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The Rate of Chloroacetic Acid Alkaline Hydrolysis: Medium Effect

G. G. Midyana[a], R. G. Makitra[a†], and E. Ya. Pal'chikova[b]

[a] *Department of Physical Chemistry of Fossil Fuels InPOCC, National Academy of Sciences of Ukraine, ul. Nauchnaya 3a, Lviv, 79053 Ukraine*
e-mail: gmidyana@gmail.com

[b] *Institute of Fossil Fuels Geology and Geochemistry, Ukraine National Academy of Sciences, Lviv, Ukraine*

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Abstract—Rate constant of chloroacetic acid alkaline hydrolysis in the mixed aqueous-organic solvents depends on the organic co-solvent nucleophilic solvation; however, the effect of the medium polarity on the rate constant is not clear. The rate constant can be reasonably estimated with a multi-parameter equation accounting for the organic co-solvent basicity as well as its density of cohesion energy and molar volume.

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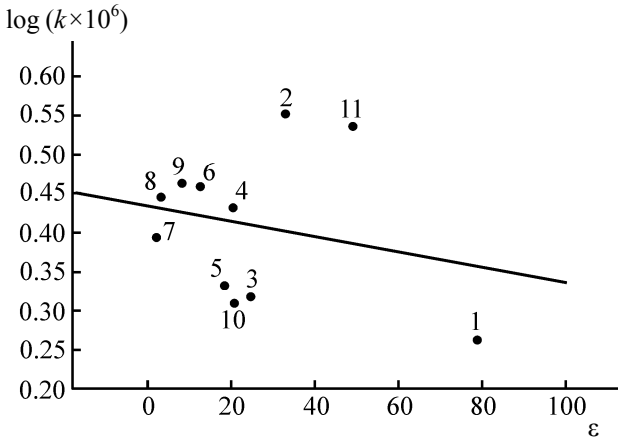
Kinetics and mechanism of solvolysis, including hydrolysis of halogenated hydrocarbons, have been thoroughly studied. It has been concluded that the medium effect on the reaction rate is fairly complex; however, it can be generalized taking advantage of the multi-parametric equations [1–3]. The respective relations summarizing the rate of halogenated acids hydrolysis have been scarce so far.

Kinetics of the Meyer reaction (the interaction of chloroacetic acid and sodium arsenite in the excess of NaOH) in a series of ten water–organic (4 : 1) mixed solvents was studied in [4]; the respective second-order rate constants of the side reaction of alkaline hydrolysis of sodium chloroacetate were determined. It was suggested that decrease of the medium polarity should have been the decisive factor accelerating the hydrolysis due to delocalization of charges in the transition state. However, such dependence was not clearly observed (see figure), even within the subset of homologous alcohols: in the case of less polar propanol-2 (ε = 18.30), the hydrolysis of sodium chloroacetate was slower than in the case of propanol-1 (ε 20.33). Hence, the rate of chloroacetic acid hydrolysis should have been a complex function of several factors.

In general, the change of the solvolysis rate due to the substrate–solvent interaction depends on the interaction free energy, which is in turn a sum of independent energetic effects of distinct solvation processes. Furthermore, model calculations should account for the cohesion energy of the medium that can favor the reaction due to the cage effect. Noteworthily, in the case of other processes, in particular, solid dissolution, the solvent self-association, on the contrary, can suppress the intercalation of the dissolving molecules into the liquid phase. In order to elucidate the medium effect in the case of the explored hydrolysis reaction, it was reasonable to analyze the kinetic data using the multi-parametric Eq. (1).



Rate constant of alkaline hydrolysis of chloroacetic acid in the 4 : 1 mixtures of water with organic co-solvents at 25°C as function of the co-solvent dielectric constant ε. The figures near the points correspond to the table.

† Deceased.

Rate constant of alkaline hydrolysis of chloroacetic acid in the 4 : 1 mixtures of water with organic co-solvents at 25°C [4]

Run no.	Co-solvent	ε	$k\times10^6$, L mol^{-1} s^{-1}	log k		
				experimental	calculated	Δlog k
1	Water	78.5	1.830	0.2625	0.2641	0.0016
2	Methanol[a]	32.70	3.556	0.5510	0.2491	–0.3019
3	Ethanol	24.55	2.072	0.3164	0.3228	0.0064
4	Propanol-1	20.33	2.706	0.4323	0.3710	–0.0613
5	Propanol-2	18.30	2.153	0.3330	0.3811	0.0481
6	2-Methylpropanol-2	12.47	2.871	0.4580	0.4437	–0.0143
7	Dioxane	2.21	2.483	0.3950	0.4184	0.0234
8	Dimethoxyethane	2.70	2.778	0.4437	0.4504	0.0067
9	Tetrahydrofuran	7.79	2.896	0.4618	0.4536	–0.0082
10	Acetone	20.54	2.035	0.3086	0.3066	–0.0020
11	Dimethylsulfoxide	48.90	3.428	0.5350	0.5348	–0.0002

[a] The solvent was excluded from the model.

$$\log k = a_0 + a_1 f(n^2) + a_2 f(\varepsilon) + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M. \quad (1)$$

The first two variable terms if the Eq. (1) reflected the ability of the solvent towards non-specific solvation, depending on its polarity and polarizability; the next two parameters showed the solvent ability towards specific solvation, depending on the Palm basicity parameter B and the Reichardt electrophilicity parameter E_T; the squared Hildebrand solubility parameter δ accounted for the degree of self-association (or, equivalently, for the cohesion energy) of the organic solvent of the molar volume V_M [5]. The experimental data were processed using the Eq. (1) and taking into account the recommendation of the International Group for Correlation Analysis in Chemistry of IUPAC [6].

The analysis of the rate constants determined in 11 solvents (including pure water) led to the equation with unacceptably low multiple correlation coefficient, R = 0.7701. However, excluding the only outlier log k value (corresponding to methanol) gave the six-parametric Eq. (2), reasonably describing the effects of different properties of organic co-solvents on the rate of studied reaction.

$$\log (k\times10^6) = -0.6129 + (1.7291\pm1.1029) f(n^2) + (0.1724\pm0.2046) f(\varepsilon) + (0.0006\pm0.0004) B + (0.0005\pm0.0032) E_T + (0.0001\pm0.0001)\delta^2 + (0.0039\pm0.0010) V_M, \quad (2)$$
$$R = 0.9551,\ s = 0.0256.$$

The paired correlation coefficients r_i of log k with each of the equation terms were of 0.8401, –0.2103, 0.8446, –0.5674, –0.5402, and 0.6310, respectively; hence, it was not possible to evaluate the significance of the Eq. (2) terms. However, the effect of the nucleophilic solvation (reflected by B parameter) was likely the decisive one, whereas the medium polarity influence was likely negligible (the absolute value of the corresponding correlation coefficient was fairly low, of 0.2103, and its standard deviation exceeded the a_2 value). Interestingly, all the a_1–a_6 values were positive, meaning that any solvation effect predominantly stabilized the transition state, thus favoring the reaction.

In order to elucidate the significance of the Eq. (2) terms, they were excluded from the equation one by one [6], and the multiple correlation coefficients R of the reduced equations were determined. That way, the low significance of the co-solvent ability towards electrophilic solvation was demonstrated, the multiple correlation coefficient of the resulting five-parametric equation being of 0.9549. Furthermore, in the reduced equation, the exclusion procedure was repeated, and the low significance of the co-solvent polarity was stated. The so derived four-parametric Eq. (3) showed the multiple correlation coefficient of 0.9463, only slightly lower than the recommended threshold ($R \geq 0.95$ [6]).

$$\log (k\times10^6) = -0.3656 + (0.9998\pm1.0234) f(n^2) + (0.0009\pm0.0004) B + (0.0001\pm0.0000)\delta^2 + (0.0033\pm0.0010) V_M, \quad (3)$$
$$R = 0.9463,\ s = 0.0279.$$

The log k values calculated using the Eq. (3) are collected in the Table along with the respective deviations from the experimental values $\Delta\log k$. It is to be seen that indeed the individual deviations were not exceeding the standard deviation of the regression model (s = 0.0279) the exceptions being propanol and the excluded methanol. The polarizability effect was found to be negligible as well; its excluding from the model did not lead to much worse correlation (4).

$$\log (k\times10^6) = -0.2270 + (0.0012\pm0.0002)B + (0.0001\pm0.0000)\delta^2 + (0.0035\pm0.0010)V_M, \quad (4)$$
$$R = 0.9405,\ s = 0.0293.$$

To conclude, the chloroacetic acid alkaline hydrolysis rate in the mixed solvents (80% of water and 20% of the organic co-solvent) was predominantly determined by the nucleophilic solvation of chloroacetic acid salt at the electron-accepting chlorine atom. At the same time, the chlorine atom elimination was facilitated with increased cohesion energy and the solvating ability of the solvent. Taking into account the results reported in [4], such solvation effect should have been found in the case of the reaction mechanism similar to that of the Meyer reaction. As the chloroacetic acid hydrolysis was accelerated with the increasing fraction of the organic co-solvent [4], the influence of its nucleophilic solvation effect should have been simultaneously enhanced.

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