

2-Fluoro-2-chloro-2-nitroethyl diethyl phosphate (XIII). A solution of 6 g (0.03 mole) diethyl chlorophosphate in 30 ml ether was placed in a flask and at -5°C 4.3 g (0.03 mole) of (I) and then 3.03 g (0.03 mole) Et_3N were added. The reaction mixture was stirred for 4 h at 20°C and filtered. Ether was removed and the mixture was distilled to give 7.6 g (78%) (XIII), bp 106°C (2 mm). Phosphate (XIV) was obtained by analogy.

Trimethyl(2-fluoro-2-chloro-2-nitroethoxy)silane (XV). A sample of 7.6 g (0.07 mole) trimethylchlorosilane was added with stirring to 7.2 g (0.05 mole) (I) at 20°C . The mixture was maintained for 3 h at 80°C and HCl was flushed out with a nitrogen stream. The mixture was then evaporated and distilled to give 7.9 g (74%) (XV), bp $58-59^{\circ}\text{C}$ (2 mm).

CONCLUSIONS

The reaction of fluorochloronitromethane with aliphatic and aromatic aldehydes leads to the formation of the corresponding fluorochloronitroalcohols, which are capable of further transformations involving the hydroxyl group.

LITERATURE CITED

1. The Chemistry of the Nitro and Nitroso Groups, H. Feuer, ed., Wiley, New York (1969).
2. L. T. Eremenko and G. V. Oreshko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 380 (1969).
3. The Chemistry of Aliphatic and Alicyclic Nitro Compounds [Russian translation], *Izd. Khimiya, Moscow* (1974), p. 100.
4. A. V. Fokin, V. A. Komarov, K. V. Frosina, and Kh. A. Abdulganieva, *Zh. Obshch. Khim.*, 37, 152 (1967).
5. W. V. Martynov, Yu. L. Kruglyak, and S. P. Makarov, *Zh. Obshch. Khim.*, 33, 3384 (1963).

IR SPECTRUM OF THE H_5O_2^+ ION IN ACID SOLUTION

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It is difficult to separate out the vibrational spectrum of the H_5O_2^+ ion in most cases due to the superposition of the strong spectra of water molecules and acid molecules and ions superposed on it [1, 2]. In previous work [3], we established that virtually all the water in aqueous solutions of methanesulfonic acid containing more than 55 mole % $\text{CH}_3\text{SO}_3\text{H}$ is found as H_5O_2^+ ions and the IR spectra of such solutions do not contain "free" water bands. The spectrum of the H_5O_2^+ ion in the range from 1500 to 4000 cm^{-1} is observed together with the spectra of the methanesulfonic acid molecules and anions. However, these latter bands may be separated out from the overall spectrum since the equilibrium ion-molecular composition and molar absorption coefficients of the methanesulfonic acid-water system are known [3]. Thus, it is possible to obtain the IR spectrum of the H_5O_2^+ ion in "pure form."

Figure 1 gives the multiple frustrated total internal reflection IR spectrum of an aqueous solution of methanesulfonic acid, containing 58.4 mole % $\text{CH}_3\text{SO}_3\text{H}$ (curve 1). The spectrum was obtained according to our previous procedure [3] and reduced to a single effective thickness of the absorbing layer of $10\ \mu\text{m}$ for all the frequencies. Curve 2 in the figure is the result of subtracting the spectra of the methanesulfonic acid molecules and anions from curve 1, i.e., it is the IR spectrum of the H_5O_2^+ ion. The spectrum for frequencies less than 1500 cm^{-1} , given by curve 2, was taken from our previous work [2]. The spectrum of an aqueous solution containing 31 mole % $\text{CH}_3\text{SO}_3\text{H}$ (Fig. 1, curve 3) was also taken in order to confirm the validity of the assignment of the spectrum to the H_5O_2^+ ion and lack of bands for undissociated methanesulfonic acid. This spectrum lacks bands for the undissociated acid [3]. Curve 4 is the result of the subtraction of the spectra of free water (not included in H_5O_2^+) and the acid ions. Curve 4 virtually reproduces curve 2, which supports the validity of the assignment of curve 2 to the H_5O_2^+ ion.

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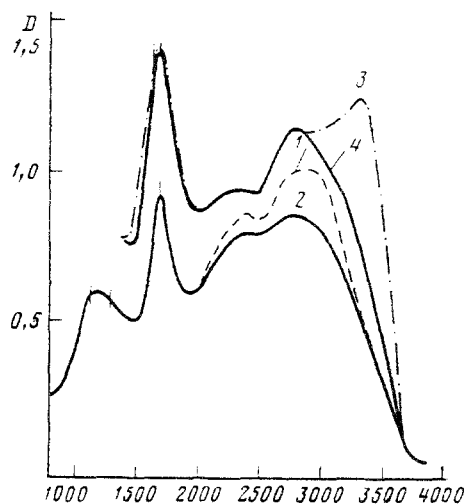


Fig. 1. Multiple frustrated total internal reflection IR spectra: 1) 58.4 mole % $\text{CH}_3\text{SO}_3\text{H}$, 3) 31 mole % $\text{CH}_3\text{SO}_3\text{H}$, and 2 and 4) spectra of the H_5O_2^+ ion separated out of spectra 1 and 3.

The assignment of the bands in the IR spectrum of the H_5O_2^+ ion was carried out in our previous work [2]. We note that the broad band with maximum about 2350 cm^{-1} was not previously considered to belong to the H_5O_2^+ ion and thus, the assignment of this band is unsure.

CONCLUSIONS

1. Presented results and literature data on the IR spectra of aqueous solutions of acids have given the IR spectrum of the H_5O_2^+ ion in the frequency range $800\text{--}3800\text{ cm}^{-1}$ at 25°C .

2. A broad band was found with a maximum at about 2350 cm^{-1} , which was not assigned previously to the H_5O_2^+ ion.

LITERATURE CITED

1. N. B. Librovich, V. D. Maiorov, and V. A. Savel'ev, Dokl. Akad. Nauk SSSR, 225, 1358 (1975).
2. N. B. Librovich, V. P. Sakun, and N. D. Sokolov, Teor. Éksp. Khim., 14, 435 (1978).
3. A. P. Kirilova, V. D. Maiorov, A. I. Serebryanskaya, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1493 (1985).