# A STUDY OF ALKALINE HYDROLYSIS OF 3'- AND 4'-SUBSTITUTED 3-PHENYLIMINOXINDOLE DERIVATIVES

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Alkaline hydrolysis of ten 3'- and 4'-substituted 3-phenyliminoxindole derivatives was studied polarographically. The effect of temperature, substituents and concentration of NaOH on the reaction rate was investigated. It was proved that the overall reaction constant $k = k_1 + k_2 c_{NaOH}$. Linear relationship between log $k$ and $\sigma$ substituent constants was found. It was shown that at 0°C the hydrolysis is a nucleophilic reaction, whereas at elevated temperatures it proceeds by two parallel mechanisms. At 90°C, some of the studied compounds undergo a catalysed nucleophilic hydrolysis whereas other react by spontaneous solvolysis.

In this paper we present results of investigation of the following 3-phenyliminoxindole derivatives $(I)$: $a$ 4'-N(CH$_3$)$_2$, $b$ 4'-NH$_2$, $c$ 4'-OH, $d$ 4'-OCH$_3$, $e$ 4'-OC$_2$H$_5$, $f$ 4'-CH$_3$, $g$ 3'-CH$_3$, $h$ H, $i$ 4'-Br, $j$ 3'-Cl. It is known[1-3] that in alkaline solutions of pH $\geq$ 13 these compounds exist in the form of anions of 3'- and 4'-substituted α-anilinisatinic acids $(II)$. In our previous papers[4-6] we studied the kinetics of alkaline hydrolysis of the compounds $Ib$, $Ih$ and $Ij$. The present study of the substituent effect is a continuation and extension of these previous investigations[4-6].

## EXPERIMENTAL

The substituted 3-phenyliminoxindole derivatives were prepared according to ref.[7-11]. All chemicals were distilled or crystallised before use. The isolation procedures and identification of hydrolysis products were the same as described in ref.[4,5].

The compounds were studied polarographically in $5 . 10^{-4}$M solutions. The ionic strength was adjusted to $I = 1$ by addition of potassium chloride. The measured solutions contained 20% of 1-propanol. The polarographic measurements were carried out on an LP-60 polarograph; the temperature in the measuring vessel was maintained with an accuracy $\pm 0.5$°C by means of a thermostat.

The reaction rates were measured by continuous recording the first cathodic wave, as well as by recording the whole polarographic curves. The rate constants, $k_{exp}$, were determined from the slopes of linear plots log $i_0/i$ against time. The values of the overall rate constants $k_{calc}$ were obtained from the Arrhenius equation using the method of least squares. Simultaneously, also the activa-

TABLE I

Overall Rate Constants, $k$ (min$^{-1}$), for the Alkaline Hydrolysis (1M-NaOH) of 3'- and 4'-Substituted 3-Phenyliminoxindole Derivatives in 20% (vol) 1-Propanol at $I = 1$ ($k_{exp}$ are arithmetic means of the overall rate constants calculated from the equation for first order reactions, $k_{calc}$ are the overall rate constants obtained from the Arrhenius equation by the method of least squares.)

| Compound Substituent | $10^2 k$ exp (calc) | | | | | |
|---|---|---|---|---|---|---|
| | 50°C | 55°C | 60°C | 65°C | 70°C | 75°C |
| *Ia*<br>4'-N(CH$_3$)$_2$ | 0·79<br>(0·78) | 1·23<br>(1·21) | 1·81<br>(1·86) | 2·66<br>(2·82) | 4·46<br>(4·23) | 6·25<br>(6·27) |
| *Ib*<br>4'-NH | 1·41<br>(1·44) | 2·20<br>(2.17) | 3·23<br>(3·22) | 4·91<br>(4·75) | 6·90<br>(6·91) | —<br>(—) |
| *Ic*<br>4'-OH | 1·65<br>(1·64) | 2·52<br>(2·1) | 3·96<br>(3·78) | 5·46<br>(5·64) | 8·16<br>(8·31) | 12·2<br>(12·1) |
| *Id*<br>4'-OCH$_3$ | 1·21<br>(1·25) | 2·10<br>(1·91) | 2·68<br>(2·87) | 4·00<br>(4·27) | 6·23<br>(6·33) | 9·03<br>(9·13) |
| *Ie*<br>4'-OC$_2$H$_5$ | 1·00<br>(0·95) | 1·51<br>(1·49) | 2·11<br>(2·28) | 3·17<br>(3·48) | 5·47<br>(5·23) | 7·93<br>(7·77) |
| *If*<br>4'-CH$_3$ | 0·91<br>(0·89) | 1·44<br>(1·38) | 2·05<br>(2·11) | 2·87<br>(3·18) | 4·85<br>(4·74) | 7·17<br>(6·98) |
| *Ig*<br>3'-CH$_3$ | 0·90<br>(0·88) | 1·43<br>(1·35) | 1·92<br>(2·03) | 2·89<br>(3·03) | 4·28<br>(4·46) | 7·05<br>(6·49) |
| *Ih*<br>H | 1·14<br>(1·34) | 2·00<br>(2·06) | 2·95<br>(3·13) | 4·74<br>(4·68) | 6·63<br>(6·93) | 10·7<br>(10·1) |
| *Ii*<br>4'-Br | 2·67<br>(2·56) | 3·88<br>(3·95) | 5·85<br>(6·02) | 9·10<br>(9·06) | 14·3<br>(13·5) | 19·2<br>(19·8) |
| *Ii*<br>4'-Br$^a$ | 1·69<br>(1·70) | 2·71<br>(2·70) | 4·19<br>(4·20) | 6·35<br>(6·48) | 10·7<br>(9·90) | 14·5<br>(14·8) |
| *Ii*<br>4'-Br$^b$ | 1·11<br>(1·02) | 1·60<br>(1·70) | 2·77<br>(2·78) | 4·29<br>(4·48) | 8·00<br>(7·13) | 10·7<br>(11·2) |
| *Ii*<br>4'-Br$^c$ | 0·61<br>(0·60) | 1·01<br>(1·07) | 1·98<br>(1·86) | 3·34<br>(3·20) | 5·92<br>(5·42) | 8·33<br>(9·03) |
| *Ij*<br>3'-Cl | 2·86<br>(2·68) | 4·05<br>(4·13) | 0·73<br>(6·09) | 9·69<br>(9·46) | 13·8<br>(14·0) | 21·6<br>(20·6) |

$^a$ 0·6M-NaOH; $^b$ 0·33M-NaOH; $^c$ 0·1M-NaOH.

tion energies, $E_a$, and frequency factors, $A_0$, were evaluated. The activation entropy, $\Delta S^{\ne}$, was calculated according to ref.[12,13]. The rate constants $k_1$ and $k_2$ were obtained from the equation $k = k_1 + k_2 c_{\mathrm{NaOH}}$. The linear plots of log $k_{\mathrm{exp}}$ against $\sigma$ were evaluated, similarly as all other linear relationships employed, by the least squares method, using trivial programs (digital computer Minsk 21). The values of the $\sigma$ constants were taken from references[14-16].

## RESULTS AND DISCUSSION

The plots of log $i_0/i$ against time are linear for all the studied derivatives *II*. The alkaline hydrolysis of these compounds is a first order reaction. The overall rate constants of this hydrolysis are given in Table I. Table II lists statistical parameters of the linear temperature dependences of rate constants.

The energies of activation in 1M-NaOH are almost identical for all studied derivatives $(18.8 - 17.3 \text{ kcal mol}^{-1})$, but in the case of the derivative *Ii* (Table III) the activation energy decreases with an increasing concentration of NaOH. An analogous situation was found for the frequency factor. These facts confirm that the irreversible alkaline hydrolysis of the C=N bond in the structures *II* is catalysed by OH⁻ ions. This is supported also by the dependence of the overall rate constant $k$ on NaOH

TABLE II

Statistical Parameters of the Linear Plots of log $k$ against $1/T$ (1M-NaOH) for the Alkaline Hydrolysis of 3'- and 4'-Substituted 3-Phenyliminoxindole Derivatives

*n* Number of measurements; $\varrho$ slope; $s_\varrho$ slope error; $q$ intercept; $s_q$ intercept error; $\varrho$ standard deviation; $r$ correlation coefficient

| Compound | $n$ | $\varrho$ | $s_\rho$ | $q$ | $s_q$ | $S$ | $r$ |
|---|---|---|---|---|---|---|---|
| *Ia* | 27 | −4 080 | 1·316 | 10·512 | 0·0039 | 0·0200 | 0·998 |
| *Ib* | 33 | −3 780 | 0·8160 | 9·859 | 0·0025 | 0·0140 | 0·999 |
| *Ic* | 30 | −3 910 | 0·8869 | 10·306 | 0·0026 | 0·0142 | 0·999 |
| *Id* | 24 | −3 890 | 2·062 | 10·125 | 0·0062 | 0·0296 | 0·996 |
| *Ie* | 25 | −4 100 | 1·887 | 10·674 | 0·0056 | 0·0275 | 0·996 |
| *If* | 20 | −4 020 | 1·840 | 10·397 | 0·0055 | 0·0238 | 0·997 |
| *Ig* | 19 | −3 900 | 2·000 | 10·009 | 0·0060 | 0·0256 | 0·996 |
| *Ih* | 25 | −3 950 | 1·709 | 10·344 | 0·0051 | 0·0256 | 0·997 |
| *Ii* | 19 | −3 990 | 1·577 | 10·762 | 0·004 | 0·020 | 0·998 |
| *Ii*[a] | 20 | −4 230 | 1·414 | 11 333 | 0·0042 | 0·018 | 0·998 |
| *Ii*[b] | 21 | −4 680 | 2·618 | 12 503 | 0·008 | 0·035 | 0·995 |
| *Ii*[c] | 21 | −5 300 | 2·230 | 14·178 | 0·007 | 0·030 | 0·998 |
| *Ij* | 25 | −3 990 | 1·805 | 10·766 | 0·0054 | 0·0263 | 0·996 |

[a] 0·6M-NaOH, [b] 0·33M-NaOH, [c] 0·1M-NaOH.

concentration in the temperature interval $50-75°C$ which can be expressed by a straight-line equation $k = k_1 + k_2 c_{NaOH}$, where $k$ is the rate constant for the overall hydrolysis, $k_1$ is the rate constant related only to the action of water molecules and $k_2$ is the rate constant for the reaction, catalysed by hydroxyl ions. The values $k_1$ and $k_2$ are listed in Table IV.

As shown in Fig. 1, the dependence of $k$ on the concentration of NaOH at 70°C is linear for all derivatives studied, however, it is obvious that an increasing basicity of the medium leads to different changes in the overall rate constants for the derivatives $Ia-Ic$ than for the remaining compounds. For the compound $Ii$ the dependence of $k$ on $c_{NaOH}$ was determined throughout the whole temperature interval, *i.e.* in the range $50-75°C$. The regression analysis shows that the plots of the overall rate constants $k$ against $c_{NaOH}$ afford high correlation coefficient values, similarly to the results for the compounds $Ib$, $Ih$ and $Ij$ (refs[4-6]).

For the alkaline hydrolysis of 3'- and 4'-substituted 3-phenyliminoxindole derivatives in the temperature interval $50-70°C$ we have found no linear relationships between log $k$ and constants expressing electron effects of substituents, which would have satisfactory statistical parameters. Since it follows from Fig. 1 that the overall rate constant, $k$, *i.e.* the quantity measured for all compounds $II$, is composed of two

TABLE III

Activation Parameters of the Overall Alkaline Hydrolysis (1M-NaOH) of 3'- and 4'-Substituted 3-Phenyliminoxindole Derivatives in NaOH Solutions Containing 20% of 1-Propanol, at Ionic Strength $I = 1$

| Compound | $E_a$ kcal mol$^{-1}$ | $A_0$ s$^{-1}$ | $\Delta S^{\ddagger}$ cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| $Ia$ | 18·7 | $5·4 . 10^8$ | $-20·7$ |
| $Ib$ | 17·3 | $1·2 . 10^8$ | $-23·8$ |
| $Ic$ | 17·9 | $3·4 . 10^8$ | $-21·7$ |
| $Id$ | 17·8 | $2·2 . 10^8$ | $-22·5$ |
| $Ie$ | 18·8 | $7·9 . 10^8$ | $-20·0$ |
| $If$ | 18·4 | $4·2 . 10^8$ | $-21·2$ |
| $Ig$ | 17·7 | $1·7 . 10^8$ | $-23·0$ |
| $Ih$ | 18·1 | $3·7 . 10^8$ | $-21·6$ |
| $Ii$ | 18·3 | $9·6 . 10^8$ | $-19·6$ |
| $Ii^a$ | 19·4 | $3·6 . 10^9$ | $-16·9$ |
| $Ii^b$ | 21·4 | $5·3 . 10^{10}$ | $-11·6$ |
| $Ii^c$ | 24·2 | $2·5 . 10^{12}$ | $-3·9$ |
| $Ij$ | 18·3 | $7·8 . 10^8$ | $-20·0$ |

[a] 0·6M-NaOH;  [b] 0·33M-NaOH;  [c] 0·1M-NaOH.

Table IV

Rate Constants $k_1$ (min$^{-1}$), $k_2$ (min$^{-1}$ mol$^{-1}$ l) and $k$ (min$^{-1}$, $k = k_1 + k_2\, c_{NaOH}$) for the Alkaline Hydrolysis of 3'- and 4'-Substituted 3-Phenyliminoxindole Derivatives

| Compound | $t, °C$ | $10^2 . k_1$ | $10^2 . k_2$ | 0°C 1M-NaOH $10^4 . k$ | 90°C 0·1M-NaOH $10^2 . k$ |
|---|---|---|---|---|---|
| Ia | 70 | 3·01 | 1·48 | 2·00 | 14·9 |
| Ib | 70 | 3·36 | 3·19 | 2·08 | 18·3 |
| Ic | 70 | 5·06 | 4·60 | 2·64 | 38·3 |
| Id | 70 | 1·91 | 4·60 | 3·27 | 13·6 |
| Ie | 70 | 1·90 | 3·73 | 3·48 | 12·7 |
| If | 70 | 1·99 | 2·97 | 3·86 | 11·3 |
| Ig | 70 | 1·93 | 2·47 | 4·79 | 9·75 |
| Ih | 70 | 2·03 | 4·74 | 5·21 | 12·6 |
| Ii | 50 | 0·35 | 2·30 | 6·89 | 22·2 |
| Ii | 55 | 0·64 | 3·20 | — | — |
| Ii | 60 | 1·46 | 4·42 | — | — |
| Ii | 65 | 2·44 | 6·57 | — | — |
| Ii | 70 | 4·98 | 9·30 | — | — |
| Ii | 75 | 7·00 | 12·26 | — | — |
| Ij | 70 | 4·15 | 9·71 | 9·12 | 28·5 |



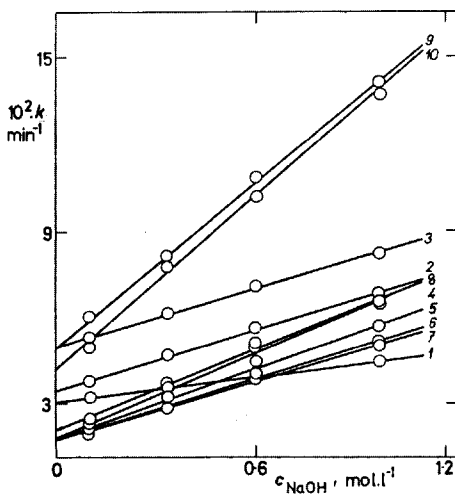Fig. 1

Plot of the Overall Rate Constants, $k$, for the Alkaline Hydrolysis of *II* against Concentration of NaOH

$c_M = 5 . 10^{-4}$M-*II*, 20% (vol) of 1-propanol, $I = 1$; $T = 70°C$. For description of substituents see the Tables.

constants, $k_1$ and $k_2$, this constant was determined under such conditions when $k \sim k_1$, or $k \sim k_2$. These conditions were found from the plots of $\log k_1$ or $\log k_2$ against $1/T$. These relationships are linear and for the compound $Ii$ the values of $\log k_1$ or $\log k_2$ can be expressed by equations $(1)$ and $(2)$:

$$\log k_1 = -6050\,(\pm 6{\cdot}3)\,.\,1/T + 16{\cdot}29\,(\pm 0{\cdot}019) \tag{1}$$

$$N = 6\,; \quad r = 0{\cdot}996$$

$$\log k_2 = -3340\,(\pm 1{\cdot}7)\,.\,1/T + 8{\cdot}69\,(\pm 0{\cdot}005) \tag{2}$$

$$N = 6\,; \quad r = 0{\cdot}999\,.$$

From these relationships we calculated the activation parameters of the non-catalysed and catalysed alkaline hydrolysis of some 3'- and 4'-substituted 3-phenyliminoxindole derivatives (Table V). It is seen from Table V that the activation energy of the catalysed reaction is lower than the activation energy of the spontaneous solvolysis. From the equations $(1)$ and $(2)$ we can calculate that at about 0°C $k_2 \gg k_1$ and therefore $k \sim k_2 \,.\, c_{NaOH}$. On the other hand, at 90°C, $k_1 > k_2$ and the measured rate constant $k \sim k_1$. The rate constants $k$, obtained under the mentioned conditions, are given in Table IV.

The similarity of the activation parameters for 1M-NaOH (Table III) is not fortuitous, as proved by the plot of $\log k$ at 70°C against $\log k$ at 50°C ($\varrho = 0{\cdot}938$; $r = 0{\cdot}985$) (ref.[12,17,18]). The value of the correlation coefficient indicates an identical mechanism of the alkaline hydrolysis of the structure $II$. It must be noted, however,

TABLE V

Activation Parameters of Non-catalysed ($k_1$) and Catalysed ($k_2$) Alkaline Hydrolysis (0·1—1M-NaOH) of Some 3'- and 4'-Substituted 3-Phenyliminoxindole Derivatives

| Compound | Non-catalyzed | | | Catalyzed | | |
|---|---|---|---|---|---|---|
| | $A_0$ $s^{-1}$ | $E$ kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ cal mol$^{-1}$. K$^{-1}$ | $A_0$ $s^{-1}$ | $E$ kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ cal mol$^{-1}$. K$^{-1}$ |
| $Ib$ | $2{\cdot}3\,.\,10^{11}$ | $21{\cdot}3$ | $13{\cdot}1$ | $4{\cdot}6\,.\,10^{6}$ | $14{\cdot}1$ | $-30{\cdot}6$ |
| $If$ | $2{\cdot}0\,.\,10^{19}$ | $35{\cdot}8$ | $27{\cdot}6$ | $6{\cdot}2\,.\,10^{4}$ | $12{\cdot}8$ | $-38{\cdot}8$ |
| $Ig$ | $3{\cdot}6\,.\,10^{20}$ | $37{\cdot}8$ | $33{\cdot}3$ | $9{\cdot}7\,.\,10^{4}$ | $13{\cdot}1$ | $-37{\cdot}8$ |
| $I^h$ | $2{\cdot}6\,.\,10^{16}$ | $31{\cdot}3$ | $14{\cdot}3$ | $5{\cdot}1\,.\,10^{6}$ | $15{\cdot}4$ | $-30{\cdot}0$ |
| $Ii$ | $3{\cdot}2\,.\,10^{14}$ | $27{\cdot}7$ | $5{\cdot}7$ | $8{\cdot}1\,.\,10^{6}$ | $15{\cdot}3$ | $-29{\cdot}1$ |
| $Ij$ | $1{\cdot}1\,.\,10^{14}$ | $27{\cdot}1$ | $3{\cdot}5$ | $6{\cdot}4\,.\,10^{7}$ | $16{\cdot}6$ | $-25{\cdot}0$ |

that in this relationship the sequence of the correlated $\log k$ does not correspond to the electronic effects of substituents. On the contrary, the correlations of $\log k$ at $0°C$ with $\log k$ at $90°C$ represent three linear relationships. The straight line with $\varrho = 0.302$, $r = 0.997$ corresponds to compounds with the most powerfully electron donating substituents, the second straight line, $\varrho = -1.187$, $r = 0.989$, corresponds to the compounds $Id-Ig$ and, finally, the straight line with $\varrho = 0.581$, $r = 0.967$ corresponds to the compounds $Ig-Ij$. In these plots the points corresponding to the particular derivatives follow the order of the electronic substituent effects.

The study of substituent effects on the reaction rates at $0°C$ revealed a linear plot $\log k$ vs $\sigma$ with a positive slope $\varrho = 0.603$, $r = 0.995$. All the points, except that corresponding to the compound $Ia$, lie on a straight line, as seen from Fig. $2A$. At temperatures, for which $k \sim k_2$, the hydrolysis is a nucleophilic reaction, in which the first step is an attack of the catalyst at the $C{=}N$ carbon. The rate determining step is the formation of the transition state $III\,2$ which reacts rapidly with water to give $IV\,2$ and this decomposes into isatinic acid anion and the corresponding substituted aniline. Acidification brings about a reversible cyclisation of $V$ into isatin $VI$.

As seen from Fig. $2B$ ($\log k$ vs $\sigma$), at $90°C$ the studied reaction of $Ia-Ic$ ($\varrho = 1.346$, $r = 0.938$) differs from the reactions of $Id-Ig$ ($\varrho = -0.696$, $r = 0.996$) and of $Ig-Ij$ ($\varrho = 1.005$, $r = 0.988$). Only compounds $Ig-Ij$ are hydrolysed also under these conditions by nucleophilic mechanism whereas in the reaction of the compounds $Id-Ig$ a spontaneous (uncatalysed) solvolysis most probably takes place. On the
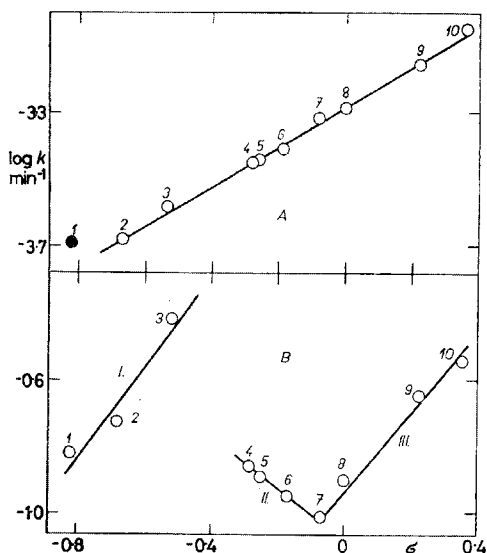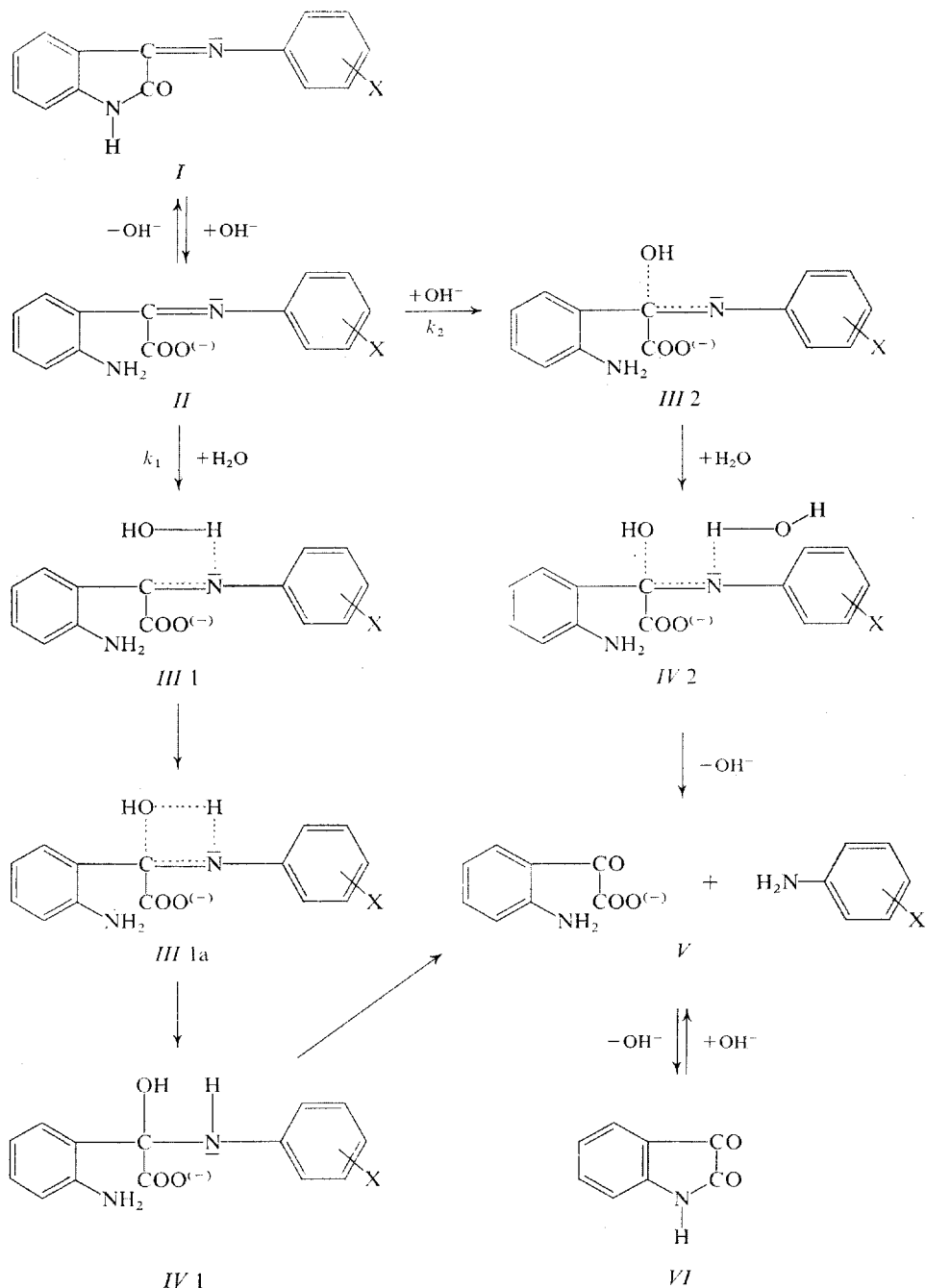


FIG. 2

Plot of Logarithms of the Overall Rate Constants, $\log k$, against Hammett $\sigma$ Substituent Constants

$A$ $c_M = 5 . 10^{-4}$M-$II$, 20% (vol) of 1-propanol, $I = 1$, 1M-NaOH, $T = 0°C$; $B$ $c_M = 5 . 10^{-3}$M-$II$, 20% (vol) of 1-propanol. $\pi = 1$, 0·1M-NaOH, $T = 90°C$.

SCHEME 1

basis of our results it is not possible to conclude which of the transition states of the spontaneous solvolysis represents the slowest step; whether *III 1* or *IV 1*. From the solvation studies of the forms[19] *I* we could judge that the slowest process is the formation of the transition state *IV 1*. However, from the suggested scheme for the acid hydrolysis of some Schiff bases[20-24] and from the obtained slope of the linear relationship between log $k$ and $\sigma$ at 90°C $(\varrho = -0.696$, Fig. 2*B)* we must assume that the slowest step is the formation of the transition state *III 1*. Thanks to their great electron donating ability, substituents in the compounds *Ia−Ic* can participate very well in the conjugated system of the molecule and thus form a quinoid structure; they are also more deeply coloured[3,11]. These structures are hydrolysed by a nucleophilic mechanism, as indicated also by the above-mentioned different slope values in the plots $k$ vs $c_{NaOH}$, log $k$ at 0°C vs log $k$ at 90°C, and log $k$ vs $\sigma$. In the region $50-70$°C, where $k_1 \sim k_2$, both reactions compete with each other. At 0°C all the compounds react by nucleophilic mechanism $(k \sim k_2)$, at 90°C the derivatives *Id−Ig* were shown to react mainly by spontaneous solvolysis $(k \sim k_1)$ whereas compounds *Ia−Ic* react by nucleophilic mechanism but their electronic structure is different from the structure of *Ig−Ij*. In the reaction of the compound *Ig*, the effect of the $OH^-$ ion in the reaction characterised by $k_2$ is the same as the effect of water molecules in the reaction, characterised by $k_1$.

On the basis of our results the most probable mechanism of the alkaline hydrolysis of compounds *II* can be expressed by Scheme 1. This Scheme does not express the mentioned different structure of the compounds *Ia−Ic*.

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