

HYDROLYTIC STABILITY OF IMIDES OF DIFFERENT STRUCTURES

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Abstract

The conversion kinetics of N(o-carboxyphenyl)naphthalimide has been studied in buffer solutions over a pH range 5-12.6 and temperature range 25-70 °C. The naphthalimide hydrolysis is shown to be a reversible reaction. The mechanism of the alkaline hydrolysis of N(o-carboxyphenyl) phthalimide is proposed. The structure dependence of the imide hydrolytic stability is explained on the basis of the suggested mechanism.

Imides are known to have low hydrolytic stability in alkaline media [1]. During multistep synthesis of polyisoindoloquinazolidione the intermediate poly(o-carboxy)-imide is affected by NH₃ and H₂O at high temperatures, which can induce polymer degradation. The influence of carboxyl group in o-position to nitrogen of the imide cycle and naphthalene ring on the imide hydrolysis rate has been investigated by the example of model compounds.

Experimental

N-(o-carboxyphenyl)-phthalimide and its degradation product—N-phthalanthranilic acid—were prepared and purified according to known procedures [2]. Melting points and acid numbers of the substances obtained corresponded to literature and theoretical data, respectively.

N-phenylnaphthalimide was synthesized according to a literature method [3].

N-(o-carboxyphenyl)naphthalimide was prepared by gradual addition of 0.0102 mole of naphthalic anhydride to 0.01 mole of anthranilic acid solution in 40 ml of dimethylformamide at 130 °C.

Complete dissolution of the anhydride was attained in about 1.5 hr and after stirring the solution for 5 hr it was cooled. The product was obtained in the form of white crystals 24 hr later with a yield of 88%.

The buffer solutions used were [4]: over the pH range 5–8 phosphate ($1/10 \text{ M NaH}_2\text{PO}_4 + 1/10 \text{ M Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$), between pH 8 and 10 borate and at pH between 10 and 13 glycine buffer. The pH of the buffer solutions was checked by a universal pH meter type Ev-74.

The kinetics of imide conversion has been studied by spectrophotometric technique. The substances investigated and their mixtures obey Beer's law. The absorbance change of the reaction solution was followed by a UV—visible spectrophotometer PU 8800 (Philips-Pye Unicam) at 295 nm and 340 nm. The experiments have been carried out in the thermostated closed cell of the instrument. The concentration of the initial model compound solutions in ethanol or dioxane was 10^{-2} mol/l . The reagent concentration in the buffer solutions was $(0.5 + 1.5) \cdot 10^{-4} \text{ mol/l}$.

The hydrolysis of N-(*o*-carboxyphenyl)phthalimide, N-phenylnaphthalimide and N-(*o*-carboxyphenyl)naphthalimide has first-order reaction kinetics. The observed rate constants of simple and reversible reactions have been calculated by known methods [5]. In Table 1 the accuracy of kinetic data obtained is listed. The effective activation energies have been calculated by least-squares method. The correlation coefficients changed over the range 0.986–0.999.

Table 1

Error of definition of k_{ob} for N-phenylnaphthalimide hydrolysis in buffer solution at pH = 11.3 and temperature 47 °C

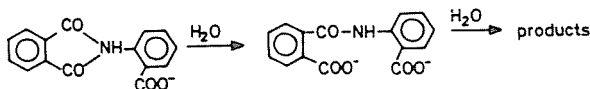
n	$\bar{k}_{\text{ob}} \cdot 10^2, \text{ s}^{-1}$	s	α	$t_{\alpha, n}$	$(\bar{k}_{\text{ob}} \pm \Delta \bar{k}_{\text{T}}) \cdot 10^2$
5	2.68	0.16	0.95	2.571	2.68 ± 0.18

n — the number of experiments,
 s — standard deviation,
 α — confidence level,
 $t_{\alpha, n}$ — Student criterion

Results and discussion

When investigating the hydrolysis of N-(*o*-carboxyphenyl)phthalimide in buffer solutions over a certain pH range the reaction is shown to be irreversible including the imide cycle opening and degradation of the N-phthalanthranilic acid formed.

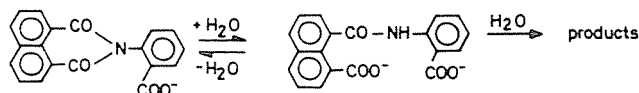
It was found that the imide hydrolysis is slow at pH < 7 and fast at pH > 7. In Scheme 1 the carboxyl groups are represented as carboxylate groups, but in neutral medium they exist in their non-ionized form. UV-spectra and molar



Scheme 1

absorption coefficients of the intermediate and reaction products coincide with those of corresponding individual substances.

N-phenylnaphthalimide and N-(o-carboxyphenyl)naphthalimide is proved to hydrolyze irreversibly in buffer solutions over the pH range 11.6–12.6. The spectra and molar absorption coefficients of the substance formed correspond to those of the intermediate N-phenylnaphthalamic and N-naphthalanthranilic acids.



Scheme 2

Under these conditions the intermediates formed are fairly stable and hydrolysis is observed only in concentrated alkaline solutions at temperatures $> 100^{\circ}\text{C}$.

In buffer solutions of pH 9.9–11.0, the ring-opening reaction of the naphthalimide cycle becomes reversible. The UV spectrum of the equilibrium reaction solution has an isobestic point and corresponds to the sum of the spectra of naphthalimide and the corresponding amide (Fig. 1).

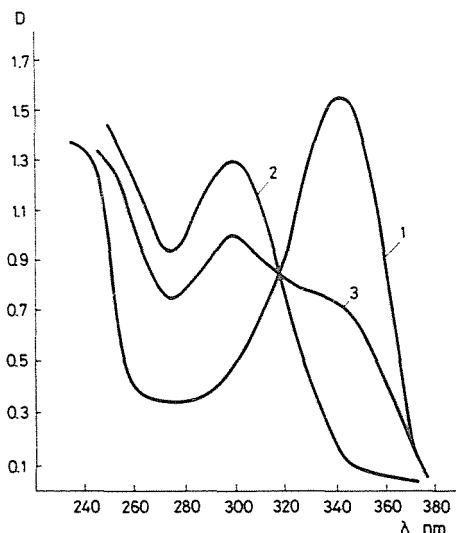


Fig. 1. UV-spectra in buffer solution at pH = 10.5: 1—N-(o-carboxyphenyl)naphthalimide, 2—N-naphthalanthranilic acid, 3—sum spectrum of N-(o-carboxyphenyl)naphthalimide and the corresponding amide, which are in equilibrium state

The mechanism of N-(o-carboxyphenyl)-phthalimide hydrolysis.

In buffer solutions in the pH range 5–6.5 the hydrolysis rate constants, obtained for N-(o-carboxyphenyl)-phthalimide do not depend on the pH of the medium (Fig. 2). Further increase in the pH of the reaction mixture causes a

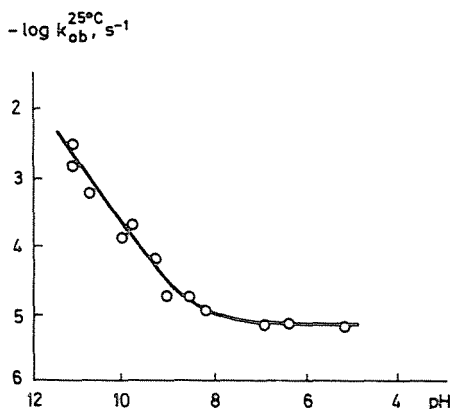
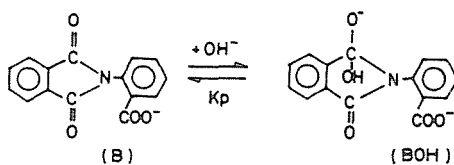


Fig. 2. pH dependence of $\log k_{ob}$ of N-(o-carboxyphenyl)-phthalimide hydrolysis at 25 °C, full line calculated using the equation and the constants obtained

sharp increase in the imide hydrolysis rate. An analogous effect has been observed for N-phenylphthalimide [1]. In basic medium the equilibrium reaction of the imide cycle ionization takes place [6].



Scheme 3

The mechanism proposed implies that the reactive form of imide appears by joining of hydroxyl ion to the carbon atom of the carbonyl group (BOH^-). The attack of the ionized form by water is suggested to be the rate-limiting step. This mechanism is described by the kinetic equation:

$$k_{ob} = k^{\circ} + k^{\text{OH}^-} \cdot K_p [\text{OH}^-]$$

where:

- k° — degradation rate constant, independent of medium composition,
- k^{OH^-} — rate constant of degradation catalyzed by hydroxyl ion,
- K_p — equilibrium constant of imide cycle ionization

A graphical solution of this equation gives the following values: $k^{\text{OH}^-} \cdot K_p = 5.62 \text{ l/mol.s}$ and $k^{\circ} = 5.0 \cdot 10^{-6} \text{ s}^{-1}$ (Fig. 3). The rate constant dependence on the hydroxyl concentration, calculated by using values obtained and by equation coincides with experimental kinetic data (Fig 2). Based on these results the increase of hydrolysis rate of N-(o-

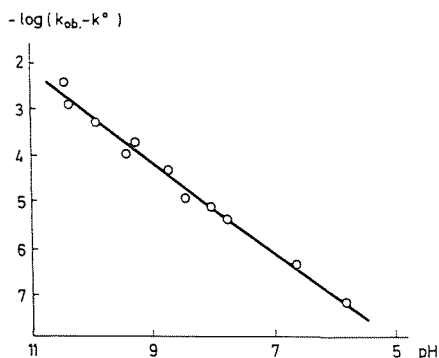


Fig. 3. Graphical solution of the equation for hydrolysis of N-(o-carboxyphenyl)phthalimide in solutions over the pH range 6-19.44

carboxyphenyl)phthalimide may be explained by the increase of concentration of ionized imide in solutions at $\text{pH} > 7$.

As can be seen from Fig. 4 for N-phenylnaphthalimide and N-(carboxyphenyl)naphthalimide the observed rate constants of hydrolysis increase with increasing pH, and the observed rate constants of cyclization remain practically constant under the conditions investigated. The degradation process of the naphthalimide cycle is defined by contribution of

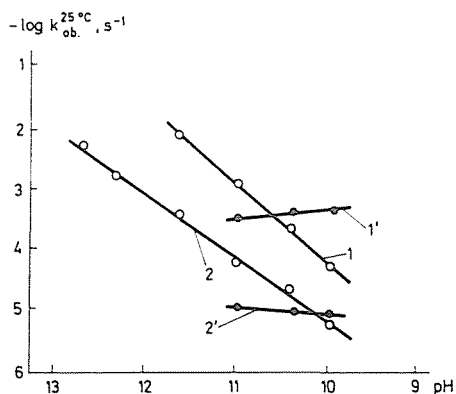


Fig. 4. pH dependence of $\log k_{\text{obs}}$ of the hydrolysis of N-phenylnaphthalimide (1) and N-(o-carboxyphenyl)naphthalimide (2) and cyclization of N-phenylnaphthalimic acid (1') and N-naphthalanthranilic acid (2') at 25 °C

hydrolysis and cyclization reactions. In solutions at $\text{pH} > 10.5$ mainly the hydrolysis of N-(carboxyphenyl)naphthalimide and N-phenylnaphthalimide takes place. A decrease in the solution pH shifts the reaction equilibrium to wards imide cycle formation.

The hydrolytic stability dependences of naphthalimide cycles on the pH are analogous to that obtained for N-(o-carboxyphenyl)phthalimide (Figs 2 and 4). It can be assumed that all the imides investigated hydrolyze via a common mechanism.

The effective activation energies of hydrolysis of both naphthalimides are approximately equal (Table 2), but are less than that of cyclization. Consequently, with rising temperature the contribution of cyclization reaction increases and that of the destruction process decreases.

Table 2

The effective activation energies of hydrolysis and cyclization

Substance	Process	pH of solution	$E \frac{\text{kJ}}{\text{mol}}$
N (o-carboxy-phenyl) phthalimide	hydrolysis	9.3	93.5
N (o-carboxy-phenyl) naphthalimide	hydrolysis	11.0	50.6
	cyclization	11.0	75.6
N-phenylnaphthalimide	hydrolysis	10.4	43.4
	cyclization	10.4	71.9

Comparison of imide hydrolytic stabilities

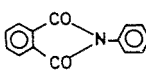
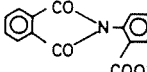
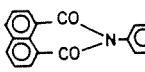
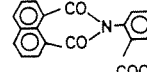
From the kinetic data listed in Table 3, it is seen that the imide hydrolytic stability increases from N-phenyl-phthalimide to N-(o-carboxy-phenyl)naphthalimide by a factor of 10^3 . This effect can be explained by the suggested mechanism of imide hydrolysis. The joining of COOH-group in o-position to the nitrogen of imide cycle results a decrease in the hydrolysis rate constant by a factor exceeding ten. In alkaline media the negative charge and steric effect of ionized carboxyl group prevent the formation of active ionized form of imide (BOH^-) and decrease its concentration in the reaction solution. This causes an increase in the imide hydrolytic stability.

The six-membered naphthalimide cycle is known to be more advantageous energetically as compared with phthalimide cycle and is consequently, more stable. Moreover, due to the stronger electron donor properties of the

naphthalene ring, the carbon atom of the carbonyl group is less electrophilic than in the case of phthalimide cycle. For this reason the equilibrium of the reaction (Scheme 3) shifts towards the formation of an unreactive form of imide (B). As a result, a 10-fold increase in the hydrolytic stability has been observed for N-phenylnaphthalimide.

Kinetic investigations of substituted naphthalimide cycle have shown that carboxyl group causes a decrease of the imide hydrolysis rate, analogously to N-(o-carboxyphenyl)phthalimide (Table 3).

Table 3

Structure dependence of imide hydrolytic stability				
Structure				
Medium				
$k_{\text{ob.}}$, $t = 25^\circ\text{C}$ pH = 10	6320	500	63.2	6.32
n (relative unit)	1	12.7	100	1000

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