Effect of Solvent on Carbonyl Stretching Frequency of Ketones

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It is well known that ketones and aldehydes show characteristic infrared absorption bands assignable to the C=O stretching vibration of molecule. In our previous works[1,2] we studied the solvent effect on $n-\pi^*$ absorption bands of some ketones on the basis of a theoretical equation proposed by McRae[3]. In these studies we found a certain relationship between the solvent-induced shift of the ultraviolet $n-\pi^*$ absorption frequencies and that of infrared C=O frequency. It is found in the present work that the same McRae's equation can also be applied to the interpretation of the solvent shift of the C=O stretching frequency for both nonpolar and polar solvents. The intensity of the C=O stretching vibration is influenced by the polarity of the solvent. The magnitude of the bond moment derivative measuring the infrared absorption intensity increases for polar solvents, especially for solvents which tend to form hydrogen bonds with the solute molecules. However, this intensification for the C=O bands is not so large as for the OH bands. In this paper we intend to estimate the bond moment derivative for the C=O bond and its increase on hydrogen bonding.

Experimental

Infrared absorption measurements of ketones were made with a Hitachi E. P. I double beam spectrophotometer with an sodium chloride prism, using 0.1 mm. cell. Solvent effects were observed for acetone, mesityl oxide, acetophenone and benzophenone. The solvents used were *n*-hexane, ethyl ether, carbon tetrachloride, benzene, dioxane, acetonitrile, chloroform, *iso*-butyl alcohol and ethyl alcohol. They were purified by the methods recommend by Weissberger and Proskauer[4]. Special care was taken to remove contaminating water in the solvents. Acetone was purified by the above method. Highest quality commercial mesityl oxide and acetophenone were further purified by repeated distillations. Benzophenone was recrystallized several times from ethanol.

Results and Discussion

The positions of the carbonyl bands of four ketones in the different solvents are given in Table I. The refractive index and dielectric constant of the solvents are given in Table II. It is seen that the carbonyl frequency in a given solvent decreases in the order of acetone, mesityl oxide, acetophenone and benzophenone. This is just the order of increase of the amount of conjugation in the respective molecules. The observed parallelism between the carbonyl frequency and the extent of conjugation may be interpreted as a result of the lowering of the double bond character of the carbonyl bond with increasing conjugation. Kirkwood and Magat[5] related the frequency shift in the infrared absorption of a solution to the dielectric constant D of the solvent by a formula

TABLE I. FREQUENCIES (cm^{-1}) OF C=O VIBRATION BANDS OF KETONES IN VARIOUS SOLVENTS

Solvent	Acetone	Mesityl oxide	Acetophenone	Benzophenone
n-Hexane	1727	1702	1701	1673
Ethyl ether	1725	1699	1697.5	1671
Carbon tetrachloride	1723	1697.5	1695	1669
Benzene	1721.5	1695	1693	1667
Dioxane	1720	1694	1693	1667
Acetonitrile	1718	1692.5	1691	1664
Chloroform	1715.5	1690	1687	1662
iso-Butyl alcohol	1714.5	1687	1684	1658
Ethyl alcohol	1713.5	1686	1683	1657

TABLE II. REFRACTIVE INDEX AND DIELECTRIC CONSTANT OF THE SOLVENTS

Solvent	n_D	D
n-Hexane	1.375	1.89
Carbon tetrachloride	1.460	2.238
Dioxane	1.422	2.209
Benzene	1.501	2.284
Ethyl ether	1.356	4.335
Acetonitrile	1.344	37.5
Chloroform	1.449	4.806
iso-Butyl alcohol	1.398	17.7
Ethyl alcohol	1.361	24.3

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[1] M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).

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

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

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

[5] W. West and R. T. Edwards, *J. Chem. Phys.*, **5**, 14 (1937); E. Bauer and M. Magat, *J. Physique Radium*, **9**, 319 (1938).

$$\Delta\nu/\nu = C(D-1)/(2D+1)$$

where ν is the frequency of an absorption band, and C is a constant. This equation has been checked experimentally for a number of substances, and it generally holds only for nonpolar solvents. The linear relation is shown in Fig. 1, in which the shift of the carbonyl stretching frequency of the ketones investigated is plotted against the value $(D-1)/(2D+1)$ of nonpolar solvents. However, such a linearity is no longer seen for polar solvents. In the case of non-hydrogen bonding polar solvents, the dipole moment effect of the solvent must be taken into consideration. In our previous paper¹⁾ on the solvent effect on the $n-\pi^*$ absorption of ketones, observed shifts were well explained by McRae's equation as mentioned above. In the same paper it was found that the solvent induced shift of the infrared carbonyl frequency relates linearly in turn with that of the ultraviolet $n-\pi^*$ absorption frequency of the same ketone. It is then expected that the solvent effect on the carbonyl frequency itself may also be explained by the same McRae's equation. With polar solvents for which D is no longer equal to n^2, the above equation tells us that if n of all the solvents used are nearly equal, the solvent induced frequency shift must be proportional to $(D-1)/(D+2)$. We took mixtures of ethyl ether and acetonitrile in various ratios as the solvents satisfying the above condition. While the n values of ethyl ether and acetonitrile are nearly the same, their D values are quite different from each other. The $\Delta\nu$ vs. $(D-1)/(D+2)$ relations are shown in Figs. 2—5 for the ketones investigated, in which the approximate linearity is clearly seen for each substance.

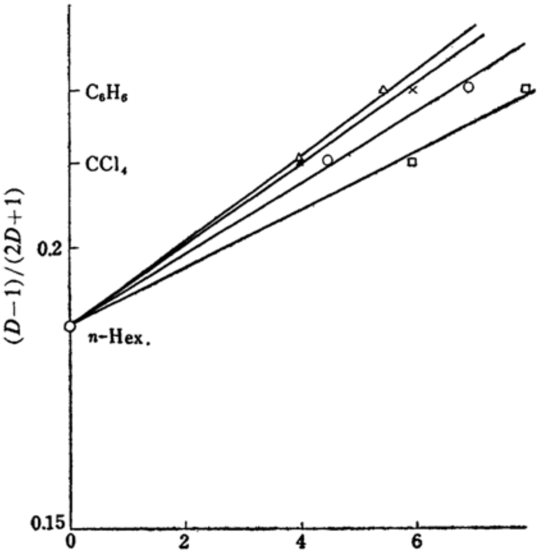

Fig. 1

From the above results it may be understood that the following McRae's equation holds well for both the cases of polar and nonpolar solvents.

$$\Delta\nu = A(n^2-1)/(2n^2+1) + B\{(D-1)/(D+2)-(n^2-1)/(n^2+2)\}$$

in which A and B are constants characteristic of the solute molecule. For nonpolar solvents D is nearly equal to n^2, thus the second term

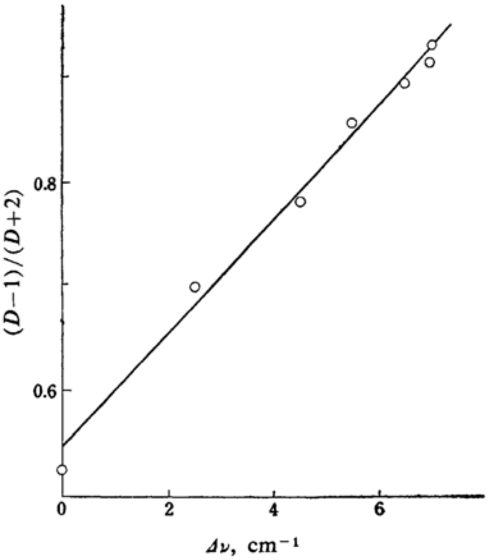

Fig. 2

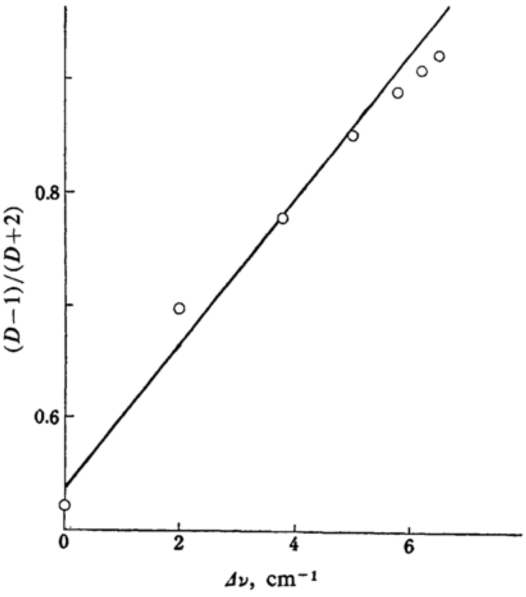

Fig. 3

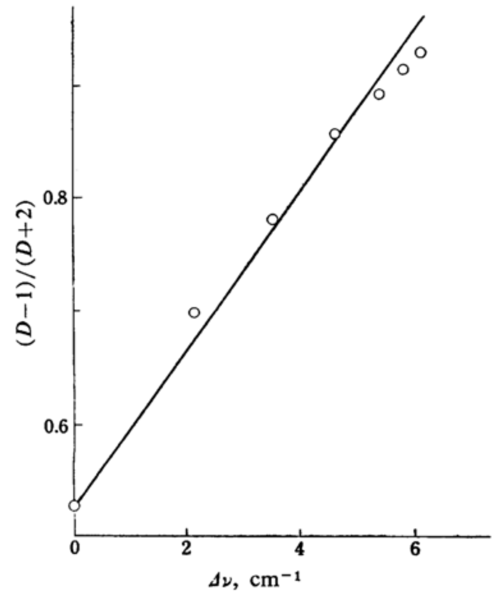

Fig. 4

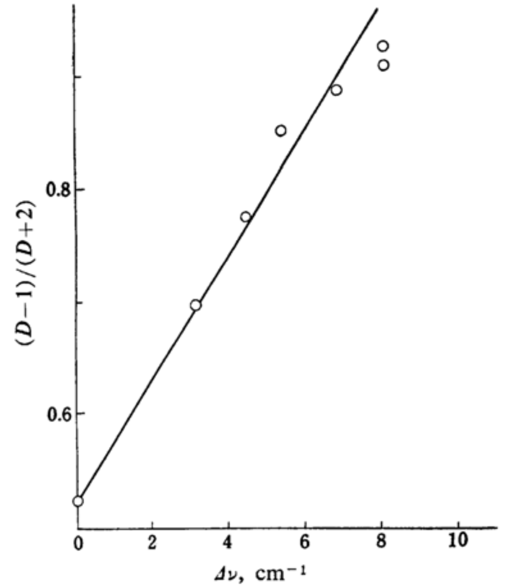

Fig. 5

vanishes. Substituting n^2 with D in the first term we obtain an equation identical with the one derived by Kirkwood and Magat. Fig. 6 shows a comparison between the observed shifts for benzophenone and those calculated from the McRae's equation, putting 65 and 9 cm^{-1} for A and B, respectively. It is seen that the points for most solvents, except those having possibilities for forming hydrogen bonds with the solute molecule, drop near to the theoretical line. For hydrogen bonding systems large deviations occur, which may be interpreted as due to the hydrogen bonding, as this effect

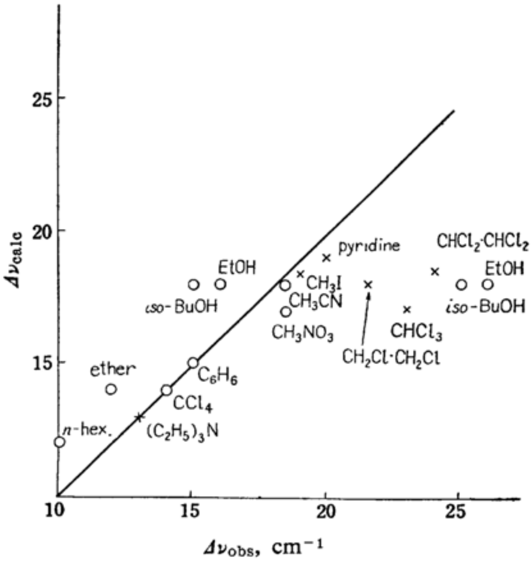

Fig. 6

is not taken care of at all by the McRae's equation. The carbonyl frequency suffers larger shifts in hydrogen bonding than in nonhydrogen bonding solvents, but this shift is much smaller than that of the hydroxyl frequency due to the same cause. In the benzophenone and ethyl alcohol system the hydroxyl frequency of the alcohol diminishes by about 150 cm^{-1}, while the decrease of the carbonyl frequency of benzophenone is only about 15 cm^{-1}. Recently Bellamy et al.[6,7] studied the solvent effect on C=O and OH bands of several molecules in various mixed solvents, suggesting that the local association effect is the dominant factor in producing the frequency shift, and that the electrostatic properties of the medium as a whole does not play an important role. If the solvent effect is principally due to the local association, two different bands will be expected for a system in which two kinds of solvents are present. Fig. 7 shows the change of the C=O frequency of mesityl oxide on changing the mixing volume ratio of ethyl ether and acetonitrile in the solvent. The band maximum changes in succession with the mixing ratio suggesting that the shift depends on the dielectric constant of the medium. The same situation obtains for acetophenone, acetone and benzophenone. These observations favor the view emphasizing the importance of dielectric constant in the solvent effect. However, the possibility of local association may not be excluded, as our experiment is not accurate enough for it.

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6) L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, 55, 220 (1959).

7) L. J. Bellamy and R. L. Williams, ibid., 55, 14 (1959).

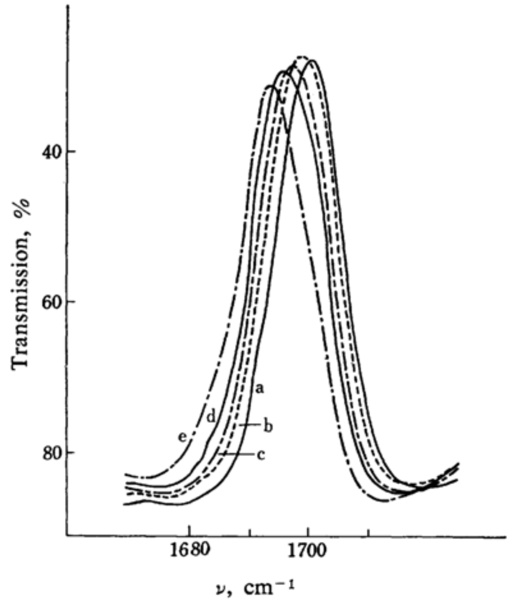

Fig. 7

On the other hand, for simplification we assumed that the C=O stretching vibration in these ketones is localized at this group and almost independent of the rest of the molecule. Therefore the normal coordinate Q contains only the pure carbonyl stretching vibration.

Then

$$\mathrm{d}\mu/\mathrm{d}r=(1/m_c+1/m_o)^{-1/2}\mathrm{d}\mu/\mathrm{d}Q$$

where μ is the dipole moment, Q the normal coordinate, m_c and m_o the masses of the carbon and oxygen atoms and r the distance between the C and O atoms.

From the observed intensities A in l. mol⁻¹ cm⁻² the change in the dipole moment with respect to the normal coordinate Q is given by

$$\mathrm{d}\mu/\mathrm{d}Q=\pm(3c^2\times 1000\ A/N\pi)^{1/2}$$

where c is the light velocity and N is the Avogadro number. Table III summarizes the values of $\mathrm{d}\mu/\mathrm{d}r$ calculated as above. They fall in the range between 4 and 6 D/Å, and show that the bond moment derivative increases with the increasing polarity of the solvent as well as with the increasing amount of conjugation, with the exception of mesityl oxide. However, the difference of the bond moment derivative for the bond of ketones in nonpolar and polar solvents is only about 1 D/Å, much smaller than the corresponding change of the OH bond moment derivatives of alcohols.

TABLE III. BOND MOMENT ($\times 10^{-10}$ e.s.u./cm.) DERIVATIVES OF KETONES IN VARIOUS SOLVENTS

Solvent	Acetone	Mesityl oxide	Aceto-phenone	Benzo-phenone
n-Hexane	4.54	4.10	4.80	5.36
Ethyl ether	4.67	4.13	5.09	5.45
Dioxane	4.67	4.41	5.28	5.58
Benzene	4.70	4.41	5.29	5.45
Carbon tetrachloride	4.87	4.50	5.45	5.32
Acetonitrile	4.87	4.28	5.64	5.60
iso-Butyl alcohol	5.07	4.41	6.72	5.56
Ethyl alcohol	5.11	4.41	5.81	5.60
Chloroform	5.28	4.54	5.81	5.81

Theoretical Calculation of dμ/dr for Ketones.—According to Coulson the value of $\mathrm{d}\mu/\mathrm{d}r$ can be evaluated from the bond polarizability defined on the simple MO theory for a π electron system. We have assumed that there is no appreciable change in the σ electron cloud during the C=O stretching vibration. Treating the acetone molecule as diatomic $\mathrm{d}\mu/\mathrm{d}r$ is expressed by

$$\mathrm{d}\mu/\mathrm{d}r=\mathrm{d}(\mathrm{q}er)/\mathrm{d}r=r_0\boldsymbol{e}(\mathrm{d}q/\mathrm{d}r)_0+q_0\boldsymbol{e}$$

where $\boldsymbol{e}$ is the electronic charge, q the formal charge density on the oxygen atom, r_0 the equilibrium distance of the C=O bond and q_0 the formal charge density for $r=r_0$. As q is a function of the exchange integral for the carbonyl bond

$$\mathrm{d}q/\mathrm{d}r=\mathrm{d}q/\mathrm{d}\beta\cdot\mathrm{d}\beta/\mathrm{d}r=\pi_{\mathrm{o,co}}\mathrm{d}\beta/\mathrm{d}r$$

where β is the exchange integral between the oxygen and carbon atoms, and $\pi_{\mathrm{o,co}}$ the atom-bond polarizability defined by Coulson et al.[8], which is calculable from the coefficients in the molecular orbital function. If we use the relation $\beta_{\mathrm{co}}=k/r^6$ as given by Kon[9] we obtain

$$\mathrm{d}\mu/\mathrm{d}r=r_0\boldsymbol{e}\pi_{\mathrm{o,co}}(-6\ \beta_{\mathrm{co}}/r_0)+q_0\boldsymbol{e}$$

for which $\pi_{\mathrm{o,co}}$ and q_0 have been calculated by the simple MO treatment for the C=O group*. If we take $r_0=1.23$ Å we obtain

$$\mathrm{d}\mu/\mathrm{d}r=8.4\ \mathrm{D/Å}$$

Instead, if the SCF molecular orbital calculated by Nagakura[10] is employed,

$$\mathrm{d}\mu/\mathrm{d}r=8.3\ \mathrm{D/Å}$$

is obtained. These calculated values are different from the observed 5 D/Å but the discrepancy is due to the rough approximation. As mentioned previously $\mathrm{d}\mu/\mathrm{d}r$ tends to be increased with the increase of the polarity of the solvent, the value of $\mathrm{d}\mu/\mathrm{d}r$ for solvents forming hydrogen

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[8] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

[9] H. Kon, This Bulletin, **28**, 275 (1955).

* Using the values of Coulomb integrals of carbon and oxygen atoms $\alpha_c=\alpha+0.2\beta$ and $\alpha_o=\alpha+2\beta$, respectively, and the carbonyl exchange integral $\beta_{co}=1.4\beta$[11], 3.1D is obtained as the value of the dipole moment of acetone, in agreement with the experimental 2.7D.

[10] S. Nagakura, ibid., **25**, 164 (1952).

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

bonds with the ketone molecule increases by about 1 D/Å compared with the case of nonpolar solvents.

Now, we may assume for a hydrogen bonding system the following two resonance forms

$$\mathrm{O{-}H\cdots O{=}C} \qquad \Phi_n \qquad \mathrm{I}$$

$$\mathrm{O^{-}H{-}O^{+}{=}C} \qquad \Phi_p \qquad \mathrm{II}$$

and represent the ground state wave function of the hydrogenbonded complex by

$$\Phi=\Phi_n+c_p\Phi_p$$

where c_p measures the extent of the charge-transferred form II to the system. During the C=O vibration c_p changes continuously. If the dipole of Φ_p is represented by μ_p, the dipole moment μ_T contributed by II is given by

$$\mu_T=\mu_p\cdot c_p{}^2$$

yielding

$$\begin{aligned} \mathrm{d}\mu_T/\mathrm{d}r_{co} &= \mathrm{d}(\mu_p c_p{}^2)/\mathrm{d}r_{co} \\ &= \mu_p \mathrm{d}c_p{}^2/\mathrm{d}r_{co}+c_p{}^2\mathrm{d}\mu_p/\mathrm{d}r_{co} \end{aligned}$$

For simplicity of calculation, we assume that firstly a C atom is fixed in a C=O vibration of acetone molecule $(CH_3)_2{=}C{=}O$ because of the great mass ratio of a $(CH_3)_2{=}C$ group to an O atom, and secondly a hydrogen bond $OH\cdots O{=}C$ is linear.

Since $\mathrm{d}r_{co}=-\mathrm{d}r_{o\cdots o}$ in the present approximation,

$$\mathrm{d}\mu_T/\mathrm{d}r_{co}=-\mu_p\mathrm{d}c_p{}^2/\mathrm{d}r_{o\cdots o}-c_p{}^2\mathrm{d}\mu_p/\mathrm{d}r_{o\cdots o}$$

Substituting $r_{OH}=1$ Å, $r_{o\cdots o}=3$ Å, and the estimated c_p value12) into the above equation, we obtain

$$\mathrm{d}\mu_T/\mathrm{d}r_{co}=1.2\ \mathrm{D/Å}$$

Thus the increase of intensity due to hydrogen bonding is 1.2 D/Å, in good agreement with the observed 1 D/Å.

Summary

The C=O stretching frequencies in acetone, mesityl oxide, acetophenone and benzophenone were measured in various solvents and the frequency shifts induced by solvents were interpreted by McRae's theoretical equation. Results show that the observed shifts can be explained in terms of the coöperating interactions between solute and solvent molecules.

Next, the intensity of the C=O group vibration bands of these ketones was observed and compared with bond moment derivatives calculated by diatomic molecular appoximation. Small changes of about 1 D/Å were observed for polar and nonpolar solvents. The increase of the bond moment derivative value in a hydrogen bonding system was attributed to the charge transfer force.

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12) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 245 (1954).