POLAROGRAPHIC STUDY OF HYDROLYSIS
OF 3-(3-CHLOROPHENYL)IMINOOXINDOLE

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Kinetics of hydrolysis of 3-(3-chlorophenyl)iminooxindole was studied in $0.1 - 1\text{M-NaOH}$ at constant ionic strength $I = 1$. Rate constants, half-times as well as activation parameters of the hydrolytic reaction were determined from polarographic measurements. Hydrolysis was found to proceed *via* an unstable intermediate to yield 3-chloroaniline and isatin, isolated and identified as final products.

The present paper is a continuation of our previous work, devoted to the kinetics of alkaline hydrolysis of 3-(4-aminophenyl)iminooxindole[1] which is reduced in alkaline medium in two cathodic waves. The more positive one of them belongs to the polarographic reduction of the C=N bond and its height decreases with proceeding hydrolysis. The more negative wave which increases in the course of hydrolysis represents the polarographic reduction of the product of hydrolysis, isatic acid anion.

The structure of 3-(3-chlorophenyl)aminoindole was studied in paper[2] where it was demonstrated that in media pH > 13 this compound occurs as anion of α-anil(3--chloro)isatic acid in the sense of analogous results[1,3−5].

EXPERIMENTAL

Preparation of 3-(3-chlorophenyl)iminooxindole is described in papers[6,7]. The prepared substance was characterized after crystallization from ethanol, by its m.p. $229-230°C$ (decomposition), by infrared spectrum and polarographically. All chemicals were of the reagent grade purity.

Isolation of the product of hydrolysis was performed as follows: 1.0 g of 3-(3-chlorophenyl)-iminooxindole was dissolved in a solution containing 20% 1-propanol and 80% 1M-NaOH. This solution was heated under steady stirring to $65°C$. After the hydrolysis had been finished (60 min) 1-propanol was removed under diminished pressure and the hydrolyzed mixture was after neutralisation extracted with benzene. The benzene layer contained 3-chloroaniline which was identified by its condensation product with isatin. The prepared 3-(3-chlorophenyl)iminooxindole was identified by its mixture melting point as well as by its differential IR spectrum. The aqueous layer was evaporated to 50 ml volume and acidified to pH 1. Crystals of isatin which separated after cooling, were identified analogously. The products were isolated in c. 65% yields.

The course of hydrolysis was checked polarographically (LP 7, Laboratorní přístroje, Prague). Constant temperature was maintained within $\pm 0.5°C$ by means of a Hoepler thermostat. A tempered Kalousek vessel was used with a separated saturated calomel electrode (s.c.e.). The measurement was carried out in nitrogen atmosphere. Hydrolysis was followed in alkaline medium with 20 vol.% of 1-propanol added, at constant ionic strength $I = 1$, which was maintained by potassium chloride. Kinetic measurements were carried out at constant voltage, i.e. by continuous recording of both the decrease of the polarographic wave, corresponding to the reduction of C=N bond, and the total polarographic waves in certain time intervals, (see Fig. 1). The time course was followed for a time longer than is the reaction half-time. Values of the over-all rate constants (k_{exp}) were determined as regression coefficients of the dependence $\log (i_0/i)$ on time. Table I presents also the values of k_{calc}, obtained by smoothing the plot $\log k$ versus $1/T$, using the method of least squares. All results are means of $3-5$ measurements. The activation energy E_a and the frequency factor A_0 were evaluated by means of the method of least squares and using the Arrhenius equation[9]. The increase of activation entropy, $\Delta S^{\ne}$, was calculated according to paper[9]. The calculations were performed on a computer Minsk 21 with the commonly used programs.

RESULTS AND DISCUSSION

The polarographic recording of the course of hydrolysis of 3-(3-chlorophenyl)-iminooxindole (I) (Fig. 1) as well as the course of hydrolysis of the 4-amino derivative[8] and other 3- and 4-substituted derivatives of phenyliminooxindole[8] indicate that in the case of I hydrolysis of the C=N bond, preceded by a fast ring cleavage, takes place which is manifested by the time decrease of the first cathodic wave. This wave $\left(E_{1/2} - 800 \text{ mV (s.c.e.)}\right)$ represents a two-electron reduction of the C=N bond in structure II. The most negative wave, increasing with time $\left(E_{1/2} - 1500 \text{ mV (s.c.e.)}\right)$, is identical with the reduction wave of the CO group of isatic acid (IV) (see[1,8]). The cathodic wave with $E_{1,2} - 1300 \text{ mV (s.c.e.)}$ corresponds to the reduction of unstable intermediate III.

From the linear dependence $\log (i_0/i)$ vs time it follows that the hydrolytic reaction studied is of the first-order. The slope of this linear dependence increases with increasing NaOH concentration and with temperature.

The values of k (over-all rate constant) are linearly dependent on the molarity of NaOH. Evidently, activation energies of the studied reaction decrease with increasing concentration of NaOH. Over-all rate constants are summarized in Table I.

Temperature dependences of the over-all rate constants at different concentrations of NaOH are expressed by Eqs $(1)-(4)$

$$\log k = -3990(\pm 1.805) \cdot 1/T + 10.766(\pm 0.0054), \tag{1}$$

$$r = 0.996, \quad \text{1m-NaOH}, \quad n = 25$$

$$\log k = -4320(\pm 1.753) \cdot 1/T + 11.570(\pm 0.0052), \tag{2}$$

$$r = 0.997, \quad \text{0.6m-NaOH}, \quad n = 27$$

$$\log k = -4610(\pm 1{\cdot}513)\,.\,1/T + 12{\cdot}285(\pm 0{\cdot}0045)\,, \tag{3}$$
$$r = 0{\cdot}998\,, \quad 0{\cdot}33\text{M-NaOH}\,, \quad n = 26$$

$$\log k = -4980(\pm 1{\cdot}543)\,.\,1/T + 13{\cdot}169(\pm 0{\cdot}0046)\,, \tag{4}$$
$$r = 0{\cdot}988\,, \quad 0{\cdot}1\text{M-NaOH}\,, \quad n = 25\,.$$

As can be seen from the dependences $\log k$ vs $1/T$, all of them are straight lines. The values of the correlation coefficients r are high $(0{\cdot}996 - 0{\cdot}998)$. With increasing concentration of NaOH from 0·1 to 1M the values of the slope of these linear dependences decrease from -4980 to -3990. Statistical evaluation of the data from Fig. 3, *i.e.*, the dependence of the total rate constants on the concentration of NaOH are described by the following equations:

$$k = 2{\cdot}55\,.\,10^{-2}(\pm 1{\cdot}6\,.\,10^{-4})\,C_{\text{NaOH}} + 2{\cdot}9\,.\,10^{-3}(\pm 0{\cdot}9\,.\,10^{-4})\,, \tag{5}$$
$$r = 0{\cdot}999\,, \quad 50{^\circ}\text{C}\,, \quad n = 19$$

$$k = 3{\cdot}38\,.\,10^{-2}(\pm 5{\cdot}7\,.\,10^{-4})\,C_{\text{NaOH}} + 5{\cdot}6\,.\,10^{-3}(\pm 3{\cdot}6\,.\,10^{-4}) \tag{6}$$
$$r = 0{\cdot}992\,, \quad 55{^\circ}\text{C}\,, \quad n = 16$$

$$k = 4{\cdot}56\,.\,10^{-2}(\pm 2{\cdot}1\,.\,10^{-4})\,C_{\text{NaOH}} + 1{\cdot}2\,.\,10^{-2}(\pm 1{\cdot}2\,.\,10^{-4})\,, \tag{7}$$
$$r = 0{\cdot}999\,, \quad 60{^\circ}\text{C}\,, \quad n = 17$$

$$k = 7{\cdot}88\,.\,10^{-2}(\pm 7{\cdot}2\,.\,10^{-4})\,C_{\text{NaOH}} + 1{\cdot}76\,.\,10^{-2}(\pm 4{\cdot}5\,.\,10^{-4})\,, \tag{8}$$
$$r = 0{\cdot}997\,, \quad 65{^\circ}\text{C}\,, \quad n = 17$$

$$k = 9{\cdot}71\,.\,10^{-2}(\pm 2{\cdot}05\,.\,10^{-3})\,C_{\text{NaOH}} + 4{\cdot}15\,.\,10^{-2}(\pm 1{\cdot}25\,.\,10^{-3})\,, \tag{9}$$
$$r = 0{\cdot}998\,, \quad 70{^\circ}\text{C}\,, \quad n = 19$$

$$k = 16{\cdot}29\,.\,10^{-2}(\pm 1{\cdot}56\,.\,10^{-3})\,C_{\text{NaOH}} + 5{\cdot}51\,.\,10^{-2}(\pm 9{\cdot}5\,.\,10^{-4})\,, \tag{10}$$
$$r = 0{\cdot}998\,, \quad 75{^\circ}\text{C}\,, \quad n = 15\,.$$

The slopes of the straight lines show that the rate constants increase with increasing temperature in the range $(2{\cdot}55\,.\,10^{-2} - 16{\cdot}29\,.\,10^{-2})$. On the basis of Eqs $(1)-(10)$ the activation parameters of the overall reaction could be summarized in Table II. With increasing NaOH concentration from 0·1 to 1M the activation energy decreases from 22·8 to 18·3 kcal mol^{-1}.

As demonstrated by Eqs $(5)-(10)$, the values of the over-all rate constants increase linearly with increasing NaOH concentration. These dependences can be

expressed by the by the relation $k = k_1 + k_2 C_{NaOH}$, where k_1 is the contribution of the over-all rate constant of the non-catalyzed process which is independent of the NaOH concentration and $k_2 C_{NaOH}$ is the rate constant, expressing the effect of the

TABLE I

Values of Over-All Rate Constants (upper value exp., lower value calc.) and of Half-Times of Decomposition of I

20 vol.% 1-Propanol, $I = 1$, $c = 10^{-3}$M. k_{exp} over-all rate constants calculated from arithmetic means of experimental values, k_{calc} over-all rate constants obtained after smoothing using the method of least squares, k over-all rate constants as calculated according to Arrhenius equation[9].

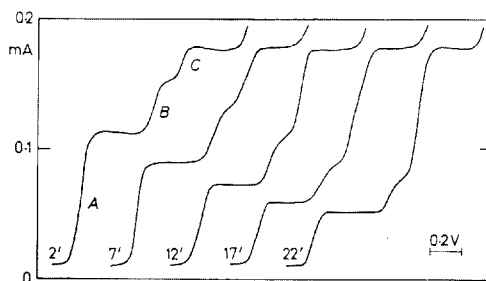| t, °C	0.1M-NaOH		0.33M-NaOH		0.6M-NaOH		1M-NaOH	
	$10^2 . k$ min^{-1}	$t_{1/2}$ min	$10^2 . k$ min^{-1}	$t_{1/2}$ min	$10^2 . k$ min^{-1}	$t_{1/2}$ min	$10^2 . k$ min^{-1}	$t_{1/2}$ min
50	0.55	122	1.10	63	1.78	39	2.86	24
	0.57	119	1.06	64	1.64	42	2.68	25
55	1.00	70	1.70	41	2.41	29	4.05	17
	0.98	72	1.75	40	2.62	27	4.13	17
60	1.62	43	2.74	26	3.97	18	5.73	12
	1.65	43	2.85	25	4.13	17	6.29	11
65	2.59	26	4.38	16	6.42	10	9.69	7.2
	2.75	26	4.56	15	6.42	11	9.46	7.5
70	4.84	14	7.78	8.9	9.83	7.1	13.8	5.1
	4.50	16	7.20	9.7	9.85	7.0	14.0	5.0
75	6.99	9.9	10.9	6.3	15.6	4.4	21.6	3.2
	7.28	9.3	11.2	6.0	14.9	4.5	20.6	3.3

FIG. 1

Polarographic Control of the Course of Hydrolysis of I in 0.6M-NaOH

$c = 10^{-3}$M, 20 vol. 1%-propanol, $I = 1$, 60°C, from -600 mV (s.c.e.).

concentration of the catalyzing species OH^-. Statistical evaluation of these effects is presented in Table III.

The temperature dependence of k_1 and k_2 can be written as

$$\log k_1 = -5.93 \cdot 10^3 (\pm 7.66) \cdot 1/T + 15.87 (\pm 0.023) . \qquad (11)$$

$$r = 0.995, \quad n = 6$$

TABLE II

Activation Parameters of the Over-All Reaction, Hydrolysis of I

$c = 10^{-3}$M, $I = 1$, 20 vol.% 1-propanol. Activation parameters are calculated according to[9].

Conditions	E_a kcal mol^{-1}	A_0 s^{-1}	$\Delta S^{\ddagger}$ cal mol^{-1} K^{-1}
1·0M-NaOH	18·3	7·8 . 10^8	−20·0
0·6M-NaOH	19·7	6·1 . 10^9	−15·9
0·33M-NaOH	21·1	3·2 . 10^{10}	−12·7
0·1M-NaOH	22·8	2·5 . 10^{11}	− 8·6

TABLE III

Constants of the Reaction Rate of Non-Catalyzed Reaction, k_1, Catalytic Coefficient k_2 ($k = k_1 + k_2 C_{NaOH}$) and Half-Times of the Hydrolysis of I in 0·1M-NaOH in Dependence on Temperature

20 vol.% Propanol, $I = 1$. Experimental values of k_1 and k_2 (upper line) were obtained by graphical analysis of Eqs $(5)-(10)$, calculated values (lower line) are these values, smoothed using the method of least squares.

t, °C	$10^2 \cdot k_1$ min^{-1}	$(t_1)_{1/2}$ min	$10^2 \cdot k_2$ min^{-1} mol^{-1}	$(t_2)_{1/2}$ min
50	0·29	243	2·55	27
	0·30	225	2·35	29
55	0·56	124	3·38	21
	0·57	123	3·48	20
60	1·12	58	4·56	15
	1·06	67	5·10	14
65	1·76	39	7·88	8·8
	1·95	37	7·38	9·6
70	4·15	17	9·71	7·2
	3·51	20	10·6	6·6
75	5·5	13	16·3	4·3
	6·21	11	15·0	4·5

$$\log k_2 = -3{\cdot}62 \,.\, 10^3 (\pm 5{\cdot}72) \,.\, 1/T + 9{\cdot}58(\pm 0{\cdot}017), \qquad (12)$$

$$r = 0{\cdot}992, \quad n = 6.$$

On the basis of the above described results, the base catalyzed hydrolysis of I can be considered a nucleophilic reaction, its first step being the binding of nucleophilic species OH$^-$, functioning as a catalyst, to the activated C=N bond. The intermediate of this reaction (III) is an unstable compound, detected polarographically at about -1300 mV (S.C.E.).

Analogously, in the acid-catalyzed hydrolysis of some Schiff bases, the authors[10-14] assume the formation of an unstable intermediate. In paper[10] a reversible reaction is assumed to proceed between the intermediate and the final product of hydrolysis, whereas in paper[11] the decomposition of intermediate is supposed to be an irreversible process. Under our experimental conditions the hydrolysis of the C=N bond in the studied compound is irreversible, whereby the rate determining step is the decomposition of III yielding the final hydrolysic product, *viz.* isatin and 3-chloroaniline, according to Scheme 1 (here reactions $I \leftrightarrows II$ and $VI \leftrightarrows IV + V$ are fast, reaction $III \rightarrow IV + V$ is slow).
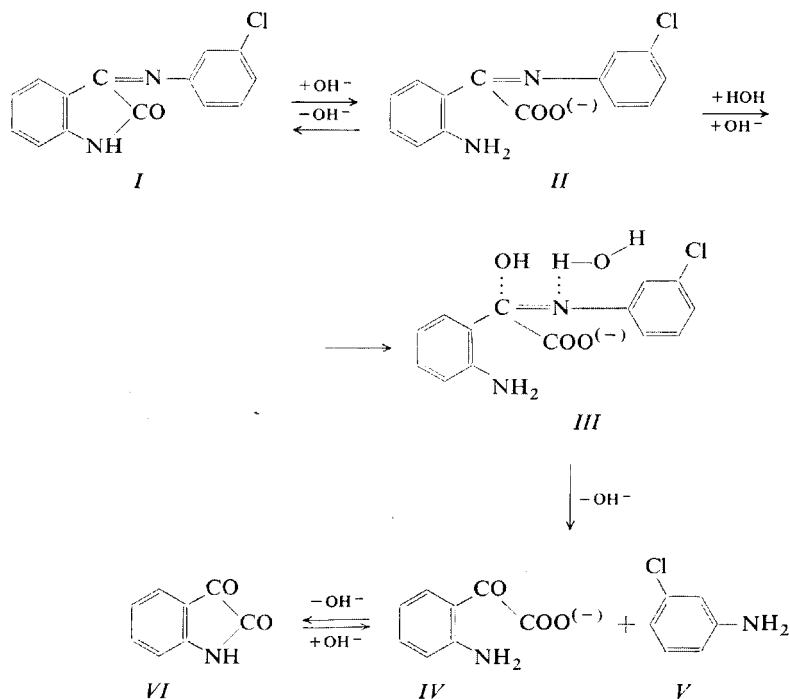
SCHEME 1

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