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Professional paper

PROTONATION OF CITRACONIC AND MESACONIC ACID IN AQUEOUS AND ETHANOLIC SOLUTIONS

Katica Jankovska*, **Ilinka Spirevska** and **Lidija Šoptrajanova**

Institute of Chemistry, Faculty of Sciences, The "Sv. Kiril & Metodij" University, POB 162, 91001 Skopje, Republic of Macedonia

The influence of the solvent on the protonation of citraconic and mesaconic acid in aqueous and ethanolic solutions of H_2SO_4 was investigated using spectrophotometric methods. The spectra were recorded, in the 190–300 nm region, from solutions with a constant concentration of the organic acid ($1.0 \cdot 10^{-4}$ mol dm^{-3} in the case of citraconic and $2.4 \cdot 10^{-4}$ mol dm^{-3} for mesaconic acid) and increasing concentration of H_2SO_4 (from 1.0 to 17.5 mol dm^{-3}). It was found that in the case of citraconic acid at H_2SO_4 concentrations higher than 8 mol dm^{-3} protonation and dehydratation take place the latter leading to the formation of protonated citraconic anhydride. In the case of mesaconic acid (the geometrical isomer of citraconic acid) only the protonation reaction takes place, most probably because of the *trans* arrangement of the carboxyl groups in it. The solvent effect is considerable and in ethanolic solutions the protonation reaction is both initiated and terminated at lower concentration of the proton donor (H_2SO_4).

Key-words: citraconic acid; mesaconic acid; protonation; dehydratation; UV spectroscopy

INTRODUCTION

The acid-base equilibria established in systems containing citraconic and mesaconic acid were studied in water [1, 2] and in organic solvents [1] and the dissociation constants of the acids were determined. Also studied was the behavior of citraconic and mesaconic acid in aqueous solutions of sulfuric and perchloric acid [3–5] and it was found that in media which are not extremely acidic these acids act as bases which are being monoprotonated, most probably at the carboxylic oxygen which has a proton affinity higher (for 0.8–1.1 eV) than the singly bonded oxygen [6]. The studies of highly acid solutions (in oleum with varying SO_3 content) [5] showed that in solutions of citraconic acid two reactions (protonation and dehydratation of the protonated acid) are taking place whereas in mesaconic acid in addition to the above two, the *trans-cis* isomerization occurs so that in oleum with an SO_3 content up to 20 % in both systems only protonated citraconic acid and its protonated anhydride are present. In variance with the studies on the influence of the proton donor described above, the effect of the solvent does not seem to have been studied and this is why we decided to study the behaviour of citraconic and mesaconic acid in aqueous and ethanolic solutions of sulfuric acid.

EXPERIMENTAL

Series of solutions were prepared in which the concentration of the proton acceptor ($1.0 \cdot 10^{-4}$ mol dm^{-3} for citraconic acid and $2.4 \cdot 10^{-4}$ mol dm^{-3} for mesaconic acid) was constant whereas the concentration of H_2SO_4 ranged from 1.0 to 17.5 mol dm^{-3}. Also prepared were corresponding series of blank solutions (without the organic acids in

*Permanent address: Tehnološko-metalurški fakultet, Univerzitet "Sv. Kiril i Metodij", Rudjer Boškovi} bb, 91000 Skopje, Republic of Macedonia.

them) containing sulfuric acid with concentrations equal to those in the studied solutions.

The ultraviolet spectra were recorded (in the 190–300 nm region) on a Hewlett-Packard 8452 A Diode Array Spectrophotometer. The measurements were carried out at room temperature. The spectra of the ethanolic solutions were recorded immediately after the preparation of the solutions, whereas those of the aqueous solutions were recorded 24 hours after preparing the solutions (the protonated forms of the studied acids are stable [5]).

Citraconic acid and mesaconic acid were *purum* products of Fluka recrystallized from a mixture of ether and ligroin (citraconic acid) or water (mesaconic acid). In the latter case the recrystallization was repeated several times. The anhydride of citraconic acid (a product of Sigma) was of p.a. purity. Sulfuric acid and ethanol were products of Merck and Alkaloid (Skopje) with a p.a. quality. The exact concentration of H_2SO_4 was determined by titration with a standard NaOH solution.

RESULTS AND DISCUSSION

The ultraviolet spectra of citraconic (1) and mesaconic (2) acid in aqueous solutions of sulfuric acid with varying concentrations (from 1.0 to 17.5 mol dm^{-3}) are shown in Fig. 1 and Fig. 2 respectively. It is easily seen that these two geometrical isomers behave differently under identical experimental conditions. Thus, in the spectra of solutions containing mesaconic acid (Fig. 1) only one absorption band is present which, on increasing H_2SO_4 concentration gradually shifts towards longer wavelengths (from $\lambda_{max} \approx 223$ nm to $\lambda_{max} \approx 243$ nm), the change in its position being a result of the protonation reaction which is taking place [3–5]. On the other hand, in the spectra of citraconic acid solutions (Fig. 2) at H_2SO_4 concentrations of 9.0 mol dm^{-3} (the corresponding spectrum is marked by an asterisk) another band appears indicating that a second species absorbing in the 190–300 nm region is being formed. Suspecting that this second band may be due to the formation of the protonated anhydride of citraconic acid, pure citraconic anhydride was dissolved in sulfuric acid solutions with three different concentrations the spectra of which are shown in Fig. 3. In each of these spectra two bands are present, the first of which is at around 226 nm and, clearly, results from a transition in the protonated citraconic acid. On the other hand, the second of the absorption bands appears in the region from $\lambda_{max} \approx 250$ nm to $\lambda_{max} \approx 270$ nm depending on the sulfuric acid concentration. Amat and co-workers [7] found a similar band in solutions of maleic anhydride in 96 % H_2SO_4 and interpreted it as due to presence of protonated maleic anhydride. Accordingly, we attribute the band found in our spectra in the 240–270 nm region (at 246 nm in the spectra of solutions containing citraconic acid) to a transition in protonated citraconic anhydride. An additional support for such a conclusion is provided by the ^{1}H and ^{13}C NMR studies by Amat and co-workers [8] on the thermal stability of the protonated forms of citraconic acid. These authors, namely, detected (at 313 K) in the systems studied by them the existence of mixtures of protonated citraconic acid and protonated citraconic

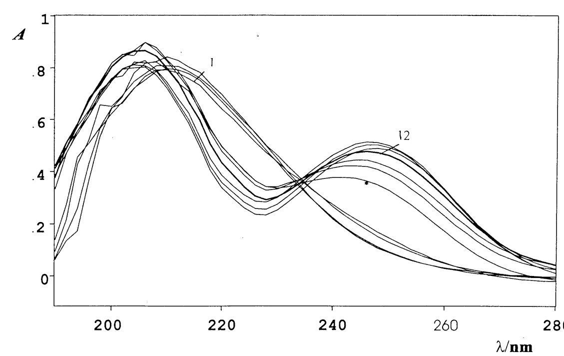

Fig. 1. UV spectra of citraconic acid (1.0·10^{-4} mol dm^{-3}) in sulfuric acid whit different cocentrations (from 1.0 mol dm^{-3} – curve 1, to 17.5 mol dm^{-3} – curve 12)

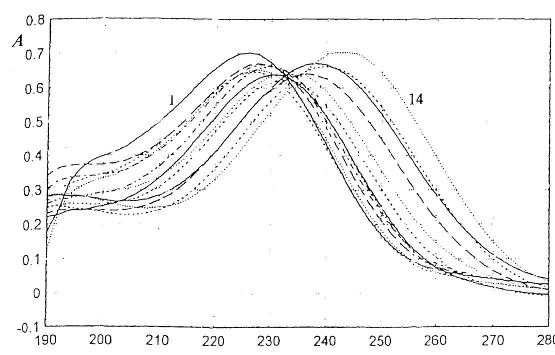

Fig. 2. UV spectra of mesaconic acid (2.4·10^{-4} mol dm^{-3}) in sulfuric acid whit different cocentrations (from 1.0 mol dm^{-3} – curve 1, to 17.5 mol dm^{-3} – curve 14)

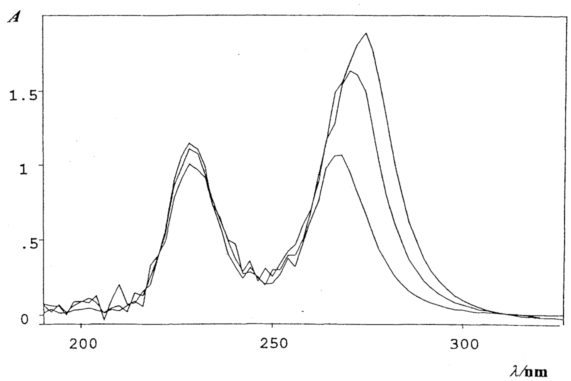

Fig. 3. UV spectra of the anhydride of citraconic acid in sulfuric acid (96 %)

anhydride, the ratio of the two species being dependent on the sulfuric acid concentration. Taken all together, we believe that our experiments show that at H_2SO_4 concentrations higher than 8 mol dm^{-3} two reaction take place in citraconic acid solutions – protonation of the acid and partial dehydratation of the formed protonated acid.

The UV spectra of citraconic and mesaconic acid in ethanolic solutions of H_2SO_4 differ insignificantly from those of the corresponding aqueous solutions with respect to both the form and the position of the bands except that, because of the lesser polarity of ethanol compared with water, a hardly detectable hypsochromic shift of the bands is present. The solvent effect is clearly visible in the spectra of citraconic acid solutions (Fig. 4) at H_2SO_4 concentrations of 13 mol dm^{-3} or higher (the intensity ratio of the bands at 246 nm and 206 nm is higher in ethanol than in water). In other words, more of the protonated anhydride is formed in ethanolic than in aqueous solutions. This result is easily understood taking into account the fact that ethanol is approximately 20 times weaker base than water and, consequently, the solvated proton $C_2H_5OH_2^+$ is a stronger acid than H_3O^+ (in other words, ethanol increases the acidity of the sulfuric acid solutions). The decrease in the relative permittivity of the ethanolic medium is an additional factor favoring the protonation reaction.

The solvent effect is even more evident from the $A = f[c(H_2SO_4)]$ curves shown in Fig. 5 for each of the studied acids. It is clear that under identical experimental conditions the protonation reaction in ethanolic solutions is more complete, especially in the case of mesaconic acid solutions. As seen, the curve 1a in Fig. 5 is almost horizontal up to an H_2SO_4 concentration of ≈ 12 mol dm^{-3} which indicates that the protonation of mesaconic acid begins at rather high sulfuric acid concentrations and is not completed even when $c(H_2SO_4) \approx 16$ mol dm^{-3}.

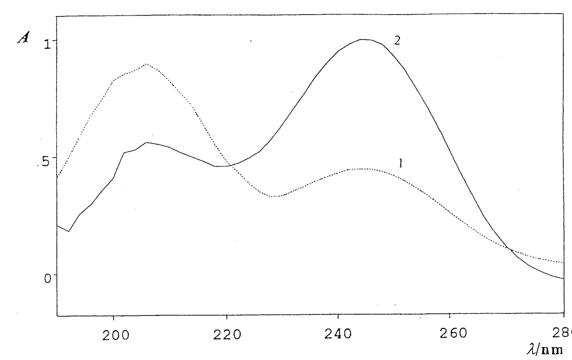

Fig. 4. UV spectra of citraconic acid (1.0·10^{-4} mol dm^{-3}) in aqueous (curve 1) and ethanolic (curve 2) solution of sulfuric acid (13.0 mol dm^{-3})

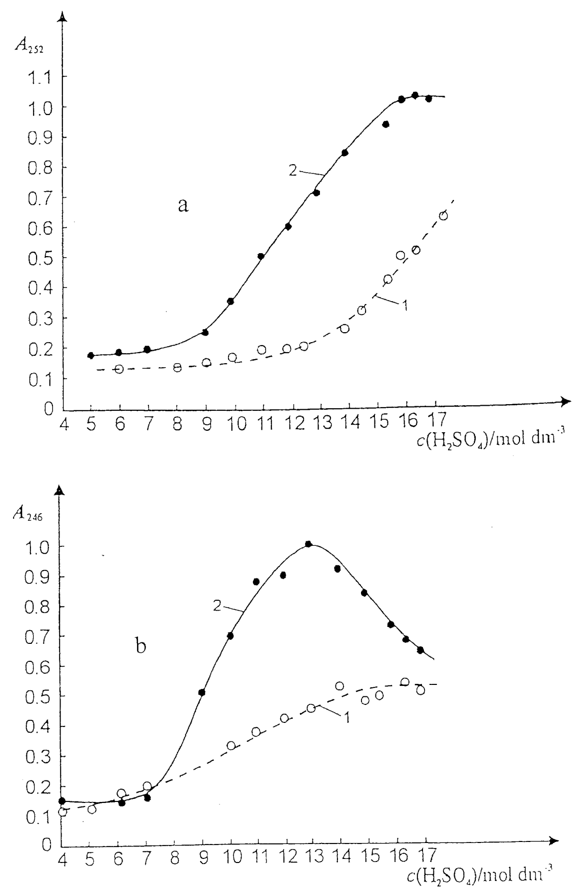

Fig. 5. a) The values of the absorbance of citraconic acid (1.0·10^{-4} mol dm^{-3}) in aqueous (curve 1) and ethanolic (curve 2) solution v.s. concentration of sulfuric acid. **b)** The values of the absorbance of mesaconic acid (2.4·10^{-4} mol dm^{-3}) in aqueous (curve 1) and ethanolic (curve 2) solution v.s. concentration of sulfuric acid

The titration curve for citraconic acid in ethanolic solutions of H_2SO_4 (curve 2b in Fig. 5) differs considerably from that obtained for the aqueous sulfuric acid solutions (curve 1b). Up to sulfuric acid concentrations of 13 mol dm^{-3} it is almost vertical indicating that in the ethanolic solutions the protonation and dehydration reactions are considerably more complete than in aqueous ones. At $c(H_2SO_4) > 13$ mol dm^{-3} the titration curve drops steeply on increasing H_2SO_4 concentrations as a result of the decrease in intensity of the band due to the presence of protonated anhydride.

The results of our studies show that in ethanolic solutions citraconic and mesaconic acid exist in their protonated form (AH_3^+) at lower concentrations of H_2SO_4 than in aqueous solutions (the protonation of mesaconic acid, however, is not complete even at the highest sulfuric acid concentrations). This finding is important for reactions taking place in acidic media in which these unsaturated acids act as intermediaries as well as for esterification processes carried out in acidic media [9].

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Р е з и м е

ПРОТОНИРАЊЕ НА ЦИТРАКОНСКА И МЕЗАКОНСКА КИСЕЛИНА ВО ВОДНИ И ЕТАНОЛНИ РАСТВОРИ

Катица Јанковска*, Илинка Спиревска и **Лидија Шоптрајанова**

Институт за хемија, ПМФ, Универзитет „Св. Кирил и Методиј", п.фах. 162, 91001 Скопје, Република Македонија

Клучни зборови: цитраконска киселина; мезаконска киселина; протонирање; дехидратација; УВ спектроскопија

Испитано е влијанието на растворувачот врз протонирање на цитраконска и мезаконска киселина во водни и етанолни раствори на сулфурна киселина со примена на спектрофотометрискиот метод. Беа снимени спектрите на серија од раствори во кои концентрацијата на органската киселина беше константна (за цитраконска киселина $1,0 \cdot 10^{-4}$ mol dm^{-3}, а за мезаконска киселина $2,4 \cdot 10^{-4}$ mol dm^{-3}), додека концентрацијата на H_2SO_4 беше растечка и се движеше од 1 до 17,5 mol dm^{-3}. Од добиените резултати беше констатирано дека при концентрации на H_2SO_4 поголеми од 8 mol dm^{-3} кај цитраконската киселина освен реакцијата на протонирање се одвива и реакцијата на дехидратација, при што се формира протониран анхидрид. Кај геометрискиот изомер на цитраконската киселина (мезаконската киселина) се одвива само реакција на протонирање што највероjатно се должи на *транс*-распоредот на карбоксилните групи во неа. Изучувањата на реакцијата на протонирање во водни и етанолни раствори на сулфурна киселина покажаа дека влијанието на растворувачот е значително. Имено, во етанолни раствори реакцијата на протонирање е поптолна, т.е. започнува и завршува при пониски концентрации на протон-донорот (H_2SO_4).