phosphite has been reported by Gerrard and Jeacocke[10] leading to the formation of dialkyl phosphobromidate and alkyl bromide. They also proposed that the reaction is initiated by the cationic attack of bromine, followed by the cleavage of the R–O bond by the nucleophilic attack of the bromine negative ion. Their explanation seems very close to the present one.

The yellow intermediate formed in the present experiment is so turbid that no absorption spectral measurements can be made. However, the yellow color seems to indicate the formation of a strong charge-transfer complex between phosphite and iodine, because most of the solutions of iodine complexes have colors which are intermediate between red and yellow, and the strongest complex of iodine so far found, the I_2-triethylamine complex, is yellow.[11] Therefore this reaction may be considered as evidence for the presence of a charge-transfer complex as the reaction intermediate.[12]

The second step of the reaction is considered to be performed by the attack of the iodine negative ion from the back side of the carbon atom of the *n*-butyl group (S_{N1} mechanism). This has been confirmed by Gerrard and Jeacocke who showed that tris {(+)-1-methylheptyl} phosphite and bromine produced (−)-1-methylheptyl bromide.

One can expect that the second step will be retarded in the case of the reaction between iodine and tri-*t*-butyl phosphite, because the attack of iodine negative ion will be much more difficult in that case due to the large *t*-butyl group. One might then reasonably hope to find an absorption band due to a charge transfer complex between iodine and tri-*t*-butyl phosphite.[13] The synthesis of tri-*t*-butyl phosphite was tried in our Laboratory by the method of Kosolapoff.[14] Unfortunately we did not succeed in that synthesis and at present no further research in this line is contemplated.

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[10] W. Gerrard and G. J. Jeacocke, *J. Chem. Soc.*, 3648 (1954).

[11] S. Nagakura, THIS JOURNAL, **80**, 520 (1958).

[12] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[13] This was suggested by Dr. Stanton Ehrenson.

[14] G. M. Kosolapoff, THIS JOURNAL, **74**, 4953 (1952).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, KYUSHU UNIVERSITY]

Effect of Solvent on n–π^* Absorption Spectra of Ketones

BY MITSUO ITO, KŌZŌ INUZUKA AND SUNAO IMANISHI

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The n–π^* absorption bands of acetone, mesityl oxide, acetophenone and benzophenone were measured in various solvents and the frequency shifts induced by solvents were analyzed on the basis of the current theory of solvent effects on absorption spectra. The results show that the well-known blue shift phenomenon in the n–π^* absorption bands can be interpreted as the result of coöperating effects of both electrostatic and hydrogen bonding interactions on solute molecules.

Introduction

It is well known that molecules having C=O groups such as ketones usually exhibit weak n–π^* absorption bands in the near ultraviolet region. n–π^* absorption bands may be distinguished easily from π–π^* absorption bands by a large blue shift on changing the solvent from one of lower to another of higher dielectric constant. The origin of the n–π^* blue shift was first explained by McConnell[1] on the basis of the general solvation hypothesis. On the other hand, Brealey and Kasha[2] attributed the phenomenon of the n–π^* blue shift essentially to the hydrogen bond formation between the solute and solvent molecules. They studied the effect of ethanol on the n–π^* absorptions of pyridazine and benzophenone and concluded that the observed frequency shifts caused by the change of solvent from hydrocarbon to ethanol represent approximately the hydrogen bond energies in the electronic ground states. This interpretation has been criticized by Pimentel[3] on the basis of the Frank–Condon principle.

It seems certain that hydrogen bonding plays an important role in the n–π^* blue shift phenomenon, but effects contributed by other origins are equally important and cannot be neglected. In fact, a blue shift frequently is observed even in cases where the system does not contain hydrogen bonds. In this paper we shall examine the role played by electrostatic interaction between the solute and solvent molecules in the n–π^* blue shift in the spectra of several aromatic ketones by applying the general expression derived by McRae[4] for the solvent effect on the absorption frequency. The extent of the contribution of hydrogen bonding to the blue shift also will be considered.

Experimental

Measurements of ultraviolet absorption spectra were made on a Hitachi model EPS automatic recording spectrophotometer, using 1 cm. cells. Infrared spectra were measured on another Hitachi model EPI double beam infrared spectrophotometer, using 0.1 mm. rock salt cells.

Solvents were purified by the methods recommended by Weissberger and Proskauer,[5] and special care was taken

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[1] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[2] G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

[3] G. C. Pimentel, *ibid.*, **79**, 3323 (1957).

[4] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

[5] A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 1955.

to remove contaminating water. Acetone was purified by the above method. Highest quality commercial mesityl oxide and acetophenone were purified further by repeated distillations. Benzophenone was recrystallized several times from ethanol.

Results and Discussion

1. Theoretical Expression for the Solvent Effect.—Recently, the effects of electric dipole interactions on electronic absorption frequencies of solution spectra have been investigated theoretically by Ooshika[6] and McRae.[4] These authors obtained independently general expressions for the solvent-induced frequency shift by applying perturbation theory. Although expressed in different forms, the physical content of their formulas is the same. We shall use here McRae's expression on account of its greater compactness. The general expression presented by McRae is

$$\Delta\nu = 2.13 \times 10^{-30}\left[\sum_{j \mp 0}\left(\frac{1}{\nu^u{}_{j0}} - L_{j0}\right)\frac{f_{j0}{}^u}{a^3}\,\frac{n_{j0}{}^2 - 1}{2n_{jo}{}^2 + 1} - \sum_{j \mp i}\left(\frac{1}{\nu^u{}_{ji}} - L_{ji}\right)\frac{f_{ji}{}^u}{a^3}\,\frac{n_{ji}{}^2 - 1}{2n_{ji}{}^2 + 1}\right] + \frac{1}{hc}\,\frac{(\mathbf{M}_{00}{}^u)^2 - (\mathbf{M}_{ii}{}^u)^2}{a^3}\cdot\frac{n_0{}^2 - 1}{2n_0{}^2 + 1} + \frac{2}{hc}\,\frac{\mathbf{M}_{00}{}^u(\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u)}{a^3}\left[\frac{D - 1}{D + 2} - \frac{n_0{}^2 - 1}{n_0{}^2 + 2}\right] + \frac{6}{hc}\,\frac{(\mathbf{M}_{00}{}^u)^2(\alpha_0{}^u - \alpha_i{}^u)}{a^5}\left[\frac{D - 1}{D + 2} - \frac{n_0{}^2 - 1}{n_0{}^2 + 2}\right]^2 \quad (1)$$

in which notations and their meaning are referred to McRae's original paper.

In equation 1, the first term represents the contribution of dispersion forces between the solute and solvent molecules, which usually gives a red shift of absorption. The second term is the contribution from interactions between solute permanent dipoles and solvent dipoles thereby induced and the third term corresponds to the contribution from interactions between permanent dipoles of the solute and solvent molecules. The last term represents the contribution from interactions between permanent dipoles of solvent molecules and solute dipoles thereby induced, which may be regarded as the quadratic Stark effect.

To make the rather complicated equation 1 more feasible to practical application, a simplification was made with the aid of several assumptions. It is assumed that the contribution of the quadratic Stark effect is small compared with other contributions, hence the last term was dropped. Moreover, refractive index extrapolated to zero frequency n_0 was replaced by the value n_D for the sodium D line. Thus we obtain

$$\Delta\nu = \textit{dispersion term} + B\,\frac{n_D{}^2 - 1}{2n_D{}^2 + 1} + C\left[\frac{D - 1}{D + 2} - \frac{n_D{}^2 - 1}{n_D{}^2 + 2}\right] \quad (2)$$

where B and C are constants characteristic of the solute molecule standing for

$$B = \frac{1}{hc}\,\frac{(\mathbf{M}_{00}{}^u)^2 - (\mathbf{M}_{ii}{}^u)^2}{a^3} \quad (3)$$

and

$$C = \frac{2}{hc}\,\frac{\mathbf{M}_{00}{}^u(\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u)}{a^3} \quad (4)$$

respectively. $\mathbf{M}_{00}{}^u$ and $\mathbf{M}_{ii}{}^u$ in equations 3 and 4 represent the dipole moment vectors of the solute molecule in its electronic ground and excited states, respectively, and a is Onsager's reaction radius of the solute molecule. The dispersion term in equation 2 depends in a complicated way on various spectroscopic properties of the solute and solvent molecules, and it is difficult to make simplified assumptions for it, especially for application of the formula to weak transitions such as the n–π^* transitions in ketone. However, since this term is always negative (red shift) and its effect is usually small compared with those of the other terms, a detailed analytical form of this term is not necessary for our present purpose, and we shall discuss the solvent effects for n–π^* absorption spectra of ketones on the basis of the simplified expression 2.

2. Effects of Electrostatic Interactions.—The $\nu_{\max}$ of n–π^* absorptions of acetone, mesityl oxide, acetophenone and benzophenone in various solvents are given in Table I. Refractive index and dielectric constant of the solvents are included in the table.

TABLE I

THE $\nu_{\max}$ OF THE n–π^* ABSORPTION SPECTRA OF KETONES (CM.$^{-1}$)[a]

Solvent	n_D	D	Acetone	Mesityl oxide	Acetophenone	Benzophenone
Non-polar						
n-Hexane	1.375	1.89	36490	30480	31000	28810
Carbon tetrachloride	1.460	2.238	35700	30760	31140	29060
Benzene	1.501	2.284	...	30950	31240	29150
Dioxane	1.422	2.209	36220	31000	...	29230
Polar						
Ethyl ether	1.356	4.335	36090	30760	31140	29060
Methyl acetate	1.362	6.68	36290	31140	31240	29230
Acetonitrile	1.344	37.5	36500	31300	31500	29510
Hydrogen bonded						
Chloroform	1.449	4.806	36220	31490	31540	29670
Isobutyl alcohol	1.398	17.7	36690	32040	...[a]	30020
Ethanol	1.361	24.3	36890	32040	...[a]	30020

[a] The absorption maxima are obscured by the tail of the π–π^* absorption.

We shall first discuss the effects of non-polar solvents on n–π^* absorption. Non-polar solvents used here are n-hexane, carbon tetrachloride, dioxane and benzene. Their refractive index increases in the above order. It is seen from the table that $\nu_{\max}$ tends to increase with the increase in the refractive index of each solvent, that is, absorption shifts to shorter wave lengths in solvents of higher refractive index, with the single exception of acetone. Plots of $\nu_{\max}$ against $(n_D{}^2 - 1)/(2\,n_D{}^2 + 1)$ for mesityl oxide, acetophenone and benzophenone are shown in Fig. 1. For each of these ketones, points for n-hexane, carbon tetrachloride and benzene are approximately on a straight line, although the point for dioxane deviates appreciably. For non-polar solvent the third term in equation 2 may be neglected since $n_D{}^2 \approx D$, and the first and second terms remain to be considered. Then if the first term is much smaller than the second term, a linear relation between $\nu_{\max}$ and $(n_D{}^2 - 1)/(2\,n_D{}^2 + 1)$ should obtain. The anomalous behavior of dioxane as a solvent already has been pointed out by McRae[4] and Lippert.[7] In this molecule the large

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(6) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

(7) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).

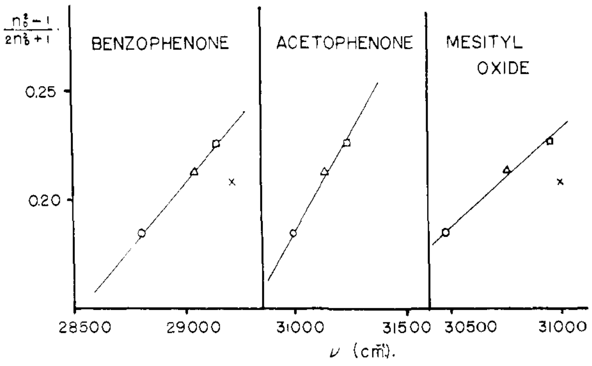

Fig. 1.—Relations between ν_{max} and $n^2_D - 1/2n^2_D + 1$: O, *n*-hexane; Δ, carbon tetrachloride; ×, dioxane; □, benzene.

bond dipole moments of the two C=O groups are canceled out on account of the high symmetry of the molecule. However, in solution the cancellation of bond dipoles may not occur owing to the interactions exerted by neighboring molecules and a permanent dipole moment may result. In such circumstances dioxane can no longer be regarded as a non-polar solvent.

As mentioned previously the frequency shift of absorption in non-polar solvents is given as the sum of two contributions from the first and the second terms in equation 2. The fact that absorption shifts to shorter wave lengths in solvents of higher refractive index indicates a greater contribution from the second term than that from the first term. The first (dispersion) term is always negative, giving red shift of the absorption frequency.[8] Then the observed blue shift must mean that the second term and hence B in equation 3 is positive for all ketones investigated here, and consequently it follows from equation 3 that $(\mathbf{M}_{00}^u)^2 > (\mathbf{M}_{ii}^u)^2$. In other words the dipole moment of ketone molecules must decrease in the excited states corresponding to the $n-\pi^*$ absorption band.

For acetone no simple relation between ν_{max} and $(n_D{}^2 - 1)/(2n_D{}^2 + 1)$ was found. This probably is due to the exceptionally small decrease of dipole moment during the $n-\pi^*$ transition and for acetone the dispersion term in equation 2 becomes more important than the second term, leading to the anomalous behavior of this molecule with respect to the linear relationship.

Next we shall proceed to the discussion about the effect of polar solvents on $n-\pi^*$ absorption frequencies. Polar solvent here means one without the ability of forming hydrogen bonds with solute molecules. For this type of solvent the frequency shift again is expressed by equation 2 but we shall use it in a more limited form here. If for any two polar solvents a and b the refractive index as well as the contribution from the dispersion term for each of them are identical, it follows from equation 2 that

$$\nu_a - \nu_b = C\left[\frac{D_a - 1}{D_a + 2} - \frac{D_b - 1}{D_b + 2}\right] \qquad (5)$$

ν_a, ν_b being ν_{max} of the solute molecule in each solvent, D_a, D_b dielectric constants of a and b. To check this relation we chose ethyl ether and acetonitrile for a and b. The refractive index is 1.356 for ethyl ether and 1.344 for acetonitrile, the two values being nearly equal. Moreover, the absorption spectra of these solvents are similar to each other in that they have no strong absorption above 2000 Å. and the dispersion term contribution from them is expected to be nearly equal.[4] On the other hand they have quite different values of dielectric constant, 4.3 for ethyl ether and 37.5 for acetonitrile. These circumstances indicate that ethyl ether and acetonitrile constitute a very suitable pair for the purpose of checking equation 5.

The ν_{max} of the $n-\pi^*$ bands of acetone, mesityl oxide, acetophenone and benzophenone were measured in solvents consisting of ethyl ether and acetonitrile mixed in various proportions. Figs. 2, 3, 4 and 5 are obtained for acetone, mesityl oxide, acetophenone and benzophenone, respectively. In each of them differences between the ν_{max} for

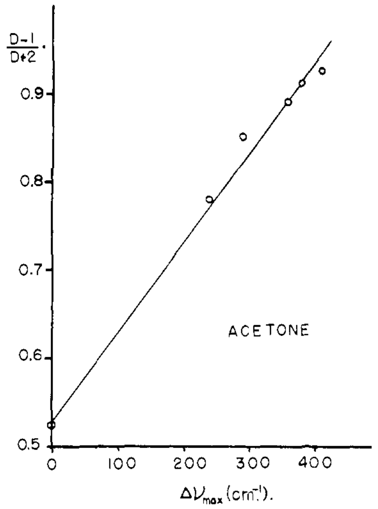

Fig. 2.—Relation between frequency difference of $n-\pi^*$ band of acetone in ethyl ether and in mixed solvent containing acetonitrile ($\Delta\nu_{max}$) and $(D - 1)/(D + 2)$ of the mixed solvent.

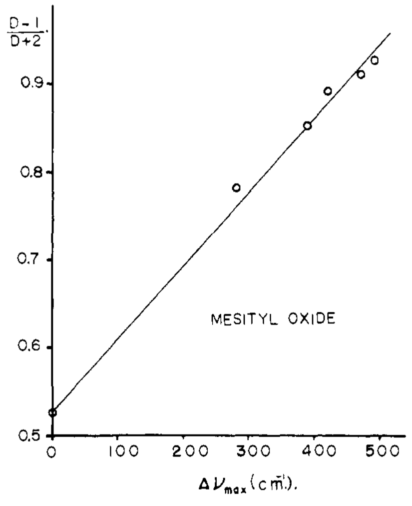

Fig. 3.—Relation between $\Delta\nu_{max}$ and $(D - 1)/(D + 2)$ for mesityl oxide.

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[8] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

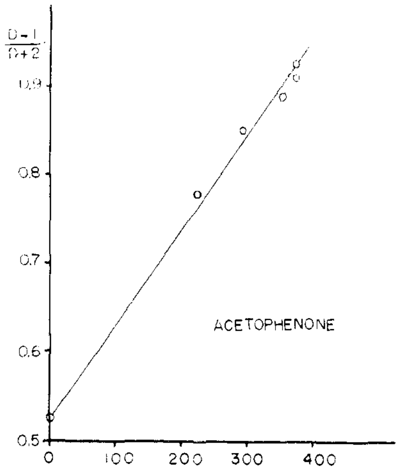

Fig. 4.—Relation between $\Delta\nu_{\max}$ and $(D - 1)/(D + 2)$ for acetophenone.

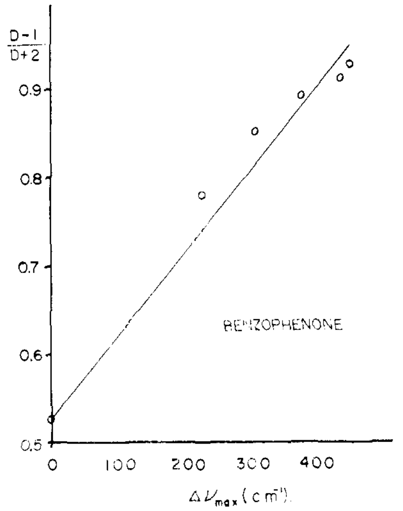

Fig. 5.—Relation between $\Delta\nu_{\max}$ and $(D - 1)/(D + 2)$ for benzophenone.

ethyl ether and those for the mixed solvents are plotted against $(D - 1)/(D + 2)$ of the latter.[9] The approximate linearity is apparent for every ketone investigated as expected from equation 5. Large deviations of points for benzophenone from the straight line probably arise from neglecting the quadratic Stark effect. From the slopes of the straight lines, the values of C in equation 5 are obtained. From these combined with equation 4 we may evaluate $\mathbf{M}_{00}^{u}(\mathbf{M}_{00}^{u} - \mathbf{M}_{ii}^{u})$ if the values of a^3 are known. Assuming a^3 proportional to the molecular volume, the relative ratio of $\mathbf{M}_{00}^{u}(\mathbf{M}_{00}^{u} - \mathbf{M}_{ii}^{u})$ for the four ketones is calculated as

Acetone		Mesityl oxide		Acetophenone		Benzophenone
1	:	1.8	:	1.4	:	2.8

A simple molecular orbital (m.o.) treatment of the $n-\pi^*$ transition in ketones also predicts just this relative order (see Appendix). That the dipole moment of ketones decreases generally very much in the process of the $n-\pi^*$ transition may be a consequence of the more extended π-conjugation.

It is difficult to evaluate the absolute magnitude of the dipole moment of a molecule in an excited state, since the appropriate a values are not easily determined and the direction of dipole vectors in the ground and excited states are not in general the same. Taking tentatively a = 4 Å.[11] for acetophenone and assuming that the ground state and the excited state dipoles are parallel, the excited state dipole moment of acetophenone is calculated to be 0.5 D. The excited state dipoles of mesityl oxide and benzophenone are expected to have values smaller than this. Anyhow, the excited state dipole moments of ketones are much smaller than their ground state values which are about 3 D. for the ketones investigated here. This fact indicates that the stabilization energies arising from the electrostatic interactions between the solute and solvent molecules are much smaller in the excited states than in the ground states. Consequently the main factor causing the blue shift of the $n-\pi^*$ absorption of ketones in polar solvents is the great stabilization in the ground states due to electrostatic interactions between solute and solvent molecules.

3. Effects of Hydrogen Bonding.—Abnormally large blue shifts of the $n-\pi^*$ absorption are observed when alcohols are used as solvents. For example, the $n-\pi^*$ absorption of benzophenone shifts to the blue by about 1200 cm.⁻¹ on changing the solvent from n-hexane to ethanol. This is much greater than expected from only the electrostatic origin. The contribution of electrostatic interactions to the frequency shift can be evaluated from equation 2, but as the refractive index of ethanol is close to that of ethyl ether or acetonitrile, equation 5 may be employed instead. From the C value for benzophenone and the dielectric constant of ethanol, the frequency shift between the $\nu_{\max}$ of benzophenone in n-hexane and in ethanol is calculated to be about 550 cm.⁻¹. Accordingly, the electrostatic interactions explain only about one half of the observed blue shift, leaving the remaining 650 cm.⁻¹ unexplained. This remaining portion of the shift probably will be accounted for on the basis of hydrogen bonding between benzophenone and ethanol molecules.

To check the formation of hydrogen bonds, infrared absorption spectra of the ketones were measured in carbon tetrachloride and ethanol mixture with various mixing ratios. The absorption curve for the C=O stretching vibration of benzophenone is shown in Fig. 6 as an example. The intensity of the higher frequency band decreases, while that of the lower frequency band increases with increasing concentration of ethanol. It is evident that these two bands correspond to free and hydrogen bonded molecules and since ethanol can be associated by itself to form polymers, many types of hydrogen bonded complexes are possible between ketone and ethanol.

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(9) Dielectric constant of a mixed solvent was calculated by $D = D_0 + bW$,[10] where D_0 is the value of dielectric constant of ethyl ether, b the difference in dielectric constants of ethyl ether and acetonitrile and W the weight fraction of acetonitrile in the solution.

(10) J. Hoigné and T. Gäumann, *Helv. Chim. Acta*, **41**, 1933 (1958).

(11) Assuming the value of a 1 Å. greater for acetophenone than for benzene for which a = 3 Å. is usually assumed.

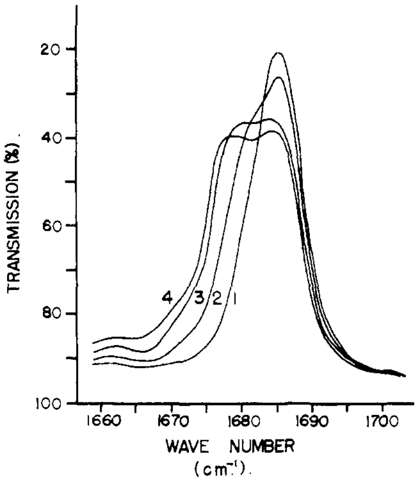

Fig. 6.—Effect of ethanol on the C=O stretching vibrational band of benzophenone: solutions of benzophenone, 0.12 mole/l., in carbon tetrachloride–ethanol solvent; ethanol in volume per cent., curve 1, 0, curve 2, 10, curve 3, 50, curve 4, 100%.

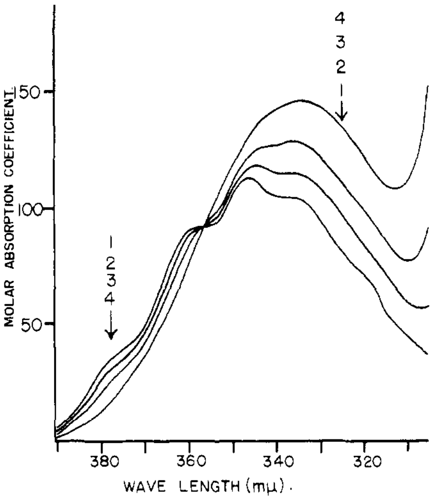

Fig. 7.—Effect of ethanol on the n–π^* absorption spectrum of benzophenone: solutions of benzophenone, 5.3×10^{-3} mole/l., in hexane–ethanol solvent; ethanol in volume per cent: curve 1, 0, curve 2, 5, curve 3, 20, curve 4, 80%.

As an aid to determine which type of complexes could be formed predominantly in ethanol solution, the concentration effect of ethanol on the n–π^* absorption spectra of ketones were examined. The latter were measured carefully in n-hexane and ethanol mixtures with 0, 5, 10, 20, 30, 50 and 80% volume per cent. of ethanol. Concentration of the solute was kept constant in a series of measurements for each ketone (5.3×10^{-3} mole/l. for benzophenone, 1.4×10^{-2} mole./l. for acetophenone, 1.7×10^{-2} mole/l. for mesityl oxide). Some of the absorption curves obtained for benzophenone as an example are shown in Fig. 7. It is found that all the curves (including the ones not shown in Fig. 7) have a common crossing point,[12] although Brealey and Kasha[2] did not observe such an isosbestic point in their measurements for benzophenone. We also observed similar isosbestic points for mesitvl oxide and acetophenone with the ethanol concentration range from 0 to 80%. Such isosbestic points may well be expected generally for systems involving two molecular species in equilibrium. An isosbestic point would most probably mean the coexistence of only two kinds of solute species in the solution.[2] In our case one of the species is free ketone and the other is hydrogen bonded ketone; the latter is most probably the 1:1 complex between ketone and ethanol. The formation of 1:2 or higher complexes seems to be unlikely and may be excluded. From the above arguments, the ethanol solution of each ketone can be regarded as a mixture consisting of solutions of free and hydrogen bonded ketone species. These two kinds of ketone species would show different n–π^* spectra. Free molecules in ethanol solution are expected to give absorption at the position predicted by equation 2, since only electrostatic interactions are operative. In the case of benzophenone, absorption by free molecules in ethanol will occur at a position shifted by about 550 cm.$^{-1}$ to the blue relative to that of n-hexane solution. On the other hand, absorption by bonded molecules in ethanol should appear at a frequency still higher than the observed $\nu_{\max}$, since the observed $\nu_{\max}$ would correspond roughly to the mean of $\nu_{\max}$ of free and bonded molecules. As the observed blue shift of benzophenone n–π^* absorption in ethanol is about 1200 cm.$^{-1}$, as stated above, relative to n-hexane solution, the difference of 650 cm.$^{-1}$ must be regarded as the lower limit of the contribution from the effect of hydrogen bonding.

In this way abnormally large blue shifts often observed in n–π^* spectra of ketones on changing solvents from non-polar to polar liquids such as alcohols can be interpreted as the result of coöperating effects of both electrostatic and hydrogen bonding interactions on solute molecules.

4. Relation Between Solvent-Induced Frequency Shift of n–π^* Absorption and Infrared C=O Stretching Band.—As seen from Table I, $\nu_{\max}$ increases in the order of solvents n-hexane, ethyl ether, carbon tetrachloride, benzene, dioxane, methyl acetate, acetonitrile, chloroform, isobutyl alcohol and ethanol for all the ketones examined, with the exception of acetone, as solutes. Although acetone shows an irregularity with respect to the order of non-polar solvents, it behaves quite in line with other ketones against polar solvents. In the infrared study of solvent effects on C=O stretching vibration frequencies, using the same series of ketones, just the same order of solvents was found.[13] The relation between the solvent-induced frequency shifts of n–π^* absorption and those of corresponding C=O vibrational bands is shown in Fig. 8, in which only benzophenone is chosen as an example for the purpose of illustration.

The linear relationship between n–π^* absorption and infrared C=O frequencies, as seen in this

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[12] After submitting this manuscript, we learned that R. S. Becker had reported (*J. Mol. Spectroscopy*, **3**, 1 (1959)) on the existence of the similar crossing point for the benzophenone–cyclohexane-valeronitrile system.

[13] M. Ito, K. Inuzuka and S. Imanishi, in *J. Chem. Phys.*, **31**, 1694 (1959).

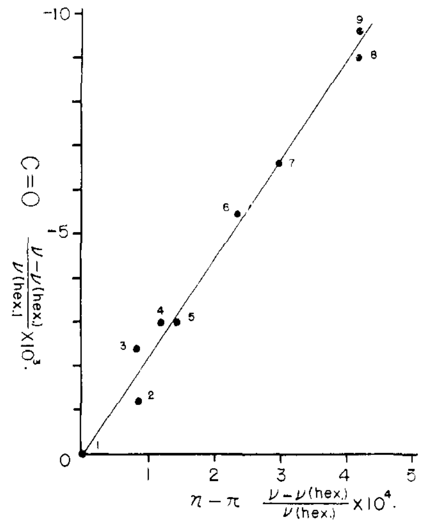

Fig. 8.—Relation between the relative shifts of the C=O vibrational bands and the n–π^* electronic absorptions of benzophenone in various solvents: 1, n-hexane; 2, ethyl ether; 3, carbon tetrachloride; 4, benzene; 5, dioxane; 6, acetonitrile; 7, chloroform; 8, isobutyl alcohol; 9, ethyl alcohol.

figure, may be understood by the following consideration. The dipole moment of a ketone molecule decreases very much as a consequence of n–π^* excitation as stated above. In addition, an excited molecule possesses a very small hydrogen bonding power since after the n–π^* transition process an electron is removed from the n-orbital and the one remaining electron is not sufficient to sustain the hydrogen bond. Then the stabilization energy of the excited solute molecule contributed by electrostatic and/or hydrogen bonding interaction with solvent molecules becomes very small and the excited state energy of the solute molecule may be approximately equal to that in the absence of such interactions. Thus the magnitude of n–π^* blue shift is mainly determined by the stabilization energy of the ground state. Since the solvent-induced frequency shift of an infrared C=O band can be regarded as a measure of the stabilization energy in the ground state, the observed linear relation between n–π^* and C=O frequencies seems quite natural.

Appendix

To estimate the changes in dipole moment of ketones during the n –π^* transition, a simple m. o. treatment was made. In an n –π^* transition, one of the non-bonding electrons originally localized on the O atom is removed and is raised into an empty antibonding π-orbital. Then $\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u$, the change in the solute dipole vector caused by the transition can be interpreted as the moment arising from the transfer of an n-electron into the π-orbital. The dipole moment of the molecule in the ground state is expressed by the sum of three moments

$$\mathbf{M}_{00}{}^u = \mathbf{M}_\sigma{}^u + \mathbf{M}_\pi{}^u + \mathbf{M}_n{}^u$$

where $\mathbf{M}_\delta{}^u$, $\mathbf{M}_\pi{}^u$ and $\mathbf{M}_n{}^u$ are moments contributed by σ-, π- and n-electrons, respectively. In ketones $\mathbf{M}_n{}^u \approx 0$, since the n-oribital has its axis perpendicular to the C=O group, the latter providing nearly the whole of the ground state moment.

In the excited state the dipole moment is given by

$$\mathbf{M}_{ii}{}^u = \mathbf{M}_\sigma{}^u + \mathbf{M}_\pi{}^u + \mathbf{M}_{\pi'}{}^u$$

where $\mathbf{M}_{\pi'}{}^u$ is the moment contributed by an electron in the antibonding π-orbital which has come from the n-orbital by the n–π^* transition. It follows, then

$$\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u = -\mathbf{M}_{\pi'}{}^u$$

$\mathbf{M}_{\pi'}{}^u$ may be calculated from the coefficients of atomic orbitals in the lowest empty π-molecular orbital. Accordingly an m.o. calculation was made, using the values of α and β adopted by Orgel, *et al.*[14] In order to compare the result with observation, the scalar product $\mathbf{M}_{00}{}^u(\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u)$[15] was calculated, assuming that the direction of the dipole vector in the ground state is along the C=O axis, since the major part of the dipole moment of a ketone molecule comes from the C=O group. If θ is the angle between the directions of the C=O axis and $\mathbf{M}_{\pi'}{}^u$, $\mathbf{M}_{00}{}^u(\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u)$ is approximately proportional to $\mathbf{M}_{\pi'}{}^u \cos\theta$. The relative ratio of $\mathbf{M}_{00}{}^u(\mathbf{M}_{00}{}^u - \mathbf{M}_{ii}{}^u)$ for acetone, etc., comes out as

Acetone	Mesityl oxide	Acetophenone	Benzophenone
1 :	2.1 :	1.7 :	2.2

in good agreement with observation described above.

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[14] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

[15] See equations 1 and 4.