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Kinetics of Reaction of Sodium Arsenite with Chloroacetic Acid in Mixed Solvents and Effect of the Nature of the Cation of Alkali Metal Hydroxide on the Rate of Meyer Reaction

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Abstract—The rate constants of the reaction of sodium arsenite with chloroacetic acid in mixtures of water with alcohols, acetone, tetrahydrofuran, dimethyl sulfoxide, dimethoxymethane, and 1,4-dioxane at 25°C were determined. By the examples of the reaction of chloroacetic acid with the lithium, sodium and potassium arsenites the effect of the nature of alkali metal hydroxide cation on the reaction rate of Meyer reaction is considered.

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Earlier [1, 2], by an example of the reaction of sodium arsenite with haloacetic acids we have studied the effect of the halogen nature on Meyer reaction. In the present study, we investigated the effect of mixed solvents and the nature of the alkali metal hydroxide cation on the reaction rate of sodium arsenite with chloroacetic acid.

$$\underset{\mathbf{I}}{AsO_3^{3-}} + \underset{\mathbf{II}}{ClCH_2COO^-} \xrightarrow[\text{MeOH}]{k} \underset{\mathbf{III}}{{}^-OOCCH_2As(O)O_2^{2-}} + Cl^-$$

The reaction under study is complicated by the alkaline hydrolysis of chloroacetic acid.

$$HO^- + \underset{\mathbf{II}}{ClCH_2COO^-} \xrightarrow[\text{MeOH}]{k_h} HOCH_2COO^- + Cl^-$$

Me = Li, Na, K.

Meyer reaction rate and the yield of alkylarsonoic acids are affected significantly by the medium. Typically, the reaction of a halogen derivatives with the alkali metal arsenite is carried out in aqueous alkaline or alcohol-aqueous alkaline media [3]. In this paper, it was interesting to determine the effect of protic and aprotic solvents additives on the rate constant of the sodium arsenite reaction with chloroacetic acid. Since Meyer reaction is accompanied by parallel alkaline hydrolysis of chloroacetic acid, we studied initially the effect of organic solvent additives on the rate constant k_h of the interaction of chloroacetic acid with sodium hydroxide.

The kinetic study of alkaline hydrolysis of chloroacetic acid was carried out at 25°C with the 20% content of organic solvent in the reaction medium. We used protic solvents: methanol, ethanol, 1-propanol, 2-propanol, and 2-methylpropan-2-ol, and aprotic: tetrahydrofuran, dimethyl sulfoxide, dimethoxymethane, 1,4-dioxane, and acetone. The reaction was monitored by argentometric titration of the resulting chloride ion. Table 1 lists the rate constants of the chloroacetic acid alkaline hydrolysis calculated along the second-order equation [4].

The addition of protic or aprotic solvent to the reaction medium slightly increases the rate constant of the alkaline hydrolysis of chloroacetic acid. Similar changes in the rate constant of alkaline hydrolysis of bromo- and iodoacetic acids in water–ethanol and water–dioxane solutions were reported in [6].

To determine the effect of mixed solvents on Meyer reaction rate constant we studied kinetics of the reaction of sodium arsenite with chloroacetic acid in water–alkaline medium in the presence of 2-propanol and 1,4-dioxane at 25°C. The reaction was monitored

Table 1. Rate constants of the reaction of chloroacetic acid with sodium hydroxide in mixed solvents at 25°C [$c^0_{\mathrm{II}}:c^0_{\mathrm{NaOH}}$ = 1:3.67]

Solvent (20 vol %)	ε (25°C) [5]	$k_\mathrm{h}\times10^6$, l mol^{-1} s^{-1}
Water (100%)	78.54	1.830±0.046
Protic solvents		
Methanol	32.70	3.556±0.0686
Ethanol	24.55	2.072±0.0907
1-Propanol	20.33	2.706±0.289
2-Propanol	18.30	2.153±0.0307
2-Methylpropan-2-ol	12.47	2.871±0.179
Aprotic solvents		
1,4-Dioxane	2.21	2.483±0.120
Dimethoxymethane	2.70 (20°C)	2.778±0.102
Tetrahydrofuran	7.39	2.896±0.180
Acetone	20.54	2.035±0.0478
Dimethyl sulfoxide	48.9 (20°C)	3.428±0.241

Table 2. Rate constant of reaction of sodium arsenite with chloroacetic acid and alkaline hydrolysis of chloroacetic acid in mixed solvents at 25°C [$c^0_{\mathrm{I}}:c^0_{\mathrm{II}}:c^0_{\mathrm{NaOH}}$ = 1:(0.87–2.63):(5.11–10.80)]

Solvent content in water phase, vol %	$k\times10^6$, l mol^{-1} s^{-1}	$k_\mathrm{h}\times10^6$, l mol^{-1} s^{-1}	k/k_h
Water (100%)	24.59±0.812	1.830±0.046	13.0
2-Propanol			
10	30.23±0.0502	2.050±0.215	14.7
20	35.91±0.0887	2.153±0.0307	16.7
30	44.03±0.182	2.509±0.185	17.5
40	47.99±0.267	2.683±0.140	17.9
1,4-Dioxane			
30	50.01±0.0637	2.617±0.0488	19.1
40	66.21±0.157	3.608±0.155	18.4

both by the rate of arsenite ion consumption measured by iodometric titration, and by the rate of the chloride ion accumulation determined by argentometri titration of the samples of the reaction mixture. The rate constant k was calculated using Eq. (1).

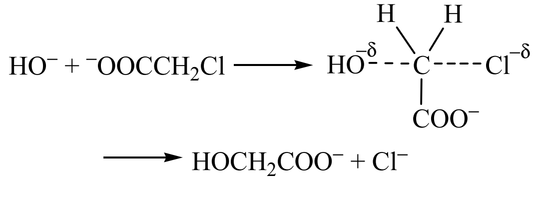
$$k = \frac{W - k_\mathrm{h}(c^0_{\mathbf{II}} - c_{\mathrm{Cl^-}})(c^0_{\mathrm{NaOH}} - 3c^0_{\mathbf{I}} - c^0_{\mathbf{II}} - c_{\mathrm{Cl^-}} + c_\mathrm{X})}{(c^0_{\mathbf{I}} - c_\mathrm{X})(c^0_{\mathbf{II}} - c_{\mathrm{Cl^-}})}. \quad (1)$$

Here, W is the rate of accumulation of chloride ion, k is the rate constant of the reaction of the compounds **I** and **II**, k_h is the rate constant of the alkaline hydrolysis of **II**, $c^0_{\mathbf{I}}$, $c^0_{\mathbf{II}}$, and c^0_{NaOH} are initial concentrations of sodium arsenite, chloroacetic acid, and sodium hydroxide, respectively; $c_{\mathrm{Cl^-}}$ and c_x are current concentrations of the generated chloride ion and hydroxycarbonylarsonic acid **III**, respectively. The reaction rate W was determined from the slope at each point of the approximated curve of the chloride ion current concentration.

Table 2 lists the rate constants for the reaction of sodium arsenite with chloroacetic acid in mixed solvents.

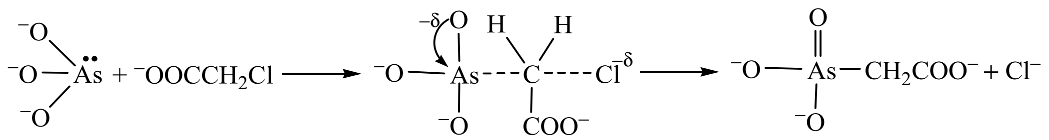
With increasing content of organic solvent in the reaction medium, Meyer reaction rate constant k increases. Ratio of Meyer reaction and the alkaline hydrolysis rate constants k/k_h compared with the reactions in aqueous phase does not change significantly. The effect of solvents on the rate of nucleophilic substitution has been described by C.K. Ingold [7]. According to the Ingold's classification, the main factors determining the effect of solvent polarity on reaction rate are the type of charge in the original state of the reagent and substrate and the changes of charges at passing from initial state to the transition state. In the studied reaction of alkaline hydrolysis and Meyer reaction, the addition of organic solvent to water decreases the medium polarity. In both the alkaline hydrolysis and Meyer reaction, in the elementary stage, which determines the reaction rate, the number of charges remains unchanged. In the transition state the charge is dispersed and transferred from hydroxy group to the halogen.

At the alkaline hydrolysis, the hydroxy ion attacks the partially positively charged α-carbon atom of chloroacetic acid, while in the transition state the negative charge is dispersed and transferred from the hydroxy ion to chlorine.



$$\mathrm{HO^- + {}^-OOCCH_2Cl} \longrightarrow \mathrm{HO^{-\delta}}\text{- -}\overset{\mathrm{H}\ \ \mathrm{H}}{\underset{\mathrm{COO^-}}{\mathrm{C}}}\text{- - - -}\mathrm{Cl^{-\delta}} \longrightarrow \mathrm{HOCH_2COO^- + Cl^-}$$

In Meyer reaction, the arsenite ion, due to the lone pair of the arsenic atom, attacks the partially positively charged α-carbon atom of chloroacetic acid, while in the transition state the charge is dispersed, and negative charge is transferred from one of arsenite ion oxygen atoms to chlorine.



The considered mechanism that involves redistribution of negative charge from the oxygen atom in the arsenite anion to chlorine underlies the importance of the alkaline environment for Meyer reaction.

As in the case of alkaline hydrolysis, in Meyer reaction the negative charge in the transition state is dispersed, and in accordance with the classification proposed by C.K. Ingold [7], with a decrease in solvent polarity an increase in the rate constant should be observed.

The nature of the cation of the alkali metal arsenite also affects the rate of Meyer reaction [3]. In this connection, it seemed interesting to study the influence of the nature of the alkali metal hydroxide cation on the rate of Meyer reaction and the alkaline hydrolysis. We studied the kinetics of alkaline hydrolysis of chloroacetic acid with the hydroxides of lithium, sodium, and potassium at 25°C. The rate constants of alkaline hydrolysis k_h are given in Table 3.

Replacing the cation in the alkali metal hydroxide along the series of Li, Na, K resulted in a slight increase in the rate constants of the chloroacetic acid alkaline hydrolysis.

Meyer reaction has been studied by the example of the interaction of chloroacetic acid and arsenites of lithium, sodium and potassium at 25°C. The values of the reaction rate constants (Table 4) were calculated with Eq. (1).

Like the case of alkaline hydrolysis, in Meyer reaction replacing alkali metal hydroxide cation in the series from lithium to potassium increases the reaction rate constant.

It is known that reactivity of a nucleophile in the ion pair composition is lower compared with the free anion [8]. The smaller the cation and anion, the more probable becomes the formation of the ion pair. Alkali metal cation having the smaller size has a more dense solvation shell, and electrostatic interaction between

Table 3. Rate constants of hydrolysis of chloroacetic acid by hydroxides of lithium, sodium, and potassium in water at 25°C

MeOH	c^0_{II}, M	c^0_{NaOH}, M	Reaction duration, $c\times10^{-2}$	Conversion, %	$k_\mathrm{h}\times10^6$, l mol^{-1} s^{-1} [a]
LiOH	0.3290	1.100	180	2.06	1.546±0.0710
	0.3268	1.100	180	2.07	1.524±0.0620
NaOH	0.2998	1.092	216	3.42	1.830±0.0462
	0.3002	1.090	216	3.74	1.826±0.0426
KOH	0.2964	1.100	216	3.85	2.291±0.157
	0.3169	1.100	216	3.87	2.335±0.0704

[a] Average value of $k_\mathrm{h}\times10^6$ for the hydroxides of lithium, sodium and potassium, respectively, equal to 1.535, 1.828, and 2.313 l mol^{-1} s^{-1}.

Table 4. Rate constants of the reaction of chloroacetic acid with lithium, sodium, and potassium arsenite in aqueous alkaline medium at 25°C

MeOH	c^0_{I}, M	c^0_{II}, M	c^0_{NaOH}, M	Reaction duration, $c\times10^{-2}$	Conversion, %	$k_\mathrm{h}\times10^6$, l mol^{-1} s^{-1} [a]
LiOH	0.1999	0.3497	1.272	180	8.79	23.34±0.356
	0.2114	0.3184	1.702	180	11.6	22.30±0.412
NaOH	0.1921	0.3020	1.700	216	13.7	25.75±2.42
	0.1951	0.2993	1.706	216	15.7	25.03±2.18
KOH	0.2099	0.2962	1.708	144	16.8	39.77±2.36
	0.2270	0.2270	1.700	216	23.4	40.77±2.59

[a] Average value of $k\times10^6$ for the lithium, sodium, and potassium arsenites is 22.82, 25.39, and 40.27 l mol^{-1} s^{-1}, respectively.

the cation and anion is a greater, which leads to a higher probability of the existence of ion pairs. In a series of lithium–sodium–potassium the increase in the cation size increases the probability of the existence of free hydroxy and arsenite ions, which leads to an increase in the rate constants of both alkaline hydrolysis and Meyer reaction.

The kinetic data obtained can be considered as a further evidence of S_N2 mechanism of the above reactions.

EXPERIMENTAL

The technique of kinetic studies of the chloroacetic acid alkaline hydrolysis and Meyer reaction have been described earlier [1].

The solvents used were purified by distillation.

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