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Kinetics of the Reaction of Sodium Arsenite with Bromo- and Iodoacetic Acids

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Abstract—By an example of the reaction of sodium arsenite with bromoacetic and iodoacetic acids the effect of halogen on the rate of Meyer reaction was evaluated. Rate constants and the activation energy and entropy values were estimated. Effects of the nature of halogen and temperature on the ratio of rate constants of the Meyer reaction and the competing alkaline hydrolysis of haloacetic acids were evaluated.

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Recently [1] we have studied the kinetics of Meyer reaction by an example of interaction of sodium arsenite **I** with chloroacetic acid in water solution of sodium hydroxide. In this work we have studied the kinetics of the reaction of sodium arsenite **I** with bromoacetic and iodoacetic acids in water–alkaline medium.

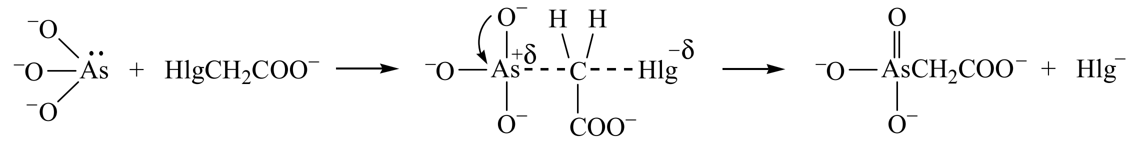
$$\underset{\mathbf{I}}{AsO_3^{3-}} + \underset{\mathbf{II,\,III}}{HlgCH_2COO^-} \xrightarrow[\text{NaOH}]{k} \underset{\mathbf{IV}}{{}^-OOCCH_2As(O)O_2^{2-}} + Hlg^-.$$

Reaction under investigation is complicated by alkaline hydrolysis of haloacetic acids.

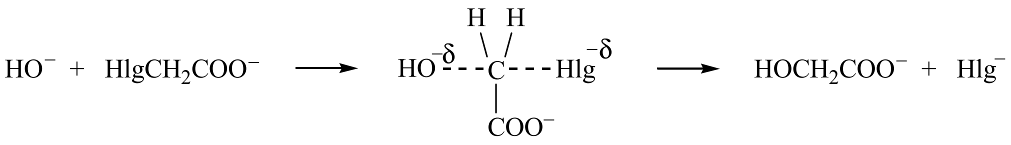
$$HO^- + HlgCH_2COO^- \xrightarrow[\text{NaOH}]{k_r} HOCH_2COO^- + Hlg^-.$$

Meyer reaction and the alkaline hydrolysis of haloacetic acids are the nucleophilic substitution reactions proceeding between the anions.

The Meyer reaction includes the attack on the partially positively charged α-carbon atom of haloacetic acid of the unshared electronic pair of arsenite ion. In the course of this process appearance of partial charges on the arsenic and halogen atoms takes place in the intermediate complex.



During the alkaline hydrolysis of haloacetic acids the hydroxy ion attacks α-carbon atom of haloacetic acid and in the transition state redistribution and transfer of negative charge from the hydroxy ion to halogen takes place.



$$HO^- + HlgCH_2COO^- \longrightarrow HO^{-\delta}\cdots\underset{COO^-}{\overset{H\ H}{C}}\cdots Hlg^{-\delta} \longrightarrow HOCH_2COO^- + Hlg^-$$

It is the main difference in mechanism of the Meyer reaction and the alkaline hydrolysis.

Rate constants of alkaline hydrolysis of haloacetic acids at 15, 25, 35, and 45°C we evaluated previously

[2]. Kinetics of the reaction of sodium arsenite **I** with bromoacetic **II** and iodoacetic **III** acids was studied at 15, 25, 35, and 45°C in water solution of sodium hydroxide. The reaction progress was monitored by iodometric titration reflecting the rate of consumption of the arsenite ion as well as by the argentometric titration of samples of the reaction mixture characterizing the rate of accumulation of halide ions.

The rate of the process is described by the kinetic Eq. (1):

$$W = kc_{\mathbf{I}}c_{\mathrm{Hlg}} + k_{\mathrm{r}}c_{\mathrm{Hlg}}c_{\mathrm{NaOH}}. \quad (1)$$

Here W is the rate of accumulation of halide ion, k is the rate constant of the reaction of compound **I** with haloacetic acid, k_{r} is the rate constant of alkaline hydrolysis of corresponding haloacetic acid, $c_{\mathbf{I}}$, c_{Hlg}, c_{NaOH} are the current concentrations of sodium arsenite, of haloacetic acid, and of sodium hydroxide respectively.

Rate constant of the reaction of compound **I** with haloacetic acid **II, III** was calculated according to Eq. (2):

$$k = \frac{W - k_{\mathrm{r}}(c^0_{\mathrm{Hlg}} - c_{\mathrm{Hlg^-}})(c^0_{\mathrm{NaOH}} - 3c^0_{\mathbf{I}} - c^0_{\mathrm{Hlg}} - c_{\mathrm{Hlg^-}} + c_x)}{(c^0_{\mathbf{I}} - c_x)(c^0_{\mathrm{Hlg}} - c_{\mathrm{Hlg^-}})}. \quad (2)$$

Here $c^0_{\mathbf{I}}$, c^0_{Hlg}, c^0_{NaOH} are the starting concentrations of sodium arsenite, of haloacetic acid, and of sodium hydroxide respectively; $c_{\mathrm{Hlg^-}}$ and c_x are current concentrations of the forming halide ions and the anion of carboxymethylarsonic acid **IV** respectively.

Reaction rate W was evaluated from the slope in each point of the approximation curve of the dependence of current concentration of the halide ion on time. Rate constant k remained practically the same independent of the reaction time (Table 1). In Table 2 the results of the kinetic studies of interaction of compound **I** with the acids **II** and **III** at different temperatures are listed.

The temperature dependence of the rate constant k of the reaction with bromoacetic [Eq. (3)] and iodoacetic [Eq. (4)] acids is evaluated.

$$\log k = 5.44 - 2.54\times10^3/T,\ r\ 0.998,\ s\ 0.03, \quad (3)$$

$$\log\ k = 9.28 - 3.59\times10^3/T,\ r\ 0.997,\ s\ 0.05. \quad (4)$$

Average value of rate constants of alkaline hydrolysis of haloacetic acids k_{r} and Meyer reaction k are presented in Table 3.

On the basis of average values of rate constants of alkaline hydrolysis of haloacetic acids k_{r} and the Meyer reaction k (Table 3) the activation energy E, kJ mol^{-1} and the activation entropy $-\Delta S$, J deg^{-1} mol^{-1} of alkaline hydrolysis were calculated. For chloroacetic acid they are 81.7, 89.1; for bromoacetic acid, 84.0, 49.4; for iodoacetic acid, 73.7 and 89.7. In the case of the Meyer reaction the same values for chloroacetic acid are 46.9, 182; for bromoacetic acid, 47.6, 153; and for iodoacetic acid, 68.9 and 75.6 respectively.

In the reaction of compound **I** with haloacetic acid at the transfer from bromoacetic acid to iodoacetic despite the significant increase in the activation energy a significant growth of the reaction rate constant takes place because of the increase in the activation entropy.

Rate constants of the Meyer reaction increase in the series Cl < Br < I. It may be explained by the increase in the polarizability of the carbon-halogen bond [3, 4] leading to the weakening of the C–Hlg bond, and by the increase of the partial positive charge on the α-carbon atom of haloacetic acid exposed to the nucleophilic attack of the arsenite ion.

Table 1. Kinetics of the reaction of sodium arsenite with bromoacetic acid in water-alkaline medium at 15°C ($c^0_{\mathbf{I}}$ 0.08874, $c^0_{\mathbf{II}}$ 0.1505, c^0_{NaOH} 0.8663 M)

Reaction time, $c\times10^{-2}$	$c_x\times10^2$, M	$c_{\mathrm{Br^-}}\times10^2$, M	Conversion, %	$W\times10^6$, mol l^{-1} s^{-1}	$k\times10^5$, l mol^{-1} s^{-1}
36	2.614	3.149	29.5	4.777	43.56
72	4.116	4.879	46.4	3.472	44.81
90	4.491	5.499	50.6	3.055	44.13
108	4.993	6.032	56.3	2.771	46.53
126	5.337	6.475	60.1	2.361	41.95
144	5.525	6.874	62.3	2.037	36.62

[a] Average k_{av} value 42.93×10^{-5} l mol^{-1} s^{-1}.

Table 2. Kinetic data on the reaction of sodium arsenite **I** with bromoacetic **II** and iodoacetic **III** acids in aqueous sodium hydroxide

Reaction temperature, °C	c_{I}×10^2, M	c^0_{Hlg}×10^2, M	c^0_{NaOH}, M	Reaction time, c×10^{-2}	Conversion, %	k×10^5, l mol^{-1} s^{-1}
			Bromoacetic acid			
15	8.874	15.05	0.8663	144	62.3	42.93
15	8.764	15.00	0.8663	144	63.2	43.52
15	9.440	14.77	0.8648	108	45.6	47.90
25	8.766	14.70	0.8663	126	75.7	70.77
25	8.752	14.99	0.8273	126	74.3	87.52
35	4.441	7.537	0.4332	54	26.7	166.4
35	8.553	15.01	0.8648	108	47.6	172.6
45	4.382	7.435	0.4332	108	47.7	304.7
45	4.460	7.549	0.4332	72	42.1	249.0
			Iodoacetic acid			
15	5.724	7.412	0.4250	180	43.2	65.60
15	6.006	7.464	0.4250	180	45.4	75.32
25	5.805	7.720	0.4250	108	62.0	147.5
25	6.606	7.711	0.4250	180	69.7	156.4
35	5.730	7.711	0.4250	162	82.5	386.6
35	5.955	7.772	0.4250	162	83.2	529.8
45	6.006	7.584	0.4250	180	85.0	1078
45	5.868	7.512	0.4250	162	84.6	898.3

Table 3. Rate constants of alkaline hydrolysis and Meyer reaction

T, °C	$\mathrm{ClCH_2COOH}$[a]			$\mathrm{BrCH_2COOH}$			$\mathrm{ICH_2COOH}$		
	k×10^4, l mol^{-1} s^{-1}	k_{r}×10^6, l mol^{-1} s^{-1}	k/k_{r}	k×10^5, l mol^{-1} s^{-1}	$k_{\mathrm{r}}^{\mathrm{b}}$×$10^6$, l mol^{-1} s^{-1}	k/k_{r}	k×10^5, l mol^{-1} s^{-1}	$k_{\mathrm{r}}^{\mathrm{b}}$×$10^6$, l mol^{-1} s^{-1}	k/k_{r}
15	0.158	0.650	24.3	44.78	29.0	14.7	70.46	13.9	50.7
25	0.246	1.83	13.4	79.14	92.1	8.59	152.0	43.3	35.1
35	0.424	5.45	7.78	169.5	282	6.01	458.2	109	42.0
45	1.01	16.0	6.31	276.8	770	3.59	988.2	257	38.4

[a] Data for chloroacetic acid are taken from [1]. [b] k_{r} Values are taken from [2].

Unlike the Meyer reaction in the case of alkaline hydrolysis of haloacetic acids at the transfer from bromoacetic to iodoacetic acid the activation energy and entropy as well as the rate constant of hydrolysis decrease. Hence, for the Meyer reaction and the alkaline hydrolysis of haloacetic acid the rate of the reaction is determined mainly by the change in the activation entropy at the transfer of the system to the active state.

Rate constants of alkaline hydrolysis of haloacetic acids grow in the series Cl < I < Br. Analogous reversion in the lability of bromine and iodine was marked in the investigation of alkaline hydrolysis of haloacetic acids [5], in the reaction of ammonia with haloacetic acids in water solution [5], in the reaction of methyl bromide and methyl iodide with sodium methylate [6], and in the aqueous hydrolysis of haloacetic acids [7].

It may be explained on the basis of the kinetic steric effects described in [8]. On the basis of these data it was explained why in some cases the substitution in alkyl iodides proceeds slower that in alkyl bromides or has the comparable rate. At the approach of atoms unbound with one another at first weak attracting and then weak repulsing forces operate. But at a definite small distance the repulsion sharply begins to increase.

The iodine atom has lager size as compared to bromine one, and due to that the distance where the increase in repulsion takes place must be larger. In some cases for the formation of the transition complex the molecules must come so close that the energy of repulsion forces becomes comparable with the energy of bond cleavage [8]. The increase of the repulsion forces between the atoms which are not bound with one another may explain evidently lower values of rate constants of alkaline as well as of water hydrolysis [7] of iodoacetic acid as compared to bromoacetic one. In this case kinetic steric effects described as steric hindrances are revealed [8].

Values of rate constants of the Meyer reaction k in all the cases exceed the values of rate constants of alkaline hydrolysis k_r for the corresponding haloacetic acids. It permits to conclude that arsenite ion AsO_3^{3-} exhibits higher nucleophilic reactivity as compared to hydroxy ion. At the increase in temperature the k/k_r ratio decreases corresponding to growth of the contribution of the alkaline hydrolysis to the total rate of the process under study. The k/k_r ratio increases in the series Br < Cl < I . Using iodoacetic acid in the Meyer reaction permits to achieve the higher rate of the process and to obtain the best yield of sodium carboxymethylarsonate **IV**.

EXPERIMENTAL

Bromoacetic acid was distilled, bp 208°C, the distilled mass solidifies on cooling to give the colorless crystals, mp 49°C (reported data [9]: bp 208°C, mp 50°C).

Iodoacetic acid was crystallized from water, mp 82–85°C (reported data [10]: mp 83°C).

Studies of kinetics of the reaction of sodium arsenite I with haloacetic acids. A weighed portion of As_2O_3 was placed in the 100 ml measuring flask and dissolved in the calculated amount of 10 N aqueous sodium hydroxide. The solution obtained was diluted with distilled water to the mark. Water solution of haloacetic acid was prepared simultaneously in the 100 ml measuring flask. The solutions were maintained at the desired temperature, and 50 ml of solution was taken from each flask. The moment of mixing was accepted as the beginning of the reaction. Two samples were taken simultaneously after definite time intervals for the evaluation of current concentrations of arsenite ion [As(III)] by iodometric titration and of halide ion by argentometic titration. The preparation of samples, iodometric titration of As(III), and argentometric titration of the halide ion was carried out as described in [1].

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