Academician B. A. ARBUZOV, O. A. ERASTOV, A. B. REMIZOV

![chemical structures I-III](image)

1965

SovietRxiv

chemical structures I-III

Figure 1: chemical structures I-III

Abstract

Full Text

CHEMISTRY

Academician B. A. ARBUZOV, O. A. ERASTOV, A. B. REMIZOV

SPECTROSCOPIC STUDY OF THE TAUTOMERISM OF 4-CARBOMETHOXY-3-KETOTHIOPHANE, 2-CARBOMETHOXY-3-KETOTHIOPHANE, AND 4-METHYL-2-CARBOMETHOXY-3-KETOTHIOPHANE

Although esters of 3-ketothiophanecarboxylic-4 acid (I) and 3-ketothiophanecarboxylic-2 acid (II) were obtained 20 years ago (1), their tautomerism has remained almost unstudied.

Budvard and Istmen (1d), who studied the conditions for the formation of I and II, indicate that with ferric chloride I gives a reddish-violet coloration. Isomer II gives with ferric chloride a transient reddish-violet coloration due to I and is readily oxidized by iodine, as Budvard and Istmen suppose, through the enol stage. These are the extent of the literature data on the tautomerism of I and II.

Since chemical methods have not given satisfactory results for keto-enols containing sulfur in the ring (2), we used infrared and ultraviolet spectra to study their tautomerism.

Ester I was obtained according to (1d) and had b.p. 118-120°/11 mm; n_D^{25} 1.5250; d_4^{25} 1.2753; MR_D exp. 38.31; MR_D ketone 37.37; MR_D enol 38.42. On standing, the ester crystallized, m.p. 38° (lit. 37.8°).

Ester II was obtained according to (1d): b.p. 118-123°/11 mm; n_D^{25} 1.5071; d_4^{25} 1.2793; MR_D exp. 37.50; MR_D ketone 37.37; MR_D enol 38.42.

Ester III was obtained analogously to I: b.p. 122-126°/14 mm; n_D^{25} 1.4969; d_4^{25} 1.2073; MR_D exp. 42.2; MR_D ketone 41.98; MR_D enol 43.04.

For comparison, spectra were taken of the methyl ester of cyclopentanone-1-carboxylic-2 acid (V), b.p. 98-101°/18 mm, n_D^{25} 1.4568 (3), and of the ethyl ester of cyclopentanone-1-carboxylic-2 acid (IV), b.p. 102-105°/12 mm, n_D^{25} 1.4510 (3).

Fig. 4

Figure 2: Fig. 4

In the literature there is no established opinion on the assignment of frequencies in the region 1800-1700 cm in the infrared spectra of esters of cyclopentanone-1-carboxylic-2 acid (4).

In the present communication we assume that, in the infrared spectra of esters I-III, in the indicated region the higher frequency belongs to the ketone group, and the lower one to the carbonyl of the ester group. We take the same assignment for esters IV and V.

Figure 1a presents the spectrum of ester I with m.p. 38° in Vaseline oil. As can be seen, ester I is the enol form (C=O chel. 1670 cm^{-1}, C=C 1630 cm^{-1}).

In the spectrum of ester II (Fig. 1b, film) there are very intense bands of the keto form (C=O ket. 1750 cm^{-1}, C=O est. 1735 cm^{-1}) and medium-intensity bands of the enol form (C=O chel. 1664 cm^{-1}, C=C 1628 cm^{-1}). Since, according to Budvard and Istmen (1d), ester II contains 20-25% ester I, which tends to be in the enol form, it is probable that ester II contains little of the enol form.

Fig. 1.

Subpanels: **a**, **b**, **c**, **d**, **e**, **f**.

Fig. 2.

Subpanels: **a**, **b**, **c**, **d**, **e**.

Fig. 3.

Subpanels: **a**, **b**, **c**, **d**, **e**.

In the spectrum of ester III (Fig. 1*c*, film) there are absorption bands of the keto form (C=O ket. 1750 cm^{-1}, C=O ester 1735 cm^{-1}) of high intensity and bands of the enol form of very low intensity (C=O chel. 1656 cm^{-1}, C=C 1605 cm^{-1}); i.e., at equilibrium the ketone form is represented mainly. For comparison, the spectra of esters IV and V are given (Fig. 1*d* and *e*, film).

Fig. 4

To study the influence of solvents on the position of the equilibrium, IR spectra of esters I-V were recorded in carbon tetrachloride and isobutyl alcohol.

Figure 2 gives the spectra of esters I-V in carbon tetrachloride. As can be seen, ester I in CCl_4 is mainly in the enol form (Fig. 2*a*). In CCl_4, for esters II and III (Fig. 2*b*, *c*) the amount of enol did not change substantially, whereas for esters IV and V (Fig. 2*d*, *e*) the content of the enol form increased noticeably. Passing hydrogen chloride through solutions of esters II and III led to a noticeable increase in the content of the enol form, and in the case of ester I, of the ketone form.

Figure 4 gives the spectra of esters I-V in isobutyl alcohol. As can be seen, in isobutyl alcohol in the case of ester I (Fig. 4*a*) the amount of keto form increased noticeably, but the enol form predominates. Esters II-V contain in solution a small amount of the enol form (Fig. 3*b*, *c*, *d*, *e*).

Table 1

Characteristic frequencies of esters I-V (cm^{-1})

Group	I	II	III	IV	V	VI	VII
A C-O ket.	1752	1750	1750	1757	1754	1740	1743
A C-O ester	1735	1737	1736	1730	1735		
A C-O chel.	1672	1664	1655	1661	1668		
A C-C	1630	1628	1605	1628	1628		
B C-O ket.	1755	1757	1754	1760	1762	1743	1745
B C-O ester	1735	1738	1738	1729	1735		
B C-O chel.	1674	1670	1658	1664	1668		
B C-C	1630	1630*	1604	1620	1623		
V C-O ket.	1752	1752	1750	1752	1756		
V C-O ester	1730	1732	1730	1730*	1730*		
V C-O chel.	1670	1669	1652	1655	1665		
V C-C	1628	1625	1605	1620	1622		
G C-O chel.	1670						
G C-C	1630						

Note. A —liquid; B —in carbon tetrachloride; V —in isobutanol; G —solid. VI —thiophanone-3, VII —4-methylthiophanone-3.

* Broad.

From comparison of the spectra (Figs. 1, 2, and 4) it is evident that replacement of the CH_2 group in the ester of cyclopentanone-1-carboxylic-2 acid by sulfur in the α-position to the ester group does not substantially change the position of the equilibrium. An analogous replacement in the β-position leads to a sharp increase in the enol content.

Table 1 gives the characteristic frequencies of esters I-V. Each value is the average of a series of determinations.

The IR spectra of esters I—V in the region 2500—3700 cm^{-1} (Fig. 3) are in agreement with the data presented above. In esters III—V (Fig. 3 , ,), absorption by the hydroxyl group is not observed. In the spectrum of ester I (Fig. 3), the broad band at 3080—3400 cm^{-1}, evidently superimposed on the absorption of the CH_2 group, may be assigned to absorption by the hydroxyl group. The analogous band in the spectrum of ester II (Fig. 3) is apparently due to an admixture of ester I.

The UV spectra data for I, II, IV, and V in methyl, ethyl, and isobutyl alcohols are presented in Table 2.

Table 2

UV absorption spectrum of esters I, II, IV, V

	I	I	II	II	IV	IV	V	V
	λ_{max}	ε	λ^*_{max}	ε	λ_{max}	ε	λ_{max}	ε
Methanol	2470	3200	2425	1020	2570	385	2570	397
Ethanol	2470	3900	2425	1190	2570	485	2570	510
Butanol	2470	4800	2425	1390	2570	800	2570	797

* Broad.

These data confirm the conclusions drawn from the IR spectra concerning the considerably greater degree of enolization of ester I in comparison with ester II (isomer II contains 20–25% I, which should be taken into account when estimating the degree of enolization of II, IV, and V).

The spectral data obtained confirm the results of the study by Woodward and Eastman (1) on the influence of temperature on the nature of cyclization in the preparation of 4-carbomethoxy-3-ketothiophane and 2-carbomethoxy-3-ketothiophane, and provide a clear qualitative picture of the tautomerism of these β-keto esters.

At present, a study of the above-mentioned tautomerism by the method of proton magnetic resonance has been begun.

The IR spectra were recorded on a Hilger H-800 spectrophotometer, and the UV spectra on an SF-4 spectrophotometer. The spectra were recorded at definite time intervals until changes in them ceased, which indicated the establishment of equilibrium.

Kazan State University
named after V. I. Ulyanov-Lenin

Received
31 XII 1964

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Note: Figure translations are in progress. See original paper for figures.