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Academician of the Academy of Sciences of the BSSR A. N. Sevchenko and I. P. Zyatkov

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Abstract

Full Text

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INFRARED SPECTRA OF UNSYMMETRICAL DIACYL PEROXIDES

The interpretation of the frequencies in the infrared absorption spectra of organic peroxides given in the literature is in a number of cases contradictory and raises doubts.

Shriv et al. (^{1}) indicate that phthaloyl, *p*-chlorobenzoyl, and benzaldehyde peroxides have a strong absorption band with a frequency of about 1000 cm^{-1}. On the other hand, di-*tert*-butyl peroxide absorbs at 880 cm^{-1}. These data were confirmed in work (^{2}). The authors of papers (^{1}, ^{2}) regard the mentioned absorption bands as characteristic of vibrations of the —O—O—group of aromatic and aliphatic peroxide compounds.

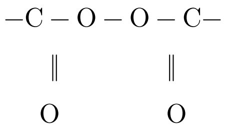
Fig. 1. Transmission spectra of solutions in CCl_4 of a mixture of *p*-chlorobenzaldehyde with acetic anhydride: before oxidation (*I*); after 3 hours of oxidation (*II*); 0.1 M solution in CCl_4 obtained in the process of the oxidation reaction of acetyl-*p*-chlorobenzoyl peroxide (*III*); 0.1 M solution in CCl_4 of *p*-chlorobenzaldehyde (*IV*).

Searches by other investigators (^{3}–^{5}) for characteristic absorption for —O—O— bonds in organic peroxides did not give positive results.

The IR spectra of compounds containing the hydroperoxide group ROOH have been studied in greater detail (^{1}, ^{6}–^{8}). A preliminary interpretation of the spectra of four unsymmetrical diacyl peroxides was given in work (^{9}).

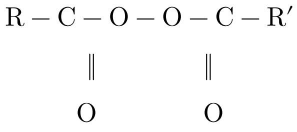
However, for the detection of organic peroxide compounds formed during an oxidation reaction, literature data on IR spectra are insufficient, especially since the presence of a frequency of 880 or 1000 cm^{-1} does not unambiguously indicate the presence of a peroxide group O—O, the vibrations of which are not characteristic ([10]).

Establishing regularities in the spectral manifestation of vibrations of the group



$$-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{O}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-$$

for peroxides of the type



$$\mathrm{R}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{O}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}'$$

requires a large amount of experimental material. It is highly advisable to trace those changes in the IR spectra which occur in the course of the oxidation reaction and the formation of peroxide compounds.

For this purpose we studied the IR spectra of four unsymmetrical diacyl peroxides: acetyl-*p*-chlorobenzoyl, acetyl-*m*-chlorobenzoyl,

acetyl-*o*-chlorobenzoyl and propionylbenzoyl. For the first three peroxides, as well as for the starting aldehydes and anhydrides, spectra were obtained (Figs. 1, 2, 3) in the transmission region of the NaCl prism of an IKS-14 spectrometer. $0.1M$ solutions of the peroxides in $\mathrm{CCl_4}$ were investigated with an absorbing-layer thickness of 0.25 mm. For propionylbenzoyl peroxide the spectra (Fig. 4) were obtained on an IKS-11 with an absorbing-layer thickness of 0.1 mm. The IR spectra of acetyl-*o*-chlorobenzoyl and propionylbenzoyl peroxides are being studied for the first time.

From the figures it is seen that during oxidation of the samples new bands appear in their spectra, which are absent from the unoxidized samples and also from the spectra of the starting aldehydes and anhydrides. These include a low-intensity band at 845-860 cm^{-1} (Fig. 1, *II*; Fig. 2, *II-IV*; Fig. 3, *II-IV*), observed in the spectra of all the peroxides presented. In the regions 1000-1030 cm^{-1} and 1030-1050 cm^{-1}, during oxidation of the samples two bands appear, very clearly expressed in the spectra of the peroxides. The intensity of the band in the spectral region 1030-1050 cm^{-1} depends on the position of the substituent in the ring, and its appearance in the spectrum is evidently not connected with formation of the peroxide chain, but rather is due to out-of-plane vibrations of

Fig. 2

Figure 2: Fig. 2

Fig. 3. Transmission spectra of solutions in CCl_4

Figure 3: Fig. 3. Transmission spectra of solutions in CCl_4

the benzene ring. In the peroxides acetyl-*p*-chlorobenzoyl (Fig. 1, *III*), acetyl-*m*-chlorobenzoyl (Fig. 2, *V*) and acetyl-*o*-chlorobenzoyl (Fig. 3, *V*) there is a very intense absorption band with a maximum at 1175 cm^{-1}, which arises in the spectrum during the oxidation reaction. The intensity and wavelength of the absorption maximum do not depend on the position of the substituent in the ring. Absorption in this region is absent from the spectrum of propionylbenzoyl peroxide (Fig. 4, *IV*). Hence it may be concluded that the above-mentioned frequency should be assigned to vibrations of the group—C—CH_3 at the end of the chain.

Fig. 2. Transmission spectra of solutions in CCl_4 of *m*-chlorobenzaldehyde with acetic anhydride: before oxidation (*I*); after 2 h oxidation (*II*); after 4 h oxidation (*III*); after 6 h oxidation (*IV*); of a 0.1M solution in CCl_4 of acetyl-*m*-chlorobenzoyl peroxide obtained in the oxidation reaction (*V*); of a 0.1M solution in CCl_4 of *m*-chlorobenzaldehyde (*VI*); of a 0.1M solution in CCl_4 of acetic anhydride (*VII*); of a 0.1M solution in CCl_4 of acetic acid (*VIII*).

Very clearly, in all the figures one can trace the appearance, during the oxidation reaction, of an absorption band in the spectral region 1220-1236 cm^{-1}, very intense in the spectra of all pure peroxides and absent from the spectra of the initial aldehydes and anhydrides. At the same time, an absorption band with a maximum at 1300 cm^{-1} appears (Fig. 1, II; Fig. 2, II–IV; Fig. 3, II–IV). The absorption band at 1300 cm^{-1} belongs to acetic acid, which is formed along with the peroxide in the course of the oxidation reaction. This is confirmed by the fact that the spectrum of acetic acid has a very intense absorption band with a maximum at 1300 cm^{-1} (Fig. 2, $VIII$). In addition, the spectrum of acetic acid contains a very intense band with a maximum at 1710 cm^{-1}, belonging to $C = O$ vibrations.

In this same spectral region, 1704-1710 cm^{-1}, the initial aldehydes also have an absorption band of the carbonyl group. During the oxidation reaction, the intensity of the carbonyl-group absorption band of the initial aldehydes should decrease. However, the intensity of this band increases somewhat during the oxidation reaction, although only slightly, which also indicates the formation of acetic acid in the reaction mixture.

Fig. 3. Transmission spectra of solutions in CCl_4 of a mixture of *o*-chlorobenzaldehyde with acetic anhydride: before oxidation (I); after 20 min of oxidation (II); after 40 min of oxidation (III); after completion of oxidation (IV); 0.1 M solution in CCl_4 of the peroxide obtained in the oxidation reaction

of acetyl-*o*-chlorobenzoyl (*V*); 0.1 M solution in CCl_4 of *o*-chlorobenzaldehyde (*VI*).

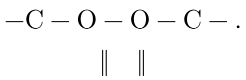
In the spectra of all samples before oxidation there are two very intense bands with maxima at 1757-1760 cm^{-1} and 1815-1820 cm^{-1}. These bands belong to the $C = O$ vibrations of the initial anhydrides (Fig. 2, *VII*; Fig. 4, *V*). In the spectra of samples during the oxidation reaction, new bands appear with maxima at 1770-1774 cm^{-1} and 1800-1805 cm^{-1}, which are very intense in the spectra of the peroxides and belong to $C = O$ vibrations.

In the spectral region 1300-1750 cm^{-1}, during the oxidation reaction of the samples, the intensity of bands with maxima at 1375-1380 cm^{-1} and 1445-1450 cm^{-1} changes. These bands are observed in the spectra of the initial aldehydes and anhydrides and may be assigned to symmetric and antisymmetric deformation vibrations of $C{-}CH_3$ and CH_2 groups.

In all spectra of the peroxides, in the region 1580-1630 cm^{-1}, a very weak absorption band is observed. It is present in the samples before oxidation, undergoes no appreciable changes during the oxidation reaction, and is also observed in the spectra of all the initial aldehydes. The position of its maximum, although only slightly, changes with the position of the substituent in the ring. It should probably be assigned to

vibrations of the benzene ring. Interpretation of the band in the region 1075-1100 cm^{-1} is difficult. Its intensity is high in the spectra of acetyl-*p*-chlorobenzoyl, acetyl-*m*-chlorobenzoyl and low in the spectrum of acetyl-*o*-chlorobenzoyl peroxide. It is not formed during the oxidation reaction and is present in the spectra of the initial aldehydes for the three above-mentioned peroxides.

Discussing the experimental data obtained, it should be noted that the absorption bands with maxima in the regions 845-860 cm^{-1}, 1000-1030 cm^{-1}, and 1220-1236 cm^{-1}, whose formation occurs during the oxidation reaction, are evidently connected with the formation of a peroxide chain of the type



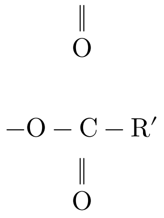
$$\begin{array}{c} -C-O-O-C-\,. \\ \|\quad\| \end{array}$$

As noted above, the authors of papers (^{1,2}) assign the band in the region 1000 cm^{-1} to vibrations of the $-O-O-$ bond of aromatic peroxides, and the band at 880 cm^{-1} to the same bond in aliphatic peroxides. In our opinion, such an interpretation is unconvincing. The presence of sufficiently characteristic vibration bands of $-O-O-$ in peroxides of the type

$$R-C-O-$$

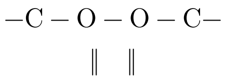
Fig. 4. Transmission spectra of solutions in CCl4

Figure 4: Fig. 4. Transmission spectra of solutions in CCl4



$$\begin{array}{c} \| \\ \mathrm{O} \\ \\ -\mathrm{O}-\mathrm{C}-\mathrm{R}' \\ \| \\ \mathrm{O} \end{array}$$

is unlikely. It is more natural to assume that the appearance of these bands is associated with vibrations of the entire chain as a whole, and not only of the $-O-O-$ bond. Probably these bands, especially the intense ones in the regions 1000–1030 cm^{-1} and 1220–1236 cm^{-1}, are characteristic of the chain of the type



$$\begin{array}{c} -\mathrm{C}-\mathrm{O}-\mathrm{O}-\mathrm{C}- \\ \|\quad\| \end{array}$$

for this class of compounds. Work on the study of the IR spectra of other peroxide compounds will be continued by us.

Fig. 4. Transmission spectra of solutions in CCl_4 of a mixture of benzaldehyde with propionic anhydride: before oxidation (*I*); after 2.5 h of oxidation (*II*); after 5 h of oxidation (*III*); 0.1 M solution in CCl_4 of propionylbenzoyl peroxide obtained in the oxidation reaction (*IV*); 0.1 M solution in CCl_4 of propionic anhydride in the spectral regions 950–1300, 1670–1900 cm^{-1} (*V*); 0.1 M solution in CCl_4 of benzaldehyde in the spectral regions 950–1050, 1100–1300, 1670–1900 cm^{-1} (*VI*).

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REFERENCES

1. O. D. Shreve, M. R. Heether et al., *Anal. Chem.*, **23**, 282 (1951).
2. L. Bellamy, *Infrared Spectra of Molecules*, IL, 1957.

3. W. H. Davison, *J. Chem. Soc.*, 1951, 2456.

4. A. R. Philpotts, W. Thain, *Anal. Chem.*, **24**, 638 (1952).

5. G. J. Minkoff, *Proc. Roy. Soc.*, A, **224**, 176 (1954).

6. A. V. Karyakin, V. A. Nikitin, *Izv. AN SSSR, ser. fiz.*, **17**, 636 (1953).

7. M. A. Kovner, A. V. Karyakin, A. P. Efimov, *Optika i spektroskopiya*, **8**, 128 (1960).

8. H. R. Williams, H. S. Mosher, *Anal. Chem.*, **27**, 517 (1955).

9. Yu. A. Ol' dekop, A. N. Sevchenko et al., *DAN*, **128**, 1201 (1959).

10. G. Herzberg, *Vibrational and Rotational Spectra of Polyatomic Molecules*, IL, 1949.

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