensation of acetone, phorone



$$[(CH_3)_2C{=}\overset{H}{C}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{C}{=}(CH_3)_2]$$

and mesitylene can also be formed. Therefore, we cannot neglect the possibility that the above absorption band may be due to either of these two substances. In order to check this point, we also measured the ultraviolet absorption of phorone and of mesitylene in sulfuric acid. The results are shown in Fig. 3. Phorone has a strong absorption band at 339 mμ in concentrated sulfuric acid, although this absorption changes remarkably with time and the absorption maximum shifts to 251 mμ (see curve 3 in Fig. 3). Under the same conditions, the strong absorption maxima of mesitylene appear at 285–280 mμ and 235 mμ, and the latter is stronger than the former. These results seem to remove the possibility that the absorption of acetone in concen-

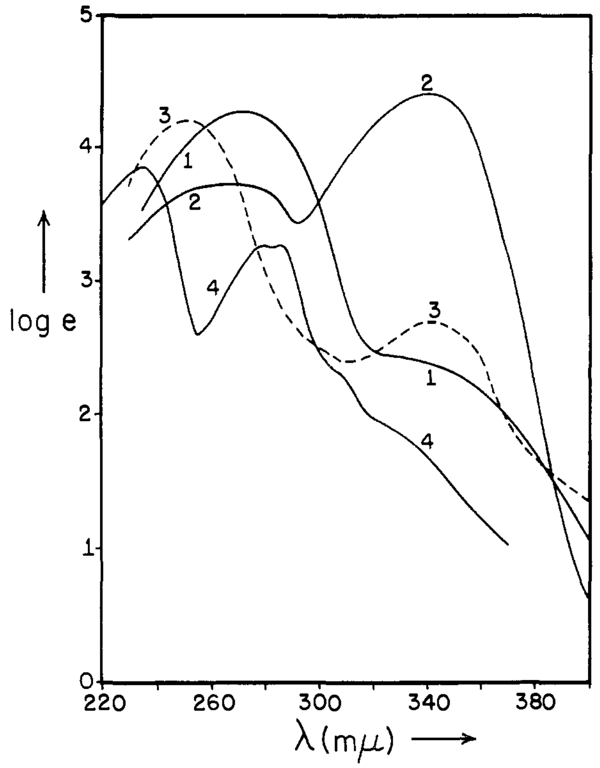


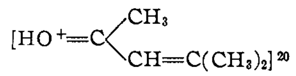
Fig. 3.—Absorption spectra of phorone and mesitylene in water and concentrated sulfuric acid: curve 1, phorone in water; curve 2, phorone in concentrated sulfuric acid; curve 3, phorone in concentrated sulfuric acid (20 hours after preparation); curve 4, mesitylene in concentrated sulfuric acid.

trated sulfuric acid under consideration may be due to phorone or mesitylene.

The above mentioned facts are concerned with the absorption spectrum of the solution where the condensation reaction occurs in the "moderate condition." In the condition where sulfuric acid is added promptly to acetone whose quantity is larger than 2 cc. and they react strongly with a large heat evolution, the color of the solution becomes deep and its tone also changes from pale yellow to dark brown. This seems to be reasonable from our interpretation that the condensation product of the acetone causes the coloration of the solution, because the concentration of mesityl oxide may probably increase as the condensation reaction proceeds, and simultaneously the possibility of the formation of phorone and mesitylene may be expected in the strong reaction. Actually, the solution which is made with a somewhat large heat evolution, increases the intensity of the 284 mμ band and at the same time shows a weak absorption maximum near 335 mμ.[15] The latter band may probably correspond to the 339 mμ band of phorone and this means that phorone takes part in the absorption to a slight extent. Anyhow, it is safely concluded that the most important condensation product of acetone in the moderate condition is mesityl oxide and the strong band at 284 mμ should be due to this substance.

Some Consideration on the Nature of the 284 mμ Band of Mesityl Oxide.—The absorption spectrum of mesityl oxide in *n*-heptane and in water is shown in Fig. 2. Mesityl oxide has a strong absorption band at 231 mμ[16] and a weak one at 325 mμ in *n*-heptane. In aqueous solution, the former shifts toward longer wave lengths (243 mμ), while the latter shifts to shorter wave lengths (about 290 mμ). This fact seems to show that the 325 mμ band corresponds to a $\pi^* \leftarrow$ n transition in accordance with the assignment by McMurry[17] and Walsh.[18] The fact that the molar extinction coefficient of this band is low (36) in *n*-heptane also supports the above interpretation. Then it may be expected that this band would shift to still shorter wave lengths in sulfuric acid than in water, like the 265 mμ band of acetone, and it might then be covered by another strong band. At least, it is impossible to consider that the $\pi^* \leftarrow$ n transition plays an important role in the strong band at 284 mμ, because the molar extinction coefficient of the latter band is 15600 and is much too high to regard it as a $\pi^* \leftarrow$ n transition.

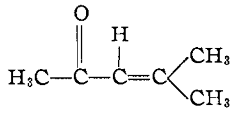
In our opinion, the most reasonable interpretation for the strong band at 284 mμ is that the 231 mμ band of mesityl oxide in *n*-heptane shows an anomalously large wave length shift and an increase of absorption intensity in sulfuric acid.[19] These changes are probably due to the attachment of a proton to the oxygen atom of the molecule, *viz.*, due to the formation of the onium ion of mesityl oxide



$$[HO^{+}{=}C(CH_3)CH{=}C(CH_3)_2]^{20}$$

A similar large red shift in acid media was observed with strong near ultraviolet bands of benzaldehyde and other aromatic molecules containing the C=O bond by Hammett, *et al.*,[11] and Thomas and Branch.[21]

Further consideration will now be given to the transition corresponding to the 231 mμ band of mesityl oxide, and we will explain why the band shows a large red shift in sulfuric acid. From the resonance viewpoint, this absorption seems to correspond to the transition between two levels caused by resonance between the non-polar structure



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[15] For instance, the absorption spectrum observed with the solution which was made by adding concentrated sulfuric acid to 3 cc. of acetone until the total volume becomes 10 cc. shows a small hump at about 332 mμ.

[16] The wave length of this band was determined as 232 and 240 mμ by McMurry (*cf.* ref. 17) and Walsh (*cf.* ref. 18), respectively. The value (215 mμ) used by Wheland is apparently in error (G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 280).

[17] H. McMurry, *J. Chem. Phys.*, **9**, 241 (1941).

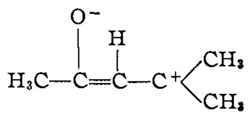
[18] A. D. Walsh, *Trans. Faraday Soc.*, **42**, 66 (1946).

[19] Another possibility is that the 284 mμ band may be an intermolecular charge transfer absorption between mesityl oxide and sulfuric acid or the hydrogen ion. But this possibility seems to be very small, because in sulfuric acid we cannot find another band corresponding to the 231 mμ band.

[20] However, we could not find experimental evidence for the existence of an equilibrium between mesityl oxide and sulfuric acid, by measuring absorption curves in various concentrations of the acid, because mesityl oxide seems to be decomposed easily in dilute acid.

[21] J. H. Thomas and G. Branch, This Journal, **75**, 4793 (1953).

and the polar structure



According to an earlier explanation based on the MO theory,[22] this can be replaced by the interaction between the highest occupied orbital of the C=C bond ($H_{C=C}$) and the lowest vacant one of the carbonyl group ($V_{C=O}$) as shown in Fig. 4a.[22] As the result of the interaction between these two orbitals, we can expect the appearance of two new orbitals ψ_n and ψ_e for mesityl oxide.[23] One of them which is filled with two electrons in the normal state W_n can be represented by a linear combination of wave functions for orbitals $H_{C=C}$ and $V_{C=O}$, namely, $\psi_n = a\psi_{C=C} + b\psi_{C=O}$. The value of b, which represents a measure of the electron migration from the C=C bond to the C=O bond in the normal state, or in other words the degree of the contribution of the polar structure to the resonance in that state, is usually small. On the other hand, the wave function of the excited level W_e, which is orthogonal to that of W_n, contains one electron in ψ_n and the second in the orbital ψ_e of the form $\psi_e = b\psi_{C=C} - a\psi_{C=O}$ $(a > b)$. Then in the W_e state, the π electron on the C=C bond migrates to the C=O bond to a large extent. Thus it may be expected that the transition from W_n to W_e can be accompanied by a large electron transfer and therefore by a strong absorption. This absorption may be called an intramolecular charge transfer absorption in analogy to the intermolecular charge transfer absorption discussed by Mulliken.[8]

According to the foregoing discussion of the absorption, the excited state of the 231 mμ band of mesityl oxide is more polar than the normal state. In other words, the oxygen atom is more negatively charged in the former state than in the latter. Then it is reasonable to consider that the attachment of a proton to oxygen results in larger energy stabilization in the upper state than in the lower state and therefore in a large red shift of the absorption band. Furthermore, the solvation energy in polar medium, which is conceivably larger in the excited state than in the normal one, should also help the red shift. Thus, the large red shift seems to be explained qualitatively on the basis of the conception of charge transfer absorption.

Experimental

C.P. acetone was treated with an aqueous alkaline solution of $AgNO_3$, distilled, dried with anhydrous K_2CO_3 and finally fractionally distilled before use. White label Eastman mesityl oxide and mesitylene were fractionally distilled. Commercial phorone was four times recrystallized from methanol. *n*-Heptane was stirred with concentrated sulfuric acid for one or two days, washed with water and aqueous alkaline solution, dried with $CaCl_2$ and finally fractionally distilled with sodium metal. Water treated by ion exchange resin was distilled with $KMnO_4$. C.P. concentrated sulfuric acid was used without further purification.

The absorption spectra were measured with a Beckman spectrophotometer model DU, using the quartz absorption cell with 10 mm. light path. The temperature of the cell compartment was kept at 25° by the use of the thermospacer.

Acknowledgments.—The authors wish to express their sincere thanks to Professor Mulliken for his kindness in reading this manuscript and in giving them some valuable advice. One of the authors (S. N.) is also indebted to Professor Mulliken and Professor Platt and other members of the Laboratory for the hospitality shown during his stay at Chicago.

[22] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955).

[23] A more accurate treatment will be published shortly.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PLASTICS DIVISION, MONSANTO CHEMICAL COMPANY]

Vapor–Liquid Equilibria in Binary Systems

BY W. F. YATES

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An equation containing two parameters has been derived from kinetic considerations which relates instantaneous vapor–liquid equilibria in binary systems. The two constants appearing in the equation have been described in terms of the thermodynamic properties of the mixtures concerned. The validity of the assumptions involved has been tested by applying them to data selected from the literature. Until recently the only adequate means of representing vapor–liquid equilibrium data involved the use of activity coefficients and rely on various integrations of the Gibbs–Duhem equation. The relationships existing, however, do not greatly contribute to the understanding of the phenomena involved in evaporation or condensation.

Spinner, Lu and Graydon[1] have observed the similarity between representations of vapor–liquid equilibrium data and copolymer–monomer composition plots and have applied the Alfrey–Price[2] relationship to predict vapor–liquid equilibria. The remarkable success of these investigations has prompted closer study to see if there is any basis in theory for the use of the equations they propose.

Considered from the standpoint of a binary liquid mixture containing components A and B in the process of evaporating, four possible processes are occurring

$$-A - A(l) \xrightarrow{k_{11}} -A(l) + A(g) \quad (1)$$

$$-B - A(l) \xrightarrow{k_{21}} -B(l) + A(g) \quad (2)$$

$$-B - B(l) \xrightarrow{k_{22}} -B(l) + B(g) \quad (3)$$

$$-A - B(l) \xrightarrow{k_{12}} -A(l) + B(g) \quad (4)$$

[1] I. H. Spinner, B. C.-Y. Lu and W. F. Graydon, *Ind. Eng. Chem.*, **48**, 147 (1956).

[2] T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).