

INFLUENCE OF THE ACIDITY OF THE IODOUS ACID SOLUTION SYSTEM ON THE KINETICS OF THE DISPROPORTIONATION REACTION

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ABSTRACT

Influence of the acidity of the iodosous acid (HOIO) solution system on the kinetics disproportionation reaction is examined in aqueous sulfuric acid solution (0.125 moldm⁻³). The disproportionation reaction rate constants were determined at 285, 291, 298 and 303 K based on data obtained under stationary conditions. The calculated rate constants increase with increasing temperature for different values of iodosous acid and iodate concentrations. The average activation energy of 46 kJmol⁻¹ was determined for the chosen temperature interval, by a graphical method. The values of *pseudo*-equilibrium concentrations of kinetically important and catalytic species H⁺, H₂OI⁺ i IO₃⁻ in the disproportionation reaction were determined for the given experimental conditions based on the equilibrium dissociation reactions of sulfuric and iodosous acids in the quasi-stationary state. The estimated values of sulfuric and iodosous acid are predominant and higher than the concentration of the protonated ion of H₂OI⁺.

Keywords: Disproportionation reaction, Iodosous acid, Activation energy, Rate constants, Kinetics.

INTRODUCTION

The iodosous acid (HOIO) disproportionation reaction was studied under different experimental conditions in the visible and ultraviolet areas of the spectrum (Noszticzius et al., 1983; Lengyel et al., 1996; Urbansky et al., 1997). The theoretical approach and explanations of experimental results represent a significant contribution to chemical kinetics for analyses of systems in which the reaction occurs in iodine complex reactions (Mäkelä et al., 2002; O'Dowd et al., 2002; Jimenez et al., 2003; De Souza & Brown., 2014).

The mechanism of the process itself, which was studied in strong acidic aqueous solutions, is complex, slow and subject to autocatalysis (Lengyel et al., 1996). A detailed, complete mechanism of this complex dynamic process has not been fully determined yet. Namely, HOIO iodosous acid decomposes in strong acidic aqueous solutions through a series of iodine-oxygen species that react with each other creating appropriate balances. Due to the complexity of the disproportionation, it is possible to followed only the reaction products that are produced during the reaction. The process depends upon the nature of the reacting species and solvents, as well as upon their acidity and temperature. High acidity is one of the kinetic factors that influences the complexity as well as the rate of the observed process. The stoichiometry of the homogeneous bimolecular redox reaction of HOIO disproportionation can be represented by the equation:



Experimental determinations are relatively difficult since the measurements are hard to perform in the same way due to the high concentration of sulfuric acid in the preparation of HOIO and very limited in terms of the observed results. Calculated kinetic parameters, based on experimental measurements such as reaction rate and the activation energy of this reaction, have been determined in relatively precise and accurate manner, whereas their published values significantly differ (Noszticzius et al., 1983; Lengyel et al., 1996).

In addition to experimental, theoretical and numerical research are of great importance for complete understanding of the process. Particularly important is the knowledge of the ionic species concentrations that are formed at the beginning of the disproportionation reaction and remain unchanged during their evolution. Our previously published studies describe the application of numerical and theoretical methods for their determination (Markovic et al., 2015).

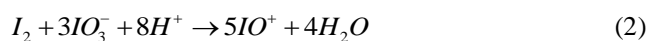
The aim of this paper is to examine the HOIO disproportionation reaction depending on the system temperature using experimental and theoretical methods. Kinetic parameters, such as rate constants and activation energy, were determined experimentally at defined acidity in aqueous sulfuric acid solution, as well as at different system temperatures. Numerical simulation of the experimentally obtained results was performed using the Hindmarsh version of the Gear's integrator (Markovic et al., 2002). Under isothermal conditions, the concentrations of the relevant species H⁺, H₂OI⁺ and IO₃⁻ were determined theoretically based on their numerical evaluation.

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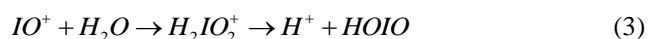
EXPERIMENTAL

The experiments are performed in a similar manner as described in our previously published papers (Markovic et al., 2002; Markovic & Petrovic, 2016). The kinetics of the iodous acid disproportionation reaction was indirectly monitored by UV-Vis spectrophotometric method in 10 mm quartz cuvettes. The absorption changes of the resulting mixture were monitored at 274 nm (absorption maximum I_2 , $\epsilon=183\text{m}^2\text{mol}^{-1}$). Fresh and thermostated solutions prepared immediately before the experiments were used for experimental determinations. Double-distilled water and analytical pure reagents (Merck, Emd Chemicals, Inc. Gibbstown, NJ) were used for the preparation of stock solutions.

Dissolution of I_2 in excess of KIO_3 (in a ratio of 1: 5) in concentrated sulfuric acid (96%) gives a mixture containing I^+ and I^{3+} ionic species (Noszticzius et al., 1983). The stoichiometry of the overall complex reaction can be described as:



Reactions were performed in iodate excess in order to prevent I^+ formation. Namely, a balance mixture containing I^+ , I^{3+} , and I^5+ ions is formed in an acidic media, where their concentration is controlled by the initial ratio of concentrations of I_2 and IO_3^- . The ionic species is added in the form of liquid iodosyl sulfate $(IO)_2SO_4$ into 50 cm^3 solution of sulfuric acid concentration of 0.125 mol/dm^3 . Then, the iodosyl ion in the aqueous solution decomposes rapidly forming I^{3+} which is presented in the form of iodous acid:



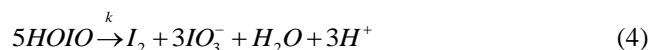
All measurements are performed in several independent series. Each new series is preceded by experiments that reproduce some of the results of previous series. The study of the disproportionation reaction was performed under conditions of a closed isothermal well-stirred reactor, where the temperature of the reaction mixture was maintained constant, with an accuracy of ± 0.2 K. The solutions were kept in closed dark quartz vessels and the experiments were performed in semi-darkness without direct overhead lighting.

RESULTS AND DISCUSSION

The experimental results are shown in Table 1. The estimated disproportionation reaction rate constants were determined at 285, 291, 298 and 303 K with constant solution acidity of 0.125 mol/dm^3 . The light absorbance is caused only by I_2 molecule absorption (Awtrey, & Connik 1951).

To determine the reaction rate constants, the experimental and numerical methods were combined in the manner shown earlier (Markovic et al., 2002). Furthermore, a previously accepted mechanism model was used, which was described in details in our previously published papers (Markovic & Petrovic,

2016). The overall stoichiometry of the disproportionation reaction can be represented as:



Due to the complexity of the system, only the I_2 generated during the reaction can be followed continuously. For the given experimental conditions, the obtained rate law for the overall disproportionation process can be presented as:

$$d[HOIO]/dt = k[HOIO]^2 \quad (5)$$

where k is the rate constant of this process.

The complex reaction was examined in the concentration range from 3.23×10^{-4} to 7.10×10^{-4} mol/dm^3 for IO_3^- , while for HOIO values the concentrations were ranging from 1.40×10^{-4} to 1.80×10^{-4} mol/dm^3 .

It can be noticed that within the analyzed concentration interval, the calculated values of the rate constants differ at different temperatures (Table 1, Fig. 1. S in the Supporting Information).

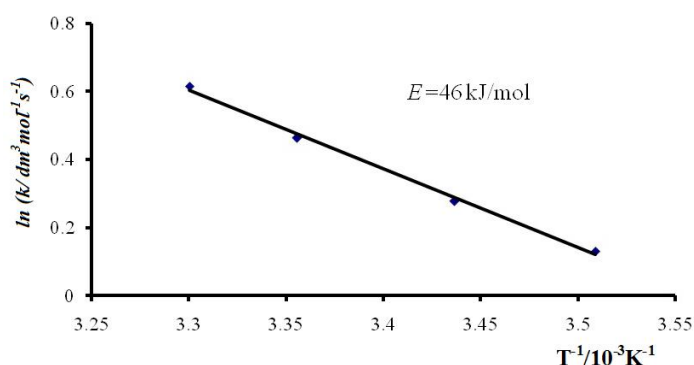


Figure 1. Dependence of $\ln k$ on $1/T$.

Their values increase with increasing temperature and obtained values are about 1.6 times lower than in the case when the concentration of Hg^{2+} was in excess by 0.18 mol/dm^3 (Markovic et al., 2002). The values of the rate constants are of the same order of magnitude (when the concentration of Hg^{2+} was in excess) and they are approximately 16 times lower than those given in the literature (Lengyel et al., 1996).

The amount of Hg^{2+} had no effect on the reaction rate constants of the process in the examined solutions, acidified with sulfuric acid; although we have predicted there would be an effect.

The influence of temperature and acidity as well as the very narrow limits of the feasible experimental conditions are probably main reasons for obtaining these diverse rate constant values. For the given experimental conditions, the average value of the activation energy was determined graphically as the slope of straight line from the dependence $\ln k = f(1/T)$, which represents the linear form of the Arrhenius equation, and is $E_a = 46$ kJ/mol . The dependence $\ln k = f(1/T)$, was plotted in Fig 1.

Table 1. HOIO disproportionation rate constants calculated at different temperatures obtained by measuring the increase in the absorption of I₂ molecular species at 274 nm.

T K	$[HOIO]$ $\text{mol dm}^{-3} \times 10^4$	$[IO_3^-]$ $\text{mol dm}^{-3} \times 10^4$	$[H^+]$ $\text{mol dm}^{-3} \times 10^4$	k $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	k_{av} $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
285	1.80	3.23	0.125	1.16	1.14±0.08
	1.74	4.80		1.14	
	1.70	5.10		1.20	
	1.54	6.00		1.12	
	1.40	7.10		1.10	
291	1.80	3.23	0.125	1.40	1.32±0.10
	1.74	3.23		1.38	
	1.70	4.80		1.35	
	1.50	5.10		1.23	
	1.40	6.00		1.26	
298	1.80	3.23	0.125	1.80	1.59±0.07
	1.70	3.23		1.70	
	1.54	5.10		1.60	
	1.40	6.00		1.40	
	1.40	7.10		1.48	
303	1.80	5.10	0.125	2.02	1.85±0.10
	1.78	4.80		1.98	
	1.74	4.80		1.80	
	1.10	6.00		1.75	
	1.20	3.23		1.68	

Table 2. Equilibrium concentrations (mol dm^{-3}) of relevant ionic species estimated numerically, $[H_2SO_4]_{\text{tot}} = 0.125 \text{ mol dm}^{-3}$, $[SO_4^{2-}]_{\text{tot}} = 0.0104 \text{ mol dm}^{-3}$, $[HSO_4^-]_{\text{tot}} = 0.083 \text{ mol dm}^{-3}$ for various values of $[HOIO]_{\text{tot}}$.

$[KIO_3]$ $\text{mol dm}^{-3} \times 10^4$	3.23	4.80	5.10	6.00	7.10
$[IO_3^-]$ (mol dm^{-3})	0.066	0.080	0.083	0.090	0.101
	0.067	0.082	0.086	0.094	0.105
	0.071	0.086	0.090	0.098	0.110
	0.074	0.092	0.096	0.105	0.116
	0.078	0.098	0.100	0.112	0.124
$[H_2OI^+]$ (mol dm^{-3})	0.052	0.077	0.082	0.096	0.114
	0.055	0.080	0.085	0.100	0.115
	0.060	0.081	0.087	0.102	0.117
	0.062	0.090	0.096	0.113	0.129
	0.066	0.095	0.106	0.124	0.142
$[H^+]$ (mol dm^{-3})	0.175	0.192	0.195	0.205	0.216
	0.187	0.202	0.210	0.215	0.228
	0.191	0.215	0.220	0.230	0.248
	0.195	0.225	0.228	0.240	0.266
	0.205	0.230	0.239	0.255	0.274

The obtained value is lower in comparison to the previously published (Markovic et al., 2002) and confirms the presence of catalytic influences in the disproportionation process, what is in agreement with previous observations (Markovic & Cekerevac 2009; Markovic & Rakicevic 2006; Hegedüs et al., 2001; Markovic & Petrovic, 2010).

During the disproportionation proces, the concentrations of catalytic and relevant species of H^+ , H_2OI^+ and IO_3^- , formed at the beginning of the reaction, are relatively high and under negligible changes. This is completely different from the

behavior I₂, and other species, such as the intermediates I, HIO, HOIO, and others (Lengyel et al., 1996). Under our isothermal conditions in the quasi-stationary state of *pseudo*-equilibrium concentrations of these relevant species, disproportionation reactions were determined during equilibrium dissociation reactions for strong acid sulfuric acid, using previously described procedure (Markovic et al., 2015) and based on the equations:

$$[SO_4^{2-}]_{\text{tot}} = [SO_4^{2-}] \left(1 + \beta_{a2} [H^+] + \beta_{a1} [H^+]^2 \right) \quad (6)$$

$$[IO_3^-]_{tot} = [IO_3^-] \left(1 + \beta_{a3} [H^+]^3 / [HIO_2] \right) + 2[HIO_2] \quad (7)$$

$$[H^+]_{tot} = [H^+] \left(1 + 2\beta_{a1} [SO_4^{2-}] + \beta_{a2} [SO_4^{2-}] \right) + \beta_{a3} [H^+]^2 + [IO_3^-] \quad (8)$$

where: $\beta_{a1} - \beta_{a3}$ are stability constants previously known or estimated.

The results are shown in Table 2, for acidity of 0.125 mol/dm³ and temperature of 298 K. The calculated concentration values are constant if HOIO concentration varies between 1.40x10⁻⁴ to 1.80x10⁻⁴ mol/dm³. Thereby, the pH value was in the range of 1.5 to 3. The concentrations SO₄²⁻, and HSO₄⁻ are small enough to be neglected, so they were not taken into account in this consideration. These results indicate that for certain values of initial sulfuric acid concentration, the *pseudo*-equilibrium concentration of iodate IO₃⁻ and H⁺ ions is a linear and monotonously increasing function of the initial concentrations of potassium iodate (Figures 2 and 3).

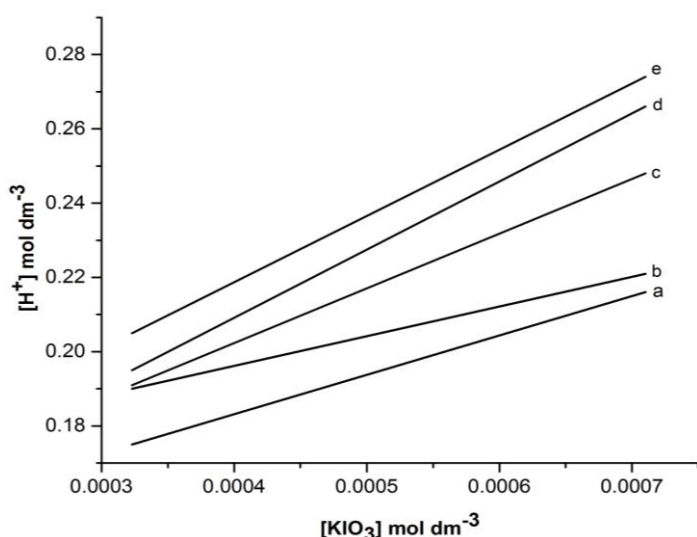


Figure 2. Equilibrium concentrations of [H⁺] as a function of [KIO₃] for various values of [HOIO]_{tot} at 298 K, a; [HOIO]_{tot} = 1.8x10⁻⁴ moldm⁻³, b; [HOIO]_{tot} = 1.74 x10⁻⁴ moldm⁻³, c; [HOIO]_{tot} = 1.70 x10⁻⁴ moldm⁻³, d; [HOIO]_{tot} = 1.54 x10⁻⁴ moldm⁻³, e; [HOIO]_{tot} = 1.40 x10⁻⁴ moldm⁻³.

The results of equilibrium concentrations at 298 K are presented here, while their trends are of a general character.

The resulting values of the observed concentrations of sulfuric and iodous acid, determined from the equilibrium dissociation reactions in the quasi-stationary state, are predominant and higher than of the protonated ion H₂OI⁺ of hypoiodic acid.

Concentrations of other species in the system are relatively small under the given conditions which can be neglected. The influence of salt was not taken into consideration because there is

no influence on the rate of the process since the neutral HOIO molecule is disproportionated.

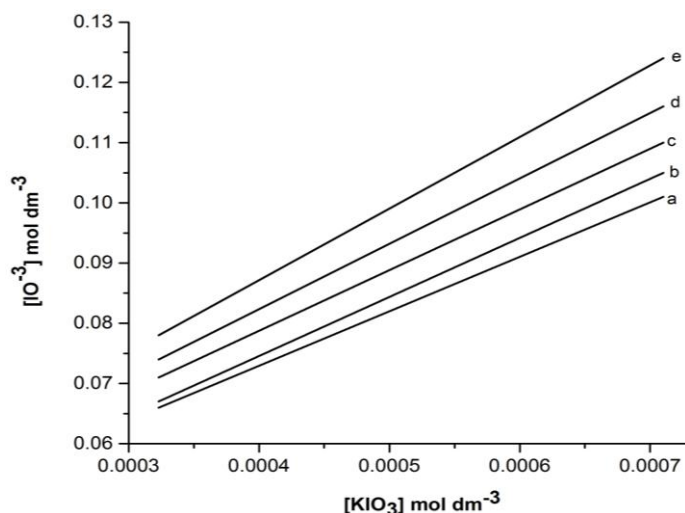


Figure 3. Equilibrium concentrations of [IO₃⁻] as function of [KIO₃] for various values of [HOIO]_{tot} at 298 K, a; [HOIO]_{tot} = 1.8x10⁻⁴ moldm⁻³, b; [HOIO]_{tot} = 1.74 x10⁻⁴ moldm⁻³, c; [HOIO]_{tot} = 1.70 x10⁻⁴ moldm⁻³, d; [HOIO]_{tot} = 1.54 x10⁻⁴ moldm⁻³, e; [HOIO]_{tot} = 1.40 x10⁻⁴ moldm⁻³.

On the base of the date obtained in the corresponding temperature interval thermodynamic parameters are calculated: $\Delta H = (-17.5 \pm 1) \text{ kJmol}^{-1}$, $\Delta S = (160 \pm 3) \text{ JK}^{-1} \text{ mol}^{-1}$. These found values shows that overall reaction (4) for disproportionation HOIO is thermodynamically possible for given values of the initial concentration of reactants and the temperature in studied system.

CONCLUSION

The HOIO iodous acid disproportionation reaction and the effect of the acidity in solutions containing 0.125 mol/dm³ sulfuric acid was analysed. Values of kinetic parameters, such as reaction rate constants and activation energy were determined based on a series of spectrophotometric measurements of absorption changes of I₂ molecular species at 274 nm, generated during the reaction. By changing concentrations from 3.23x10⁻⁴ to 7.10x10⁻⁴ mol/dm³ for IO₃⁻; and from 1.40x10⁻⁴ to 1.80x10⁻⁴ mol/dm³ for HOIO, the influence of temperature (in the range of 285-303 K) on the kinetics of this complex reaction under stationary conditions was examined. For the selected temperature range, the disproportionation average rate constants ranged from 1.14±0.08 dm³mol⁻¹s⁻¹ to 1.85±0.10 dm³mol⁻¹s⁻¹, respectively. According to the obtained results, increase of the reaction rate with increasing temperature was observed for different values of the iodous acid and iodate concentration. The average value of activation energy is determined graphically from temperature dependence of the rate constants, equals of E_a = 46 kJ/mol. The values for enthalpy and entropy activation were determined.

Under the examined isothermal conditions, the *pseudo*-equilibrium values of the concentrations of the relevant ionic species H^+ , H_2OI^+ i IO_3^- were determined from the equilibrium dissociation reactions for sulfuric acid and the iodous acid disproportionation reaction in the quasi-stationary state. Their values are predominant and higher than the concentration of the protonated H_2OI^+ ion under given conditions.

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