[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Rôle of Hydrogen Bonding in the n → π* Blue-shift Phenomenon[1]

BY GRAHAM J. BREALEY AND MICHAEL KASHA

RECEIVED MARCH 21, 1955

The change in the position of the n → π* absorption bands on changing from a hydrocarbon to a hydroxylic solvent has been investigated for a number of molecules. The large shift to shorter wave lengths (blue-shift) is shown to be mainly due to hydrogen-bonding of the n-electrons by the hydroxylic solvent, which causes a greater stabilization of the ground state compared with the excited state of the molecule. Pyridazine and benzophenone have been examined in detail in a series of different mixtures of hexane and ethanol. The families of spectra obtained indicate that essentially two species are involved, a hydrogen bonded and a non-hydrogen bonded form and it is the formation of the hydrogen bonded species that causes the main shift of the n → π* transition to the blue. From the ultraviolet data, an association constant of hydrogen bonding can be obtained and this agrees well with the association constant found by a study of the association of ethanol with the molecule in the infrared. The infrared work makes use of the shift in the O–H stretching frequency on formation of a hydrogen bond.

1. The n → π* Blue-Shift Phenomenon

Anomalous shifts of electronic absorption bands in certain unsaturated molecules to *shorter* wave lengths on changing the solvent from one of low to one of high dielectric constant were first studied by Scheibe.[1a,2] Scheibe investigated the influence of different solvents on the low intensity (molar absorption coefficient, ϵ_{max} 10 to 300) near ultraviolet absorption bands of acetone and other molecules containing the carbonyl group. He attempted, unsuccessfully, to correlate quantitatively the position of the absorption maximum with dielectric constant of the solvent used. Burawoy[3,4] investigated ketones, thioketones, aldehydes and azo compounds and found in all these molecules the presence of a comparatively weak absorption band that moved to shorter wave lengths on changing the solvent from hexane to ethanol.[5] He studied also the effect of dissolving the molecule in sulfuric acid and came to the conclusion that the bands disappeared completely in this solvent.

In the following discussion, the low intensity absorption bands which move to shorter wave lengths on changing the solvent from hexane to ethanol will be referred to as *blue-shift* bands, after the nomenclature of McConnell.[6]

The earlier workers recognized the *blue-shift* bands as associated with compounds containing carbonyl, thiocarbonyl, azo and certain other groups. It was only much later that Kasha,[7] Platt,[8] Halverson and Hirt,[9] and McConnell[6] recognized such absorption bands as generally arising from *singlet-singlet* n → π* transitions. This generalization followed the tentative assignment by McMurry and Mulliken[10] and McMurry[11] of the weak long wave length absorption band in aldehydes and ketones as an n → π* band. An n → π* transition in a planar conjugated molecule corresponds to the excitation of an n-(non-bonding or "lone-pair") electron from an orbital symmetric to the molecular plane, to an antibonding *pi* (π*) molecular orbital, antisymmetric to the molecular plane. This definition may still be applied but less strictly to molecules like benzophenone and thiobenzophenone which may be non-planar.

The *blue-shift* phenomenon has been used to characterize n → π* transitions, and to distinguish them from π → π* transitions. This criterion was suggested by Kasha[7] and developed by McConnell.[6] McConnell catalogued the solvent *blue-shifts* or *red-shifts* of certain electronic absorption bands in 17 compounds and assigned them to n → π* or π → π* transitions, respectively. He compared data on the frequencies of band maxima for the molecules in the solvents: paraffin hydrocarbon, ethanol and water. He examined data also on solutions in sulfuric acid, but decided that the latter solvent was poor for classification purposes. McConnell gave the explanation that the *blue-shift* originates from the solvent molecules orienting themselves around the solute molecules to fit in with the ground state charge distribution of the solute molecule. On excitation, if the charge distribution of the solute changed markedly (as in the case of n → π* transitions), the solvent molecules would not have the position and orientation to bind most strongly with the excited state charge distribution. This would give rise to the *blue-shift* phenomenon, since (relative to a non-polar solvent) a polar solvent would give a greater solvation energy for the ground state of the solute than for the excited state.

In this paper we shall show that specific hydrogen bonding of the solvent with the solute plays an important part in the *blue-shift* phenomenon of n → π* transitions on changing the solvent from a hydrocarbon to a hydroxylic one. Other workers[12] have dealt with the connection of hydrogen bond-

(1) Work supported by the Office of Naval Research, U. S. Navy.

(1a) G. Scheibe, E. Felgor and G. Rossler, *Ber.*, **60**, 1406 (1927).

(2) G. Scheibe, *ibid.*, **59**, 2619 (1926).

(3) A. Burawoy, *J. Chem. Soc.*, 20 (1941).

(4) A. Burawoy, *ibid.*, 1177 (1939); *Ber.*, **63**, 3155 (1930).

(5) Burawoy[3,4] designated these weak bands, which shift toward shorter wave lengths with the change of solvent hexane to ethanol, as R-bands (*radikal-artig*); and those generally strong bands which shift toward longer wave lengths with the same solvent change as K-bands (*konjugierte*). These designations refer to the supposed type of electronic origin of these respective bands. It is now commonly accepted that Burawoy's R-bands correspond to n → π* transitions, and his K-bands to π → π* transitions, both cases involving *no* change of multiplicity.

(6) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(7) M. Kasha, *Faraday Soc. Disc.*, No. 9, 14 (1950).

(8) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

(9) F. Halverson and R. C. Hirt, *ibid.*, **19**, 711 (1951).

(10) H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.*, **26**, 312 (1940).

(11) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

(12) (a) N. D. Coggeshall and E. M. Lang, THIS JOURNAL, **70**, 3283 (1948); (b) H. Baba and S. Nagakura, *J. Chem. Soc. (Japan)*, **71**, 560, 610 (1950); *ibid.*, **72**, 3 (1951); (c) S. Nagakura and H. Baba, THIS JOURNAL, **74**, 5693 (1952); (d) S. Nakakura, *ibid.*, **76**, 3075 (1954).

ing with the *red-shift* of π → π* transitions in molecules such as phenol and aniline, when the solvent is changed from a hydrocarbon to an ethereal one. In their case the solute molecule acted as the hydrogen donor in forming the hydrogen bond; in all n → π* cases considered here the solvent acts as the hydrogen donor.

2. Outline of the Present Investigation

Most of the experimental literature on the *blue-shift* phenomenon involves hydroxylic solvents in comparison with hydrocarbon solvents. The former are notably hydrogen bonding solvents, and the presence of a lone-pair of electrons on a relatively electronegative atom (N,O,S) in all n → π* cases suggests strongly that a specific hydrogen bonded complex between solvent and solute could form. Moreover, the binding of a proton to a lone-pair orbital is a well recognized chemical result of dissolving such molecules in acidic solvents, and is substantiated by the spectral changes observed.

To test for the formation of a specific complex between solvent and solute in hydroxylic solvents, a new series of measurements of absorption spectra was made to provide information missing in the published literature. In all previous papers on the *blue-shift* phenomenon, spectral data for discontinuous solvent changes (*e.g.*, pure hydrocarbon *versus* pure ethanol) are given. In order to test our hypothesis, spectral data for a continuous solvent change from pure hydrocarbon to pure ethanol were required; a continuous range of mixtures of hexane and ethanol was used. This technique offered the possibility of distinguishing qualitatively between the general solvation hypothesis suggested by McConnell and the specific hydrogen bonding hypothesis favored by us.

In the general solvation case, a progressive shift of the absorption band to higher frequency proportional to the mean dielectric constant of the solvent mixture might be expected. In the specific hydrogen bonded complex case, the absorption band of the non-complexed molecule would be expected to be replaced by the shifted absorption band of the complexed molecule. Thus, one absorption maximum should gradually fall in intensity, to be replaced by another at higher frequency. The previously published data could fit either of the above alternatives, since of course the end result would be identical in the two cases.

As an independent check on the hydrogen bonding hypothesis, absorption measurements were made in the appropriate infrared region of the spectrum. This well established method is based on the alteration of the O–H stretching frequency upon formation of a hydrogen bond involving this hydroxyl group.[13]

In choosing molecules to work with we used several criteria. Although we may reasonably expect the general results to be analogous for all n → π* transitions, for practical purposes some molecules present essential advantages. The criteria are (a) the n → π* absorption band should be clearly separated from π → π* transitions, (b) there should be a relatively large *blue-shift* of the n → π* band upon changing solvent from hydrocarbon to ethanol, (c) vibrational structure of the electronic band should be discernible in the hydrocarbon solvent, (d) there should be no possibility of keto–enol tautomerism upon changing the solvent. Another criterion might be a high association constant of solute with solvent, but in our work this became apparent only in retrospect.

(13) (a) N. D. Coggeshall and E. L. Saier, THIS JOURNAL, **73**, 5415 (1951); (b) L. P. Kuhn, *ibid.*, **74**, 2492 (1952); (c) J. Errera, R. Gasport and H Sack, *J. Chem. Phys.*, **8**, 63 (1940).

3. Experimental Details

Measurement of ultraviolet spectra were made on the Beckman Model DU Spectrophotometer using 1, 10 and 20 mm. glass stoppered fused silica cells. Infrared spectra were measured on the Perkin–Elmer Model 21 double beam infrared spectrophotometer, using 0.5 mm. matched rock salt cells and rock salt optics; the work was subsequently repeated in 1 mm. quartz cells.

Carbon tetrachloride (Baker and Adamson C.P. grade) was fractionally distilled (reflux ratio 10 to 1) through a 20 inch column packed with glass helices. The distillate was refluxed with phosphorus pentoxide and again fractionally distilled. The distillate from the phosphorus pentoxide was tested for water by measuring the infrared spectrum in a 14 mm. quartz cell; a negligible amount of water was found to be present.

The hydrocarbon solvents methylcyclohexane (Phillips pure) and hexane (Phillips commercial) were purified by fractionally distilling through a 20 inch column (packed with glass helices) and passing the fraction, which distilled within a very narrow temperature range of the appropriate boiling point, through a freshly activated silica gel column.[14] The solvent obtained was again passed through a freshly activated silica gel column. After some experience it was found better to use fresh silica gel every time instead of reactivating silica gel that had been used previously.

U.S.I. 100% Absolute alcohol was used without further purification (this alcohol contained about 0.005% benzene, as determined by its ultraviolet absorption).

Pyridazine ($C_4H_4N_2$) was synthesized to order by Delta Chemical Company. It was purified by first forming the crystalline picrate and then recrystallizing this from alcohol; the recrystallized picrate was decomposed with 5 *N* hydrochloric acid and the liberated picric acid extracted with ether and nitrobenzene mixture (the nitrobenzene forms a complex with the picric acid). The aqueous solution of pyridazine hydrochloride was made alkaline by the slow addition of a concentrated solution of potassium hydroxide. The solution, after being saturated with potassium carbonate, was repeatedly extracted with ether. The ether solution was distilled in a partial vacuum at room temperature, and the residue of pyridazine was distilled from freshly activated quicklime at room temperature and in a hard vacuum.

Eastman Kodak White Label benzophenone and azobenzene were used without further purification. Spectral studies indicated these were of sufficient purity to be usable directly.

Mesityl oxide (Paragon Testing Laboratories) was carefully fractionated twice each time taking the middle third of the distillate. The distillations were carried out in subdued light and the product was stored in the dark.

The benzophenone solutions were prepared by separately weighing out the benzophenone for each solution. As near as possible the same quantity was weighed out every time.

Pyridazine solutions were prepared by diluting a stock solution in hexane with the required amount of hexane and ethanol. Because of this method the highest ethanol concentration was 80%. The pure dry pyridazine was kept either in a sealed evacuated tube or in a nitrogen atmosphere. No special precautions were used to prevent the pyridazine solution from absorbing water vapor except that the solutions were prepared rapidly with the minimum contact with air and were used immediately after preparation. Ethanol was either added directly to the hexane solutions or if the required volume was small, a stock solution of ethanol in hexane was used.

All experiments were carried out in a laboratory thermostated at 21°.

(14) W. J. Potts, Jr., *ibid.*, **20**, 809 (1952).

4. Discussion of Ultraviolet Absorption Results

(a) **The n → π* Blue-shift in Pyridazine.**—Pyridazine shows an absorption band with a maximum at 29450 cm.$^{-1}$ in hexane solution (Fig. 1). This absorption band has been assigned to an n → π* transition by Halverson and Hirt,[9] and its large *blue-shift* (4000 cm.$^{-1}$) on changing solvent from hexane to water has been observed by them. We found that the *blue-shift* on changing from hexane to 80% ethanol in hexane (Fig. 2) although smaller than the hexane–water shift is still very large (2440 cm.$^{-1}$).

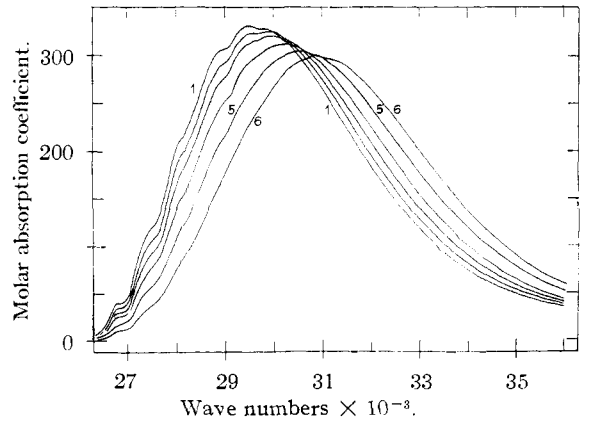

Fig. 1.—Effect of ethanol as solvent on the near ultraviolet n → π* absorption band of pyridazine. Solutions of pyridazine, 1.01 × 10^{-2} *M*, in hexane–ethanol solvent, from zero to 3.2% by volume ethanol. Ethanol concentrations: curve 1, zero; curve 2, 0.0343 *M*; curve 3, 0.0686 *M*; curve 4, 0.137 *M*; curve 5, 0.274 *M*; curve 6, 0.549 *M*.

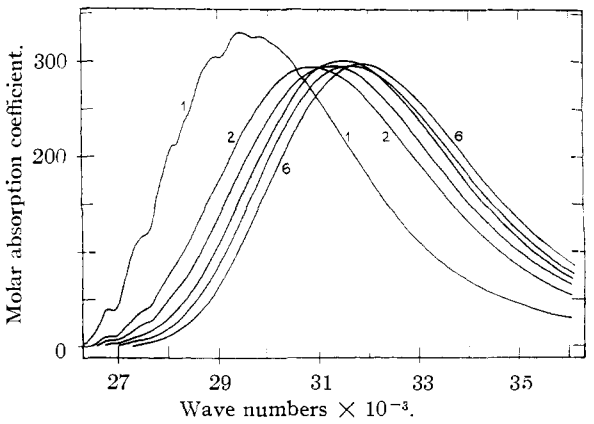

Fig. 2.—Effect of ethanol as solvent on the near ultraviolet n → π* absorption band of pyridazine. Solutions of pyridazine, 0.979 × 10^{-2} *M*, in hexane–ethanol solvent, from 3.125 to 80% by volume ethanol, with reference curve in hexane. Ethanol in volume per cent.: Curve 1, zero; curve 2, 3.125%; curve 3, 6.25%; curve 4, 12.5%; curve 5 25%; curve 6, 80%.

We studied the n → π* 29450 cm.$^{-1}$ band (hexane) using mixtures of hexane and alcohol. Figure 1 shows the series of absorption curves obtained as the solvent was changed from pure hexane to hexane containing 0.549 *M* (3.2% by volume) ethanol through intermediate concentrations of 0.0343 *M* (0.2%), 0.0686 *M* (0.4%), 0.137 *M* (0.8%) and 0.274 *M* (1.6%) ethanol in hexane solution. During the addition of this small quantity of ethanol there is a remarkable change leading to an almost complete blurring of the vibrational structure and a large shift (1450 cm.$^{-1}$) in the maximum to higher frequency. Figure 2 shows the change in spectrum in changing from 3.125 to 80% ethanol with a reference curve of the spectrum in pure hexane. Intermediate curves correspond to 6.25, 12.5 and 25% ethanol in hexane solutions. During the addition of alcohol from 3.125 to 80% ethanol, the maximum shifts still more to higher frequency but the shift is only about $^2/_3$ that which occurs during the addition of the first 3% ethanol.

In Fig. 1 it is seen that although the maximum moves considerably to higher frequency the position of the individual bands (often showing only as shoulders) are unchanged in position but merely smoothed out. Figure 3 illustrates this point very clearly for the vibrational peak at 26800 cm.$^{-1}$.

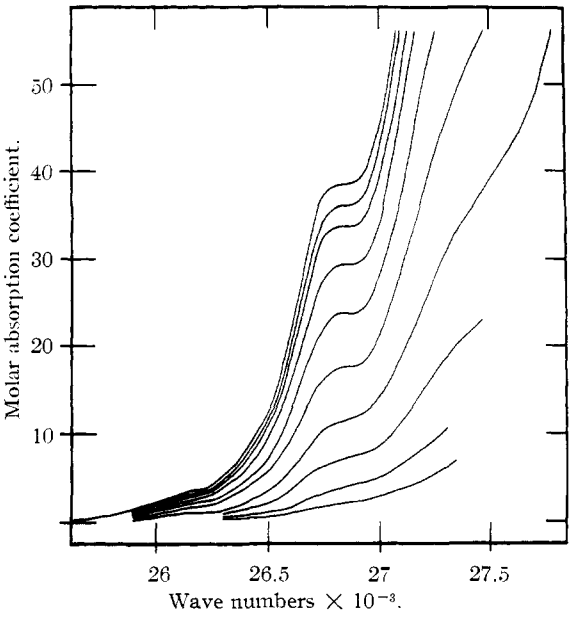

Fig. 3.—Effect of ethanol as solvent on the 26800 cm.$^{-1}$ vibrational peak of the n → π* absorption band of pyridazine. Concentrations: seven highest curves, 1.01 × 10^{-2} *M* pyridazine; three lowest curves, 0.979 × 10^{-2} *M* pyridazine; all in hexane–ethanol solvent mixtures. Ethanol concentrations (top to bottom): zero, 0.0172, 0.0343, 0.0686, 0.137, 0.274, 0.549, 1.07, 2.14, 4.27 *M*.

This shows the absorption spectrum in solution consisting of pure hexane and hexane–ethanol solutions containing up to 25% ethanol by volume. The peak (shoulder) stays in the same position over this range of solvent variation while the maximum of the whole band moves by 2190 cm.$^{-1}$. The peak becomes less well pronounced during this change probably owing to the superposition of another absorption band rising to shorter wave lengths. The behavior of the n → π* absorption band as the ethanol concentration is increased indicates definitely that essentially two forms of pyridazine are involved, namely, non-complexed pyridazine and pyridazine complexed with ethanol (hydrogen bonded). An equilibrium should exist between

these two species and the ethanol; this equilibrium was tested by using the absorption of the low frequency side of the 26800 cm.$^{-1}$ peak as a measure of the concentration of non-hydrogen bonded pyridazine. If the hydrogen bonded species absorbed at all near this frequency, the intensity of the band could not be taken as a direct measure of the concentration of the non-complexed species. The lower the frequency at which the optical density is taken, the less would be the error due to the absorption tail of the hydrogen bonded species, but, of course, the greater the error in measurement of the optical density owing to its smaller value.

The best value of the concentration of the non-complexed pyridazine was therefore determined as follows.

Log D_0 − log D_c was plotted against the frequency (cm.$^{-1}$) for various values of c. The D_0 is the optical density (log I_0/I) of the pyridazine in pure hexane and D_c is the optical density of the same concentration of pyridazine in a hexane solution containing ethanol of concentration c moles/liter. The ethanol concentration was varied between 0 and 0.549 mole/liter. This plot gave a line which was straight and horizontal below 26730 cm.$^{-1}$ and dropped off at higher frequencies because of the overlap of the tail of the absorption band of the complexed pyridazine. The value of D_c on the best straight line below 26730 cm.$^{-1}$ was then used as a measure of the concentration of the non-hydrogen bonded form for each value of c.

A graph of log $\{[C_4H_4N_2]/[C_4H_4N_2\cdot(EtOH)_r]\}$ against log $[EtOH]_{added}$ gave a good straight line and a value of r in the equation

$$C_4H_4N_2 + r\ EtOH \rightleftharpoons C_4H_4N_2\cdot(EtOH)_r$$

of 0.97. Because of the closeness of the value of r to 1 it was assumed that one ethanol molecule was adding to one pyridazine molecule to give a hydrogen bonded complex. Therefore, the equilibrium was replotted, this time using log $[EtOH]_{calc.}$ instead of log $[EtOH]_{added}$. Again an excellent straight line was obtained (*cf.* Fig. 4) giving r = 0.93 and

$$K_a = \frac{[C_6H_4N_2\cdot(EtOH)_r]}{[C_6H_4N_2][EtOH]^r} = 4.9$$

(b) **The n → π* Blue-shift in Benzophenone.**—The solvent effect on the n → π* absorption band of benzophenone (max. at 28850 cm.$^{-1}$ in methylcyclohexane) on changing the solvent from pure methylcyclohexane to pure ethanol is shown in Fig. 5. The behavior of this absorption band has many features in common with the behavior of the pyridazine n → π* absorption band discussed above. On changing from a hydrocarbon to ethanol solvent the vibrational structure is completely blurred out and the maximum shifts considerably (1170 cm.$^{-1}$) to higher frequencies. Although the maximum apparently shifts, the position of the individual vibrational peaks remain constant and they merely become smoothed out, as in the case of pyridazine. However, with benzophenone, several times the ethanol concentration is required to cause the same degree of spectral change. An association constant of 0.4 was obtained by approximate calculations based on the data obtained. More exact data would be determined by measuring the tail at low frequencies in a much longer path length, but in view of the uncertainty of the degree of association of ethanol at these high concentrations, it was felt that more accurate work was not justified.

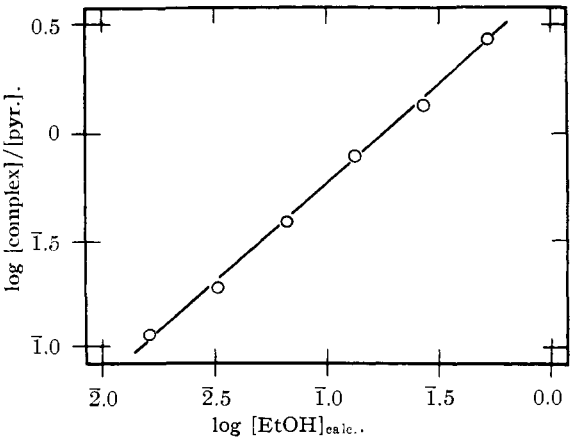

Fig. 4.—Proof of complex formation of pyridazine with ethanol, in hexane–ethanol solutions, based on ultraviolet absorption data. Concentration of pyridazine, 1.01 × 10^{-2} *M*; ethanol concentrations, 0.0172, 0.0343, 0.0686, 0.137, 0.274 and 0.549 *M*.

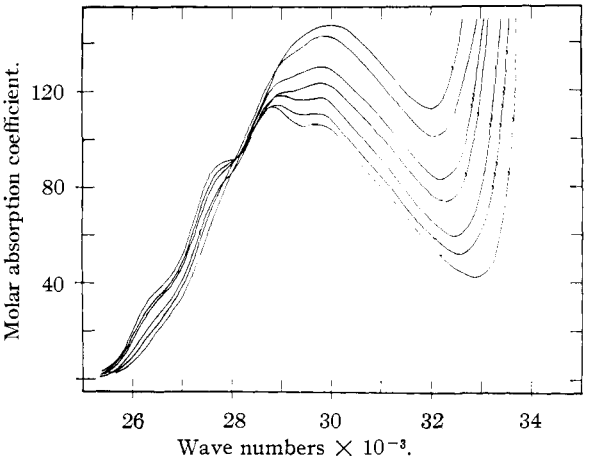

Fig. 5.—Effect of ethanol as solvent on the near ultraviolet n → π* absorption band of benzophenone. Solutions in hexane–ethanol solvent mixtures. Concentrations (B = benzophenone, E = ethanol; top to bottom): B, 2.92 × 10^{-3} *M*, E = 100%; B = 2.83 × 10^{-3} *M*, E = 50%; B = 2.94 × 10^{-3} *M*, E = 25%; B = 2.90 × 10^{-3} *M*, E = 14%; B = 2.94 × 10^{-3} *M*, E = 3.4%; B = 3.12 × 10^{-3} *M*, E = 1%; B = 2.94 × 10^{-3} *M*, E = zero per cent., (all per cent. by volume).

(c) **The n → π* Blue-shifts of Other Molecules.**—Ultraviolet absorption spectra were measured for acetone (band maximum at 35960 cm.$^{-1}$) and mesityl oxide (band maximum at 30760 cm.$^{-1}$) in methylcyclohexane. The *blue-shifts* are quite large, 1200 and 1180 cm.$^{-1}$, respectively, on changing the solvent to ethanol; but since there is no vibrational structure in the absorption bands, even when these molecules are dissolved in the hydrocarbon solvent, a detailed study did not seem promising. When the possibility of keto–enol tautomerism be-

came apparent, these cases were not considered further.

Azobenzene has an n → π^* absorption band at 22360 cm.$^{-1}$ in methylcyclohexane which moves only 160 cm.$^{-1}$ to the blue when dissolved in ethanol. This small shift will be discussed further, later in the paper.

5. Proof of Hydrogen Bond Formation by Infrared Studies

To check the formation of a hydrogen bond, the fundamental stretching frequency of the O–H bond in ethanol was measured in the absence and presence of the solute molecule being investigated.

Hexane and methylcyclohexane are solvents of poor transparency for work in the region of the O–H stretching frequency (3640 cm.$^{-1}$). For this reason the infrared investigation was carried out using carbon tetrachloride as solvent, although the results will not be stringently comparable with the work carried out in the hydrocarbon solvents. The dielectric constant of carbon tetrachloride is small (2.238 at 20°) and comparable in value to hexane (2.023 at 20°) and methylcyclohexane (2.020 at 20°). Therefore the change in dielectric constant should not cause any large change in the association constant. Work was carried out initially in 0.5 mm. rock salt cells using 0.2 M ethanol in carbon tetrachloride but the work was later repeated in 1 mm. quartz cells with 0.1 M ethanol. The lower alcohol concentration gave less interference from the absorption bands of polymer ethanol.

Figure 6 shows the absorption curve of 0.1 M ethanol in carbon tetrachloride in a 1 mm. cell *versus* a carbon tetrachloride blank. The narrow band at 3640 cm.$^{-1}$ is due to the fundamental O–H stretching frequency in ethanol.[13a,15] The small peak at 3510 cm.$^{-1}$ probably is due to a trimer of ethanol and the very diffuse band with a maximum at about 3370 cm.$^{-1}$ is due to hydrogen bonded polymeric forms of ethanol.[13b,16] Figure 6 shows the effect on the O–H spectrum of adding approximately 0.1 M pyridazine. A new intense band at 3415 cm.$^{-1}$ appears and the band at 3640 cm.$^{-1}$ decreases in intensity. The bands at 3510 and 3370 cm.$^{-1}$ must also decrease in intensity but in the figure this is not obvious owing to the masking of these bands by the new 3415 cm.$^{-1}$ band. Pyridazine itself does not have any significant absorption bands in the region shown in the diagram and the new band arises from the modified O–H frequency of the ethanol O–H bond, hydrogen bonded to a nitrogen of the pyridazine molecule. An association constant between pyridazine and ethanol, based on ethanol concentration calculated as monomer and assuming one ethanol for each pyridazine complexed, was calculated from the infrared data shown in Fig. 6. Knowing the initial concentration of ethanol, the fraction of the monomeric form was calculated from published data.[17,18] By relating this to the intensity of the monomer peak (Fig. 6), corrected for overlap by the trimer band, it is possible to calculate the monomer concentration in the pyridazine–ethanol mixture in carbon tetrachloride (Fig. 6). From this the total ethanol concentration uncomplexed with pyridazine can be calculated and hence the association constant of the pyridazine with ethanol. A value of 6.8 was obtained for the association constant as defined in part 4.

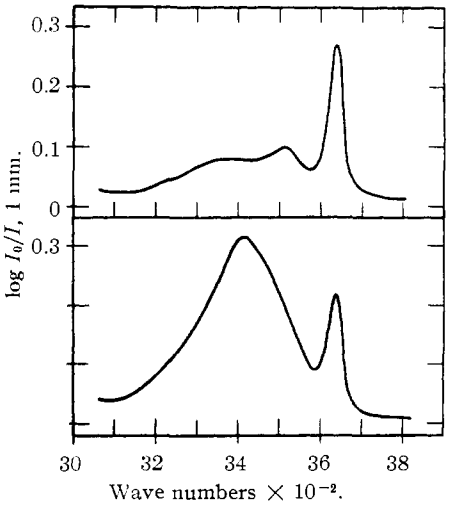

Fig. 6.—Infrared absorption study of pyridazine–ethanol hydrogen bonded complexing; modification of the fundamental O–H stretching frequency of ethanol by pyridazine. Upper curve, 0.0981 M ethanol in carbon tetrachloride; lower curve, 0.123 M pyridazine plus 0.0981 M ethanol in carbon tetrachloride; both in 1 mm. quartz cells.

Figure 7 again shows the absorption curve of an approximately 0.1 M ethanol solution in carbon tetrachloride in a 1 mm. cell. Figure 7 shows the effect of adding 0.3 M benzophenone to the solu-

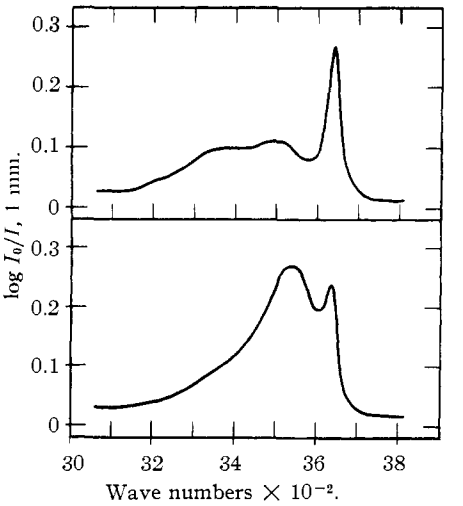

Fig. 7.—Infrared absorption study of benzophenone–ethanol hydrogen bonded complexing; modification of the fundamental O–H stretching frequency of ethanol by benzophenone. Upper curve, 0.0970 M ethanol in carbon tetrachloride; lower curve, 0.284 M benzophenone plus 0.0970 M ethanol in carbon tetrachloride; both in 1 mm. quartz cells.

(15) J. Errera and P. Mollet, *Nature*, **138**, 882 (1936).

(16) F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 145 (1951).

(17) C. B. Kretschmer and R. Wiebe, THIS JOURNAL, **76**, 2579 (1954).

(18) W. Coburn, Ph.D. Thesis, Florida State University, Tallahassee, 1954.

tion. As before, an intense new band is formed (max. at 3535 cm.$^{-1}$) and the fundamental O–H vibration band decreases in intensity. The new peak found was closer in frequency value to the fundamental O–H peak than was the pyridazine ethanol O–H peak. It is possible to relate the difference in frequency between the fundamental O–H peak and the modified O–H peak to the energy of formation of the hydrogen bond.[19,20] This method gives a value of 2.2 kcal. for benzophenone and 4.6 kcal. for pyridazine. The absolute value of these figures is uncertain but certainly their relative values are of the right order. The association constant between benzophenone and ethanol based on the infrared data and calculated in the same way as before gave a value of K_a of about 1.4. The K_a obtained does not represent of course a simple equilibrium constant, as it is based on ethanol concentration expressed as monomer, when in fact an appreciable proportion of it is polymerized.

Similar studies were carried out with azobenzene and ethanol in carbon tetrachloride. Unlike pyridazine and benzophenone only very slight evidence of hydrogen bonding was found, indicating an association constant of only about $^1/_{20}$ the value of the constant found for benzophenone.

The agreement between the association constant calculated from the n → π* *blue-shift* (K_a = 4.9) and the infrared method (K_a = 6.8) is good for pyridazine; this is probably because low ethanol concentrations (*ca.* 0.1 *M*) were the critical ones in determining the K_a in both methods. For benzophenone the concentration of ethanol for the infrared work was 0.1 *M*, but for the work in the ultraviolet the critical concentration used in deriving the association constant was *ca.* 2.8 *M*. At this high ethanol concentration the ethanol is greatly associated with itself, and this would reduce the apparent association constant with benzophenone by a considerable amount. Thus it was found that the association constant from the infrared data is 1.4 but that from the n → π* *blue-shift* work is only 0.4 for the benzophenone case.

6. Discussion

The experimental results given in this paper indicate that hydrogen bonding of the solute by the solvent can be directly correlated with the *blue-shift* phenomena of n → π* electronic absorption bands in changing the solvent from a saturated hydrocarbon to ethanol. The observation that the individual pyridazine and benzophenone vibrational peaks remain at the same frequency during a large increase in the ethanol concentration indicated that the general solvent effect[21,22] is of little importance.

On the basis of one non-complexed form and of one hydrogen bonded form of the molecule, a family of absorption curves such as measured would be expected to give a simple *isosbestic* point; this is not found experimentally (Figs. 1, 2 and 5). Further considerations show that at all but the lowest ethanol concentrations more than one species of hydrogen bonded complex will be formed, owing to trimers and polymers of ethanol bonding to the hydrogen-acceptor molecule. As the ethanol concentration is increased the ratio of the various polymeric forms of ethanol will change and therefore the average absorption curve of the complexed molecule will alter. In the case of a molecule like pyridazine which has two hetero-centers at which hydrogen bonding can take place, the situation is still more complicated. If there are two centers of hydrogen bonding possible, however, the two association constants are expected to be different. Thus, it should be possible to study the addition to one center of hydrogen bonding before there is any appreciable bond formation at the second center.

The oscillator strength of the n → π* band in pyridazine (proportional to the area under the absorption band) does not vary greatly on changing the solvent from hexane to ethanol. The n → π* band in benzophenone on the other hand seems to increase in strength as the solvent is changed from a hydrocarbon to ethanol. This increase however is apparent only, and is mainly or entirely caused by the increased overlap of the tail of the adjacent π → π* absorption band, which moves to the red[21,22] at the same time as the n → π* band moves to the blue.[6,7] The overlap of the π → π* tail with the n → π* band will also cause the apparent position of the maximum to be at higher frequencies than the real value. By extrapolating the intrinsic intensity of the π → π* tail, the corrected *blue-shift* of n → π* band is found to be 900 cm.$^{-1}$ instead of 1170 cm.$^{-1}$ as given earlier in this paper.

The large *blue-shift* of n → π* absorption bands on hydrogen bonding can be explained on the following basis: The formation of a hydrogen bond with the n-electrons lowers the energy of the n-orbital by an amount equal to the energy of the hydrogen bond. In the n → π* transition, one of the electrons is removed from the n-orbital and goes to an empty antibonding π-orbital. The n-electron remaining is not sufficient to sustain the hydrogen bond; when the hydrogen bond is broken, the energy of the excited state should be approximately equal to the energy of the same excited state of the molecule in the absence of a hydrogen bond. Thus the magnitude of the *blue-shift* should be of the same order as the energy of the hydrogen bond formed; any dielectric effect would tend to reduce the magnitude of the *blue-shift*. A strict comparison of the magnitude of the *blue-shift* with the strength of the hydrogen-bond would require the value of the *blue-shift* corresponding to a *single* ethanol molecule bonding onto the acceptor molecule, but this value is hard to obtain experimentally. Taking the value of the band maximum for pyridazine in the 0.549 *M* ethanol (for higher ethanol concentrations hydrogen bonding will also occur at the 2nd nitrogen), we obtain an energy shift equivalent to 4.2 kcal.; this can be compared with the value of 4.6 kcal. determined from the infrared hydrogen bonding data.

For benzophenone the value of the maximum in 100% ethanol was chosen, but the value was corrected because of the n → π* band being over-

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lapped by the tail of the $\pi \rightarrow \pi^*$ transition. The corrected *blue-shift* corresponds to an energy of 2.6 kcal. which is of the same order as the value 2.2 kcal. obtained from the infrared data.

The infrared work with azobenzene indicates a very small association constant of azobenzene with ethanol. Thus although the hydrogen-bonded azobenzene molecule might have its $n \rightarrow \pi^*$ transition moved by a considerable amount to higher energies compared with the non-hydrogen bonded molecule, the apparent maximum of azobenzene in ethanol would correspond to the average spectrum of mainly uncomplexed azobenzene with a few per cent. of hydrogen bonded molecules. This would account for the very small (160 $cm.^{-1}$) *blue-shift* of the azobenzene $n \rightarrow \pi^*$ transition from methylcyclohexane to ethanol which is actually observed.

Polar solvents like ethers and nitriles which are not expected to hydrogen bond strongly with the solute molecule also cause a *blue-shift* of $n \rightarrow \pi^*$ absorption bands. This shift is generally much less than the *blue-shift* caused by hydrogen bonding in hydroxylic solvents, but is nevertheless appreciable. Preliminary investigations with propionitrile–hexane mixtures and pyridazine show a similar behavior to ethanol–hexane mixtures, except that the shift is smaller and the concentration of the nitrile necessary to cause the same relative change is much greater. It is unlikely that a definite complex is formed between the nitrile and the pyridazine. But it is probable that the nitrile solvent molecules preferentially orient themselves around the pyridazine molecules, and thus have a higher concentration than average in the neighborhood of the solute molecules.

In conclusion it should be said that the primary object of this work was not to obtain association constants for hydrogen bonding but merely to show that hydrogen bonding is the main influence in the $n \rightarrow \pi^*$ *blue-shift* phenomenon in hydroxylic solvents. The method however has shown itself to be capable of giving accurate association constants from ultraviolet data.

TALLAHASSEE, FLA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY]

Methyl Affinities of Quinones

BY A. REMBAUM AND M. SZWARC

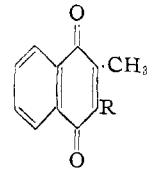
RECEIVED APRIL 12, 1955

Addition of CH_3 radicals to a series of quinones has been investigated. The relative rates of reaction $Q + CH_3 \rightarrow Q{\cdot}CH$ referred to as methyl affinities, decrease rapidly along the series Q = *p*-benzoquinone (15,200), 1,4-naphthoquinone (4900) phenanthraquinone (700), and *t*-butylanthraquinone (90). This scale of methyl affinities is based on a value of unity for benzene. It was found that a successive methylation of quinones decreases the methyl affinity, the introduction of a methoxy group decreases the reactivity even more. On the other hand, the methyl affinity increases when chlorine atoms are introduced into the molecule. The results are discussed tentatively in terms of reactivities of the C=C double bonds, and in terms of effects due to steric hindrances, the low reactivity of chloranil being the most striking example of the latter effect. By comparing the reactivities of quinones toward methyl radicals and toward styryl radicals, the relative intrinsic reactivity of styryl radical has been determined. It has been found that the latter radical is 2.2 less reactive than the former.

The high reactivity of quinones toward free radicals is well recognized, and this property of quinones accounts for their inhibitory action on many chain processes, such as radical initiated oxidations and the polymerization of vinyl monomers. Although it is generally agreed that reaction (1)

$$Q + R \longrightarrow Q{\cdot}R \qquad (1)$$

is involved in the inhibitory action of quinones, the nature of the primary adduct Q·R is still unsettled. Some workers suggest that the attacking radical R is added initially to the oxygen atom of a quinone, while others favor the idea that the primary addition process involves the C=C double bond. These conclusions are based on results of investigations into the structure of the *final* products formed in reactions inhibited by quinones. Thus, the isolation of di-ethers like $R{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}R$ is taken as evidence for an O-addition process,[1] while isolation of compounds such as



is considered an argument in favor of an addition mechanism involving the C=C double bond.[2] It seems, however, that the above evidence might be misleading, since an intramolecular rearrangement may accompany the process which converts the *initial* addition product into the *final* product eventually isolated from the reacting mixture. Whether or not such a rearrangement takes place will depend on the nature of the quinone used, on the type of radical attacking, and on the conditions prevailing in the experiment performed.

Quinones differ considerably in their inhibitory power, which can be measured by studying the kinetics of a chain reaction inhibited by these com-

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