Yu. G. Borod' ko and Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. G. Borod' ko and Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin

INTENSITY OF INFRARED ABSORPTION OF THE CARBONYL BOND IN SYDNONES AND TROPONE AND ITS POLARITY

It is often asserted that the lower the frequency of the stretching vibration of the carbonyl group $> C = O$, the lower its bond order and the greater the polarity of its bond. Thus, comparing the vibrational frequencies of the $C = O$ bond in different molecules with the frequency of this bond in acetone (dipole moment 2.7D, frequency 1710 cm^{-1}), it is assumed that, in the presence of conjugation, the frequencies decrease in accordance with an increase in the polarity of this bond, a decrease in its bond order ($> \overset{+}{C} - \overset{-}{O}$), and an increase in the dipole moment. This conclusion is based on empirical observations of the frequency of $> C = O$ in various organic molecules.

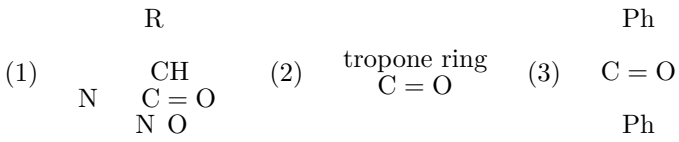
An increase in frequency is often attributed to an increase in bond order, on the assumption that oxygen is to some extent oxonium-like with a displacement of an electron toward a halogen, for example in the molecule acetyl chloride (CH_3COCl). However, in our opinion, there are not sufficient grounds for such an assertion. In any case, the converse assertion is unjustified: that if the vibrational frequency of the carbonyl bond is higher than in acetone, then its bond order is also higher. Here one cannot argue from the known progression of frequencies in single, double, and triple bonds $> C - C <$, $> C = C <$, $-C \equiv C-$, where the bond is due to one, two, and three pairs of electrons. It is more natural, when judging the polarity of a given bond, to use data on the absorption intensity of the carbonyl bond in the infrared spectrum. It is known that, for a series of diatomic molecules (HCl, HBr, HJ), the intensities of the infrared absorption spectra, determined by matrix elements of the dipole moment, increase in parallel with the increase in the dipole moment μ. There is a parallelism between the known values of $d\mu/dr$ and the quantity μ_{exp}/r_0, where r_0 is the equilibrium distance and is a measure of bond polarity. It is also known that, as a rule, the absorption intensity of ionic bonds in the infrared spectrum is greater than for covalent ones.

Particular caution must be exercised in estimating the bond order and polarity of the carbonyl bond in those cases where there is a new class of molecules with a specific structure, for example, in five-membered rings in sydnones (1), in

Fig. 1

Figure 1: Fig. 1

seven-membered rings of the tropone type (2), or in three-membered rings, for example in compounds of the diphenylcyclopropenone type (3).



The indicated compounds have large dipole moments, considerably exceeding the moment of acetone, and elevated frequencies of stretching vibrations: in the case of diphenylcyclopropenone $\nu_{C=O} = 1845$ cm^{-1}, and in sydnones 1760 cm^{-1}. This shows that the correspondence between the vibrational frequency and the dipole moment characterizing its polarity is not general

Fig. 1

for all molecules. The frequency of vibrations of the carbonyl group can hardly be a characteristic of bond polarity, since it is not directly related to the dipole moment and is a complex function of a large number of variables.

To characterize the polarity of the carbonyl bond, as indeed of any other, it is natural to use the intensity of the i.r. absorption band corresponding to the stretching vibration. The intensity due to the transition of the molecule from a vibrational state with quantum number v_1 to a state with quantum number v_2 is determined by the square of the matrix element $M_{v_1 v_2}(Q)$, which is equal to

$$\int \psi^*_{v_1}(Q)\, M(Q)\, \psi_{v_2}(Q)\, dQ,$$

where $M(Q)$ is the operator of the dipole moment of the molecule having configuration Q ([1]). Therefore, an increase in the integral intensity of the i.r. absorption band corresponding to the stretching vibration of the carbonyl group indicates an increased polarity of its bond.

Table 1

Compound	μ, D	$\nu_{C=O}$, cm^{-1}	$I_{C=O}$, $1.2 \cdot 10^4$ mol$^{-1} \cdot$ l $\cdot$ cm^{-2}
Acetone	2.7	1710	1.6
Acetophenone	2.9	1692	2.1
Benzophenone	3.0	1668	2.2
Tropone	4.3 (3)	1590	2.6

Fig. 2

Figure 2: Fig. 2

Compound	μ, D	$\nu_{C=O}$, cm^{-1}	$I_{C=O}$, $1.2 \cdot 10^4$ $mol^{-1} \cdot l \cdot cm^{-2}$
Diphenylcyclopropenone	5.08 *	1845	6.4
3-Phenylsydnone	6.48 (4)	1760	10
3-Ethylsydnone	~ 6	1745	11

* According to measurements by A. N. Shidlovskaya and Ya. K. Syrkin.

Table 1 presents the results of measurements of the frequencies and integral intensities of i.r. absorption bands corresponding to the stretching vibration of the carbonyl group in a series of compounds (the experiments were carried out on a two-beam UR-10 spectrometer). The intensities were determined by the method described in Ramsay' s work ([2]). As is seen from Table 1, the intensity increases strongly with increasing dipole moment, but there is no simple relation between frequency and dipole moment. Table 1 gives the value of the intensity of the band

tropone with a frequency of 1590 cm^{-1}, instead of the band with a frequency of 1635 cm^{-1} accepted in the literature ([5]). The basis for this was our investigation of the frequencies and intensities of the 1590 cm^{-1} and 1635 cm^{-1} bands in various solvents and at different temperatures. (In Fig. 1 the IR absorption spectrum of tropone is given ([2]).) The intensity of the tropone band

Fig. 2. Observed contours of the absorption bands of tropone with frequencies 1590 cm^{-1} and 1635 cm^{-1} at 30° in solutions: 1 —CCl_4 (conc. $12.3 \cdot 10^{-2}$ mol/l; $d = 0.1$ mm); 2 —$CHCl_3$ (conc. $11.2 \cdot 10^{-2}$ mol/l, $d = 0.1$ mm)

at 1635 cm^{-1} in CCl_4 solution is $1.2 \cdot 10^4$ $mol^{-1} \cdot l \cdot cm^{-2}$, i.e., less than in the case of acetone. This, in our opinion, is inconsistent with the large value of the dipole moment of tropone (4.3 D). In chloroform solution the intensity of this band decreases to $0.9 \cdot 10^4$ $mol^{-1} \cdot l \cdot cm^{-2}$ without a noticeable change in frequency, which clearly contradicts the numerous available experimental data showing that the formation of a hydrogen bond with chloroform leads to an increase in intensity and a decrease in the vibrational frequency of the carbonyl group ([6]). At the same time, the intensity of the band with frequency 1590 cm^{-1} increases from $2.6 \cdot 10^4$ $mol^{-1} \cdot l \cdot cm^{-2}$ in CCl_4 to $3.4 \cdot 10^4$ $mol^{-1} \cdot l \cdot cm^{-2}$ in $CHCl_3$, while the frequency decreases from 1590 cm^{-1} to 1574 cm^{-1} (Fig. 2). Measurements in the temperature interval from 20 to 60° did not introduce substantial changes into the results.

Fig. 3

Figure 3: Fig. 3

Fig. 4. Observed contour of the carbonyl band of 3-phenylsydnone.

Figure 4: Fig. 4. Observed contour of the carbonyl band of 3-phenylsydnone.

Fig. 3. Change in the ratio of the integral intensities of the absorption bands of tropone I_{1635}/I_{1590} in various solvents: 1 —cyclohexane, 2 —tetrachloroethane, 3 —carbon tetrachloride, 4 —benzene, 5 —pyridine, 6 —chloroform, 7 —acetic acid

Figure 3 shows the decrease in the ratio of the band intensities I_{1635}/I_{1590} when the 1590 cm^{-1} band is shifted toward lower frequencies. A solvent can be chosen in which the intensity of the band with frequency 1635 cm^{-1} will correspond to the intensity of a second-order line. This result apparently indicates that the 1635 cm^{-1} band is a combination tone (837 cm^{-1} + 789 cm^{-1}), enhanced in intensity due to Fermi resonance with the carbonyl band. As the frequency of the carbonyl group moves away from the combination tone toward lower frequencies (as a result of interaction with the solvent), the conditions for resonance become worse, which leads to a sharp decrease in the intensity of the combination tone ([7]).

Thus we arrive at the conclusion that the carbonyl band is the most intense absorption band in the IR spectrum of tropone, with frequency 1590 cm^{-1}.

It should be noted that the carbonyl bands of 3-phenylsydnone and 3-ethylsydnone are doublets. Figure 4 shows the change in the frequencies and intensities of the components of the 3-phenylsydnone band as a function of solvent and temperature.

Fig. 4. Observed contour of the carbonyl band of 3-phenylsydnone, *A*—in CCl_4 (conc. $7.2 \cdot 10^{-4}$ mol/l): 1—at 12°, 2—at 50°. *B*—in $CHCl_3$ (conc. $7.24 \cdot 10^{-4}$ mol/l): 3—at 9°, 4—at 50°.

At present we are continuing work on the investigation of the nature of the splitting of this band in different sydnones. In conclusion, we express our gratitude to M. E. Vol' pin and V. S. Yashunskii for kindly providing the substances.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
1 VII 1960

CITED LITERATURE

1. G. Herzberg, *Vibrational and Rotational Spectra of Polyatomic Molecules.* Moscow, 1949; S. S. Savvantam, *Theory of Groups and Its Application to*

Physical Problems. Moscow, 1959.

2. D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 1, 72 (1952).

3. A. Giacomo, C. P. Smyth, *J. Am. Chem. Soc.*, **74**, 17, 4411 (1952).

4. R. A. W. Hill, L. E. Sutton, *J. Chem. Soc.*, 1949, 746.

5. K. Kuratani, *Bull. Chem. Soc. Japan*, **25**, 250 (1952); P. L. Pauson, *Chem. Rev.*, **55**, 1, 9 (1955).

6. H. W. Thompson, D. J. Jewelle, *Sp. Acta*, **13**, 3, 254 (1958); G. Borrow, *J. Chem. Phys.*, **21**, 11, 2008 (1953); A. K. Syrkin, Yu. G. Borodko, *DAN*, **131**, No. 4, 868 (1960).

7. L. J. Bellamy, R. L. Williams, *Trans. Farad. Soc.*, **55**, 1, 16 (1959).

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