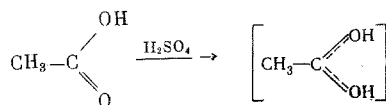


MECHANISM OF THE INTERACTION OF CONCENTRATED
SULFURIC ACID AND GLACIAL ACETIC ACID

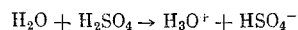
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An investigation of the interaction of various mineral acids with acetic acid [1-5] is not only of theoretical but also of practical importance in connection with the ability of anhydrous acetic acid to differentiate the strength of acids dissolved in it. A study of the interaction of acetic and sulfuric acids involves a consideration of the state and structure of these acids when they are mixed. In [6] it was proposed on the basis of the data of the Raman spectra and IR spectra that the structure of acetic acid changes in the following way when an aqueous solution of sulfuric acid is added:

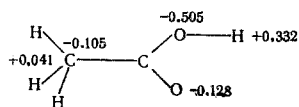


The authors apparently did not take into consideration the fact that water participated in this interaction and that, consequently, instead of the two-component system $\text{H}_2\text{SO}_4 - \text{CH}_3\text{COOH}$, they were actually studying a system of three components, $\text{H}_2\text{SO}_4 - \text{H}_2\text{O} - \text{CH}_3\text{COOH}$. At the same time, it is known that even a small quantity of water is sufficient for the dissociation of sulfuric acid according to the scheme:



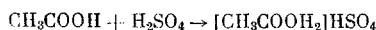
Acetic acid also dissociates partially, forming the anion $[\text{CH}_3\text{COOH}]^-$. Thus, in a three-component system the most varied types of interaction both of ionic and of molecular forms become possible.

In the second place, it was not shown in this work in what mole ratios the acids react (i.e., whether they are monobasic $[\text{CH}_3\text{COO}]\text{H}$, $\text{H}[\text{SO}_4\text{H}]$ or dibasic $\left[\text{CH}_3\overset{\text{O}^-}{\underset{\text{O}^-}{\text{C}}} \right]$, $\text{H}_2[\text{SO}_4]$). In addition, it seems not entirely justified to us to extrapolate the data on the electronic structure of the $[\text{COO}]^-$ group obtained from a calculation of benzoic acid by the Hückel molecular orbital method (HMO) to the electronic structure of acetic acid. We calculated the charges on the atoms of acetic acid according to the method of Del Rey in the neutral form:



The parameters for the calculation were taken from [7].

The calculation showed that a substantially larger negative charge is concentrated on the oxygen atom in the hydroxyl group than on the carbonyl oxygen. We believe that the interaction of acetic and sulfuric acids is determined chiefly by the charges on the atoms, and that there should primarily be a protonation of the hydroxyl oxygen:



It may be assumed that two cases are possible here: a) as a result of protonation, two equivalent OH bonds arise, which are arranged symmetrically with respect to the plane of the molecule, which leads to the appearance of symmetrical and antisymmetrical valence vibrations of the OH group; b) as a result of protonation, an OH bond arises, which is energetically close to an intermolecular hydrogen bond and

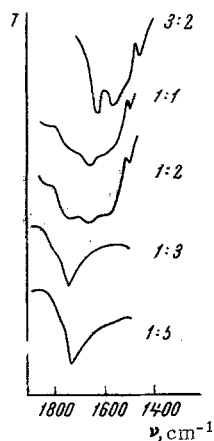


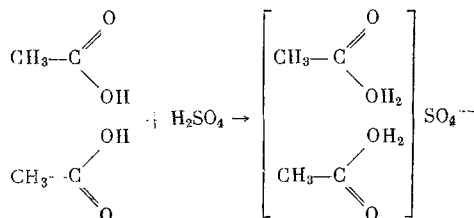
Fig. 1. IR spectra of mixtures of conc. H_2SO_4 and glacial CH_3COOH at various mole ratios.

therefore does not introduce any significant changes into the force field of the acetic acid molecule. After protonation of the hydroxyl oxygen atom, the distribution of charges in the molecule of $[CH_3COOH_2]^+$ is such that the carbonyl oxygen becomes more negative, and in the presence of excess sulfuric acid, there should be a further interaction with it.

EXPERIMENTAL METHOD

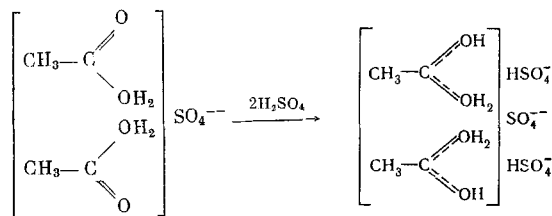
IR spectroscopy was used as the method of investigating the mechanism of the interaction of sulfuric and acetic acids. The vibrational spectra were measured on a UR-10 instrument (Fig. 1). The mixture of acids was placed between two polyethylene films and fixed in a holder. Sulfuric acid was placed in the reference channel between polyethylene films to compensate for the spectra of polyethylene and sulfuric acid. By gradually increasing the concentration of sulfuric acid in acetic acid, we succeeded in determining that until the mole ratio $H_2SO_4:CH_3COOH$ reaches 1:2, no significant changes are observed in the spectrum of acetic acid in the region of $1800-1500\text{ cm}^{-1}$.* The band at 1715 cm^{-1} , assigned to the valence vibrations of the $C=O$ group in the dimer of acetic acid, on the basis of the calculations of [8, 9] and the experimental data of [10], shows no change in intensity and is not shifted. Beginning with a ratio $H_2SO_4:CH_3COOH = 1:2$ up to a ratio 3:2, there is a gradual decrease in the intensity of the absorption band at 1715 cm^{-1} and the appearance of new bands at 1635 and 1570 cm^{-1} , which we assigned to the symmetrical and antisymmetrical vibrations of the $C(OH)_2$ group. At a ratio $H_2SO_4:CH_3COOH = 3:2$, the band at 1715 cm^{-1} disappears entirely, and further addition of sulfuric acid does not lead to any changes in the spectrum of acetic acid.

Thus, it may be imagined that the process of interaction proceeds in two steps. In the first step sulfuric acid behaves as a dibasic acid and combines with two molecules of acetic acid:



This is also confirmed by data on conductometric [11] and high-frequency titration [12, 13] of a solution of sulfuric acid in acetic acid. Actually, as long as the two protons of sulfuric acid are added to two molecules of acetic acid, they are equivalent. The replacement of one of the protons by potassium during titration of this solution with a solution of potassium acetate in acetic acid leads to a redistribution of the electron density in the sulfuric acid molecule and changes the nature of the bond of the second proton to acetic acid, as a result of which it is titrated separately.

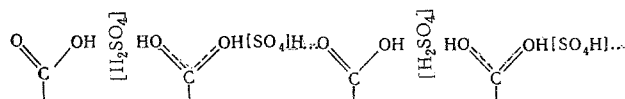
In the second stage of the interaction there is a sharp change in the structure of acetic acid, accompanied by a change in the force field of the molecule, which also leads to the observed strong changes in the spectrum.



* Changes in the spectrum of acetic acid begin within the interval between ratios 1:3 and 1:2, but closer to 1:2, which was due to the use of 95% sulfuric acid.

As can be seen, the structure obtained has substantial differences in comparison with that cited in [6].

To demonstrate the presence of an interaction of H_2SO_4 and CH_3COOH even before a 1:2 ratio was reached, we measured the viscosity of solutions of H_2SO_4 in CH_3COOH according to the procedure described in [14]. It might be expected that since there is a breakdown of the dimer of acetic acid in the interaction of H_2SO_4 and CH_3COOH , and a polymer structure is formed, the viscosity of the system should increase, which was observed experimentally. Measurements indicated that the maximum viscosity corresponds to a 1:1 ratio; when the H_2SO_4 content was further increased, the viscosity of the system decreased (which agrees with studies citing data on the measurement of the viscosity of systems of mixtures of mineral acids with acetic acid [5]). The data obtained can be explained by representing the process of interaction of H_2SO_4 and CH_3COOH in the following way: as was indicated above, at the first stage a structure is formed in which the forces binding sulfuric and acetic acids are probably close to hydrogen bonds. At a 1:1 mole ratio of the acids, half the carbonyl groups are protonated; in this case one of the protons of sulfuric acid combines with the oxygen of the carbonyl group, while the second proton, remaining free, is capable only of forming a hydrogen bond with the carbonyl oxygen.



This hydrogen bond should cross-link aggregates of molecules into a polymer. From the considerations cited it is clear that the optimum condition for the formation of a polymer structure is that in which the number of free protons of sulfuric acid is equal to the number of carbonyl oxygens of acetic acid, i.e., at a 1:1 ratio. Further increasing the amount of sulfuric acid in the system under consideration reduces the total number of carbonyl oxygens participating in the hydrogen bond, and consequently shortens the polymer chain; which finds reflection in a decrease in the viscosity of the system.*

CONCLUSIONS

1. It was established by investigations of the IR spectra that the reaction between sulfuric and acetic acids proceeds in two steps: at the first step the H_2SO_4 and CH_3COOH molecules interact in a 1:2 ratio; at the second stage two more molecules of H_2SO_4 are added to the product obtained.
2. The stoichiometric ratio of the acids in the final product is 3:2.

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* The presence of a small amount of water in the system (0.3 mole H_2O per mole of H_2SO_4) can change only the absolute magnitude of the measured viscosity, and cannot distort the general nature of the process.