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Kinetics of the Reactions of [Chloro(phenyl)arsanyl]acetic Acid with Bromo- and Iodoacetic Acids

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Abstract—Quternization of [chloro(phenyl)arsanyl]acetic acid with bromo- and iodoacetic acids in aqueous alkali follows S_N2 mechanism and is accompanied by alkaline hydrolysis of haloacetic acids. The rate constants and thermodynamic parameters of the process were determined

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We previously [1] studied the kinetics of the Meyer reaction of [chloro(phenyl)arsanyl]acetic acid (**I**) with chloroacetic acid in aqueous alkali at 25, 35, 45, and 55°C. In the present work we examined the kinetics of the reactions of acid **I** with bromoacetic acid (**II**) and iodoacetic acid (**III**) in aqueous sodium hydroxide.

$$\underset{\textbf{I}}{PhAs(Cl)CH_2COO^-} + \underset{\textbf{II, III}}{HlgCH_2COO^-} \xrightarrow[NaOH]{k} \underset{\textbf{IV}}{PhAs(O)(CH_2COO^-)_2} + Cl^- + Hlg^-,$$

II, Hlg = Br; **III**, Hlg = I.

[Chloro(phenyl)arsanyl]acetic acid (**I**) was synthesized according to the procedure described in [2].

$$PhAsO(OH)_2 \xrightarrow[KI]{SO_2,\ HCl} PhAsCl_2 \xrightarrow{NaOH} PhAsO$$
$$\xrightarrow{ClCH_2COOH} PhAs(O)(OH)CH_2COOH$$
$$\xrightarrow[KI]{SO_2,\ HCl} PhAs(Cl)CH_2COOH.$$

The structure of **I** was additionally confirmed by electron-impact mass spectrometry. The mass spectrum (*A*) is given in Experimental. The mass spectrum of **I** taken from “Wiley Registry of Mass Spectral Data 1988-2001, version 3.2.1” (B) is also given for comparison.

(1) The experimental mass spectrum (A) contains all ion peaks given in B. The fragmentation pattern is consistent with structure **I**.

(2) The molecular ion peak had *m*/*z* 246, the ion peak with *m*/*z* 210 corresponds to the rearrangement ion $[M - HCl]^+$, and the presence of a strong peak with *m*/*z* 187 is related to formation of the fragment ion peak $[M - C_2H_3O_2]^+$ as a result of cleavage of the As–CH_2 bond. The subsequent decomposition of the $[M - HCl]^+$ ion (*m*/*z* 210) with elimination of C_2HO species is responsible for the appearance of an intense ion peak with *m*/*z* 169. The ion peak with *m*/*z* 91 belongs to the rearrangement ion $[C_6H_5CH_2]^+$.

The formation of 2,2'-(phenylarsoryl)diacetate (**IV**) was proved by the formation of 2,2'-(phenylarsamediyl)diacetic acid (**V**) via reduction of **IV** with sulfur dioxide directly in the reaction mixture [2].

$$\underset{\textbf{IV}}{PhAs(O)(CH_2C\Theta O\ )_2} + SO_2$$
$$\xrightarrow{HCl + KCl} \underset{\textbf{V}}{PhAs(CH_2COOH)_2}.$$

After recrystallization from water, compound **V** had mp 127°C (published data [2]: mp 126–127°C).

It was identified by mass spectrometry (EI). The molecular ion peak (m/z 270, $[M]^{+\cdot}$) had low intensity due to the presence of CH_2COOH groups which considerably reduced its stability. Ions with m/z 253 and 252 resulted from elimination of OH group and water molecule, respectively, from the molecular ion. Loss of CH_2COOH from the molecular ion gives ion with m/z 211. The most abundant peak was that with m/z 169. Presumably, it is rearrangement ion $[As(OH)C_6H_5]^+$ formed via fragmentation of the ion with m/z 211 via elimination of C_2H_2O. Expulsion of water and benzene molecules from $[As(OH)C_6H_5]^+$ yields ions with m/z 151 and 91, respectively. The other ion with low m/z values originate from successive decomposition of the above ions.

The reaction of [chloro(phenyl)arsanyl]acetic acid with haloacetic acids in aqueous alkali is complicated by alkaline hydrolysis of the latter.

$$HlgCH_2COO^- + HO^- \xrightarrow{k_h} HOCH_2COO^- + Hlg^-.$$

To estimate the contribution of the hydrolysis process to the overall Meyer reaction rate we initially studied the kinetics of alkaline hydrolysis of haloacetic acids at 15, 25, 35, and 45°C. The progress of the reaction was monitored following the concentration of liberated halide ions by argentometric titration. The rate constants of alkaline hydrolysis (k_h) were calculated using the second-order equation [3]. The average values are collected in Table 1.

The temperature dependences of k_h for chloroacetic (1), bromoacetic (2), and iodacetic acids (3) were determined:

$$\log k_h = 8.58 - 4.26\times10^3/T;\ r = 0.982,\ s = 0.192; \quad (1)$$

$$\log k_h = 8.95 - 3.86\times10^3/T;\ r = 0.999,\ s = 0.544; \quad (2)$$

$$\log k_h = 7.91 - 3.67\times10^3/T;\ r = 0.999,\ s = 0.455. \quad (3)$$

The energy of activation E (kJ mol^{-1}) and entropy of activation $-\Delta S$ (J mol^{-1} K^{-1}) for alkaline hydrolysis are as follows: chloroacetic acid, 82.1, 87.6 [4]; bromoacetic acid, 74.0, 82.0; iodoacetic acid, 70.2, 102. The rate constants of alkaline hydrolysis of haloacetic acids change in the series Cl < I < Br. An analogous dependence for the same reaction was reported in [5], where the following rate constants were given (60°C): $k_h\times10^6$ = 76.7, 2030, and 1575 l mol^{-1} s^{-1} for chloro-, bromo-, and iodacetic acids, respectively. For comparison, Table 1 also contains k_h values calculated by Eqs. (1)–(3) for the temperature 60°C.

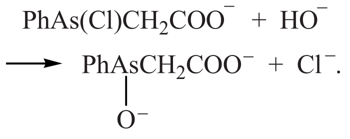
Anomalous relation between the reactivities of bromo and iodo derivatives was observed for the first time while studying reactions of methyl bromide and methyl iodide with sodium methoxide in methanol [6]. The opposite directions in the variations of halogen mobility and C–Hlg bond energy was also noted in the reaction of ammonia with haloacetic acids in aqueous solution [5], as well as in the alkaline hydrolysis and ammonolysis of haloacetic acids in aqueous ethanol and aqueous dioxane [7].

The kinetics of the reactions of [chloro(phenyl) arsanyl]acetic acid (**I**) with bromoacetic acid (**II**) and iodoacetic acid (**III**) were studied at 15, 20, 25, and 30°C. The reaction rate is described by kinetic Eq. (4).

$$\omega = k\, c_I\, c_{Hlg} + k_h\, c_{Hlg}\, c_{NaOH}, \quad (4)$$

where ω is the rate of accumulation of halide ions; k is the rate constant for the reaction of compound **I** with haloacetic acid **II** or **III**; k_h is the rate constant for alkaline hydrolysis of haloacetic acid **II** or **III**; and c_I, c_{Hlg}, and c_{NaOH} are the current concentrations of acid **I**, haloacetic acid **II** or **III**, and sodium hydroxide, respectively. Apart from argentometric tirtraion, the reaction rate was also monitored by iodometric titration, following the the consumption of arsinite ion.

The As–Cl bond undergoes complete hydrolysis by the action of alkali [8, 9] to produce chloride ion. Dissolution of compound **I** in aqueous alkali was accompanied by formation of an equivalent amount of chloride ion, which was confirmed by argentometric titration. Most probably, acid **I** is thus converted into arsinite ion **VI** [10].



$$PhAs(Cl)CH_2COO^- + HO^- \longrightarrow Ph\underset{\displaystyle O^-}{\underset{|}{As}}CH_2COO^- + Cl^-.$$

VI

Table 1. Average rate constants for alkaline hydrolysis of haloacetic acids

Temperature, °C	$k_h \times 10^6$, l mol^{-1} s^{-1}		
	$ClCH_2COOH$[a]	$BrCH_2COOH$	ICH_2COOH
15	0.650	29.0	13.9
25	1.83	92.1	43.3
35	5.45	282	109
45	16.0	770	257
60[b]	57.5	2291	776

[a] Data of [4]. [b] The rate constants k_h at 60°C were calculated from the corresponding temperature dependences [Eqs. (1)–(3)].

The argentometric titration curves for the reactions of acid **I** with haloacetic acids **II** and **III**, plotted in the E_{mV}–V_{ml} coordinates, showed two clearly defined jumps. Model studies performed on KCl–KBr and KCl–KI mixtures showed that the first jump corresponds to bromide and iodide ion, respectively, and that the second jump corresponds to chloride ion. The current concentration of halide ion was calculated at the equivalence point of the first jump. The rate constants for the reactions of **I** with haloacetic acids **II** and **III** were calculated using Eq. (5).

$$k = \frac{\omega - k_h(c^0_{Hlg} - c_{Hlg^-})(c^0_{NaOH} - 2c^0_{\mathbf{I}} - c^0_{Hlg} - c_{Hlg^-} + c_X)}{(c^0_{Hlg} - c_{Hlg^-})(c^0_{\mathbf{I}} - c_X)}. \quad (5)$$

Here, $c^0_{\mathbf{I}}$, c^0_{Hlg}, and c^0_{NaOH} are the initial concentrations of acid **I**, haloacetic acid **II** or **III**, and sodium hydroxide, respectively, and c_{Hlg} and c_X are the current concentrations of halide ion and 2,2'-(phenylarsoryl)diacetate.

The reaction rate ω was determined from the slope of the tangent at each point of the approximated time dependence of the halide ion concentration. The rate constant k almost did not change with time. Table 2 contains the result of the kinetic study on the reactions of [chloro(phenyl)arsanyl]acetic acid (**I**) with haloacetic acid **II** and **III** at different temperatures. For comparison, average rate constants for the reaction of compound **I** with chloroacetic acid in aqueous alkali [1] are given, $k \times 10^3$ (l mol^{-1} s^{-1}): 0.0158 (15°C), 0.0246 (25°C), 0.0424 (35°C), 0.101 (45°C). On the basis of these data we constructed temperature dependences of the rate constants k for the reactions of **I** with chloroacetic, bromoacetic, and iodacetic acids [Eqs. (6)–(8), respectively].

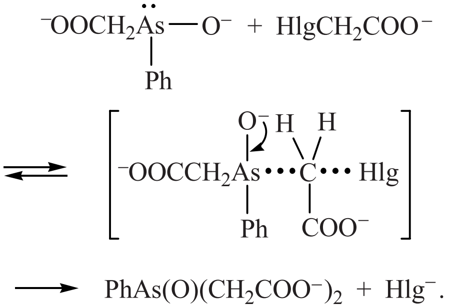
$$\log k = 8.58 - 4.26 \times 10^3/T;\ r = 0.998,\ s = 0.772; \quad (6)$$

$$\log k = 10.8 - 3.67 \times 10^3/T;\ r = 0.999,\ s = 0.250; \quad (7)$$

$$\log k = 18.1 - 5.66 \times 10^3/T;\ r = 0.999,\ s = 0.493. \quad (8)$$

The energies of activation E (kJ mol^{-1}) and entropies of activation $-\Delta S$ (J mol^{-1} K^{-1}) are as follows: chloroacetic acid, 69.9, 92.4 [1]; bromoacetic acid, 70.3, 46.0; iodoacetic acid, 108.5, –93.3. Positive value of the entropy of activation for the reaction of **I** with iodoacetic acid must be noted. Increase in the entropy of activation from negative values to positive was also observed by us while studying the kinetics of quaternization of 10-phenylphenoxarsinine with methyl iodide in different solvents. The entropy of activation increased from –143 to 9.9 J mol^{-1} K^{-1} in going from acetone to propan-2-ol [11].

The rate of the reaction of [chloro(phenyl)arsanyl] acetic acid (**I**) with haloacetic acids in aqueous alkali increases in the series Cl > Br < I, which may be regarded as an evidence in favor of the S_N2 mechanism of this process.



EXPERIMENTAL

The mass spectra (electron impact, 70 eV) were recorded on a Finnigan Trace mass spectrometer (USA); ion source temperature 200°C; batch inlet probe was heated in a programmed mode from 35 to 250°C at a rate of 35 deg min^{-1}. The spectral data were processed using Xcalibur program; m/z values of ions containing the most abundant isotopes are given below.

Bromoacetic acid (**II**) was distilled before use, bp 208°C; the distillate crystallized on cooling to form colorless crystals with mp 49°C; published data [12]: bp 209°C, mp 51°C. Iodoacetic acid was recrystallized from water, mp 82–85°C; published data [13]: mp 83°C.

[Chloro(phenyl)arsanyl]acetic acid (I). mp 102–103°C; published data [2]: mp 103°C. Found, %: As 30.03; Cl 14.27. $C_8H_8AsClO_2$. Calculated, %: As 30.39; Cl 14.39. Mass spectrum, m/z (I_{rel}, %): *A*: 246 (17.1) $[M]^{+\cdot}$, 248 (5.1), 229 (5.0), 210 (26.4) $[M - HCl]^+$, 206 (4.5), 204 (15.5), 189 (75.0), 187 (95.0) $[M - C_2H_3O_2]^+$, 169 (65.0), 140 (60.5), 119 (76.5), 91 (100.0), $[C_6H_5CH_2]^+$, 65 (40.0), 51 (73.3), 36 (70.0); *B*: 248 (3.2), 246 (12.1) $[M]^{+\cdot}$, 210 (26.4) $[M - HCl]^+$, 206 (1.5), 204 (3.5) 189 (29.0), 187 (100.0) $[M - C_2H_3O_2]^+$, 169 (19.7), 140 (14.5), 91 (85.7) $[C_6H_5CH_2]^+$.

2,2′-(Phenylarsanediyl)diacetic acid (V). Mass spectrum, m/z (I_{rel}, %): 270 (2.8) $[M]^{+\cdot}$, 253 (0.42) $[M - OH]^+$, 252 (3.37) $[M - H_2O]^+$, 211 (40.0) $[M - C_2H_3O_2]^+$, 169 (100.0) $[M - C_2H_3O_2 - C_2H_2O]^+$, 152 (3.4) $[AsC_6H_5]^+$, 151 (11.0) $[AsC_6H_4]^+$, 125 (1.3), 109 (2.6), 91 (29.4) $[AsO]^+$, 77 (4.3) $[C_6H_5]^+$, 75 (0.60) $[As]^+$, 45 (0.90) $[C_2H_5O]^+$, 43 (2.8) $[C_2H_3O]^+$.

The kinetics of alkaline hydrolysis of bromo- and iodoacetic acids were studied as described previously for chloroacetic acid [4].

Table 2. Kinetic data for the reactions of [chloro(phenyl)arsanyl]acetic acid (**I**) with bromoacetic acid (**II**) and iodoacetic acid (**III**) in aqueous sodium hydroxide

Temperature, °C	$c_{\mathrm{I}}^{0} \times 10^{2}$, M	$c_{\mathrm{Hlg}}^{0} \times 10^{2}$, M	c_{NaOH}^{0}, M	Reaction time, $s \times 10^{-2}$	Conversion, %	$k \times 10^{3}$,[a] $\mathrm{l\,mol^{-1}\,s^{-1}}$
Bromoacetic acid						
15	0.617	0.891	0.8262	162	59.9	10.8
15	0.682	0.785	0.8262	180	57.5	9.7
15	0.525	0.777	0.8160	186	55.2	9.8
20	0.735	0.908	0.8262	54	50.3	21.7
20	0.732	0.902	0.8262	54	46.3	22.2
20	0.745	0.979	0.8262	54	48.7	20.9
25	0.820	0.565	0.8691	87	44.5	29.8
25	0.892	0.524	0.8691	54	40.1	30.7
25	0.650	0.612	0.8660	132	51.5	27.3
30	0.442	0.389	0.8262	54	30.5	45.6
30	0.475	0.432	0.8262	54	41.8	46.0
30	0.338	0.483	0.8160	96	36.3	44.0
Iodoacetic acid						
15	0.545	0.454	0.8262	162	63.3	26.7
15	0.694	0.527	0.8262	162	58.3	26.0
15	0.470	0.436	0.8160	180	72.9	29.7
20	0.539	0.640	0.8262	54	58.0	62.4
20	0.550	0.508	0.8262	78	64.6	64.4
20	0.550	0.393	0.8160	93	62.5	61.9
25	0.686	0.605	0.8262	63	72.1	119.9
25	0.825	0.719	0.8262	63	80.2	110.5
25	0.735	0.463	0.8262	75	64.6	121.2
30	0.422	0.200	0.8262	57	46.8	214.6
30	0.196	0.245	0.8262	57	62.6	226.2
30	0.237	0.237	0.8160	96	64.7	280.9

[a] The average $k \times 10^{3}$ values, $\mathrm{l\,mol^{-1}\,s^{-1}}$, for bromoacetic acid are 10.1 (15°C), 21.6 (20°C), 29.3 (25°C), and 45.2 (30°C); for iodoacetic acid: 27.5 (15°C), 62.9 (20°C), 116.9 (25°C), and 240.6 (30°C).

Kinetic study on the reaction of [chloro(phenyl) arsanyl]acetic acid (I) with haloacetic acids. A sample of acid **I** was placed into a 50-ml volumetric flask and dissolved in an aqueous solution of sodium hydroxide with a required concentration. The volume of the solution was adjusted to 50 ml, and the solution was kept at a specified temperature. A sample of haloacetic acid was weighed in a reaction flask, a required amount of the alkaline solution of acid **I** was added, and the mixture was thoroughly stirred. The moment of addition of acid **I** was taken as reaction start. Samples were withdrawn from the mixture at definite time intervals, and the concentrations of arsinite ions and halide ions were determined by iodometric and argentometric titration, respectively, according to the procedure described in [4].

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