KINETICS AND MECHANISM OF THE ACID CATALYTIC HYDROLYSIS OF 1-ALKYLTHIO-1-BUTEN-3-YNES

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UDC 541.127:541.124:
542.97:542.938

Protolysis in the acid catalytic hydrolysis of 1-alkoxy-1-buten-3-ynes (AB) [1] proceeds according to a different mechanism from the protolysis of structurally close vinyl ethers. In this work we studied the influence of replacement of an oxygen atom by a sulfur atom in the C^1 position of AB on the kinetics and mechanism of hydrolysis. For this purpose we made a spectrophotometric investigation of the kinetics of the acid catalytic hydrolysis of a series of 1-alkylthio-1-buten-3-ynes (ATB).

EXPERIMENTAL METHOD

1-Alkylthio-1-buten-3-ynes were synthesized according to [2]. According to the data of IR and PMR spectroscopy, all the compounds were cis isomers. The measurements were performed on a Unicam SP-8000 spectrophotometer in a thermostatically controlled cuvette (1 cm). The initial ATB had one absorption band at 273-274 nm.

The reaction of hydrolysis was conducted in aqueous and aqueous methanol (2:1 by volume) media at 40-50° (accuracy of thermostatic control ± 0.5°). The initial concentration of the substrate was varied in the range 0.0001-0.0002 M, HCl concentration 0.2-0.9 M.

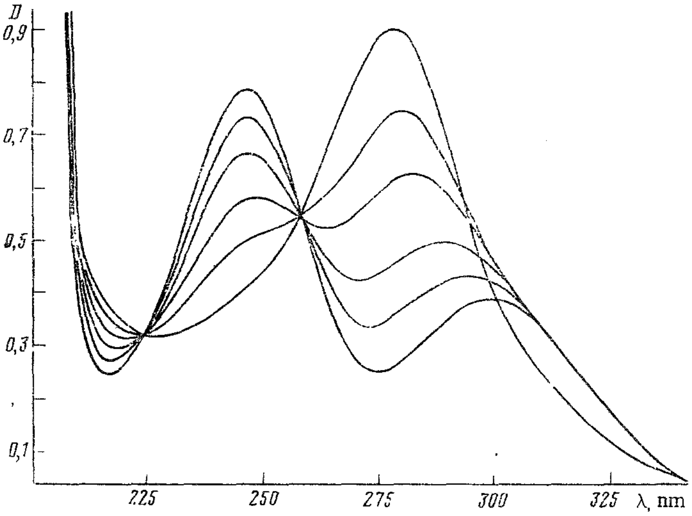

Fig. 1. Variations in the UV spectrum in the hydrolysis of $HC \equiv CCH = CHSC_4H_9$ (40°, water, concentration of substrate 0.0001 M, 0.5 M HCl — curves obtained at 7-min intervals).

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1975-1979, September, 1975. Original article submitted October 29, 1974.

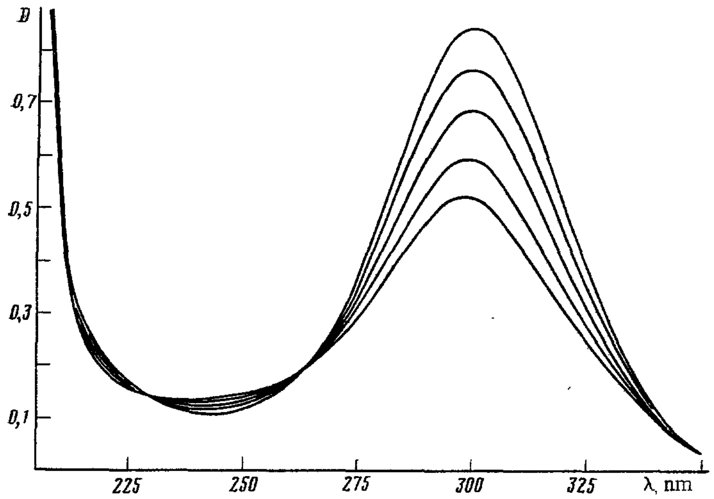

Fig. 2. UV-spectral monitoring of the hydrolysis of $C_2H_5SCH = CHCOCH_3$ (50°, water, substrate concentration 0.00005 M, 0.5 M HCl, curves obtained at 10-min intervals).

The spectra of the hydrolyzate (Fig. 1) contained three absorption bands (λ_{max} 246, 273, 300 nm), where λ_{max} of the initial ATB was gradually shifted to 246 nm with the simultaneous appearance of the third band (300 nm). The reaction rate was measured according to the decrease in the absorption of the initial ATB (273 nm) and according to the rate of absorption at 246 nm. In this case the same patterns were maintained as in the hydrolysis of AB [1].

In the hydrolytic cleavage of ATB, 1-alkylthio-1-buten-3-ones can be formed; as a control we synthesized 1-ethylthio-1-buten-3-one, which actually absorbs in the region of 300 nm. In this case, in the presence of acid a decrease in the concentration of 1-ethylthio-1-buten-3-one is observed; however, the appearance of the absorption maximum of acetoacetaldehyde (246 nm) is not observed, although the consumption of thiobutenone is evident (Fig. 2). The rate of decrease in 1-ethylthio-1-buten-3-one at 50° is characterized by a pseudofirst-order rate constant $k_1 = 2.1 \cdot 10^4\ sec^{-1}$ at a HCl concentration of 0.5 M.

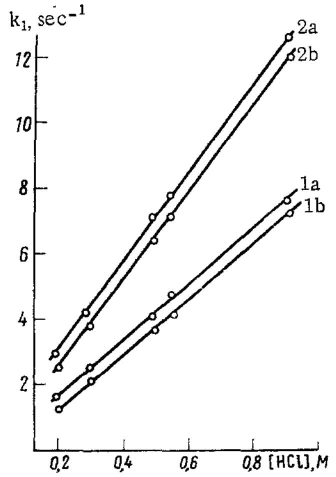

Fig. 3. Dependence of k_1 on the HCl concentration: 1) $R = C_3H_7$; 2) $R = C_4H_9$. a) Calculation according to the decrease in the concentration of the initial sulfide; b) calculation according to the increase in the concentration of acetoacetaldehyde.

DISCUSSION OF RESULTS

According to [3], the acid hydrolysis of 1-ethylthio-1-buten-3-yne (10% H_2SO_4, 60-95°) proceeds chiefly through the step of hydration of the triple bond, as a result of which ethylthiobutenone is formed, and is then saponified to acetoacetaldehyde; the latter is trimerized to triacetylbenzene (λ_{max} in aqueous medium 228 nm)

$$HC{\equiv}CCH{=}CHSR \xrightarrow[H_2O]{H^+} CH_3COCH{=}CHSR \rightarrow CH_3COCH_2CHO \rightarrow 1,3,5\text{-}(CH_3CO)_3C_6H_3 \quad (1)$$

The kinetics of the investigated reaction is identical with the kinetics of acid catalytic hydrolysis of AB [1] (first order with respect to the substrate and acid). At a constant acid concentration the reaction proceeds as a pseudo monomolecular process. Within the interval of acidities studied, the pseudofirst-order rate constant k_1 is a linear function of the acid concentration (Fig. 3). Evidently at first there is a protonation of the triple bond. The decrease in the absorption at λ_{max} 273 nm characterizes the rate of this step:

$$HC{\equiv}CCH{=}CHSR + H^+ \rightarrow [H_2C{=}\overset{+}{C}CH{=}CHSR \leftrightarrow H_2C{=}C{=}CH\overset{+}{C}HSR \leftrightarrow H_2C{=}C{=}CHCH{=}\overset{+}{S}R]\ (I) \quad (2)$$

However, the similarity of the hydrolysis of 1-alkoxy- and 1-alkylthio-1-buten-3-ynes ends in this.

The observed rate constant k_2 of the consumption of ATB is significantly greater than the rate constant of accumulation (k_2') of

TABLE 1. Second-Order Rate Constants and Parameters of Activation of Hydrolysis of HC ≡ CCH = CHSR, Calculated according to the Decrease in the Concentration of the Initial Sulfide

R	$(k_2 \pm s_{k_2}^*)\cdot 10^4$, liters·mole^{-1}·sec^{-1} (correlation coefficient)						ΔH≠, kcal /mole	ΔS≠, cal /mole·deg
	40°		45°		50°			
CH_3	10,86±0,05 *	(0,998)	14,82±0,09	(0,997)	18,20±0,07	(0,998)	12,2	—10,7
C_2H_5	12,02±0,12	(0,998)	17,08±0,17	(0,991)	20,40±0,05	(0,998)	13,8	—9,4
C_3H_7	13,00±0,06	(0,998)	19,28±0,13	(0,995)	22,40±0,04	(0,992)	15,5	—8,6
i-C_3H_7	11,62±0,05	(0,999)	16,60±0,07	(0,998)	29,98±0,09	(0,999)	14,1	—9,1
C_4H_9	14,10±0,09	(0,996)	23,68±0,06	(0,999)	32,60±0,01	(0,999)	19,1	—6,5
i-C_4H_9	10,88±0,07	(0,995)	16,34±0,12	(0,996)	29,30±0,40	(0,990)	16,0	—8,2
t-C_4H_9	8,74±0,05	(0,996)	15,10±0,07	(0,998)	22,00±0,14	(0,996)	20,6	—6,1

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*Here and henceforth, the standard deviation.

TABLE 2. Second-Order Rate Constants and Parameters of Activation of Hydrolysis of HC ≡ CCH = CHSR, Calculated according to the Accumulation of Acetoacetaldehyde

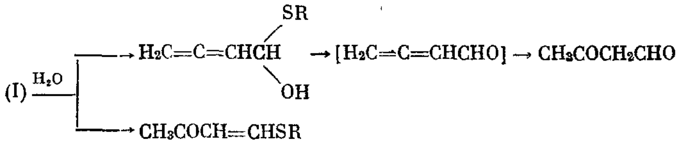
R	$(k'_2 \pm s_{k_2})\cdot 10^4$, liters·mole^{-1}·sec^{-1} (correlation coefficient)						ΔH≠, kcal /mole	ΔS≠, cal /mole·deg
	40°		45°		50°			
CH_3	9,85±0,02	(0,999)	13,44±0,03	(0,999)	17,00±0,05	(0,999)	15,3	—8,0
C_2H_5	8,80±0,01	(0,998)	11,98±0,08	(0,998)	15,54±0,08	(0,998)	14,4	—8,5
C_3H_7	8,54±0,05	(0,997)	8,72±0,09	(0,991)	13,98±0,05	(0,997)	13,5	—8,9
i-C_3H_7	4,60±0,04	(0,995)	7,72±0,03	(0,999)	10,20±0,04	(0,999)	12,5	—9,5
C_4H_9	7,64±0,06	(0,999)	8,02±0,03	(0,999)	10,60±0,07	(0,996)	10,2	—10,8
i-C_4H_9	6,22±0,04	(0,996)	7,98±0,02	(0,999)	8,14±0,06	(0,995)	9,6	—11,0
t-C_4H_9	4,90±0,03	(0,998)	6,72±0,03	(0,998)	10,88±0,04	(0,999)	16,3	—7,5

TABLE 3. Second-Order Rate Constants $(k_2 \pm sk_2) \cdot 10^4$, liters · $mole^{-1}$ · sec^{-1} of the Hydrolysis of $HC \equiv CCH = CHSR$ in Water–Methanol Medium (2 : 1)*

R	40°		50°	
	1	2	1	2
C_3H_7	6,21±0,02	2,24±0,04	14,01±0,12	3,55±0,02
i-C_4H_9	5,11±0,05	1,56±0,03	13,90±0,09	2,04±0,04

*1) Calculation according to the decrease in the concentration of the initial sulfide; 2) calculation according to the increase in the concentration of acetoacetaldehyde.

acetoacetaldehyde (Tables 1 and 2). This means that the primary cation (I) is further converted in two directions: one leads to acetoacetaldehyde, the other to 1-alkylthio-1-buten-3-one. Moreover, the latter, as shown by a special experiment, is not hydrolyzed to acetoacetaldehyde:

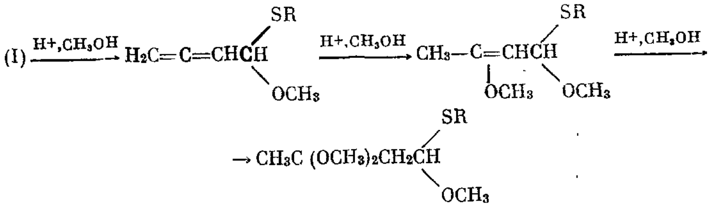


$$(\mathrm{I}) \xrightarrow{H_2O} \begin{cases} H_2C{=}C{=}CHCH(SR)(OH) \rightarrow [H_2C{=}C{=}CHCHO] \rightarrow CH_3COCH_2CHO & (3) \\ CH_3COCH{=}CHSR & (4) \end{cases}$$

The differences in the behavior of the cation (I) and its oxygen analog [1] are probably due to the different degree of stabilization of the charge in the C^1 position. The sulfur atom is a substantially poorer partner in p–π conjugation than the oxygen atom [4]; therefore, the C^1 carbon in the cation (I) should be more strongly subject to nucleophilic attack of the water molecule than in the oxygen analog. In other words, the transition state of step (2) in this case lies closer to the cation than in the case of AB.

As can be seen from a comparison of the data (Tables 1-3), the reaction is extremely sensitive to additions of methanol. In aqueous methanol (2 : 1) the rate of protonation [step (2)] decreases ~twofold, while the rate of formation of acetoacetaldehyde (step 3) decreases ~fourfold. At a water: methanol ratio of 1 : 1, the absorption at 245 nm practically does not appear in the UV spectrum of the hydrolyzate. These results can serve as evidence of the participation of water molecules in the transition state of the step of protonation, analogously to the case in the protolysis of vinyl ethers [5].

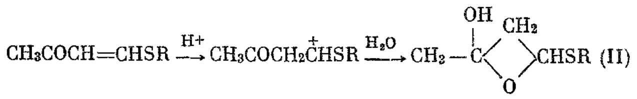
The influence of methanol on step (3) evidently is due to the following competing reactions:



$$(\mathrm{I}) \xrightarrow{H^+, CH_3OH} H_2C{=}C{=}CHCH(SR)(OCH_3) \xrightarrow{H^+, CH_3OH} CH_3{-}C(OCH_3){=}CHCH(SR)(OCH_3) \xrightarrow{H^+, CH_3OH} CH_3C(OCH_3)_2CH_2CH(SR)(OCH_3) \qquad (5)$$

An interesting peculiarity of the reaction is the very weak dependence of its rate on the structure of the radical R (see Tables 2 and 3); moreover, just as in the hydrolysis of AB [1], branched radicals somewhat slow it down. The possibility remains that the cation (I) is also stabilized by the heteroatom through space. Moreover, it should be considered that cis–transisomerization in the fragment $-CH = CH-SR$ is possible in the cation (I), and the stability of this cation should also depend on this. Then stabilization, and perhaps the reaction rate as well, may prove to be an extremely complex function of the induction, steric, and hyperconjugation properties of the substituent. In any case, the paired dependences of log k_2 on the induction and steric constants are not linear. However, the values of the isokinetic temperatures, both in plots of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ and in Palm–Exner coordinates, practically coincide (405 and 417°K).

In conclusion, let us consider the question of the further conversions of the second intermediate product of the reaction – the ketone $CH_3COCH = CHSR$. Its hydrolysis (see Fig. 2) under the conditions used does not lead to acetoacetaldehyde. An acceptable explanation might be the fact that the protonation of such ketones in very dilute aqueous solutions leads to a comparatively stable cyclic hemiacetal (II)



$$CH_3COCH{=}CHSR \xrightarrow{H^+} CH_3COCH_2\overset{+}{C}HSR \xrightarrow{H_2O} CH_2{-}\overset{OH}{C}\langle{}^{CH_2}_{O}\rangle CHSR\ (II) \qquad (6)$$

CONCLUSIONS

The kinetics of the acid catalytic hydrolysis of 1-alkylthio-1-buten-3-ynes was studied, and it was shown that the reaction includes a step of protonation of the triple bond and the formation of the $H_2C = \overset{+}{C}H = CHSR$ cation, which is further converted into two directions with the formation of acetoacetaldehyde and alkylthiobutenone.

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