

## THE BEHAVIOR OF CITRACONIC AND MESACONIC ACID IN OLEUM

Katica Jankovska, Lidija Šoptrajanova, Pinka Spirevska

**A b s t r a c t:** The behavior of citraconic and mesaconic acid in oleum was studied at room temperature using the methods of UV/VIS spectroscopy. The changes in the absorption spectra recorded in the 190–300 nm region, at constant concentration of the organic acid ( $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) and increasing content of  $\text{SO}_3$  in oleum (from  $w = 0.047$  to  $w = 0.2$ ) show that in the case of citraconic acid two reactions (protonation of the acid and its dehydration) occur, both protonated citraconic acid and its protonated anhydride being present in the system. On the other hand an isomerization reactions in the case of mesaconic acid (the *trans* isomer of citraconic acid) equilibrium between protonated citraconic acid and its protonated anhydride being afterwards established.

The spectral appearance 24 hours after the preparation of the solutions shows that the formation of the anhydride of mesaconic acid goes more slowly, most probably due to the *trans* arrangement of the carboxyl groups in it.

**Key words:** citraconic acid, mesaconic acid, oleum, protonation, protonated citraconic anhydride, UV-VIS spectroscopy

### *Introduction*

It is well-known that the unsaturated dicarboxylic acids, citraconic and mesaconic, are easily polymerized and used in the production of polymers [1]. This is why their behavior in various reaction media was studied by a number of authors. In the beginning, the acid-base equilibria in water [2, 3] and in organic

solvents [2] were studied and the dissociation constants of the acids were determined. More recently, the behavior of these two geometrical isomers in acidic media (aqueous solutions of sulfuric and perchloric acid [4–6], as well as in ethanolic solutions of  $\text{H}_2\text{SO}_4$  [6]) was investigated. In the course of these studies it was found that both unsaturated carboxylic acids behave like bases, a reaction of monoprotection taking place. According to Benoit and Harrison [7] the hydrogen is bound to the carboxylic oxygen (the value of the proton affinity of the singly bonded oxygen in the carboxylic acids and esters, is for 0.8–1.1 eV lower than the proton affinity of the carboxylic oxygen).

Our previous studies [6] showed that in solutions of citraconic acid in  $\text{H}_2\text{SO}_4$  (when the concentration of the latter was higher than  $8 \text{ mol dm}^{-3}$ ), besides the protonation, dehydration of the protonated acid is also taking place, the protonated anhydride of citraconic acid being simultaneously present in the reaction system. In order to deepen these findings and to supplement our previous studies on the behavior of citraconic and mesaconic acid in various acidic media [4–6], we studied the influence of an superacid, such as oleum, on the behavior of the above-mentioned carboxylic acids (according to Gillespie [8], the superacids are systems in which the acidic function  $H_0 \leq -12$ ; for oleum with 20 % of  $\text{SO}_3$ ,  $H_0 = -13.02$  [9, 10]).

The solution of oleum is more acidic than the sulfuric acid. Namely, the increase of the concentration of  $\text{H}_3\text{SO}_4^+$  ions in the latter case is related solely to autoprotolysis of  $\text{H}_2\text{SO}_4$ . In oleum the reaction of  $\text{HSO}_4^-$  with  $\text{SO}_3$  leads to the formation of complex  $\text{HS}_3\text{O}_{10}^-$  ions:



Data for the thermal stability of the protonated forms of citraconic and mesaconic acid in oleum with 63 % of  $\text{SO}_3$  at 313 K were obtained by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [11].

### Experimental

Two series of solutions of citraconic and mesaconic acid with concentration  $1.0 \cdot 10^{-4} \text{ mol dm}^{-3}$  were prepared while the mass fractions of  $\text{SO}_3$  in the oleum solutions were 4.68 %, 9.99 %, 15.20 % and 20 %, respectively. Oleum (with appropriate composition) was used as a referent solution.

The ultraviolet spectra were recorded in the 190–300 nm region, using the Hewlett-Packard 8452 A Diode Array Spectrophotometer. The measure-

ments were conducted immediately after the preparation of the solutions and their cooling down to the room temperature and, also at room temperature, 24 hours after their preparation.

Citraconic and mesaconic acid were products of Fluka (of a *purum* quality). Citraconic acid was purified by recrystallization from a mixture of ether and ligroin whereas mesaconic acid was repeatedly recrystallized from water. The anhydride of citraconic acid (a product of Sigma) was of p.a. purity. The sample of oleum (a Carlo Erba product) was of p.a. quality containing 20 % of  $\text{SO}_3$ .

### Result and discussion

Two absorption bands (due to  $\pi$ - $\pi^*$  transitions) appear in the ultraviolet spectra of citraconic acid in oleum with different mass fractions of  $\text{SO}_3$  (Fig. 1). By increasing the mass fraction of  $\text{SO}_3$  in oleum, the band at shorter wavelengths ( $\lambda_{\text{max}} \approx 220$  nm) shifts insignificantly, while the second band ( $\lambda_{\text{max}} \approx 248$  nm) towards longer wavelengths (to about 270 nm). All spectral curves go through a clearly defined isobestic point at 255 nm. Its occurrence shows that both absorbing molecular species are in the system in equilibrium.

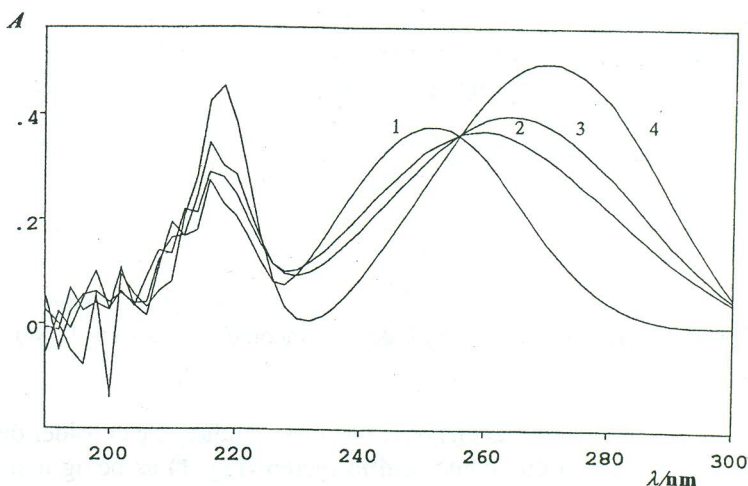


Fig. 1. UV spectra of citraconic acid ( $1.0 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ ) in oleum with 4.68 %  $\text{SO}_3$  (1), 9.99 %  $\text{SO}_3$  (2), 15.20 %  $\text{SO}_3$  (3) and 20.00 %  $\text{SO}_3$  (4) recorded immediately after preparing the solutions

As we have found previously [6], two bands also appear in the absorption spectra of citraconic acid solutions (in concentrated aqueous sulfuric acid), at concentrations of  $\text{H}_2\text{SO}_4$  greater than  $8 \text{ mol dm}^{-3}$ . When  $c(\text{H}_2\text{SO}_4) = 17.5 \text{ mol dm}^{-3}$  the first band (originating from a transition in the protonated acid) appears with  $\lambda_{\text{max}} \approx 210 \text{ nm}$ , and the second (due to the presence of the protonated anhydride of citraconic acid) is characterized by  $\lambda_{\text{max}} \approx 246 \text{ nm}$ .

In order to determine the origin of the bands in the spectra of citraconic acid in oleum, we recorded the spectrum of the anhydride of citraconic acid in 96 %  $\text{H}_2\text{SO}_4$  (Fig. 2). Two absorption bands are present in this spectrum. The band around 275 nm originates from an electronic transition in the protonated anhydride, whereas the other one (found at shorter wavelengths) is apparently related to the presence of protonated citraconic acid. Similar conclusion was reached by Amat and coworkers [12] using NMR spectroscopy. They have, namely found that in the case when the anhydride of maleic acid is dissolved in 96 %  $\text{H}_2\text{SO}_4$ , a mixture of protonated maleic anhydride and protonated maleic acid in 1:9 ratio is formed. The same authors [11], concluded that citraconic acid in oleum (with 63 %  $\text{SO}_3$  at 313 K), completely transforms into its protonated anhydride.

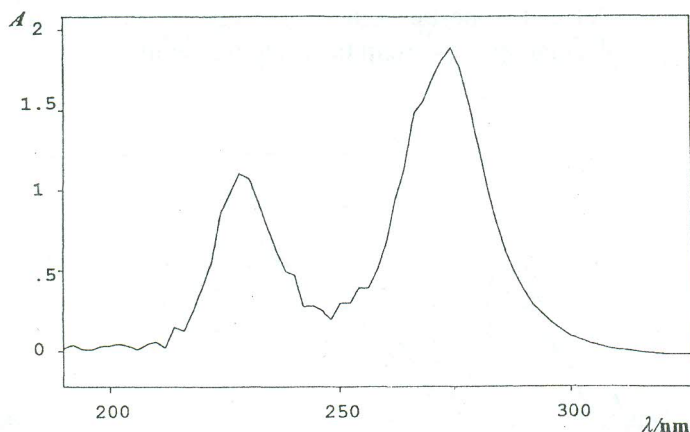
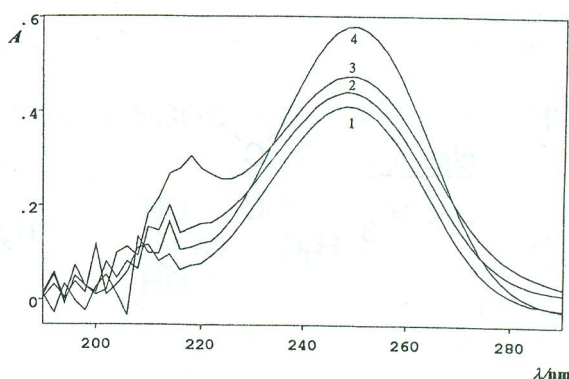


Fig. 2. UV spectra of the anhydride of citraconic acid in 96 %  $\text{H}_2\text{SO}_4$

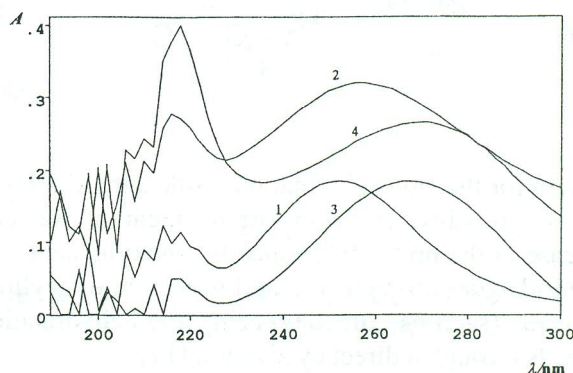
In line with the conclusions based on these studies, we consider the isobestic point in the spectra of citraconic acid in oleum (Fig. 1) as being a sign of the equilibrium between the protonated citraconic acid and its protonated anhydride.

The UV spectra of mesaconic acid (the geometrical isomer of citraconic acid) recorded immediately after the preparation and cooling of the solutions to

room temperature (Fig. 3), differ significantly from the spectra of citraconic acid. Here the absorption band with  $\lambda_{\max} \approx 250$  nm does not shift towards longer wavelengths with the increase of the mass fraction of  $\text{SO}_3$  in the reaction system, but gains in intensity. Around 218 nm there is another band with considerably lower intensity which, due to the absorption of oleum itself in the same spectral region is rather different to the distinguished. However, the spectra recorded 24 hours after the preparation of the solutions (Fig. 4) show that the reaction is still taking place, apparently going towards the formation of the anhydride of citraconic acid. If this indeed happens, then the second band which, on increasing the mass fraction of  $\text{SO}_3$  in oleum, shifts towards longer wavelengths (up to  $\lambda_{\max} \approx 270$  nm), originates from the protonated anhydride of citraconic acid.



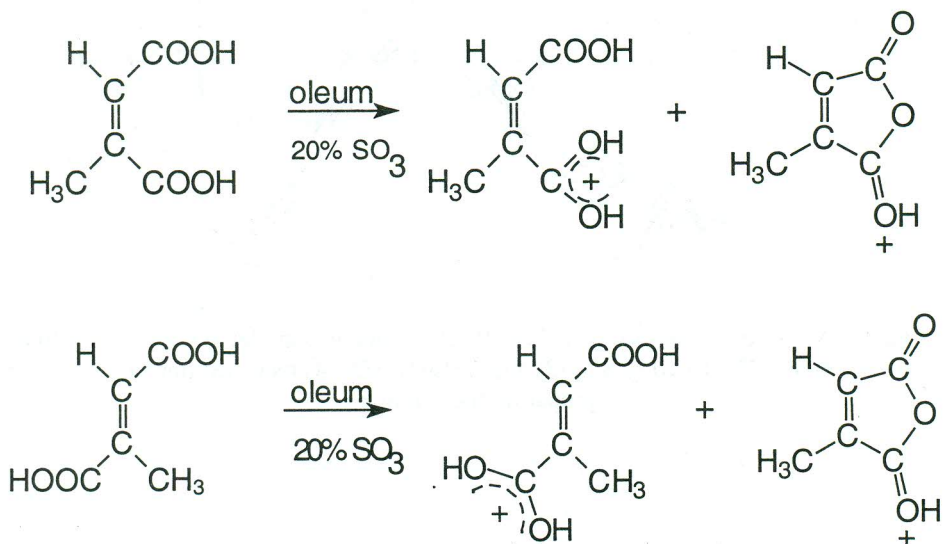
**Fig. 3.** UV spectra of mesaconic acid ( $1.0 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ ) in oleum with 4.68 %  $\text{SO}_3$  (1), 9.99 %  $\text{SO}_3$  (2), 15.20 %  $\text{SO}_3$  (3) and 20.00 %  $\text{SO}_3$  (4) recorded immediately after preparing the solutions



**Fig. 4.** UV spectra of mesaconic acid ( $1.0 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ ) in oleum with 4.68 %  $\text{SO}_3$  (1), 9.99 %  $\text{SO}_3$  (2), 15.20 %  $\text{SO}_3$  (3) and 20.00 %  $\text{SO}_3$  (4) recorded 24 hours after preparing the solutions

This agrees with the above mentioned studies of Amat *et al.* [11] who found out that mesaconic acid in oleum with 63 %  $\text{SO}_3$  at 313 K completely transforms into the protonated anhydride of citraconic acid, the intermediary in the fast *trans-cis* isomerization being the acilium ion  $\text{RC}\equiv\text{O}^+$ .

The above described studies lead us to the conclusion that, at room temperature, in oleum with an  $\text{SO}_3$  content up to 20 %, two reactions (protonation and dehydration) are taking place in the case of citraconic acid. On the other hand three reactions are taking place in succession in the corresponding solutions of mesaconic acid: isomerization, protonation and dehydration. As a result, in both systems the same types of cations are present – the protonated citraconic acid and its protonated anhydride. The equations of the reactions would be as follows:



The reason for the slower formation of the anhydride in mesaconic acid solutions is, most probably, the *trans*-arrangement of the carboxyl groups. Namely, in the case of the protonated *trans*-dicarboxylic acids, the formation of protonated anhydride goes through an initial formation of acylium ions, while in the case of *cis* acids (such as citraconic acid), the dehydration of the protonated acid proceeds through a direct cyclization [11].

The differences in the medium (i.e. the different nature of the proton donor), obviously leads to even more pronounced differences in the behavior of the studied organic acids. Thus, when oleum is the proton donor, the protona-

tion and dehydration reactions of citraconic acid are more complete compared to the case when  $H_2SO_4$  plays this role [5, 6]. The differences in the behavior are more pronounced in the case of the *trans*-isomer (i.e., mesaconic acid). Even in solutions with the highest  $H_2SO_4$  concentration ( $17.5 \text{ mol dm}^{-3}$ ), the protonated mesaconic acid is the unique product, while in oleum, a mixture of protonated citraconic acid and its protonated anhydride is formed as a result of the reactions of isomerization and dehydration.

## REFERENCES

- [1] I. A. Askarov, B. L. Tafurov, *Sintez i polimerizaciya itakonatov*, Fan, Tashkent, 1979.
- [2] W. Simon, P. Mencke, E. Heillbrouner, *Helv. Chim. Acta*, **39** (1956) 290.
- [3] N.W. Ashton, J.R. Partington, *Trans. Faraday Soc.*, **30** (1937) 598.
- [4] I. Spirevska, L. Šoptrajanova, B. Andonovski, *Bull. Chem. Technol. Macedonia*, **8** (1990) 151.
- [5] L. Soptrajanova, I. Spirevska, *Bull. Chem. Technol. Macedonia*, **10** (1991) 21.
- [6] K. Jankovska, *Ph.D. Thesis*, Tehnolosko-metalurski fakultet, Skopje, 1997.
- [7] F. M. Benoit, A. G. Harrison, *J. Amer. Chem. Soc.*, **99** (1977) 3980.
- [8] R. J. Gillespie, T. E. Peel, *J. Amer. Chem. Soc.*, **95** (1973) 5173.
- [9] J. C. D. Brand, W. C. Horning, M. B. B. Thornely, *J. Chem. Soc.*, (1952) 1374.
- [10] M. I. Vinik, R.S. Ryabova, *Zh. Fiz. Khim.*, **38** (1964) 606.
- [11] A. M. Amat, G. Asensio, M. A. Miranda, M. J. Sabater, A. Simon-Fuentes, *J. Org. Chem.*, **53** (1988) 5480.
- [12] A. M. Amat, G. Asensio, M. J. Castello, M. A. Miranda, A. Simon-Fuentes, *Tetrahedron*, **43** (1987) 905.

## Резиме

### ОДНЕСУВАЊЕ НА ЦИТРАКОНСКАТА И МЕЗАКОНСКАТА КИСЕЛИНА ВО ОЛЕУМ

Проучено е однесувањето на цитраконската и мезаконската киселина во средина на олеум, на собна температура, со примена на методите на УВ-ВИД спек-

троскопија. Промените во апсорпционите спектри се регистрирани во подрачјето на бранови должини од 190 до 300 nm при константна концентрација на органската киселина ( $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) и растечки удел на  $\text{SO}_3$  во олеумот (од 0,047 до 0,200). При тоа е покажано дека во случај на цитраконската киселина, се одвиваат реакциите на протонирање и дехидратација, додека во случај на мезаконската киселина (*trans*-изомер на цитраконската киселина) се одвива реакцијата на изомеризација заради што во системот се присутни протонирана цитраконска киселина и нејзиниот протониран анхидрид.

Katica Jankovska<sup>1</sup>, Lidija Šoptrajanova<sup>2</sup>, Ilinka Spirevska<sup>2</sup>

<sup>1</sup>Faculty of Technology and Metallurgy,  
The "Sv. Kiril & Metodij" University,  
P. O. Box 580, MK-1001 Skopje, Republic of Macedonia

<sup>2</sup>Faculty of Natural Sciences and Mathematics,  
Institute of Chemistry, The "Sv. Kiril & Metodij" University  
P. O. Box 162, MK-1001 Skopje, Republic of Macedonia