which accounts for the formation of ethylene and products of complete oxidation, depending on the oxygen content in the gaseous phase.

LITERATURE CITED


STUDY OF INTERMOLECULAR INTERACTIONS OF ALDEHYDES WITH TRIALKYLPHOSPHINE OXIDES FROM ABSORPTION SPECTRA IN THE INFRARED REGION


The H-bonds of aldehydes (acetaldehyde and its mono-, di-, and trichloro derivatives) acting as proton donors in solutions and in carbon tetrachloride were studied by IR absorption spectroscopy. Triethylphosphine oxide, one of the strongest acceptors, was used as the proton acceptor. The investigations were carried out in the frequency region of $\nu$(C-H) of aldehydes and $\nu$(P=O) of phosphine oxide. It was found that changes in the spectra corresponding to an H-bond formation are observed only in the case of chlorine derivatives of acetaldehyde, and they are most evident in the case of chloral. This corresponds to the increase in the protonation of the C-H group hydrogen by the action of a constantly increasing inductive effect with increase in the degree of chlorine substitution. It was shown that a characteristic feature of the H-bond with the participation of the aldehydes studied is the appearance of a doublet in the $\nu$(C-H) region with a $\sim 100$ cm$^{-1}$ splitting having Fermi resonance nature.

In discussing the molecular association of aldehydes as a result of local intermolecular interactions, the possibility most frequently accepted in the literature is the participation of the aldehyde group CHO in the complexation as a proton acceptor in the H-bond [1]. At the same time, the proton-donor capability of the aldehyde C-H group is still disputed. Thus, in [2, 3] the observed indications of perturbations of frequencies of the C-H stretching vibrations in the spectra of o-substituted benzaldehydes are interpreted as the result of the existence of an intramolecular hydrogen bond. In [4] a high frequency shift was observed of the $\nu$(C-H) band in the spectra on transition from gaseous form aldehyde to the crystalline phase. However the authors believe that the intermolecular interaction leading to such spectroscopic effects, is not the hydrogen bonding. Direct spectroscopic proof of the participation of the aldehyde group C-H proton in the formation of the intermolecular hydrogen bonds was reported in [5] for a mixture of trichloracetaldehyde with pyridine and...
Fig. 1. Absorption spectra of solutions of acetaldehyde (1, 2: \(C = 0.5\) mole/liter, d = \(2.6 \cdot 10^{-2}\) cm), mono- (3, 4: \(C = 0.2\) mole/liter, d = \(3.9 \cdot 10^{-2}\) cm), di- (5, 6: \(C = 0.1\) mole/liter, d = \(4 \cdot 10^{-1}\) cm), trichloracetaldehyde (7, 8: \(C = 0.5\) mole/liter, d = \(2.6 \cdot 10^{-2}\) cm) in CCl₄ and in CCl₄ + Et₃PO mixtures containing phosphine oxide at concentrations (mole/liter): 0.39 (2); 0.2 (4); 0.02 (6); 0.39 (8).

Fig. 2. Absorption spectra of solutions (0.5 mole/liter) of trichloroacetaldehyde in CCl₄ (1) and in CCl₄ + Et₃PO mixtures containing phosphine oxide at concentrations (mole/liter): 0.1 (2); 0.39 (3); d = \(3.9 \cdot 10^{-2}\) cm.

in [6] for a mixture of trichloroacetaldehyde with azine. The ambiguity concerning the conclusions on the proton-donor properties of the aldehydes may be due to two reasons: the relatively low value of the observed spectroscopic effects [7] and the absence of a reliable interpretation of the spectra in the stretching vibration region of the C-H group.

In the present work, triethylphosphine oxide (Et₃PO) was used as a proton acceptor in the investigation of the proton-donor capability of the aldehydes [8, 9]. Because of its high polarity [10], the P=O group of this compound is one of the strongest proton acceptors in the H-bonding [11, 12]. To observe the H-complexes C-H...O=P, the spectra of solutions in CCl₄ containing an aldehyde and the Et₃PO groups in given ratios were studied.

The absorption spectra of the solutions studied in the frequency region of the stretching vibrations of the C-H (2600-2950 cm⁻¹) and P=O groups (1050-1250 cm⁻¹) were obtained on a UR-20 IR spectrometer. To determine the accurate parameters of the overlapping absorption bands, the experimental spectra were processed using an EC-1020 computer.

Figure 1 shows the absorption spectra of solutions of a series of simple aldehydes in CCl₄, and a mixture of carbon tetrachloride with triethylphosphine oxide, from which it is seen that the presence of trialkylphosphine oxide in the ternary system in fairly large amounts practically does not influence the spectra of acetaldehyde solutions. In the spectra of the chlorine-substituted analogs, definite changes are observed under the influence of the phosphine oxide molecules — a broad absorption band appears in the 2700 cm⁻¹ region, the intensity of the band with a maximum at 2850 cm⁻¹, which we attributed to the stretching vibrations of the C-H groups of monomeric molecules of the aldehydes, increases. Since this observation is somewhat unusual for complexation through a hydrogen bond, in order to establish the character of the intermolecular interactions in the aldehyde-trialkylphosphine system, we studied the absorption spectra of the ternary systems both in the frequency region of the stretching vibrations of the proton-donor C-H group and in the stretching vibrations region of the proton-acceptor P=O group. Solutions of trichloracetaldehyde were studied in detail, since this compound is clearly characterized by the highest degree of protonation of the C-H group hydrogen atom in the series of chlorinated aldehydes.

Figure 2 shows that with the addition of triethylphosphine oxide to a solution of trichloroacetaldehyde in CCl₄, the absorption intensity substantially increases over a wide range of frequencies. A new maximum appears in the spectrum with a frequency of 2715 cm⁻¹,