ON DIPOLE–DIPOLE INTERACTIONS IN SOLUTIONS OF COMPOUNDS WITH CARBONYL GROUPS

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When investigating dipole–dipole interactions the majority of investigations pay most attention to the influence of the mean field of molecules in solution on the parameters of a band of a given oscillator [1-3]. The results of studies in which fine structure detected in the ν(C =O) band of the IR spectrum of certain ketones and which have been explained, in particular, by the presence of an equilibrium between monomeric molecules and molecules associated by a dipole–dipole mechanism, are apparently unreliable [4]. In the present communication the interaction of molecules containing a carbonyl group with molecules possessing a large dipole moment has been investigated by IR spectroscopy. Solutions of carbonyl compounds in CCl_4 were studied in the presence of tetraalkylammonium halides and in acetonitrile in certain cases. To reduce errors linked with atmospheric absorption the work was conducted at a point in a diffraction spectrometer with a small amount of diffuse light [5], the monochromator of which was dried with phosphoric anhydride.

In Fig. 1, (a) represents the IR absorption spectrum in the ν(C =O) region of acetophenone in a solution containing $(C_8H_{17})_4NI$. It is seen that on introducing a salt molecule ($\mu \simeq$ 10 to 12 D) into the solution, the ν(C =O) band at 1692 cm^{-1} acquires doublet structure; a new band appeared on the low frequency side at 1688 cm^{-1}, the intensity of which grew with increasing salt concentration. In spite of the small size of the shift ($\sim$4 cm^{-1}) the fact that the displacement of the band is distinct does not raise doubt since there are no absorption bands due to atmospheric water in the range 1696-1685 cm^{-1}. As was recorded in [4] the cause of the appearance of the apparent splitting of the ν(C =O) band is included in precisely this. An increase in solution temperature leads to a weakening of the 1688 cm^{-1} band and a strengthening of the 1692 cm^{-1} band; these changes with temperature are reversible. This indicates the presence in solution of an equilibrium between two types of acetophenone molecule viz., free and bonded with salt molecules. In the presence of dioxan or triethylamine a discrete band shift is not observed which indicates the absence of interactions of a donor–acceptor bill.

The distinct displacement of the ν(C =O) band on interaction with salts was also observed for γ-butyrophenone, benzophenone (Fig. 1, b), and methyl vinyl ketone. In all cases the shift to lower frequency amounted to 4-6 cm^{-1}. A similar picture was observed on the band at 1688 cm^{-1} for dimethylformamide (Fig. 1b), and the lower frequency on forming a complex with Bu_4NBr amounted to 8 cm^{-1}. A distinct shift - of the ν(C = O) band of dimethylformamide also arose on interaction with acetonitrile which indicates the formation of a complex of an electrostatic type. A distinct shift has been observed previously on the ν(C $\equiv$ N) band of acetonitrile [6] and the ν(P = O) band of phosphine oxide [7] on interaction with salts.

In the presence of ammonium salts the ν(C =O) band of aliphatic ketones (acetone, methyl ethyl ketone, diethyl ketone, and cyclohexanone) is displaced to lower frequency by approximately 4 cm^{-1} and its half-width is increased. The frequency of the band in esters (ethyl formate, benzyl acetate, and dioctyl phthalate) is reduced by 1-2 cm^{-1}; the increase in half width is also less than in ketones. It is interesting that the band parameters of $(CH_3)_3CCOCH(CH_3)_2$ are unchanged in the presence of salt which is seemingly caused by steric hindrance towards the interaction. Clearly the structure expressed for the band in esters and ketones was not observed; therefore, there is no basis for explaining the picture obtained as the manifestation of an equilibrium between molecules which are free or interacting with salt.

Analysis of the data obtained showed that the maximum size of band shift on interaction with salts, which register in the spectrum as a splitting of this band, are observed for compounds in which the frequency

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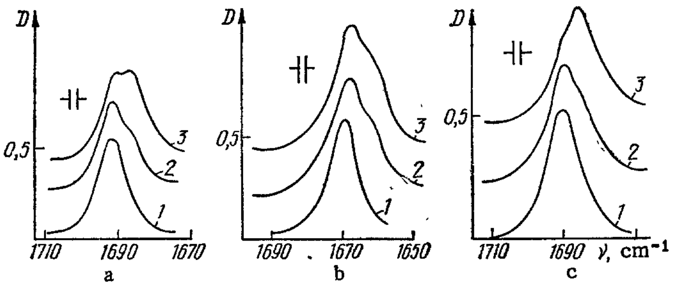

Fig. 1. IR spectra of solutions (0.02 M) in CCl_4: a) acetophenone 1) without additions, 2) and 3) with added 0.02 and 0.2 M $(C_8H_{17})_4NI$ respectively; b) benzophenone 1) without additions, 2) and 3) with added 0.5 M $(C_4H_9)_4NBr$ at temperatures of 47 and 16°C respectively; c) dimethylformamide 1) without additions, 2) and 3) with added 0.3 and 1.0 M acetonitrile respectively.

of ν(C =O) lies relatively low, i.e., in the range 1660-1700 cm^{-1}. The presence of delocalization of the π electrons of the C =O bond (resonance effect) is a characteristic of these compounds and this leads to an increase in the polarity of the C =O bond in comparison with aliphatic ketones, for example. For molecules in which ν(C =O) lies higher at 1780-1810 cm^{-1} (acetyl chloride, methyl trifluoracetate, significant changes were not observed in the frequency and shape of the ν (C =O) band in the presence of salt. The high frequency of ν (C =O) in these compounds reflects the lowering of the polarity of the C =O bond due to the inductive effect and the field effect. In esters the increase in bond polarity due to the resonance effect is compensated by the inductive effect of the ester oxygen which also apparently causes the intermediate character of the observed spectral picture. We record that the shift of ν (C =O) has a tendency to increase with the growth of the dipole moment of the compounds being investigated. All compounds showed no sign of association with dioxane or triethylamine.

The results of the present study, and also of the studies in [6-8], show that oriented van der Waals interactions of dipolar molecules may lead to the formation of molecular complexes, the dissociation energy of which significantly increases the size of kT even at temperatures of the order of 300°K. These data supplement the existing concept of van der Waals molecules (see review [9]) and demonstrate the convention of the spectral criterion (distinct or smooth shift of frequency), frequently used for the identification of interaction type.

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