The temperature dependence of the disproportionation reaction of iodous acid in aqueous sulfuric acid solutions

SMILJANA MARKOVIĆ,[1] NOVICA RAKIĆEVIĆ[2] and DJURO MIŠLJENOVIĆ[3]

[1]*Faculty of Technological Sciences, University of Priština, Kneza Miloša 7, YU-38220 Kosovska Mitrovica,* [2]*Faculty of Natural Sciences, University of Priština, P. O. Box 131, YU-37000 Kruševac and* [3]*Faculty of Mathematics, University of Belgrade, Studentski trg 16, P. O. Box, 550, YU-11001 Belgrade, Yugoslavia*

The aim of this work was to examine the disproportionation reaction of iodous acid, HOIO, in aqueous 0.18 mol/dm^3 H$_2$SO$_4$ solution, by spectrophotometric measurements of the absorbance. The absorbing HgI$^+$-ion species were generated during the observed disproportionation process. The specific rate constants of disproportionation were calculated in the temperature range from 12 to 30 ºC. The average values ranged from 1.20 to 2.94 mol^{-1}dm^3 s^{-1}, respectively. In addition, the values of the activation energies were determined by a graphical method. An average value of 71.20 kJ/mol was found for the chosen temperature interval.

Keywords: iodous acid, disproportionation reaction, iodine compounds, activation energy, specific rate constants.

INTRODUCTION

Iodous acid as significant molecule species appears in many investigated iodine complex reactions in chemical kinetics. It was claimed that disproportionation of HOIO could be expected in some systems.[1,2] In this sense, the magnitude of some kinetic parameters, such as the specific reaction rate constants, the activation energies and Arrhenius constant of this reaction have not been thoroughly determined. More precisely, in the literature some results exist for the rate constants at 25 ºC which, however, differ from author to author. In this paper experimental and numerical comparisons are made between our results and the results obtained in some other investigations.

The homogeneous disproportionation of HOIO in aqueous solutions of H$_2$SO$_4$ is well known. In this case iodous acid is simultaneously oxidized to iodate and reduced to hypoiodous acid, as can be seen from the stoichiometry of the tested bimolecular chemical reaction:

$$2HOIO \rightarrow IO_3^- + H^+ + HOI \qquad (1)$$

On the basis of electrochemical measurements, Noszticzius[3] reported values of the rate constants of less or equal to 5.4 mol^{-1} dm^3 s^{-1} in aqueous solutions of 0.05 – 0.15 mol/dm^3 sulfuric acid at 25 ºC. In addition, by spectrochemical absorbance measurements, Furrow[4] found values of about 50 mol^{-1} dm^3 s^{-1} or lower in 0.13 – 0.51 mol/dm^3 H_2SO_4 at 25 ºC.

A complex mechanism for the decomposition HOIO in the presence Hg^{2+} ions, in solutions of H_2SO_4, was observed with the net reaction being:

$$3HOIO + Hg^{2+} \rightarrow HgI^+ + 3H^+ + 2IO_3^- \tag{2}$$

The I^--ions generated relatively fastly in the elementary reaction: HOI + HOIO $\rightarrow 2H^+ + I^- + IO_3^-$, could be rapidly removed, in the presence of excess of Hg^{2+}-ion, by the reaction: $Hg^{2+} + I^- \rightarrow HgI^+$. Therefore, the disproportionation of HOIO, given by reaction (1), is the slowest process, which determines the total reaction rate.

Following the above-described results ,we have determined the specific rate constants in the temperature range from 12 to 30 ºC. In order to avoid the dependence of the reaction rate on the concentration of Hg^{2+}, the Hindmarsh version of the Gear's integrator[5] was used for the numeric simulation of the experimentaly obtained data.

EXPERIMENTAL

Mixtures of the intermediates of the iodine species, I^+ and I^{3+}, were prepared by disolving I_2 and KIO_3 in concentrated sulfuric acid (96 %) according to the stoichiometry of the chemical reaction:[6]

$$I_2 + 3IO_3^- + 8H^+ \rightarrow 5IO^+ + 4H_2O \tag{3}$$

The iodine species I^{3+} is stable in the presence of excess of iodate, when the ratio of KIO_3 to I_2 is larger than 5:1. Thus, excess iodate was used to prevent the formation of I^+. The produced compound was formulated as $(IO)_2SO_4$, which in the presence of sulfuric acid reacts rapidly with water and produces the chemical species: HOIO and IO_3^-, and, naturally, H_2SO_4.

The spectrophotometric measurements of the absorbance changes at a wavelength of 274 nm, absorbed by the HgI^+-ion species, were performed using a Perkin Elmer Hitachi 2000 spectrophotometer with thermostated cells.

The temperatures of the reaction solutions were held constant with an accuracy of ±0.2 ºC by circulating water from a thermostated bath.

Doubly distilled water, which had been tested by electric conduction, was used for the experiments. The stock solutions were prepared by using chemicals produced by "Merck". The solutions were stored in dark vessels. The stock solutions were diluted immediately before each measurement. Most experiments were carried out in semidarkness without direct overhead light.

RESULTS AND DISCUSSION

New values of the activation energies were determined graphically for the temperature interval from 12 to 30 ºC using the Arrhenius equation: $k = A \exp(-E_a/RT)$, where A is a constant, E_a the activation energy and T the absolute temperature. Constant A was determined as the intercept on the ordinate for $1/T = 0$.

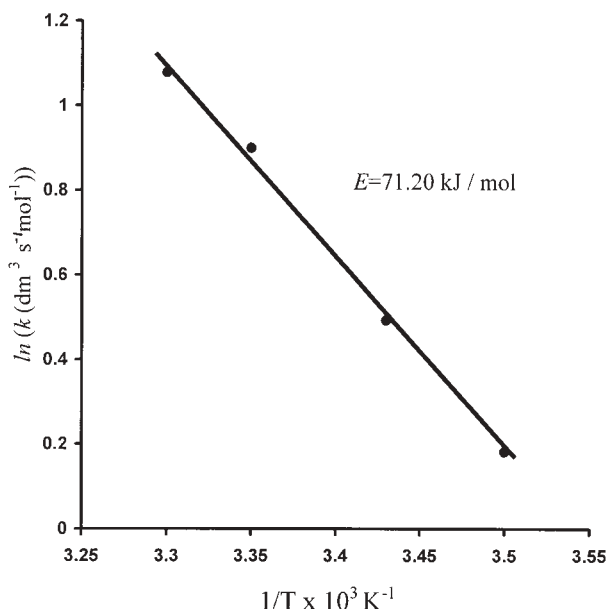The activation energy was determined as the slope of the straight line of the equation. $\ln k = f(1/T)$ (see Fig. 1).

Fig. 1. The Arrhenius dependence between ln k and $1/T$. The rate constants $k(2)$ are listed in Table I.

By integration of the expression for a symmetric second-order reaction: $-dc/dt = k_2c^2$ with the boundaries from c to c_0 one obtains: $k_2 = 1/t\,(1/c - 1/c_0)$, where k_2 is the specific rate constant for a second-order reaction, c and c_0 are the concentrations during and at the start of a process. This equation is solved in the form: $t = (-1/kc_0) + 1/kc$ and can be used to graphically determine the rate constant; the slope of the straight line obtained by plotting t against $1/c$ gives the reciprocal value of the rate constant.

For our investigation we used the equation in the form: $k_2 = 1/t\,[1/(A_\infty - A_t) - 1/(A_\infty - A_0)]$, where A_∞, A_t and A_0 are the absorbance at the end, during and at the start of the experiment, respectively. The obtained experimental data and calculated values are presented in Table I, with the division into A, B, C and D parts, (with the corresponding units), which was used for the calculation of the specific reaction rates, on the basis of the observed absorbance changes during the process. The examined reaction is second-order, because a straight line is obtained when the function is plotted: $1/(A_\infty - A_t) = f(t)$ and because constant values of k_2 are obtained at successive times.

The rate constant of disproportionation increases with increasing temperature, which is normal, but they are somewhat different from those cited in the literature, although they have the same order of magnitude in some cases. Thus, the value at 30 °C is 2.94 and at 12 °C is 1.20 dm^3 mol^{-1} s^{-1}. Their quotient of 2.45 indicates that the chemical rate increased by the same value, for a temperature difference of 18 °C. In our case, these values are approximately one-half those of Noszticzius and twenty times lower than the values of Furrow. Such are the results of our investigation.

For this concrete reaction, the average activation energy of 71.20 kJ/mol is relatively high, which shows that the disproportionation process is slow, thus the experiment must be performed very precisely. One measurement lasted several hours. The

found value for the Arrhenius constant was 9×10^{12} dm^3 mol^{-1} s^{-1}. In general, the agreement between our experimental results and the results of the mathematical approximation is good, with the percent errors lying between 0.13 and 4.73.

TABLE I. Disproportionation rate constants of HOIO from the absorbtion changes at various temperatures

A. At 12 ºC

c_M(HOIO) (mol/dm³)×10⁴	c_M(IO₃⁻) (mol/dm³)×10⁴	c_M(Hg²⁺) (mol/dm³)×10⁴	c_M(H₂SO₄) (mol/dm³)	k_2 (dm³ mol⁻¹s⁻¹)
5.5	3.23	5.00	0.18	1.02
5.8	3.23	5.00		1.21
6.0	3.23	6.00		1.09
7.5	5.10	7.00		1.30
7.5	5.10	10.00		1.38
				k_{av} = 1.20
B. At 18 ºC				
5.8	3.23	5.00	0.18	1.45
6.0	3.23	5.25		1.62
6.0	3.23	6.00		1.71
7.5	5.10	7.00		1.62
7.5	5.10	10.00		1.81
				k_{av} = 1.64
C. At 25 ºC				
5.5	3.23	4.61	0.18	2.50
5.5	3.23	5.25		2.62
7.5	5.10	6.00		2.42
7.5	5.10	7.00		2.28
8.8	6.00	10.00		2.48
				k_{av} = 2.46
D. At 30 ºC				
5.5	3.23	4.61	0.18	2.69
5.8	3.23	5.00		2.84
7.5	5.10	6.00		2.93
7.5	5.10	7.00		3.02
8.8	6.00	10.00		3.22
				k_{av} = 2.94

Under our experimental conditions, there was no oscillation of the reaction, as some authors had predicted. The amount of Hg^{2+} had no effect on the rate of the process in the examined solutions, acidified with sulfuric acid, although we had secretly hoped there would be. Probably, there was a small autocatalytic effect of the HgI^+-ion on the

rate of disproportionation. The effect of sulfuric acid was evident with the rate of the investigated reaction increasing with increasing sulfuric acid concentration. The effect of salt was not taken into consideration, because the ionic strength of the examined solutions was constant. Likewise, it is important to realize that a good deal of the former work, particularly on ionic reactions, in chemical kinetic was uselles.

CONCLUSION

On the basis of spectrophotometric measurements of the absorbance change of the HgI$^+$ species at 274 nm, generated during the chemical reaction, the rate constants for the disproportionation of the molecular species HOIO in the temperature interval from 12 ºC to 30 ºC have been calculated. The average values were from 1.20 to 2.94 mol^{-1} dm^3 s^{-1}, increasing with temperature. In the given temperature interval of 18 ºC, the disproportionation rate of HOIO increased by about 2.45 time. An average activation energy of 71.20 kJ/mol was determined graphically as the coefficient of the slope of the straight-line dependence between ln k and 1/T. Subsequently the Arrhenius constant was calculated and found to have a value of 9×10^{12} dm^3 mol^{-1} s^{-1}.

И З В О Д

ЗАВИСНОСТ РЕАКЦИЈЕ ДИСПРОПОРЦИОНИСАЊА HOIO ОД ТЕМПЕРАТУРЕ У ВОДЕНОМ РАСТВОРУ СУМПОРНЕ КИСЕЛИНЕ

СМИЉАНА МАРКОВИЋ,[1] НОВИЦА РАКИЋЕВИЋ[2] и ЂУРО МИШЉЕНОВИЋ[3]

[1]*Факулѿеѿ ѿехничких наука, Универзиѿеѿ у Пришѿини, Кнеза Милоша 7, 38220 Косовска Миѿровица,* [2]*Природно-маѿемаѿички факулѿеѿ, Универзиѿеѿ у Пришѿини, ѿ. ѿр. 131, Крушевац и* [3]*Маѿемаѿички факулѿеѿ, Сѿуденѿски ѿрг 16, 11001 Београд*

Испитана је реакција диспропорционисања у киселом раствору (0,18 mol/dm^3 H$_2$SO$_4$) на основу низа спектрофотометријских мерења апсорпционих промена светлости са временом. Апсорбујућа HgI$^+$-јонска врста добијена је током посматрања процеса диспропорционисања. Експериментални подаци били су неопходни да би се израчунале специфичне константе брзине на температури од 12 ºC до 30 ºC, које су имале просечне вредности од 1,20 до 2,94 mol^{-1} dm^3 s^{-1}, респективно. Поред тога, вредности активационих енергија биле су одређене графичком методом уз просечну вредност 71,20 kJ/mol за одабрани температурни интервал.

REFERENCES

1. W. C. Bray, H. A. Liebhafsky, *Am. Chem. Soc.* **53** (1931) 38
2. D. O. Cooke, *Int. J. Chem. Kinet.* **12** (1980) 683-98
3. Z. Noszticzius, E. Noszticzius, Z. A. Schelly, *J. Phys. Chem.* **87** (1983) 510
4. S. Furrow, *J. Phys. Chem*. **91** (1987) 2129
5. C. Hindmarch, *GEAR: Ordinary Differential Equation System Solver* Livemore CA 1974
6. I. Masson, C. Argument, *J. Chem. Soc.* (1938) 1702.