KINETICS OF THE SOLVOLYSIS OF α-BROMO KETONES OF THE THIOPHENE AND SELENOPHENE SERIES IN AQUEOUS ETHANOL

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A comparative study of the kinetics of the solvolysis of α-bromo ketones of the selenophene, thiophene, and benzene series in 50% ethanol at 55, 70, and 80°C has been performed. The activation parameters of the reactions have been determined and it has been shown that solvolysis takes place mainly by an S_N2 mechanism. The rate of solvolysis rises in the sequence selenophene → thiophene → benzene.

It is known that the bromine in α-bromo ketones of the furan, thiophene, and selenophene series is readily replaced in reactions with, for example, amines [1-3]. However, there is no information in the literature on a quantitative comparison of the mobilities of the bromine atoms in α-bromo ketones of five-membered heterocycles but only isolated reports on the kinetics of the solvolysis of phenacyl halides [4]. In the present work we have investigated the kinetics of the solvolysis of α-bromo ketones of the selenophene and thiophene series in 50% aqueous ethanol. For comparison, the solvolysis of phenacylbromide was performed under the conditions given in [4], the solvolysis rate constant at 55°C found ($0.326 \cdot 10^{-3}$ min^{-1}) agreeing well with that given in the literature ($0.292 \cdot 10^{-3}$ min^{-1}) [4].

The solvolysis of α-bromo ketones in an excess of solvent took place by first-order kinetics. The rate constants of the reaction were calculated from formula (1):

$$K=\frac{1}{t}\ln\frac{c_0}{c_0-c_t}, \tag{1}$$

where K is the first-order rate constant in min^{-1}, t is the time in minutes from the beginning of the experiment, c_0 is the initial concentration of bromo ketone, and c_t is the concentration of hydrogen bromide at time t.

TABLE 1. Rate Constants, Parameters of the Arrhenius Equation, and Activation Entropy of the Solvolysis of α-Bromo Ketones

Substance	$K_1 \cdot 10^3$ min^{-1}			E, kcal/mole	lg pZ	ΔS, cal/deg
	55°	70°	80°			
Phenacyl bromide	0,326	1,31	3,02	20,5	10,17	−23,9
2-Bromoacetylthiophene	0,169	0,686	1,72	21,4	10,43	−22,7
2-Bromoacetylselenophene	0,168	0,645	1,59	20,1	9,61	−26,6
2-Bromoacetyl-5-methylthiophene	0,152	0,633	1,27	18,9	8,76	−30,4
2-Bromoacetyl-5-methylselenophene	0,151	0,600	1,05	16,9	7,44	−36,6
2-Bromoacetyl-5-nitrothiophene	1,49	4,18	9,34	16,4	8,07	−33,7
2-Bromoacetyl-5-nitroselenophene	0,649	2,88	5,73	19,4	9,72	−26,1

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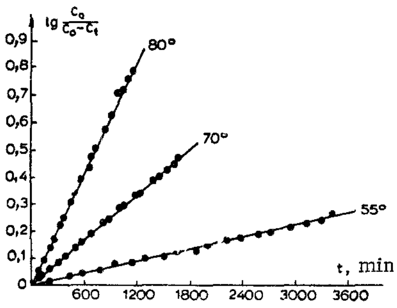

Fig. 1

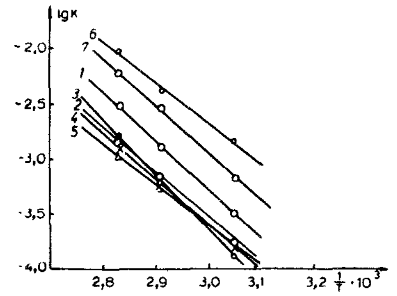

Fig. 2

Fig. 1. Dependence of log $[C_0/(C_0-C_t)]$ on the time for the solvolysis of 2-bromoacetylselenophene.

Fig. 2. Temperature dependences of the rate constants of the solvolysis of phenacyl bromide (1), 2-bromoacetylthiophene (2), 2-bromoacetylselenophene (3), 2-bromoacetyl-5-methylthiophene (4), 2-bromoacetyl-5-methylselenophene (5), 2-bromoacetyl-5-nitrothiophene (6), and 2-bromoacetyl-5-nitroselenophene (7).

The activation energy E (see Table 1) was determined graphically as the tangent of the angle of slope of the straight line of a plot of log K versus 1/T°.

$$\lg K - \frac{1}{T^\circ}.$$

The values of log pZ of the Arrhenius equation were calculated from formula (2) for T = 328°K:

$$\lg pZ = \lg K + \frac{E}{2.303\,RT^\circ}. \tag{2}$$

The values of the entropy of activation were calculated from formula (3) for T = 328°K:

$$-\Delta S^{\neq} = 2.303\,R\,\lg\frac{kT}{h} - 2.303\,R\,\lg K - \frac{E}{T} + R, \tag{3}$$

where k is Boltzmann's constant ($1.38 \cdot 10^{-16}$ erg/deg), h is Planck's constant ($6.62 \cdot 10^{-27}$ erg/sec), K is the rate constant of solvolysis in $\sec^{-1}$, E is the activation energy in cal/mole, and R is the gas constant (1.987 cal/deg).

On the basis of the figures given, it may be concluded that the reactivity of the α-bromo ketones in the solvolysis reaction rises in the sequence selenophene ≤ thiophene < benzene, which agrees with information for the reactivity of the selenophene series in electrophilic substitution reactions (see, for example, [5]).

Apparently, α-bromo ketones of the thiophene and selenophene series solvolyze by a bimolecular reaction, since:

in the first place, the rate constants of their solvolysis are close to the rate constants for the corresponding α-bromoacetophenones [4], for which a bimolecular mechanism of solvolysis has been established without doubt;

in the second place, the introduction of substituents into position 5 of the heterocyclic nucleus affects the rate of solvolysis in accordance with the influence of the substituents on the rate of bimolecular substitution (an electron-donating group decreases and an electron-accepting group increases the partial positive charge on the α-carbon atom), this influence apparently being mainly inductive and not mesomeric; and

in the third place, the influence of the entropy factor on the rate of solvolysis frequently masks the opposite influence of the activation energy.

The opposite relationship is characteristic for a monomolecular mechanism.

EXPERIMENTAL

The solutions were prepared with ethanol and distilled water. The bromo ketones were twice recrystallized from hexane or methanol or, if liquid, were twice redistilled. They possessed the following constants. 2-Bromoacetylselenophene: mp 48-49°C (from hexane); [1], mp 48-49°C. 2-Bromoacetylthiophene: bp 101-107°C (1 mm); n_D^{20} 1.6291; [6], bp 143-145°C (14 mm); n_D^{20} 1.5308. 2-Bromoacetyl-5-methylselenophene: mp 45-46°C (from methanol); [1], mp 45-47°C. 2-Bromoacetyl-5-methylthiophene: bp 105-110°C (1 mm); n_D^{20} 1.6182; [7], bp 160°C (12-13 mm). 2-Bromoacetyl-5-nitroselenophene: mp 122-124°C (from methanol); [8], mp 125.5-126°C. 2-Bromoacetyl-5-nitrothiophene: mp 102-103°C; [9], mp 103-104°C.

A weighed sample of a bromo ketone was dissolved in 50% (by volume) aqueous ethanol in a 100-ml measuring flask, and 5-ml portions of this solution were sealed into glass tubes which were placed in a thermostat at 55, 70, or 80°C and the time reckoning was begun. Tubes were opened periodically, and their contents were rinsed out with distilled water into a flask and titrated with a standard solution of caustic soda (with phenolphthalein as indicator). In the treatment of the bromo nitro ketones, the contents of the tubes were extracted with ether,the ethereal layer was washed twice with water, and the aqueous layers were combined and titrated with a solution of alkali. In this way, 19 points were obtained in each case.

In order to take into account the experimental errors connected with the indeterminacy of the point of zero time, a graph was plotted on log $[C_0/(C_0-C_t)]$ versus t_{exp}, where t_{exp} is the time, C_0 is the initial concentration of bromo ketone, and C_t is the concentration of hydrogen bromide at time t_{exp}. The experimental points lay satisfactorily on a straight line which did not always pass through the origin of coordinates. The intercept Δt cut off by this straight line on the axis of abscissas was used to correct the experimental time t_{exp}, the corrected time being $t = t_{exp} + \Delta t$. As a rule, the value of Δt did not exceed the time elapsing from the beginning of the experiment to the moment of the first measurement and was basically small in comparison with the period of half-transformation.

Solvolysis was performed at two initial concentrations for each temperature; the rate constants obtained in these experiments did not differ from one another by more than 10%. A linear dependence of log $[C_0/(C_0-C_t)]$ on the time was observed (Fig. 1). The temperature dependence of the solvolysis rate constant is given in Fig. 2.

The rate constants were determined with an accuracy of 5% and the values of E with an accuracy of ±5 kcal/mole, and the values of log pZ were calculated with an accuracy of ±0.07 and the values of $\Delta S^{\neq}$ with an accuracy of ±1.5 cal/deg.

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