Molecular Complexes between Ketones and Alkali Salts

By Haruka YAMADA

(Received December 14, 1959)

Sodium or lithium perchlorate and sodium iodide have high solubilities in ketones. These salts form a sort of molecular complex with ketones. From infrared studies[1,2] it has been shown that the change of the ketone band with salt concentration differs from that in general solvation case, and the non-complexed ketone band is replaced by the shifted band of the complexed ketone; namely, one absorption maximum falls gradually in intensity to be replaced by another. Further, it has been shown that the separation between the complexed and non-complexed ketone bands is independent of anion species. Based on these facts, it has been understood that the formation of the complex is due to the bonding between the $C=O$ group and metallic cation.

These complexes are of interest, because they will give information upon the covalent bond formation, besides the other intermolecular interactions such as ion-dipole, dipole-dipole interaction, London force etc., of alkali metallic ions with some electron donor molecules. The present studies are undertaken to elucidate the electronic states of the complexes.

In ultraviolet absorption spectra, the shifts caused by the formation of the complexes are measured for the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands. In order to know whether or not the experimental results obtained here are interpreted based on the theory of charge transfer complex[3], the covalent characters and the stabilization energies of the complexes have been estimated by use of Pauling's " bond-length " relation[4]. By these estimated values, the $n\rightarrow\pi^*$ transition energies of the complexes have been calculated and compared with the observed data.

Experimental

Ultraviolet absorption spectra were taken with a modified* Perkin-Elmer Model 112 Infrared Spectrophotometer equipped with LiF prism. A H_2-lamp and a 1P28 photomultiplier were used as light source and detector, respectively. Wavelength calibration was made by means of the spectra of Hg-lamp and benzene vapor. Cells had quartz windows and lead Spacers. The thickness of the cell was measured by interference method. Spectral slit width ranged from 10 cm^{-1} to 20 cm^{-1}.

Infrared spectra were taken with the spectrophotometer mentioned above, by use of CaF_2 prism.

Organic compounds were purified by fractionating after drying. Guaranteed commercial anhydrous sodium iodide was used without further purification. Anhydrous sodium perchlorate was obtained heating $NaClO_4\cdot H_2O$ in an air bath. Lithium perchlorate was prepared by neutralizing lithium carbonate with a slight excess of 60% perchlorate acid, and digesting the mixture on a hot plate until evolution of carbon dioxide ceased, and a clear solution remained. The solution was heated to remove excess acid and the white solid remained. The salt was dehydrated by heating in vacuo to approximately 100°C over phosphorus pentoxide. The anhydrous salts were stored in the dark in a desiccator. Measurements were made for pure ketones and the ketone solutions of the salts. No diluent was added, as no suitable solvent for the complexes was found.

Experimental Results

Infrared Absorption Spectra.—The wave numbers for $C=O$ stretching bands are tabulated in Table I. From this table, it can be seen that the wave numbers for the NaI- and the $NaClO_4$-ketone system are about the same and that the observed shifts are larger for lithium salt than for sodium salt and exhibit a similarity between the acetone- and the cyclohexanonesalt system.

TABLE I. WAVE NUMBERS FOR $C=O$ STRETCHING BANDS

	Pure liquid	NaI-ketone complex	$NaClO_4$-ketone complex	$LiClO_4$-ketone complex
Acetone	1717	1709	1710	1702
Cyclohexanone	1714	1706	1706	1702
Acetophenone	1685	(1684)	(1680)	(1677)

Ultraviolet Absorption Spectra.—The curves obtained for the $NaClO_4$- and the $LiClO_4$-acetone systems both in 1 : 4 mole ratio are shown in Fig. 1. The non-complexed acetone band attributed to the $n\rightarrow\pi^*$ transition has a maximum at 36400 cm^{-1}. By the addition of the salt the band shifts to higher frequencies with

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[1] A. D. E. Pullin and J. McC. Pollock, *Trans. Faraday Soc.*, **54**, 11 (1958).

[2] H. Yamada, This Bulletin, **33**, 666 (1960).

[3] R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); ibid., **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[4] L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

* Thanks are due to Mr. W. Suëtaka and Mr. S. Saito for their help in this modification.

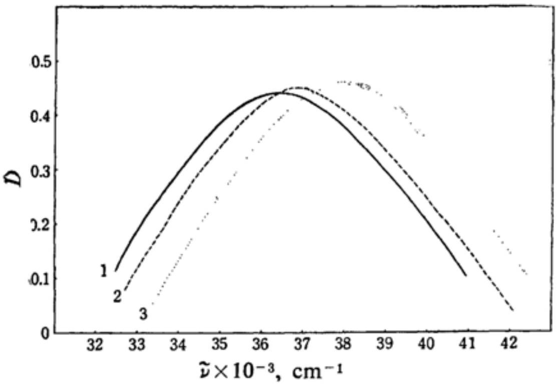

Fig. 1. $n\rightarrow\pi^*$ bands of acetone and acetone-salt solutions.
1. Pure acetone.
2. Acetone-$NaClO_4$ solution (in 4 : 1 mole ratio).
3. Acetone-$LiClO_4$ solution (in 4 : 1 mole ratio).

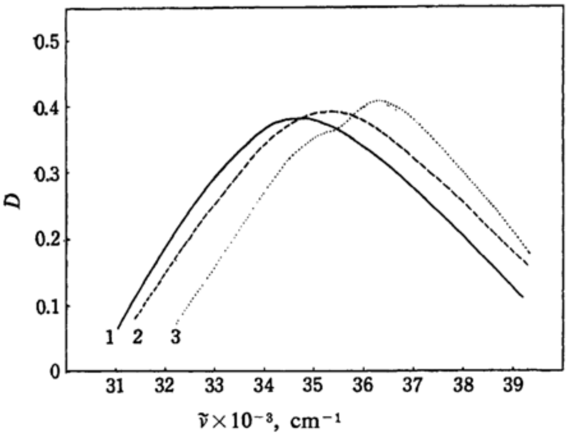

Fig. 2. $n\rightarrow\pi^*$ bands of cyclohexanone and cyclohexanone-salt solutions.
1. Pure cyclohexanone.
2. Cyclohexanone-$NaClO_4$ solution (in 4 : 1 mole ratio).
3. Cyclohexanone-$LiClO_4$ solution (in ca. 6.5 : 1 mole ratio).

the maximum at 36900 cm^{-1} for the $NaClO_4$-acetone system and at 38000 cm^{-1}for the $LiClO_4$-acetone system. The band for the $LiClO_4$-acetone system shows a contour with two peaks at a lower perchlorate concentration. In 1 : 4 mole ratio, almost all the acetone molecules are, therefore, regarded as forming the complex with the salt. For the $NaClO_4$-acetone system the separation between acetone and the complex bands is relatively small and the variation of band contour is not found for changing mole ratio.

The observed curves for the $NaClO_4$- and the $LiClO_4$-cyclohexanone system are shown in Fig. 2. The $n\rightarrow\pi^*$ band maximum of cyclohexanone at 34700 cm^{-1} shifts to 35300 cm^{-1} by the addition of $NaClO_4$ and to 36400 cm^{-1} by that of $LiClO_4$. The curves for the $LiClO_4$-cyclohexanone system measured for various concentrations are shown in Fig. 3. Each band shows the contour of two components. Since all these curves intersect at about 35600 cm^{-1} and the number of cyclohexanone molecules in unit volume, calculated from the specific gravity of the solution, is almost constant over this range of concentration, this point at about 35600 cm^{-1} is the so-called isosbestic point for the $LiClO_4$-cyclohexanone system.

The curves for the $NaClO_4$- and the $LiClO_4$-acetophenone system are shown in Fig. 4. Acetophenone shows a $\pi\rightarrow\pi^*$ band together with the $n\rightarrow\pi^*$ band in ultraviolet region. Although the solubilities of the salts in acetophenone are relatively low, the shifts are observed distinctly. By adding the salt the $n\rightarrow\pi^*$ band, having a maximum at 31250 cm^{-1}, shows the blue shift similar to the $n\rightarrow\pi^*$ bands of the other ketones. The red shift of the $\pi\rightarrow\pi^*$ band was observed, although the band maximum was difficult to determine owing to the high intensity. As shown in Fig. 4, the peak of $n\rightarrow\pi^*$ band for the $LiClO_4$-acetophenone system is hardly ever found in 1 : 10 mole ratio and can not be found in 1 : 6 mole ratio, because it is covered with the $\pi\rightarrow\pi^*$ band shifted to lower frequencies.

Although it might be expected from the results of infrared studies that the ultraviolet spectrum of the sodium iodide-ketone system is similar to that of the sodium perchlorate-ketone system, it is not actually the case.

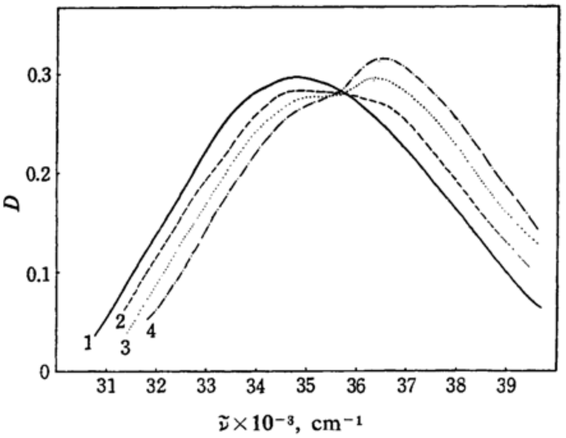

Fig. 3. Curves for cyclohexanone-$LiClO_4$ solutions in various concentrations (27.2 μ cell).
1. Pure cyclohexanone.
2. ca. 15 : 1 mole ratio.
3. 8.1 : 1 mole ratio.
4. 6.5 : 1 mole ratio (saturated).

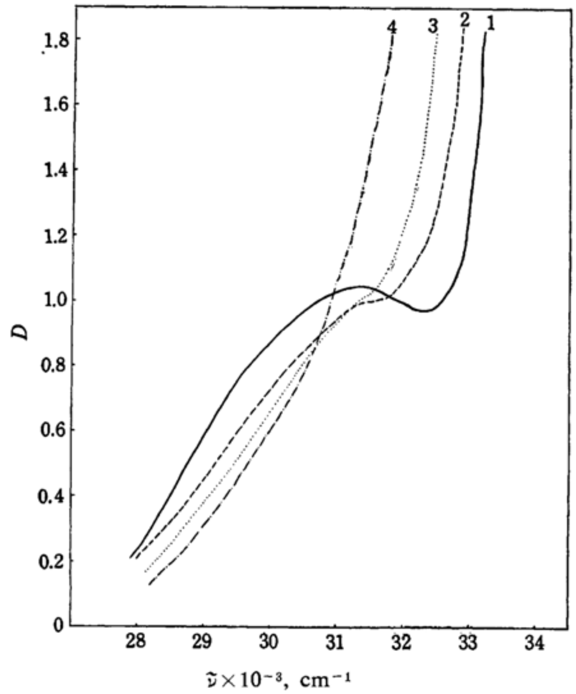

Fig. 4. Spectra of acetophenone and acetophenone-salt solutions.

1. Pure acetophenone.
2. Acetophenone-$NaClO_4$ solution (in ca. 12 : 1 mole ratio).
3. Acetophenone-$LiClO_4$ solution (in ca. 10 : 1 mole ratio).
4. Acetophenone-$LiClO_4$ solution (in ca. 6 : 1 mole ratio).

The curve measured for the sodium iodide-ketone system, however, has a strong absorption ranging from about 31000 cm^{-1} to higher frequencies, which is probably caused by the iodide ion in the solution.

The $n\rightarrow\pi^*$ blue shift and $\pi\rightarrow\pi^*$ red shift phenomena observed here are similar to but generally much larger than those usually observed as general solvent effects. The band contours can be separated into two components. These phenomena are just like those observed for the hydrogen bond formation.

Interpretations

Infrared Spectra.—Although only the C=O bands are shown in Table I, the slight changes for the other ketone bands were also found similar to the sodium iodide-acetone complex[2]. From the fact that the $NaClO_4$-ketone and NaI-ketone complexes show the same frequencies, it follows that the formation of the complexes is independent of anion species. The solubilities of the salts in acetophenone are low and the spectra of the saturated solutions are not those of the complexes but those of the complexed acetophenone overlapped with the non-complexed one. The observed shifts for the acetophenone-salt systems, therefore, are small.

Covalent Contribution to the Intermolecular Bond.—By considering a charge transfer force between C=O group and metallic ion, besides the other intermolecular interactions such as ion-dipole, dipole-dipole interaction, London force etc., the intermolecular bonding is expressed as a resonance between following two structures.

$$(\mathrm{A})\quad \mathrm{C{=}O}\quad \mathrm{M^+}$$

$$(\mathrm{B})\quad \mathrm{C{=}\overset{+}{O}{-}M}$$

The structure A expresses a no-bond structure and the structure B dative one which is formed by the transfer of the lone pair electrons of oxygen atom to the cation.

To estimate the contribution of the B structure to the complex, Pauling's "bond-length" relation[4] seems to be useful for the complex[5], since this relation holds for intermetallic compounds and also for organic compounds. The relation is represented by

$$R(n)-R(1)=-C\log_{10}n$$

Here, R expresses the atomic radius, n is the number of shared electron pairs involved in the bond and is proportional to the bond order[5], and C a constant. As for the bond length L the following formula is obtained from the formula described above.

$$L(n)-L(1)=-2C\log_{10}n$$

The values of $L(n)$ are estimated to be 2.15 and 2.46 Å for O—Li$^+$ and O—Na$^+$ bonds, respectively. These values are the same as those obtained for $LiClO_4\cdot3H_2O$[6a] and $Na_3SbS_4\cdot9H_2O$[6b] or $Na\cdot Al(SO_4)_2\cdot12H_2O$[6c] crystals in which the Li$^+$ or Na$^+$ ion combines with the ligands of six water molecules by the coordination of the lone pair electrons of oxygen atoms. As C is usually 0.30 for intermetallic compounds and 0.35 for organic compounds, the mean value of them, 0.325, is used for these complexes. By use of the usual covalent radii for $R(1)$[7], the relation $L(1)=R_O(1)+R_M(1)$ and the values of $L(n)$, the values of n are obtained. The suffixes O and M refer to

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[5] Coulson and Danielson applied in to the hydrogen bonds to estimate the contribution of the B structure, and reported that the results obtained agreed satisfactorily with the results calculated by a semi-empirical method. C. A. Coulson and U. Danielson, *Arkiv För Fysik*, **24**, 239 (1954).

[6] a) C. D. West, *Z. Krist.*, **88**, 198 (1934).
b) A. Grund and A. Preisnger, *Acta Cryst.*, **3**, 363 (1950).
c) H. Lipson, *Proc. Roy. Soc.* (*London*), **A151**, 347 (1935).

[7] The covalent radii used are $R_O(1)=0.66$, $R_{Li}(1)=1.34$ and $R_{Na}(1)=1.54$Å.

oxygen and metal, respectively. From the meaning of n, the following formula should hold for the complexes,

$$b^2 = n \times (\text{covalent character of the } L(1) \text{ bond})$$

Since the covalent character of the $L(1)$ bond can be estimated from the difference between the electronegativities of two atoms, the covalent character of $L(n)$ bond, b^2, is calculated. The results are contained in Table II.

TABLE II

	n	Difference of electronegativities	Covalent character of the $L(1)$ bond	b^2
$O-Li^+$	0.59	2.5	22%	0.13
$O-Na^+$	0.40	2.6	20%	0.08

The covalent character of $O-Li^+$ is 13% and that of $O-Na^+$ 8%. It can be seen that these complexes mainly consist of the no-bond structure and the covalent character of $O-Li^+$ is about 1.5 times that of $O-Na^+$.

Stabilization Energy of the Complex.—By use of the amount of contribution of the B structure obtained above, the stabilization energy of the complex per one ketone molecule was estimated. According to Mulliken[3], the ground state wave function of the complex is written by

$$\Psi_N = a\phi_A + b\phi_B$$

and the stabilization energy of the complex in ground state is given by

$$W_{AA} - W_N = (W_{BB} - W_{AA}) b^2/a^2$$

where ϕ_A is the no-bond wave function and ϕ_B the dative one,

$$W_{AA} = \int \phi_A \mathrm{H} \phi_A d\tau$$

$$W_{BB} = \int \phi_B \mathrm{H} \phi_B d\tau = I_P - E_A + V$$

In this case, I_P is the ionization potential of the oxygen atom for lone pair electrons, E_A the electron affinity of the metallic ion and V the energy of the covalent bond between the oxygen atom and the ion. Although the exact values of I_P and E_A are not available, the following ones seem to be reliable, i.e. $I_P = 10.1$ eV., $E_A = 5.39$ eV. for Li^+ and 5.14 eV. for Na^+. The energy V may be expressed by Morse's function, i. e.

$$V = D_e(e^{-2a(L-L_e)} - 2e^{-a(L-L_e)}),\ L_e = L(1)$$

where the dissociation energy, D_e, is given by the geometric mean of the bond energies $D(O-O)$ and $D(M-M)$, and a is determined by Badger's rule.

$$a = (k/2D_e)^{1/2}$$

where k expresses the force constant.

TABLE III

	D_e (kcal./mol.)	k (dyne/cm.)	a (Å^{-1})	V (eV.)
$O-Li^+$	30.8	0.808×10^5	1.37	−1.29
$O-Na^+$	25.3	0.847×10^5	1.55	−0.977

The formation energy of the complex bond, namely the stabilization energy of the lone pair electrons is determined as follows.

$$W_{AA} - W_N = (I_P - E_A + V) b^2/a^2$$
$$= 0.51 \text{ eV. } (O-Li^+)$$
$$0.34 \text{ eV. } (O-Na^+)$$

where W_{AA} is taken to be zero.

Computation of the $n \rightarrow \pi^*$ Transition Energies of the Acetone-salt Complexes.—By taking into account the stabilization energies, the $n \rightarrow \pi^*$ transition energies of the complexes can be calculated. As the energy level of lone pair electrons is approximately expressed by the coulomb integral of oxygen atom, the stabilization energy of the complex is due to the decrease of the coulomb integral of oxygen atom. The stabilized energy level may be expressed by

$$\alpha_O' = \alpha_O + (W_{AA} - W_N)/2$$

Here, α_O expresses the coulomb integral of oxygen atom. As for the other numerical values required for the computations, Nagakura's values[8] for acetone molecule are used. They are, $X_C = 2.5$, $X_O = 3.5$, $k = 4.1$, $\alpha_C = 4.35\beta$, $\alpha_O = 5.44\beta$ and $\beta_{CO} = 0.838\beta$ in his notation. The calculated results are shown in Table IV(A), in which the $n \rightarrow \pi^*$ transition energy is expressed by $E_2 - \alpha_O'$. In Table IV(B) the calculated $n \rightarrow \pi$ transition energies are shown in wave number unit, together with the observed data. Here, $\beta = 2.84$ eV. $= 23000$ cm^{-1}. It seems more reasonable to compare the calculated

TABLE IV

(A)

	Acetone	$NaClO_4$-acetone complex	$LiClO_4$-acetone complex
E_1	5.895β	5.94β	5.96β
E_2	3.895	3.91	3.92
α_O'	5.44	5.50	5.53
$E_2 - \alpha_O'$	−1.55	−1.59	−1.61

(B)

	Acetone	$NaClO_4$-acetone complex	$LiClO_4$-acetone complex
Cal.	35600	36600	37000
Obs.	35800 (in non-polar solvent) 36400 (in liquid)	36900	38000

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[8] S. Nagakura, This Bulletin, 25, 164 (1952).

value for acetone with the observed value in non-polar solvent than that in liquid.

Although the formation of the complexes is mainly due to the no-bond structures, the $n \rightarrow \pi^*$ blue shift phenomenon is interpreted by use of the results calculated by considering the charge transfer interaction.

The author wishes to express her sincere thanks to Professor K. Kozima for his kind guidance.

Research Laboratory of Spectroscopy
Tokyo Institute of Technology
Meguro-ku, Tokyo