INVESTIGATIONS IN THE FIELD OF VINYL ESTERS OF THE FURAN SERIES

XI.* INVESTIGATION OF THE KINETICS OF THE ALKALINE HYDROLYSIS OF VINYL ESTERS OF ACIDS OF THE FURAN SERIES BY A POLAROGRAPHIC METHOD

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UDC 547.725: 547.29.02'26: 541.127

The kinetics of the alkaline hydrolysis of vinyl esters of furan-2-carboxylic, trans-β-(2-furyl)acrylic, and trans-cinnamic acids and also the comparative electrochemical activities of these compounds and of vinyl esters of 5-bromofuran-2-carboxylic, 5-nitrofuran-2-carboxylic, and benzoic acids have been studied by a polarographic method. A symbatic increase in the rate of hydrolysis of the esters with a shift of the potential of the half-wave of reduction into the more negative region has been established. Both the polarity and the polarizability of the molecules have a fundamental influence on the properties of the esters.

At the present time, a large amount of material has accumulated in the literature on the kinetics and mechanism of the alkaline hydrolysis of vinyl esters [2, 3]. In the present work, we have investigated the hydrolytic cleavage of vinyl esters of trans-β-(2-furyl)acrylic (I), trans-cinnamic (II), furan-2-carboxylic (III), benzoic (IV), 5-bromofuran-2-carboxylic (V), and 5-nitrofuran-2-carboxylic (VI) acids in order to determine the influence of the furan ring with different substituents in position 5 on the reactivity of the esters in alkaline hydrolysis. As follows from the results obtained (Table 1), the replacement of a phenyl radical by a furyl radical leads to a decrease in the rate of hydrolysis of (II) and (I). At the same time, the greatest reactivity is possessed by the ester (III). If one takes into account the original slow addition of OH^- ions to the carbonyl carbon atom, the greatest electron-donating capacity is possessed by the furan ring.

The introduction of a double bond between the furan ring and the carbonyl group reduces the rate of hydrolysis of the ester (I). A comparison of the reactivities of the esters (I) and (III) shows that the influence of the furan ring is not purely inductive but also includes a mesomeric effect.

The thermodynamic parameters of the hydrolysis reaction of these compounds are in good agreement with one another. The regular changes in the free energy ΔF, enthalpy ΔH, entropy ΔS, and the activation energy E in agreement with the change in the hydrolysis rate constant permits the conclusion that there is a single mechanism of the hydrolysis of the esters (I-III) from the point of view both of the geometry of the transition state and of the electronic influence of substituents.

It was interesting to compare the hydrolysis rate constants with the polarographic properties of these compounds. Table 2 gives information characterizing the electrochemical activity of compounds (I-VI) on electroreduction at a dropping mercury electrode. This comparison is based on the fact that their electrophilicity is a common factor for the esters both in hydrolysis and in electroreduction. At the same time, the capacity for being reduced at an electrode is more sensitive to the dynamic polarization of a molecule, which explains the presence of two waves on the polarograms of compounds (I) and (II) and of one wave on

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*For Communication X, see [1].

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 33-36, January, 1974. Original article submitted September 22, 1972.

TABLE 1. Kinetic Characteristics of the Hydrolysis of the Vinyl Esters $RCOOH{=}CH_2$

Compound	R*	$k_{II}^{298} \cdot 10^3$, $l \cdot mole^{-1} \cdot sec^{-1}$	E, kcal/mole sec^{-1}	ΔF, kcal/mole	ΔS, eu	ΔH, kcal/mole
I	$C_4H_3OCH{=}CH$	3,66	10,8	20,8	−35,4	10,2
II	$C_6H_5CH{=}CH$	4,12	11,6	20,7	−32,5	11,0
III	C_4H_3O	5,60	12,4	20,6	−29,4	11,8

*C_4H_3O – 2-furyl.

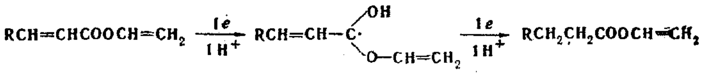
TABLE 2. Polarographic Characteristics for the Vinyl Esters $RCOOCH{=}CH_2$

Compound	R	$-E_{1/2}$, V	n
I	2-(2-Furyl)vinyl	1,52 1,86	0,95 0,94
II	Styryl	1,55 1,86	1,20 0,77
III	2-Furyl	1,85	2,11
IV	Phenyl	1,83	1,71
V	5-Bromo-2-furyl	1,79	2,90
VI	5-Nitro-2-furyl	0,37 1,52	

the polarograms of compounds (III–V). This is connected with the presence of double bonds adjacent to the ester group, so that the mechanism of the reduction of a structure of type (III) is apparently limited by a two-electron stage with the formation of the corresponding semiacetal [4]:

$$RCOOCH{=}CH_2 \xrightarrow[2H^+]{2e} RCH(OH)OCH{=}CH_2$$

The presence of an ethylenic bond in the α position to the carbonyl carbon atom extends to chain of conjugation, modifying the mechanism of electroreduction in such a way that the latter takes place through two one-electron stages [5] (I, II):



$$RCH{=}CHCOOCH{=}CH_2 \xrightarrow[1H^+]{1e} RCH{=}CH{-}\dot{C}(OH){-}O{-}CH{=}CH_2 \xrightarrow[1H^+]{1e} RCH_2CH_2COOCH{=}CH_2$$

The closeness of the potentials of the second waves is due to the small difference in the delocalization energies of the radicals formed after the addition of the first electron in electroreduction. Of compounds (I) and (II), the greater tendency to delocalization is possessed by the styryl radical. Because of the lower degree of aromatization of the furan ring as compared with the benzene ring, the polarizability of the molecule of the ester (I) is greater than that of (II), but the mesomeric effect of a furan ring is more positive than that of a benzene ring.

The reduction of the esters (V) and (VI) takes place in more complex fashion, since the bromine atom and the nitro group present in position 5 of the furan ring are themselves reduced under our conditions. However, in our opinion, the probability of the formation in the first stage of the reduction of the ester (VI) of an anion radical in a neutral aqueous alcoholic medium and, all the more, their subsequent reduction at potentials of the order of −1.5 V appears unlikely. Consequently, the second wave of the ester (VI) must be assigned to a process of reducing the ester group. Unfortunately, we have not been able to study the polarography of the esters considered over a wider range of changes of pH of the medium because of their tendency to undergo both alkaline and acid hydrolysis. Nevertheless, in spite of the difference in the nature of the electroreduction of the esters discussed, it is possible to find a symbatic increase in the rate of hydrolysis of the esters (I–III) with a displacement of the half-wave reduction potential to a less negative region [for the esters (I) and (II), the potentials of the second waves]. This feature enables us to evaluate the tendency to hydrolysis of those esters that could not be studied under our conditions, as well. On the basis of the reduction potentials, the esters (I–VI) can be arranged in the following sequence with respect to their resistance to alkaline hydrolysis: (I) > (II) > (III) > (IV) > (V) > (VI). One must take into account the fact that this sequence is due not only to the inductive properties of the substituents but also to the tendency of the molecules to undergo dynamic polarization.

EXPERIMENTAL

The kinetics of the alkaline hydrolysis of the vinyl esters, which were obtained by known methods [1, 6-8], was studied by means of a LP-7 polarograph. The reaction was performed in the polarographic cell. During the course of the reaction, a decrease in the height of the wave of polarographic reduction of the corresponding vinyl ester with time was observed at temperatures of 20, 25, 30, and 35°C (±0.1°C) in 45% aqueous ethanolic solutions. The concentrations of the vinyl esters amounted to 0.0025, 0.005, and 0.01 M. The concentrations of the catalyst (LiOH) were varied between 0.2 and 0.08 M. The support was a 0.1 N solution of lithium chloride. The results of the measurements were used to calculate the hydrolysis rate constants k_{II} according to the equation:

$$k_{II}=\frac{\frac{2.3}{t}\cdot\log\frac{a}{a-x}}{c}, \qquad (1)$$

where t is the time, sec; a is the initial height of the wave corresponding to the concentration of ester at time t = 0; $(a-x)$ is the height of the wave corresponding to the concentration of ester at time t; and c is the concentration of catalyst (M).

Calculation of the hydrolysis rate constant k_{II} by the equation:

$$k_{II}=\frac{2.3}{t}\cdot\frac{1}{c_{A_1}{}^0-c_{A_2}{}^0}\cdot\log\frac{(c_{A_1}{}^0-x)\,c_{A_2}{}^0}{(c_{A_2}{}^0-x)\,c_{A_1}{}^0}, \qquad (2)$$

where $c^0_{A_1}$ is the initial concentration of LiOH (M); $c^0_{A_2}$ is the initial concentration of vinyl ester (M); $(c^0_{A_1}-x)$ is the concentration of alkali at time t; and $(c^0_{A_2}-x)$ is the concentration of vinyl ester at time t, showed the closeness of the results of calculation to those obtained by means of Eq. (1), which is explained by the fact that the observations were made only in the initial stage of the reaction and also by the considerable excess of catalyst in relation to the initial ester.

The polarographic parameters were found with the aid of a LP-60 polarograph at 25°C on a support of lithium acetate buffer at pH 6.70 in 50% aqueous ethanol. The reduction potentials were measured relative to a saturated calomel electrode. The error in the measurements of the potentials amounted to ±5 mV. The characteristics of the capillary were: $m = 1.803\ \text{mg}\cdot\text{sec}^{-1}$, $\tau = 4.24\ \text{sec}^{-1}$. The diffusion coefficient D was calculated by a modified Stokes–Einstein equation, and the number of electrons n by the Ilkovic equation [9]. The concentration of the esters was 0.001 M.

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