

UV STUDY OF THE FORMATION OF SUPERACIDS IN A SULFURIC ACID MEDIUM

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The methods of ultraviolet (UV) spectroscopy were used to study the changes in the composition of the reaction systems consisting of a monocarboxylic (acrylic or methacrylic) or dicarboxylic (itaconic or glutaconic) acid, on the one hand and sulfuric acid, on the other. It was concluded that protonation of the carboxylic acids is taking place and that *monoprotonated* superacids are formed. The pK values for the protonation reactions were estimated numerically and graphically.

1. INTRODUCTION

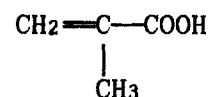
The ultraviolet (UV) spectroscopy has been used as a convenient method for the study of the protonation of various types of compounds which can undergo such reactions (see [1-10] and the references given therein). Relatively little is known about the UV studies of the formation of superacids by protonation of carboxylic acids by strong mineral acids such as H_2SO_4 . Among the not so numerous examples, the communications by Pospíšil *et al.* [2] and by Mchedlov-Petrosyan *et al.* [6] as well as our own [9,10] may be quoted.

Utilizing various techniques, the equilibrium constants for the protonation reactions could be determined [1-10] or, rather, estimated. Usually the pK values are given.

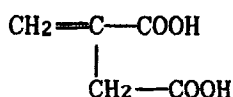
As mentioned above, we have already studied [9,10] the formation of superacids by protonation in aqueous solutions of sulfuric and/or perchloric acids. Extending these studies, we now report the results of the investigation of the protonation of acrylic (I) and methacrylic (II) acids as representatives of the monocarboxylic and of itaconic (III) and glutaconic acids (IV) as examples of the dicarboxylic acids.



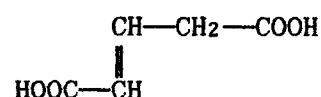
I



II



III



IV

2. EXPERIMENTAL

For each investigated acid, three parallel series of solutions with a constant concentration of the carboxylic acid ($\approx 1 \cdot 10^{-4}$ mol dm $^{-3}$) were prepared. The concentrations of itaconic and glutaconic acids were $1.0 \cdot 10^{-4}$ mol dm $^{-3}$, that of acrylic acid was $1.4 \cdot 10^{-4}$ mol dm $^{-3}$ whereas the concentration of methacrylic acid was $1.6 \cdot 10^{-4}$ mol dm $^{-3}$.

In order to ensure appropriate conditions for the protonation reactions to take place, the concentration of sulfuric acid in its aqueous solutions was varied from 0.1 to 17.5 mol dm $^{-3}$.

The UV spectra of each solution were recorded between 190 and 250 nm on a Hewlett-Packard 8452A Diode Array Spectrophotometer.

For each solution, four suitable wavelengths were chosen and the absorbance values were determined at each of them.

At each wavelength, the molar absorption coefficients for the respective organic acid were determined from separately prepared solutions with a constant concentration of the organic acid and a *low* (0.1 mol/dm 3) concentration of H $_2$ SO $_4$. The absorption coefficients for the corresponding superacids were estimated in a similar way, but using solutions with a *high* (17.5 mol/dm 3) sulfuric acid concentration. Three parallel determinations were carried out in each case.

The molar absorption coefficients were used to estimate the concentrations of the acid (HA) and the superacid (H $_2$ A $^+$) from the measured absorbance values.

All employed chemicals were reagent grade Merck products.

3. RESULTS AND DISCUSSION

The UV spectra of the four investigated acids are rather similar in their appearance. This is why only the spectra of two of them (I and III) or, rather, of their solutions in aqueous sulfuric acid are shown in Figs. 1 and 2 respectively.

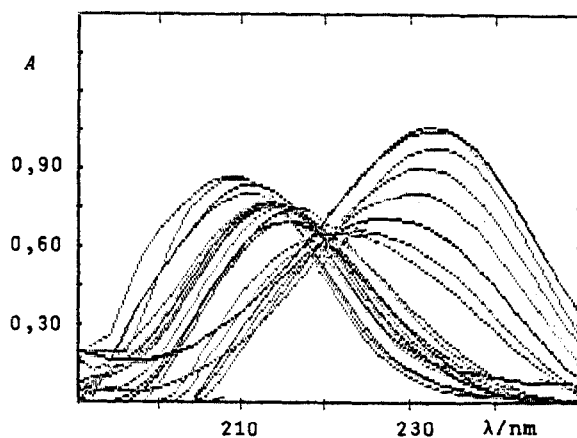


Fig. 1. The UV spectra of methacrylic acid in sulfuric acid solutions

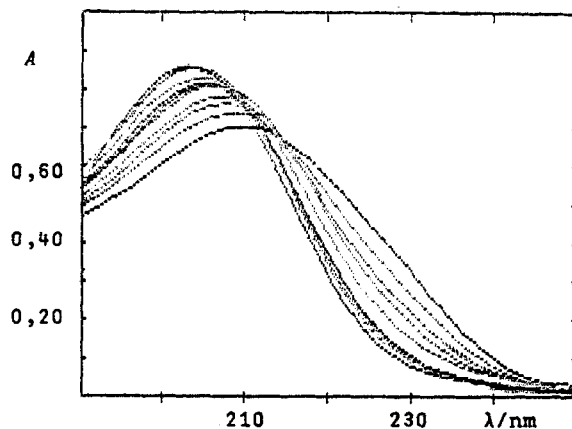


Fig. 2. The UV spectra of itaconic acid in sulfuric acid solutions

As seen, the change in the sulfuric acid concentration leads to spectral changes as well. The maxima of the absorption bands (only one band is observed for each acid) shift towards higher wavelengths whereas, as a rule, the intensities of the bands at first decrease and then increase when the sulfuric acid concentration is increased. Only in the case of itaconic acid the intensity of the band monotonously decreases.

The spectral changes described above show that a chemical change is taking place and the only (and expected) possibility is that the carboxylic groups are protonated and superacids are formed as a result.

As anticipated, the changes are such that the plots of the absorbance vs. the Hammett's acidity function H_0 [11] or of the wavelength of the absorption maximum vs. H_0 yield sigmoidal curves (Figs. 3 and 4). Merely as a reminder, we note that the Hammett's function reflects the sulfuric acid concentration.

The existence of *only one* step on the sigmoidal curves (such as those presented in Figs. 3 and 4) shows that the reaction leads to a formation of a *monoprotonated* acid not only when this is the only possibility (the two monocarboxylic acids) but also in the case of the dicarboxylic acids. Apparently, the sulfuric acid concentration is not sufficiently high to ensure the protonation of the second carboxylic group in the case of the dicarboxylic acids. This sounds reasonable since the protonation of the second COOH group would require a proton to be transferred to an already positively charged particle.

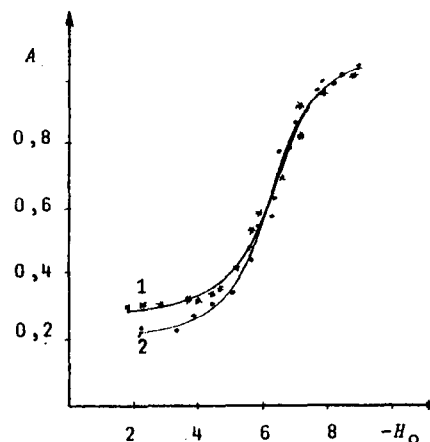


Fig. 3. A vs. H_0 curves for methacrylic acid (1) and itaconic acid (2)

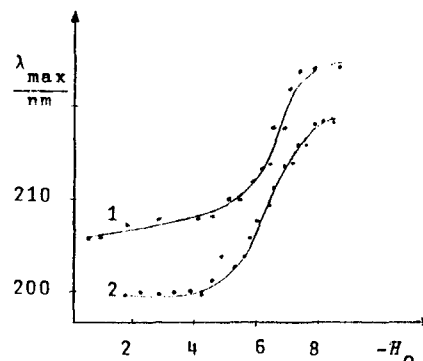
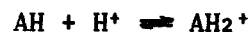


Fig. 4. The plot of the maximum of the absorption band in the spectrum of glutacetic acid (1) and acrylic acid (2) vs. H_0

For the equilibria



the protonation constants of the studied reactions were calculated

using the Hammett's equation [11] :

$$pK = H_0 + \log[c(AH_2^+)/c(AH)]$$

and *estimated* from the inflection points on the sigmoidal $A = f(H_0)$ curves.

The data obtained from the parallel determinations were averaged and the standard deviations were calculated. The pK values (with the standard deviations given in parentheses) are summarized in Table 1.

Table 1. Numerically and graphically determined pK values for the four investigated carboxylic acids

Acid	- pK	
	Numerically	Graphically
I	6.31 (0.41)	6.27
II	6.27 (0.36)	6.23
III	6.50 (0.39)	6.60
IV	6.37 (0.32)	6.30

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