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POLAROGRAPHIC STUDY ON THE KINETICS AND MECHANISM OF THE HYDROLYSIS OF 1,2,3,-CYCLOHEXANETRIONE 1,3-DIOXIME

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Abstract

The hydrolysis of 1,2,3-cyclohexanetrione 1,3-dioxime was studied polarographically in the presence of different concentrations of the perchloric acid, by measuring the diffusion current intensity of the first polarographic wave with $E_{\frac{1}{2}} = -440$ mV. First order rate constants were derived and the influence of perchloric acid concentration and temperature was studied. The results are discussed by presuming a reaction mechanism consisting of a protolytic pre-equilibrium, followed by a slow competitive water addition onto both the protonated and non-protonated forms of the dioxime. The final step is presumed to be a fast elimination of hydroxylamine.

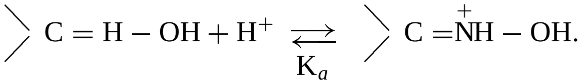
Keywords: 1,2,3-cyclohexanetrione 1,3-dioxime; kinetics and mechanism of oxime hydrolysis, protonation of oximes; acidity constants.

1. Introduction

Both aliphatic and alicyclic α-dioximes are very weak acids with $pK_1 = 10 \ldots 11$ [1-3]. 1,2,3-cyclohexanetrione 1,3-dioxime and especially 1,2,3-cyclohexanetrione-trioxime are much stronger acids due to electronic effects in the delocalized π-bond system [4]. All these substances are stable in neutral and basic aqueous solutions. In acidic media protonation of an N-atom occurs. The corresponding protonation constants have been determined by means of UV spectrophotometric and potentiometric measurements [5–7]. The spectrophotometric investigations showed the dioximes not to be stable in acidic solutions, to undergo hydrolysis with liberation of hydroxylamine and the corresponding diketone [7].

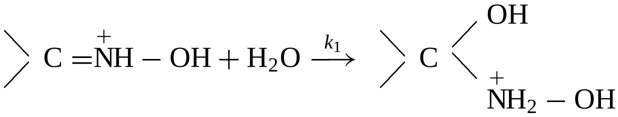
The hydrolysis of the oximes can be studied by means of polarography. 1,2,3-cyclohexane-trione-trioxime at pH = 6 exhibits a single wave with $E_{1/2} = -670$ mV (vs.SCE). If it is treated with $HClO_4$, a second wave appears with $E_{1/2} = -440$ mV [8] and it is due to 1,2,3-cyclohexane-trione 1,3-dioxime, as proved by means of amperometric titration with nickel salts.

Polarographic measurements are suitable also for kinetic studies. It has been observed that the hydrolysis of 1,2,3-cyclohexane-trione-trioxime [8], 1,2-cycloheptane-dione-dioxime [9] and of 1,2-cyclohexane-dione-dioxime [10] are apparently first order reactions. The rate constants were observed to increase with increasing acidity, but there is no direct proportionality between the rate constants and the perchloric acid concentration, indicating a protolytic pre-equilibrium



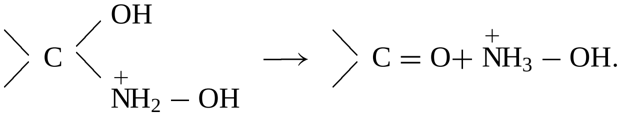
$$>C = H - OH + H^+ \underset{K_a}{\rightleftarrows} >C = \overset{+}{N}H - OH.$$

In order to explain the experimental results, a water addition onto the protonated form has been presumed as the rate determining step:



$$>C = \overset{+}{N}H - OH + H_2O \xrightarrow{k_1} >C\begin{matrix} OH \\ \overset{+}{N}H_2 - OH \end{matrix}$$

followed by a fast elimination of hydroxylamine



$$>C\begin{matrix} OH \\ \overset{+}{N}H_2 - OH \end{matrix} \longrightarrow >C = O + \overset{+}{N}H_3 - OH.$$

By presuming the above mechanism, the observed rate constant obeys the following expression:

$$k_{\text{obs}} = \frac{[H^+]}{K_a + [H^+]} k_1$$

and by performing polarographic measurements at different perchloric acid concentrations, k_1 and K_a values could be derived [8–10].

In the present paper a similar study is described on 1,2,3-cyclohexane-trione-1,3-dioxime (CTD).

2. Results and Discussion

The polarogram of CTD in Britton–Robinson's buffer solution of pH $= 6.09$ exhibits a single wave with $E_{1/2} = -440$ mV (vs.SCE). After a treatment of the dioxime with $HClO_4$, two more waves appear and the first one diminishes. In *Table 1* the diffusion current intensities (i_d) are given for the first wave as a function of the perchloric acid concentration and of the time of treatment.

A graphical plot of $\lg i_d$ vs. t showed a good linearity, pleading for an apparent first order reaction and allowed us to derive apparent rate constants by means of linear regression. The results are presented in *Table 2*.

As seen from this table, k_{obs} increases with increasing perchloric acid concentration, but very slowly, suggesting a protolytic pre-equilibrium, implying very fast protonation and deprotonation processes. It is worth mentioning that with the

Table 1. Time dependence of the diffusion current intensity of the first wave (i_d, in μA). 20 °C. $[CTD] = 1.667 \times 10^{-3}$ M. Samples 1 . . . 6.

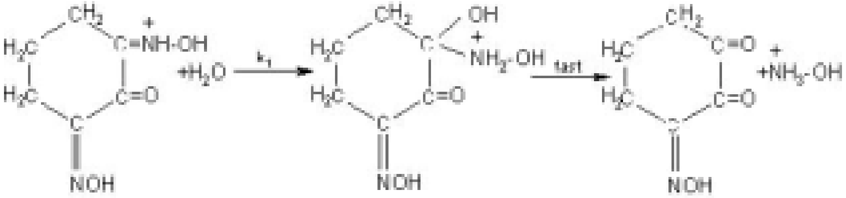
Time, s	$[HClO_4]$, mol · L^{-1}					
	0.222		0.4		0.6	
	1	2	3	4	5	6
180	0.816	0.888	0.852	0.888	0.840	0.892
300	0.792	0.840	0.840	0.792	0.804	0.804
600	0.768	0.792	0.720	0.720	0.702	0.756
900	0.696	0.696	0.672	0.708	0.636	0.642
1200	0.624	0.672	0.612	0.636	0.576	0.612
1500	0.588	0.624	0.552	0.576	0.552	0.552
1800	0.552	0.588	0.504	0.504	0.432	0.468

Table 2. Apparent rate constants of the hydrolysis at 20 °C

$[HClO_4]$, mol L^{-1}	Sample	$k_{obs} \cdot 10^4$, s^{-1}	Mean value
0.222	1	2.523	2.523
	2	2.524	
0.4	3	3.192	3.113
	4	3.034	
0.6	5	3.516	3.518
	6	3.520	

1, 2-cyclohexane-dione-dioxime we obtained for the recombination constant of the protonated form $k_r = 9.6 \times 10^{11}$ s^{-1} [11].

Protonation of the nitrogen atom entails the polarization of the π-bond, facilitating water addition. Nevertheless, in our view the water addition onto the non-protonated form cannot be excluded either. Consequently, we propose a mechanism with two competing paths:



It can be easily shown that on the basis of the above mechanism the apparent rate constant will obey the following equation:

$$k_{\text{obs}} = \frac{[\text{H}^+]k_1 + K_a k_2}{K_a + [\text{H}^+]},$$

where K_a stands for the acidity constant of the protonated form. The above equation can be written as

$$[\text{H}^+]k_1 + K_a k_2 - k_{\text{obs}} K_a = k_{\text{obs}}[\text{H}^+],$$

which is a linear equation with three variables, viz. k_1, $K_a k_2$ and K_a. Since we determined three k_{obs} values for three H^+ concentrations, we have a system of linear equations which can be easily solved and one obtains:

$$k_1 = 5.086 \times 10^{-4}\ \text{s}^{-1}, \qquad k_2 = 1.000 \times 10^{-4}\ \text{s}^{-1}, \qquad K_a = 0.3735.$$

We mention 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.

We can see that the consideration of the second reaction path, consisting in water addition onto the non-protonated form is perfectly justified since k_2 cannot be neglected beside k_1 although it is much less as compared to the latter one.

Concerning the acidity constant of the protonated form, it is interesting to compare it with other data obtained in a similar way.

Table 3. Acidity constants of the protonated forms derived from hydrolysis kinetics data. 20 °C

Oxime	K_a	Reference
1,2 – cycloheptane-dione-dioxime	0.110	[9]
1,2 – cyclohexane-dione-dioxime	0.141	[10]
1,2,3 – cyclohexane-trione-dioxime	0.3735	this paper
1,2,3 – cyclohexane-trione-trioxime	1.34	[8]

As seen, the α-dioximes are the weakest acids. The CTD is stronger since the electron withdrawing effect of the $\text{CO}-\text{C}=\text{NOH}$ moiety is larger as compared to $\text{C}=\text{NOH}$. The strongest acid is the protonated trioxime, for which the protonation occurs in position 2, where the effects of the oxime groups in both positions 1 and 3 are cumulated. Thus, our results seem to be quite realistic.

Furthermore, the influence of the temperature was studied, but only at a single perchloric acid concentration. The results are presented in *Table 4*.

The apparent rate constants have been worked up by means of the Eyring–Polányi–Evans equation

$$\ln\frac{k_{\text{obs}}}{T} = \ln\frac{k}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T},$$

Table 4. Temperature dependence of the rate constant. $[\mathrm{HClO}_4] = 0.222$

T, K	$k_{\mathrm{obs}} \times 10^4,\ \mathrm{s}^{-1}$
293	2.523
298	3.464
303	5.962
308	6.555

where k and h stand for Boltzmann's and Planck's constants, respectively. The activation parameters calculated by performing a linear regression, are as follows:

$$\Delta H^{\ddagger} = 48.72\ \mathrm{kJ\ mol}^{-1} \quad \text{and} \quad \Delta S^{\ddagger} = -147\ \mathrm{JK}^{-1}\ \mathrm{mol}^{-1}.$$

The meaning of these parameters is not precisely defined. At any rate, the activation enthalpy of the water addition must be lower than the above value in the case of the protonated form and higher for the non-protonated one. The relatively important negative activation entropy value is in perfect agreement with the presumption that the rate determining step is an addition reaction.

3. Experimental

The 1, 2, 3-cyclohexane-trione-1, 3-dioxime was dissolved in distilled water to obtain a 10^{-2} M parent solution. Samples were prepared by mixing the CTD solution with perchloric acid solution in such a way as to ensure a final concentration of CTD equal to 1.667×10^{-3} M, HClO_4 concentrations of 0.222, 0.4 and 0.6 M, respectively. NaClO_4 was added to ensure a constant ionic strength. Samples were kept under thermostated conditions at 20, 25, 30 and 35°C, respectively. After the time interval indicated in *Table 1*, the hydrolysis reaction was chemically frozen by adding calculated volumes of NaOH solution. Polarograms were recorded in Britton–Robinson's buffer solutions with pH = 6.09, on a Radelkis-Type OH–120 polarograph. A conventional polarographic cell with dropping mercury electrode was used by applying the forced dropping method. The reference electrode was a saturated calomel electrode (SCE).

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