was 12.8 kcal mol^{-1} for the exchange of the primary hydrogen atom and 11.2 kcal mol^{-1} for the exchange of the secondary atom (MP2/6-31G*) with analogous transition state structures.

For the hydrogen exchange reaction at the alanine β-atom the activation energy was found to be 11 kcal mol^{-1} by the AM1 method with the same transition state structure (R^1 = $CH(NH_2)COOH$, R^2 = H, R^3 = H); for the α-atom it was 21 kcal mol^{-1} (R^1 = COOH, R^2 = NH_2, R^3 = CH_3). The calculation results obtained allow us to offer a new interpretation of the hydrogen isotope exchange reaction conducted under conditions of high-temperature solid-state catalytic isotopic exchange (HSCIE)[11] of organic compounds with activated tritium. In this reaction, methyl groups are the most reactive groups in aliphatic amino acids. Isotope exchange at the asymmetric carbon atoms proceeds with retention of the configuration. These particular features of the HSCIE reaction can be accounted for by the suggested mechanism of synchronous transfer at one catalytic center. Later we intend to undertake a theoretical study of isotope exchange for aromatic and heteroaromatic molecules.

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Ions with a strong symmetric H-bond in solutions of sodium acetate in acetic acid

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The multiple attenuated total reflection IR spectra of solutions of sodium acetate in acetic acid have been recorded in the range from 900 to 4000 cm^{-1}. The CH_3COO^- anion and an acid molecule form the complex $(CH_3COO...H...OOCCH_3)^-$ with a strong symmetric H-bond.

Key words: IR spectra; hydrogen bond; solutions, acetic acid.

Nonaqueous solutions of strong acids are efficient catalytic systems, whose activity is determined in many cases by proton solvates formed due to symmetric H-bonds.[1,2] When a salt of one of these acids is dissolved in a strong oxygen-containing acid, negatively charged complexes with a strong symmetric H-bond are formed, for example, $(HO_3SO...H...OSO_3H)^-$.[3,4] In aqueous solutions of acetic acid, the concentration of dissociated protons is low, and the acid molecules form strong hydrates.[5–7] In this work, solutions of CH_3COONa in CH_3COOH have been studied by multiple attenuated total reflection (MATR) IR spectroscopy[8] with the purpose of elucidating the ability of acetic acid to form ions with strong symmetric H-bonds in nonaqueous solutions.

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Experimental

For the preparation of 100 % CH_3COOH, acetic acid (reagent grade) was distilled at 117.7 °C and frozen and then thawed out 5 times.

Sodium acetate was prepared from $CH_3COONa \cdot 3H_2O$ (reagent grade) by drying *in vacuo* at 200 °C.

Molar concentrations of solutions of CH_3COONa in CH_3COOH were measured by their densities. The maximum solubility of the salt was 14 mol. %, which corresponds to 2.4 mol L^{-1} CH_3COONa. The content of water did not exceed 0.1 mol L^{-1}.

MATR IR spectra were obtained at 30 °C on a UR-20 spectrophotometer with a MATR attachment made at the Institute of Chemical Physics of the Russian Academy of Sciences. A germanium prism with an incident irradiation angle of 30° and 4 or 8 reflections was used. Spectra were recorded relative to air. The effective thicknesses of the absorbing layer determined from the spectra of water using its optical constants[9] were 1.60 or 3.20 mm, respectively, at a frequency of 2000 cm^{-1}. Spectra of solutions of sodium acetate in CH_3COOH (0 to 2.3 mol L^{-1} CH_3COONa) were recorded in the range from 900 to 4000 cm^{-1}. Optical densities of bands were measured relative to basis lines. Optical densities of continuous absorption (CA) were determined relative to an empty cell.

Results and Discussion

The IR spectrum of pure acetic acid contains the following bands[5–7]: 1227—1290 and 1410 (ν(C—O), or δ(O—H)), 1710 (ν(C=O)), and 2500—2750 and 3050 (ν(OH)) cm^{-1}. When sodium acetate is added, the intensity of these bands decreases noticeably, and new bands at 1255, 1370, and 1542 cm^{-1} as well as continuous absorption in the range from 1000 to 2600 cm^{-1} appear (Fig. 1). These changes in the spectrum do not correspond to the formation of CH_3COO^- anions, whose spectrum (the spectrum of an aqueous solution of CH_3COONa) is also presented in Fig. 1.

The bands of the ν(C=O) and ν(OH) vibrations of CH_3COOH are the most convenient for quantitative analysis. The absorption coefficients at 1710 and 3000 cm^{-1} were determined from the spectra of the pure acid. The concentrations of acetic acid molecules in solutions were calculated from the D_{1710} and D_{3000} values for solutions of CH_3COONa in CH_3COOH. A comparison of the obtained values with stoichiometric concentrations of the acid C^0_{AcOH} shows that 1.5 to 2 CH_3COOH molecules are consumed in the solvation of one CH_3COONa molecule (see Table 1). It can be assumed that one acid molecule is strongly bound to the anion to form a complex with a strong symmetric H-bond: $(CH_3COO...H...OOCCH_3)^-$.

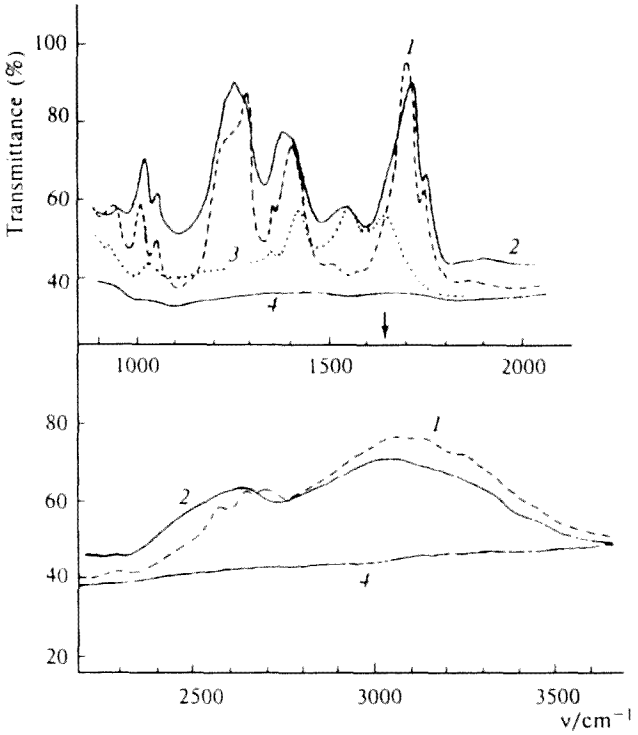

Fig. 1. MATR IR spectra of: *1*, CH_3COOH; *2*, 2.23 mol L^{-1} CH_3COONa in CH_3COOH; *3*, 2.30 mol L^{-1} CH_3COONa in H_2O; and *4*, empty cell. The position of the maximum of the absorption band of deformation vibrations of water in the spectrum of the $CH_3COONa—H_2O$ system is marked with an arrow.

Table 1. Stoichiometric composition of the $CH_3COONa—CH_3COOH$ system, densities of solutions (ρ/g cm^{-3}), optical densities (D) of the bands at 1710 and 3000 cm^{-1}, and concentrations (mol L^{-1}) of "free" (C_{AcOH}) and "bound" (ΔC) acids

C^0_{AcONa}[a]	C^0_{AcOH}[a]	ρ	D_{1710}	C_{AcOH}[b]	ΔC[c]	n	D_{3000}	n
—	17.45	1.049	1.084	—	—	—	0.333	—
0.93	17.10	1.100	0.923	14.9	2.2	2.4	0.297	1.6
1.39	16.58	1.110	0.813	13.1	3.5	2.5	0.284	1.2
1.96	16.28	1.116	0.780	12.6	3.7	2.3	0.268	1.3
1.96	16.08	1.126	0.754	12.2	3.9	2.0	0.260	1.3
2.23	15.87	1.138	0.747	12.0	3.9	1.7	0.245	1.3

[a] C^0_{AcONa} and C^0_{AcOH} are the stoichiometric concentrations of CH_3COONa and CH_3COOH, respectively; [b] C_{AcOH} are the concentrations of CH_3COOH determined from D_{1710} and D_{3000}; [c] $\Delta C = C^0_{AcOH} - C_{AcOH}$; $n = \Delta C / C^0_{AcONa}$.

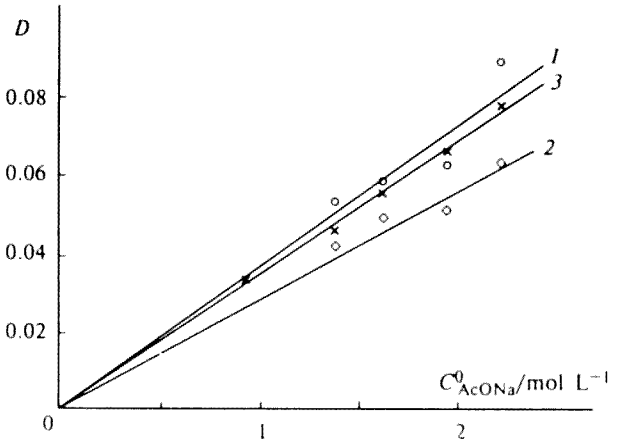

Fig. 2. Dependence of optical densities of absorption bands at 1542 (*1*) and 2500 cm^{-1} (*2*) and of the continuous absorption at 2000 cm^{-1} (*3*) on the concentration of sodium acetate.

When these anionic complexes are solvated by acid molecules, stronger hydrogen bonds can be formed than those in acetic acid dimers, which results in a noticeable shift of the band of stretching vibrations of the OH groups to a the longwave region and the appearance of a broad band in the range from 2350 to 2700 cm^{-1} (Fig. 1). In our opinion, this band corresponds to the ν(OH) vibrations of acid molecules strongly solvating the $(CH_3COO)_2H^-$ anion. The optical density of this band is proportional to the concentration of CH_3COONa (Fig. 2). When the Na^+ cations are solvated, the acid dimers can also decompose and the intensities of the bands of the C=O and O—H vibrations can change. The dissolution of the salt in the acid results in noticeable broadening of the ν(C=O) band at 1710 cm^{-1}. The optical density at the longwave wing of this band (at 1650 cm^{-1}) in the spectrum of pure acetic acid is 12 % of the optical density at the maximum. In solutions of sodium acetate the optical density at 1650 cm^{-1} is 38 %. The relative intensity of the absorption of monomers of acetic acid at 1755 cm^{-1} also increases.

The bands of the proton disolvate appearing in the spectra of solutions of CH_3COONa in CH_3COOH occur against the background of the bands of acetic acid, which makes the exact measurement of their optical densities difficult. The absorption in the maxima of these bands is caused both by proton disolvates and by acid molecules. For example, the optical density at 1255 cm^{-1} can be presented as follows:

$$D_{1255} = \varepsilon_1 l C_{AcOH} + \varepsilon_2 l C_{(AcO)_2H^-}, \quad (1)$$

where l is the effective thickness of the absorbing layer at 1255 cm^{-1}, C_{AcOH} is the concentration of CH_3COOH molecules in solution ($C_{AcOH} = C^0_{AcOH} - C^0_{AcONa}$; C^0_{AcOH} and C^0_{AcONa} are the analytical concentrations of the acid and sodium acetate); $C^0_{(AcO)_2H^-}$ is the concentration of proton disolvates $(CH_3COO)_2H^-$; and ε_1 and ε_2 are the extinction coefficients of the acid and proton disolvates, respectively. We assume that the salt is completely dissociated, and that all CH_3COO^- anions are bound to proton disolvates, *i.e.*, $C_{(AcO)_2H^-} = C^0_{AcONa}$.

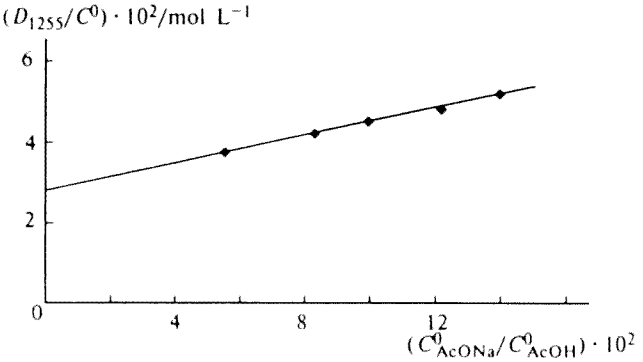

Fig. 3. Graphic solution of Eq. (2) for the band at 1255 cm^{-1}.

From Eq. (1) we obtain

$$D_{1255}/C^0_{AcOH} = \varepsilon_1 l + (\varepsilon_2 - \varepsilon_1) l C^0_{AcONa}/C^0_{AcOH}. \quad (2)$$

This dependence is a straight line in the coordinates $D_{1255}/C^0_{AcOH} - C^0_{AcONa}/C^0_{AcOH}$ (Fig. 3), which confirms both the assumption that the radiation is absorbed at 1255 cm^{-1} by proton disolvates and acid molecules and the assumption that the salt dissociates completely and the anions formed bind completely to proton disolvates.

A characteristic feature of the IR spectra of complexes with a strong symmetric H-bond is a broad-band of continuous absorption.[10] We measured its optical density at 2000 cm^{-1} taking into account the absorption of acetic acid at this frequency (Fig. 2). The linear character of the dependence of D_{2000} on the concentration of sodium acetate also confirms the assumption that CH_3COO^- anions bond completely to complexes with a strong symmetric H-bond. The absorption coefficient at this frequency (106±10 L mol^{-1} cm^{-1}) almost coincides with the coefficient of continuous absorption of the $(HO...H...OH)^-$ ion (120±10 L mol^{-1} cm^{-1}).

Thus, it follows from the analysis of the IR spectra of solutions of CH_3COONa in CH_3COOH that CH_3COO^- anions with CH_3COOH molecules form complexes with a strong symmetric H-bond $(CH_3COO...H...OOCCH_3)^-$.

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Synthesis of 1,3,4-thiaza- and 1,3,4-oxazaphosphol-2-ines based on *N*-phosphorylated (thio)ureas

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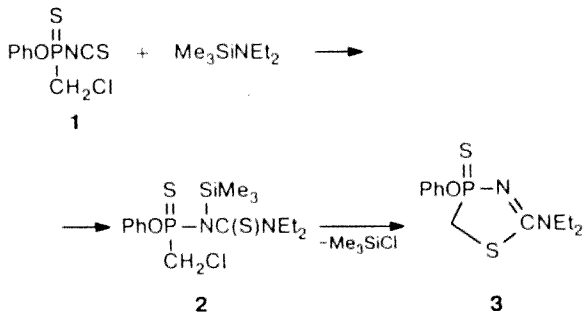
The reactions of *O*-phenyl chloromethylisothiocyanatothioxophosphonate and *O*-phenyl chloromethylisocyanatophosphonate with trimethylsilyldiethylamine lead to the formation of 1,3,4-thiazaphosphol-2-ine and 1,3,4-oxazaphosphol-2-ine, respectively. Phosphorylation of *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea with *O*-phenyl chloromethylchlorophosphonate gives 1,3,4-diazaphospholidin-2-one.

Key words: chloromethylphosphonates, silylated amines and ureas, heterocyclization, 1,3,4-oxazaphosphol-2-ine, 1,3,4-diazaphospholidin-2-one.

The synthesis of various 2-substituted 1,3,4-thiazaphospholines based on chloromethylisothiocyanato(thio)phosphonates has been previously developed.[1—3] It includes the addition of protonic nucleophiles (amines, mercaptans, and phosphines) to form *N*-phosphorylated thioureas, dithiocarbamates, and thioamides as intermediates followed by their intramolecular alkylation at the sulfur atom of the thio group by a chloromethyl group.

It has been established that silylated derivatives can be used instead of protonic nucleophiles themselves. The addition of trimethylsilyldiethylamine to *O*-phenylchloromethylisocyanatothioxophosphonate (**1**) is accompanied by the intermediate addition of silicon-containing *N*-phosphorylated thiourea (**2**). The latter is very unstable and immediately cyclizes to 2-diethylamino-4-thioxo-4-phenoxy-1,3,4-thiazaphospholine (**3**) accompanied by the elimination of trimethylchlorosilane.



1 **2** **3**

The similar reaction of *O*-phenylchloromethylisocyanatophosphonate (**4**) with trimethylsilyldiethylamine occurs readily at room temperature. After 1 day the spectrum contains two signals at δ_P 24 and 51 ppm in a ratio of 5 : 1 assigned to phosphorylated urea (**5**) and oxazaphospholine (**6**), respectively.

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