STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVIII, 1, 2003

KINETIC STUDY ON HYDROLYSIS REACTION OF DIOXIMES

G. SZABÓ, J. ZSAKÓ, I. BÂLDEA and CS. BOLLA

Babe¿-Bolyai University, Faculty of Chemistry and Chemical Engineering
Department of Physical Chemistry

ABSTRACT. The hydrolysis of 1,2,3-cyclohexanetrione-1,3-dioxime (CTD) and 1,2,3-cyclohexanetrione-2-imine-1,3-dioxime (CTDI) was studied polarogaphically at different concentrations of perchloric acid. It was followed the time course of diffusion current intensity of the polarographic wave. First order rate constants were derived and the influence of perchloric acid concentration was studied. A mechanism of hydrolysis reaction consisting of a protolytic pre-equilibrium, followed by a slow competitive water addition onto both the protonated and non-protonated forms of the dioxime has been suggested. The final step is presumed to be a fast elimination of hydroxylamine. On the basis of this mechanism it was derived a relationship among the rate constants, acidity constant and the hydrogen ion concentration. Acidity constants were calculated for the protonated oximes.

Introduction

Both aliphatic and alicyclic α-dioximes are stable in neutral and basic aqueous solutions. The spectrophotometric investigations showed that the dioximes are not stable in acidic solutions, they undergo hydrolysis with liberation of hydroxilamine and the corresponding diketone [1-3]. In presence of mineral acids protonation of a nitrogen atom occurs.

The hydrolysis of the oximes can be studied by means of polarography as well. Polarographic measurements are suitable also for kinetic studies.

It has been observed that hydrolysis of the alicyclic α-dioximes, namely the 1,2-cycloheptanedione-dioxime [4] and 1,2-cyclohexanedione-dioxime [5] and the alicyclic trioximes as 1,2,3-cyclohexanetrione-trioxime [6] are apparently first-order reactions. It has been observed that the increasing acidity causes the increase of rate contants, without existing of a direct proportionality between them. This indicates that protolytic pre-equilibrium is established. In order to explain the experimental results, it was presumed that a water addition onto the protonated form is the rate-determining step, followed by a fast elimination of hydroxylamine.

The aim of the present paper was to study the hydrolysis reaction of the 1,2,3-cyclohexanetrione-1,3-dioxime (CTD) and 1,2,3-cyclohexanetrione-2-imine-1,3-dioxime (CTDI) at 20°C, to suggest a mechanism for hydrolysis reaction, to derive a mathematical relation among rate constants, acidity constant and hydrogen ion concentration and to calculate acidity constant for the protonated oximes. The influence of the group in position 2 was studied on the value of acidity constant of protonated oximes and rate constants.

Experimental

Experiments were performed in a 25-ml double-walled, water-jacketed, temperature controlled by a circulating water bath (VEB-MLW type thermostat) glass cell. A dropping mercury electrode was used by applying the forced dropping method (RADELKIS OH-991 type "Fast rapid adapter") and the reference electrode was a saturated calomel electrode (SCE). Polarograms were recorded on a Radelkis OH-120 type polarograph.

The CTD and CTDI were dissolved in distilled water to obtain a 10^{-2} M stock solution. It has been prepared before each set of measurements. Samples were prepared with perchloric acid solutions in order to ensure a final concentration of CTD and CTDI equal to $2.5 \cdot 10^{-3}$ M and the perchloric acid concentrations: 0.05, 0.1, 0.2, 0.5 M. Sodium perchlorate was added to ensure a constant ionic strength. The oxygen was eliminated from the solutions with purified methane gas.

From our previous paper [7] we can conclude that it is not necessary the chemical freezing of the reaction and addition of buffer solution. The reaction is sufficiently slow and can be investigated by the simple registration of the polarograms at different time steps.

Results and Discussion

In Table 1 the diffusion current intensities (i_d) are given as a function of the perchloric acid concentration and of the time elapse for the hydrolysis of CTD to occur.

Table 1.

Time dependence of the diffusion current intensity of the wave; $c_{CTD}=2.5 \cdot 10^{-3}$ M.

T(K)	$[H^+]$ (M)	t(s)	i_d (μA)	lg i_d	k_{app} (s^{-1})
293	0.05	50	9.76	0.989	$0.92 \cdot 10^{-4}$
		185	9.48	0.977	
		535	9.20	0.964	
		963	8.90	0.949	
		1260	8.78	0.943	
		1560	8.42	0.925	
		1860	8.14	0.911	

A plot of lg i_d vs. time indicates a good linearity, pleading for an apparent first order reaction. It allows determination of apparent rate constants by means of linear regression. The apparent rate constants for the hydrolysis of CTD are presented in Table 2 and for the CTDI in Table 3.

Table 2.

Apparent rate constants of the hydrolysis at 20℃; $c_{CTD}=2.5 \cdot 10^{-3}$M.

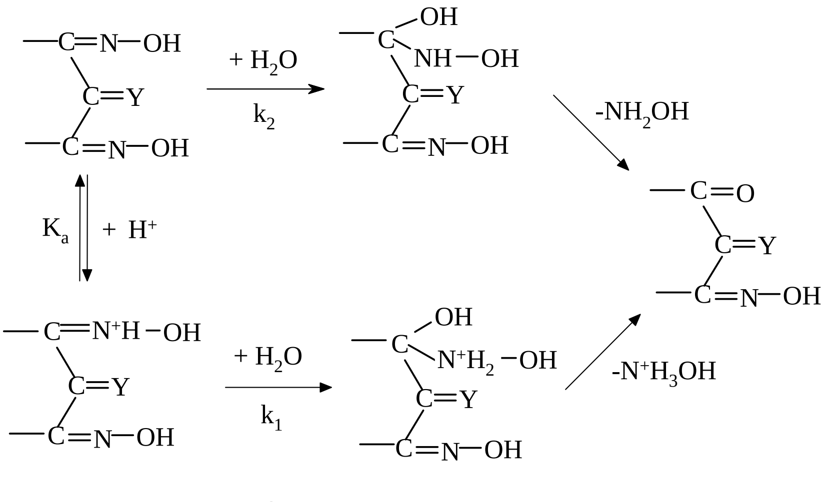
$[H^+]$ (M)	$k_{app} \cdot 10^4$ (s^{-1})
0.05	0.92
0.1	1.41
0.2	2.10
0.5	3.15

Table 3.

Apparent rate constants of the hydrolysis at 20℃; $c_{CTDI}=2.5 \cdot 10^{-3}$M.

$[H^+]$ (M)	$k_{app} \cdot 10^4$ (s^{-1})
0.05	1.42
0.1	2.08
0.2	2.88
0.5	3.88

As it can be observed in these tables, apparent rate constant increases with increasing perchloric acid concentration, but very slowly, suggesting a protolytic pre-equilibrium, implying very fast protonation and deprotonation processes. Protonation entails the polarization of the π-bond, facilitating water addition. Nevertheless the water addition onto the non-protonated form cannot be excluded either. The proposed mechanism contains two competing paths: the hydrolysis of protonated oxime and the non-protonated one.



Y: =O, =NH

On the basis of the above mechanism the apparent first-order rate constant can be described well by the following equation:

$$k_{app} = k_1 \cdot \frac{[H^+]}{[H^+] + K_a} + k_2 \cdot \frac{K_a}{K_a + [H^+]} \tag{1}$$

Table 4.

The hydrolysis rate constants and acidity constant of CTD at 20°C.

$[H^+]$ (M)	**$10^4 \cdot k_{app}$ (s^{-1})**	**$10^4 \cdot k_1$ (s^{-1})**	**$10^5 \cdot k_2$ (s^{-1})**	**K_a**
0.05	0.92	4.93	2.73	0.310
0.1	1.41			
0.2	2.10			
0.5	3.15			

By determining four values for four H^+ concentrations, we obtained a system of equations, which can be easily solved. The results for the CTD are presented in Table 4.

In case of CTDI, the Table 5 presents the rate constants and acidity constant.

Table 5.

The hydrolysis rate constants and acidity constant of CTDI at 20°C.

$[H^+]$ (M)	**$10^4 \cdot k_{app}$ (s^{-1})**	**$10^4 \cdot k_1$ (s^{-1})**	**$10^5 \cdot k_2$ (s^{-1})**	**K_a**
0.05	1.42	5.16	4.04	0.183
0.1	2.08			
0.2	2.88			
0.5	3.88			

It is worth be mentioning that k_1 and k_2 are pseudo first-order rate constants since water addition is a bimolecular reaction, but the water is the solvent and its concentration practically does not vary.

It can be observed that in both cases the value of rate constant k_2 represents approximately 10 % of value of k_1. This fact is in a good agreement with the presumption that the water addition onto the non-protonated form cannot be neglected. For the hydrolysis of CTDI both rate constants have a greater value than in case of CTD, reactions are carried out easier.

It is interesting to compare the value of acidity constants of protonated forms with other data obtained in a similar way (see Table 6).

If one compares the values of acidity constants in Table 6 it is obvious that α-dioximes are the weakest acids. The strongest acid is 1,2,3-cyclohexanetrione-trioxime, in case of which protonation occurs in position 2 and the effects of the oxime groups in both positions 1 and 3 are cumulated [4].

The CTD and CTDI are stronger acids than α-dioximes. The electron withdrawing effect of groups situated in position 2 can explain this. Since the electron withdrawing effect of =O group is larger than that of =NH, protonation of CTDI occurs much easier and acidity constant of protonated form is smaller.

Table 6.

Acidity constants of the protonated forms derived from hydrolysis kinetics' data, at 20ºC.

Oxime	**K_a**
1,2-cycloheptanedione-1,2-dioxime	0,110
1,2-cyclohexanedione-1,2-dioxime	0,133
1,2,3-cyclohexanetrione-2-imine-1,3-dioxime	0,183
1,2,3-cyclohexanetrione-1,3-dioxime	0,310
1,2,3-cyclohexanetrione-trioxime	1,340

Value of acidity constant of protonated oximes calculated on the basis of hydrolysis reaction kinetics is used for determination of the recombination reactions rate constant.

REFERENCES

1. P.R. Elefson, I. Gordon: *Talanta,* 1967, p. 409.
2. A.N. Alibina, V.M. Peshkova: *Vestnik Moskovsk Univ.Ser.II, Khim,* 1970, p. 260.
3. V.I. Shlenskaya, T.I. Tikhvinskaya: *Vestnik Moskovsk Univ.Ser.II, Khim,* 1970. p. 337.
4. F. Mánok, E. Kőszegi, Cs. Várhely: *Acta Chim.Hung.* 1984, p. 51.
5. F. Mánok, G. Dénezsi, Cs. Várhelyi, A. Benkő: *Studia Univ. Babeş-Bolyai,* 1986, p. 3.
6. F. Mánok, Cs. Várhelyi, A. Benkő, M. Tarsoly-Magyari: *Monatsh. Chem.*, 1978, p. 1329.
7. J. Zsakó, G. Szabó: *Periodica Polytechnica ser. Chem. Eng.,* 1999, p. 35