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Abstract

Full Text

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MOLECULAR COMPOUNDS OF DIPHENYLCYCLOPROPENONE, TROPONE, AND BENZOPHENONE WITH HYDROGEN CHLORIDE

Using the method of infrared absorption spectra, we investigated the intermolecular interaction of ketones that do not have an enol form with HCl. The objects studied were diphenylcyclopropenone (DPCP), tropone, and benzophenone. The first two substances are of interest because they contain three- and seven-membered rings, which readily pass into a cationic form and, it would seem, are capable of stronger interaction with HCl.

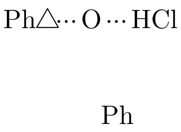
Fig. 1. Infrared absorption spectra: *a* –DPCP + HCl in $CHCl_3$, $t = 20°$; $C_{\text{DPCP}} = 6.6 \cdot 10^{-2}$ mol/l; *b* –the same at $t = 52°$; *c* –DPCP in chloroform, $t = 30°$, $C_{\text{DPCP}} = 6.8 \cdot 10^{-2}$ mol/l; *d* –DPCP pressed in KBr, $t = 30°$.

The infrared absorption spectrum of DPCP was recorded in solutions of CCl_4, C_2Cl_4, $CHCl_3$, and C_6H_6, through which gaseous HCl was passed. The temperature range studied was from 10 to 60°. The concentration of HCl in solution was determined by titration. As is seen from Fig. 1, when HCl is passed through a solution of DPCP in $CHCl_3$, the intense absorption in the region of 1845 cm^{-1} (corresponding to the stretching vibration of the carbonyl group ([1])) and 1623 cm^{-1} (stretching vibration of the C=C bond in the cyclopropenone ring) is greatly decreased, and a new intense band appears at about 1420 cm^{-1}.

The intensity of absorption in the region of the stretching vibrations of the $C \cdots C$ and C–H bonds of the phenyl rings increases considerably, although the frequencies remain practically unchanged. Absorption appears in the region of 2780 cm^{-1}, as well as a number of other less intense bands, the positions of which are indicated in Table 1. When the temperature is raised from 20 to 50° (Fig. 1), the intensity of the new bands decreases and the spectrum approaches that of individual DPCP in chloroform (a similar picture is also observed in other solvents).

From the temperature dependence of the integral intensity of the carbonyl band (in the concentration range $10^{-2} \div 10^{-4}$ mol/l), the enthalpy (ΔH), entropy (ΔS), and free energy (ΔF) of the formation reaction of the molecular compound (I) were estimated; they proved to be, respectively:

$$\Delta H = -6000 \text{ cal/mol}, \qquad \Delta S = -14 \text{ entropy units.}$$



$$\mathrm{Ph}\triangle\cdots\mathrm{O}\cdots\mathrm{HCl} \quad (I)$$

$$\mathrm{Ph}$$

Table 1

Frequencies of IR absorption bands of DPCP, tropone, and molecular compounds with HCl and HBr (cm^{-1})

DPCP, frozen in KBr	DPCP in CHCl$_3$, $c = 6.8\cdot10^{-2}$ mol/l	DPCP + HCl in CHCl$_3$, $c = 6.4\cdot10^{-2}$ mol/l	DPCP + HBr, crystal	Tropone	Tropone + HCl, crystal	Tropone + HBr, crystal	DPCP, frozen in KBr	DPCP in CHCl$_3$, $c = 6.8\cdot10^{-2}$ mol/l	DPCP + HCl in CHCl$_3$, $c = 6.4\cdot10^{-2}$ mol/l	DPCP + HBr, crystal	Tropone	Tropone + HCl, crystal	Tropone + HBr, crystal
513				492	504	505	1625	1623	1505*	1511			
687				580	595	592	1760	1760	1572*	1575			
702				715	707	710	1780	1780	1597	1598	1525	1510	1512
764				790	785	789	1807	1807	1620	1650	1590	1612	1618
786				840	855	860	{1840	{1840	1807		1640		
1023				908	938	944	{1855	{1850	{1840		1708		
1082				1025	960	985	1887	1887	{1850				
{1165				1221	1229	1230				2380			2393
{1180				1260	1254	1251			2780*			2790	
1314				1315	1295	1285			2820				
1344	1343	1340		1416	1345	1335						2950	
1446	1447	1420*	1416	1478	1495	1410		2960	2960	2960			2960
1485	1485	1448	1452			1460	3030				2997		
1594	1595	1483	1482			1492							

* Frequencies belonging to the molecular compound are marked.

ed., and $\Delta F = -1840$ cal/mol. The experiments showed that ΔH, ΔS, and ΔF do not depend on the nature of the solvents used by us.

It is significant that in the spectrum there is no absorption in the region of the stretching vibrations of the OH group, while absorption near 2780 cm^{-1} indicates the presence in solution of undissociated, but perturbed, HCl molecules. The experimental data presented, in our opinion, show that a hydrogen bond is formed between DPCP and HCl. A stronger interaction with formation of an OH bond and the appearance of two ions apparently does not occur.

In the spectrum an intense band with frequency 1420 cm^{-1} is observed, corresponding, in our opinion, to the bond C O. The disappearance of the band near 1623 cm^{-1} (the high intensity of which is due to conjugation of the C=C bond with two phenyl rings) indicates equalization of the bonds in the three-membered ring. The increase in absorption in the region of vibrations of the C=C bonds (1597 cm^{-1}) and C–H (2960 cm^{-1}), without a noticeable shift of the frequencies, indicates a change in the electron density in the phenyl rings (^{2}). Formation of a hydrogen bond leads to a marked lowering of the frequency of the stretching vibration of HCl. If in chloroform solution $\nu_{\mathrm{HCl}} = 2820\ \mathrm{cm}^{-1}$, then in the molecular compound $\nu_{\mathrm{HCl}} = 2780\ \mathrm{cm}^{-1}$.

In the case of tropone we investigated the IR spectrum of the crystalline compound that is obtained by passing gaseous HCl through a benzene solution (^{3}) (see Table 1). In the spectrum the carbonyl band with frequency 1590 cm^{-1} (^{1}) is absent, and in the region of 1495 cm^{-1} an intense band appears which, apparently, corresponds to the C O bond. In the region of 2790 cm^{-1} there is absorption corresponding to the perturbed vibration of the HCl molecule; absorption in the region of the stretching vibrations of OH is absent.

These data show that in the case of tropone as well a molecular compound (II) is formed through a hydrogen bond.

$$\text{(tropone)} \cdots \mathrm{O} \cdots \mathrm{HCl} \quad \text{(II)}$$

It was not possible to measure ΔH for the formation of this molecular compound, since no suitable inert solvent was found. It should be noted that molecular compound (II) is readily soluble in water and tetrahydrofuran, and the spectrum recorded in these solvents proved to be the spectrum of individual tropone. This means that dissolution of the molecu-

polar compound, for example, in tetrahydrofuran, leads to regeneration of pure tropone:

$$\text{tropone} \cdots \mathrm{HCl} + \mathrm{C_4H_8O} \rightleftharpoons \text{tropone} + \mathrm{C_4H_8O} \cdots \mathrm{HCl}$$

The enthalpy of formation of the complex $\mathrm{C_4H_8O} \cdots \mathrm{HCl}$ is $\sim 9 \div 10$ kcal/mole (according to preliminary results obtained in our laboratory). Regeneration of

Fig. 2. Contours of carbonyl bands.

Figure 2: Fig. 2. Contours of carbonyl bands.

tropone from compound (II) by the action of H_2O, C_4H_8O confirms the presence between tropone and HCl of only a hydrogen bond. An analogous result was obtained in the case of DPhCP. The frequencies of the IR spectra of crystalline compounds of DPhCP and tropone with HBr are given in Table 1. In this case molecular compounds are also formed.

Fig. 2. Contours of carbonyl bands. I: *a*—benzophenone in C_2Cl_4, $C_{\mathrm{BPh}} = 1.9 \cdot 10^{-3}$ mole/l, $t = 30°$; *b*—benzophenone + HCl in C_2Cl_4, $C_{\mathrm{BPh}} = 1.9 \cdot 10^{-3}$ mole/l, $C_{\mathrm{HCl}} = 7 \cdot 10^{-2}$ mole/l, $t = 25°$; *v*—the same at $t = 55°$. II: *g*—DPhCP in CCl_4, $C = 1.1 \cdot 10^{-3}$ mole/l, $t = 10°$; *d*—the same at $t = 55°$. III: *e*—DPhCP in $CHCl_3$, $C = 5 \cdot 10^{-4}$ mole/l, $t = 10°$; *zh*—the same at $t = 55°$.

Upon saturation of a benzophenone solution with gaseous HCl, no substantial changes are observed in the spectrum of the latter. Only the contour of the band corresponding to the carbonyl bond, with frequency 1664 cm^{-1}, changes; near it a peak appears with frequency 1642 cm^{-1} (Fig. 2), attributable to vibrations of the $C = O$ group perturbed as a result of formation of a weak hydrogen bond. The exceptionally large lowering of the vibration frequency of the carbonyl group of tropone and DPhCP as a result of formation of a molecular compound with HCl and HBr is noteworthy. Such frequency shifts were observed only in the formation of complexes of ketones with compounds of the type $AlCl_3$, $SnCl_4$, $TiCl_4$ (4). Thus, for example, in the complexes $AlCl_3$—benzophenone $\nu_{C \cdots O} = 1515\ \mathrm{cm}^{-1}$, acetone–$SnCl_4$ $\nu_{C \cdots O} = 1545\ \mathrm{cm}^{-1}$. Formation of a hydrogen bond between ordinary ketones and acetic, formic, and hydrohalic acids lowers the vibration frequency of the CO group by $15 \div 30\ \mathrm{cm}^{-1}$.

In the case of diphenylcyclopropenone and tropone, the tendency toward formation of stable aromatic systems of cyclopropenylium and tropylium leads to a very large lowering of the vibration frequency, probably as a consequence of a decrease in the bond order of $C = O$.

It should be noted that in a number of works (3,5) it is assumed that, upon interaction of tropone and DPhCP with gaseous HCl, HBr, and HI, salt-like compounds are formed, containing ions (III), for example,

$$\text{cyclopropenylium/tropylium-type cation—O—H and } Cl^- \quad \text{(III)}$$

The absence in the IR absorption spectrum, in the region of stretching vibrations of the OH group, of absorption; the presence of a band with frequency 2780 cm^{-1}, attributable to undissociated HCl molecules; the small reaction enthalpy ($\Delta H = -6000$ cal/mol), characteristic of the interaction of ketones and ethers with HCl (6); and the regeneration of ketones under the action of water

Fig. 3. Absorption of tropone in the region 2700-3600 cm^{-1} in C_2Cl_4 solution: a –C_trop = 0.27 mol/l; b –C_trop = 4.6 • 10^{-2} mol/l

Figure 3: Fig. 3. Absorption of tropone in the region 2700-3600 cm^{-1} in C_2Cl_4 solution: a –C_trop = 0.27 mol/l; b –C_trop = 4.6 • 10^{-2} mol/l

and tetrahydrofuran indicate, it seems to us, that the interaction is limited solely to the formation of a hydrogen bond. This is also supported by the temperature reversibility, since salt (III) could not decompose so readily with a slight rise in temperature.

Fig. 3. Absorption of tropone in the region 2700-3600 cm^{-1} in C_2Cl_4 solution: a –$C_{\text{trop}} = 0.27$ mol/l; b –$C_{\text{trop}} = 4.6 \cdot 10^{-2}$ mol/l.

The statements in the literature (7) that tropone absorbs in the region of 3425 cm^{-1} prompted us to study this region of the spectrum, since, by its structure, tropone cannot have fundamental vibrational frequencies lying in the region of stretching vibrations of the OH and NH bonds. Experiments showed that in this region absorption is indeed present (Fig. 3), but its intensity is two orders of magnitude smaller than that of bands corresponding to fundamental vibrations.

Therefore we believe that the absorption near 3425 cm^{-1} is a second-order line.

We also note that the contour of the carbonyl band of DPhCP is double; moreover, its change as a function of solvent and temperature (Fig. 2) is analogous to the previously noted (1) case of the carbonyl band of sydnones. The nature of the splitting will be discussed by us separately.

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Note: Figure translations are in progress. See original paper for figures.