

## KINETICS AND MECHANISM OF SOLVOLYSIS OF SUBSTITUTED PHENYL N-PHENYLBENZIMIDOESTERS

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Received June 13th, 1986

Kinetics of hydrochloric acid-catalyzed solvolysis of substituted phenyl and methyl N-phenylbenzimidesters have been studied in methanol, 50 vol. % aqueous methanol, and 50 vol. % aqueous tetrahydrofurane, and the composition of the reaction products has been determined. The rate-limiting step consists in addition of water or methanol to the protonated substrate. The reaction of methyl N-phenylbenzimidester with both water and methanol and that of substituted phenyl N-phenylbenzimidesters with methanol produce aniline, the ester (or orthoester) and the corresponding phenol. The reaction of substituted phenyl N-phenylbenzimidesters with water gives both the neutral tetrahedral intermediate (which is decomposed into phenol and anilide) and the protonated intermediate (which produces aniline and the ester). At the same proton concentration the phenol content increases with increasing value of the  $\sigma$  constant of the substituent.

The hydrolysis of  $R^1-N=C(R)-OR^2$  imidoesters has been paid considerable attention, because it involves the same tetrahedral intermediates as those in the aminolysis of the corresponding esters or hydrolysis of amides. Thus, studies of the hydrolysis of imidates contribute to a more detailed estimation of the reaction mechanisms of these reactions and to the differentiation between the rate- and the product-determining steps<sup>1-16</sup>. Depending on structure and reaction conditions, the rate-limiting step can consist in either formation or decomposition of one of the intermediates or in the proton transfer. In most cases  $R^1$  and  $R^2$  are alkyl groups, only exceptionally used was an aromatic amine ( $R^1$ ) (ref.<sup>17</sup>) or a phenol derivative ( $R^2$ ) (refs<sup>3,7,11</sup>).

The present communication deals with a study of solvolysis of substituted phenyl N-phenylbenzimidesters (both  $R^1$  and  $R^2$  are aryl groups) in mixtures water-tetrahydrofurane and water-methanol and in neat methanol.

### EXPERIMENTAL

#### Reagents

Phenyl N-phenylbenzimidate (*I*), 4-nitrophenyl N-phenylbenzimidate (*II*), 3-nitrophenyl N-phenylbenzimidate (*III*), and 4-chlorophenyl N-phenylbenzimidate were prepared from N-phenyl-

benzimidoyl chloride<sup>18</sup> and phenol (chloro-, and nitrophenols, respectively) according to the known procedure<sup>19</sup>. The melting points 104–106°C (*I*), 73.5–75.5°C (*II*), 80–81.5°C (*III*), and 91–92°C (*IV*) agree with literature data<sup>19–21</sup>. Methyl *N*-phenylbenzimidate (*V*): A solution of 8.6 g (40 mmol) *N*-phenylbenzimidoyl chloride in 100 ml dry benzene was stirred and treated with 50 ml 1 mol l<sup>-1</sup> sodium methoxide. The separated sodium chloride was filtered off and washed with benzene. The filtrate was distilled, and the fraction boiling at 127–128°C at 650 Pa was taken; yield 5.5 g (65%). <sup>1</sup>H NMR spectrum:  $\delta(\text{OCH}_3) = 3.96$ . For C<sub>14</sub>H<sub>13</sub>NO (211) calculated: 79.62% C, 6.16% H; found 79.50% C, 6.20% H.

#### Estimation of Aniline in the Methanolysis and Hydrolysis Products

A methanolic solution of compounds *I–IV* (0.5 ml 1 · 10<sup>-2</sup> mol l<sup>-1</sup>) and methanolic solution of hydrogen chloride (to make its final concentration of 4 · 10<sup>-3</sup> to 2 · 10<sup>-1</sup> mol l<sup>-1</sup>) was injected into 40 ml methanol or mixtures (1 : 1 by vol.) methanol–water or tetrahydrofuran–water. After the solvolysis was complete (which was proved photometrically at 240–350 nm) aniline was determined by azo coupling reaction: Four 4.5 ml samples were taken from the reaction solution and placed in 10 ml calibrated flasks, whereupon 1 ml 1 mol l<sup>-1</sup> potassium bromide in 0.2 mol l<sup>-1</sup> hydrochloric acid was added (in the case of the most acidic reaction media aqueous 1 mol l<sup>-1</sup> potassium bromide was only added) followed by two drops of 1 mol l<sup>-1</sup> sodium nitrite. The reaction mixtures were left to stand 0.5, 1, 2, and 4 min. After these intervals, 2 ml 0.01 mol l<sup>-1</sup> 3-hydroxynaphthalene-2,7-disulphonic acid and 2 ml 0.5 mol l<sup>-1</sup> sodium hydrogen phosphate were added to each sample. The reaction mixtures thus prepared were diluted with methanol (to 10 ml final volume) and, after 5 min, the absorbance was measured in a 1 cm cell at 500 nm. Along with these experiments, similar measurements were carried out in which, instead of the imidoester *I–V* solutions, aniline of the same concentration was used.

#### Kinetic Measurements

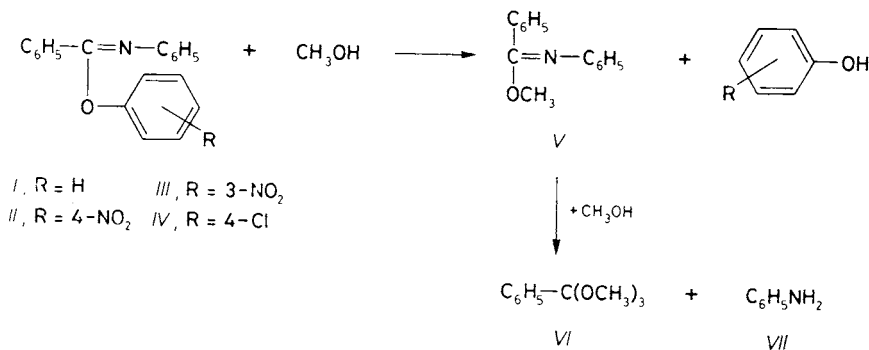
A 1 cm quartz cell was charged with 2 ml solution (25°C) of hydrogen chloride in the given medium (methanol, methanol–water, tetrahydrofuran–water), and 20  $\mu$ l fresh methanolic solution of compounds *I–V* (0.01–0.03 mol l<sup>-1</sup>) was added. The cell was closed, placed into the thermostated compartment of spectrophotometer, and the absorbance–time course was followed. The rate constants  $k_{\text{exp}}$  (s<sup>-1</sup>) were calculated from the relation  $k_{\text{exp}}t = -2.3 \log \Delta A + \text{const.}$ , where  $\Delta A$  means the absorbance differences ( $A_{\infty} - A_t$ ) or ( $A_t - A_{\infty}$ ) depending on the absorbance course (increase or decrease, resp.) at the analytical wavelength chosen (see Tables). The  $k_{\text{exp}}$  differences between three independent experiments were less than 5%.

## RESULTS AND DISCUSSION

### *Methanolysis*

The solvolyses of the imidoesters *I–V* were carried out in three media: methanol, 50 vol. % aqueous methanol, and 50 vol. % aqueous tetrahydrofuran. As the compounds *I–V* are almost insoluble in water, the kinetic experiments could not be performed in pure water. The methanolysis of compounds *I–IV* is subject to acid catalysis, the reaction product comprising the substituted phenol, protonated aniline, and methyl orthobenzoate. The composition of the reaction mixture was

confirmed by comparison with a separately prepared mixture of these compounds in methanolic hydrochloric acid and after addition of  $1 \text{ mol l}^{-1}$  sodium methoxide and by quantitative determination of aniline after the finished reaction. When followed in the 230–380 nm wavelength interval the reaction was found to proceed in two steps. In the first step the respective phenol is formed along with compound *V* which is transformed into aniline and the orthoester (*Scheme 1*).



SCHEME 1

The methanolysis rate constants of the methyl ester *V* were determined in the hydrochloric acid concentration range of  $2 \cdot 10^{-4}$  to  $5 \cdot 10^{-3} \text{ mol l}^{-1}$ . The dependence of  $k_{\text{exp}}$  on the proton concentration is represented in Fig. 1. The theoretical curve was calculated from Eq. (1) in which  $k_1 = (9.5 \pm 0.6) \cdot 10^{-2} \text{ s}^{-1}$

$$k_{\text{exp}} = k_1[\text{H}^+]/(K_A + [\text{H}^+]) \quad (1)$$

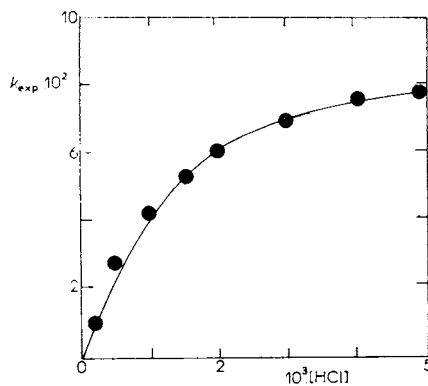


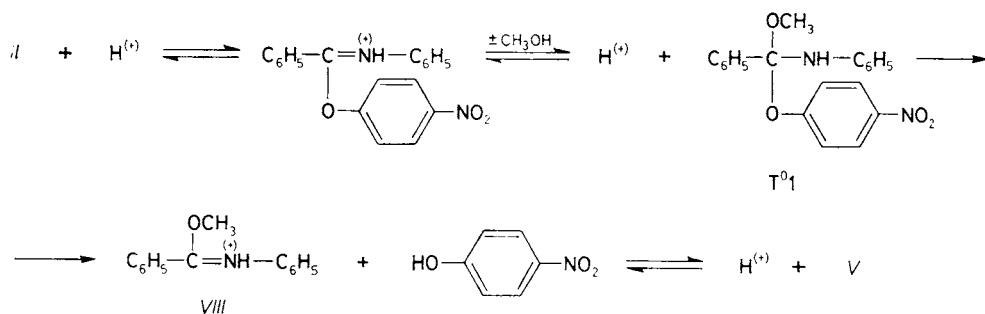
FIG. 1

Dependence of rate constants  $k_{\text{exp}} (\text{s}^{-1})$  (●) of methanolysis of compound *V* on molar concentration of hydrogen chloride. The curve was calculated from Eq. (1) for  $k_1 = 9.5 \cdot 10^{-2} \text{ s}^{-1}$  and  $K_A = 1.1 \cdot 10^{-3}$

is the methanolysis rate constant of the protonated compound *V* and  $K_A = (1.1 \pm \pm 0.08) \cdot 10^{-3}$  is the acidity dissociation constant of compound *V*.

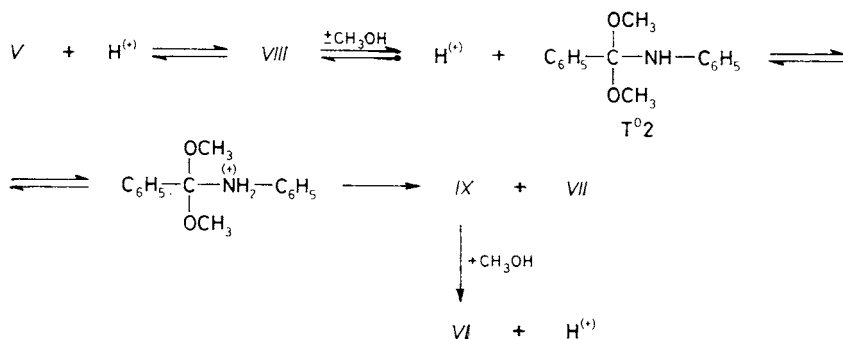
The methanolysis rate of the 4-nitro derivative *II* was determined from the absorbance increase of the 4-nitrophenol produced at 345 nm at which wavelength neither compound *V* nor its methanolysis products absorb. The observed rate constants increase linearly with the hydrochloric acid concentration and obey the relation  $k_{\text{exp}} = k_{\text{H}^+}[\text{H}^+]$ , where  $k_{\text{H}^+} = 24.4 \pm 2.2 \text{ l mol}^{-1} \text{ s}^{-1}$ .

With the derivatives *I*, *III*, *IV* no reliable values of the methanolysis rate constants to compound *V* were obtained, because both the absorbance changes and the rate constants are similar to those of the subsequent methanolysis of compound *V*.



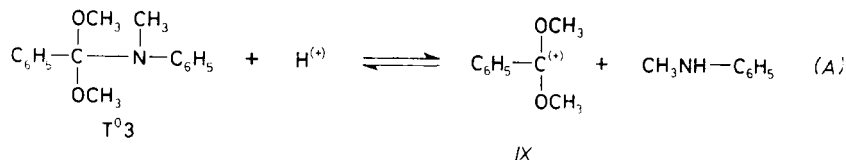
SCHEME 2

The rate-limiting step of the methanolysis of the nitro derivative *II* consists in an attack of the protonated imidoester by methanol (Scheme 2), because  $k_{\text{exp}}$  is directly proportional to the proton concentration. If the decomposition of the intermediate  $T^0 1$  were rate limiting, the  $k_{\text{exp}}$  value would be independent of the proton concentration.



SCHEME 3

The reaction mechanism of methanolysis of compound *V* is given in Scheme 3. The rate-limiting step can consist either in the addition of methanol or in the splitting off of aniline. The acid-catalyzed splitting of the tetrahedral intermediate  $T^{03}$  (Eq. (A)), which is structurally very similar to  $T^{02}$  in Scheme 3, exclusively produces



the carbocation<sup>22</sup>, which means that the splitting off of aniline is much faster than the reverse reaction (splitting off of methanol), and hence it cannot be rate limiting.

#### Hydrolysis in Water-Tetrahydrofuran Medium

The hydrolysis kinetics in the water-tetrahydrofuran medium was followed in the hydrochloric acid concentration ranges of 0.1 to 2.5 mol l<sup>-1</sup> (with compounds *I* and *IV*) and 0.1 to 1.0 mol l<sup>-1</sup> (with the nitro compounds *II* and *III*). At the same time the hydrolysis kinetics of the methoxy derivative *V* was followed in the hydrochloric acid concentration range of 0.01 to 2.5 mol l<sup>-1</sup>, although this compound is not formed as an intermediate in the hydrolyses of compounds *I-IV*. The dependence of logarithm of the absorbance change on time was linear in all the cases within the whole interval investigated. From the kinetical point of view the reaction is of pseudo first order. The  $k_{\text{exp}}$  values obtained are given in Table I. The acidity of medium is expressed by the acidity function. No such function is known for the water-tetrahydrofuran (1 : 1 by vol.) medium, hence we used the  $H_0$  function for 40% aqueous dioxane<sup>23</sup>, because the two media should be similar. The dependence of  $k_{\text{exp}}$  on the acidity function mentioned is represented in Fig. 2. At the lowest proton concentrations the log  $k_{\text{exp}}$  vs  $H_0$  dependence is practically linear with the slope one. The rate-limiting step consists in the addition of water to the protonated substrate whose concentration is negligible (in comparison with that of the neutral substance) and increases linearly with the acidity of medium. Further acidity increases are connected (except for the nitro compounds *II* and *III*) with a slope decrease. A considerable part of the substrate is transformed into the protonated form and its concentration increases then more slowly than the acidity of medium. At the highest proton concentrations, predominant parts of compounds *I*, *IV*, and *V* are present in their protonated forms. The  $k_{\text{exp}}$  value should be independent of a further acidity increase. The found decrease is due to the effect of medium on the rate constant of the addition of water to the protonated substrate.

The effect of acidity of medium on values of equilibrium and rate constants is expressed more suitably by the acidity expressions of the form  $H_0 + \log [\text{H}^+]$  and

TABLE I

Experimental<sup>a</sup> rate constants  $k_{\text{exp}}$  ( $\text{s}^{-1}$ ) of hydrolyses of compounds *I*–*V* in water–tetrahydrofuran mixture (1 : 1 by vol.) at 25°C at various hydrogen chloride concentrations  $c_{\text{HCl}}$  ( $\text{mol l}^{-1}$ )

| $10 \cdot c_{\text{HCl}}$ | $10^2 \cdot k_{\text{exp}}$ |           |            |           |          |
|---------------------------|-----------------------------|-----------|------------|-----------|----------|
|                           | <i>I</i>                    | <i>II</i> | <i>III</i> | <i>IV</i> | <i>V</i> |
| 0.1                       | —                           | —         | —          | —         | 0.77     |
| 0.2                       | —                           | —         | —          | —         | 1.25     |
| 0.5                       | —                           | —         | —          | —         | 3.08     |
| 1.0                       | 0.87                        | 0.34      | 0.29       | 0.63      | 5.66     |
| 2.0                       | 1.80                        | 0.78      | 0.68       | 1.33      | 10.66    |
| 4.0                       | 3.85                        | 1.82      | 1.57       | 3.38      | —        |
| 5.0                       | 5.15                        | 2.52      | 2.17       | 4.47      | 16.31    |
| 7.5                       | 8.66                        | 4.20      | 4.33       | 9.24      | —        |
| 10                        | 11.55                       | 7.49      | 7.30       | 12.60     | 15.40    |
| 15                        | 14.59                       | —         | —          | 19.80     | 11.55    |
| 20                        | 13.86                       | —         | —          | 19.80     | 6.76     |
| 25                        | 9.56                        | —         | —          | 18.23     | 5.13     |

<sup>a</sup> Measured at  $\lambda_{\text{anal}}$  (nm): *I* (312), *II* (350), *III* (322), *IV* (322), *V* (294).

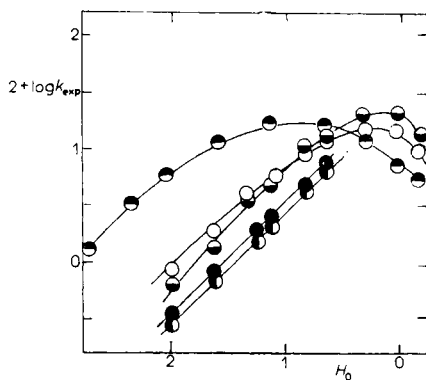


FIG. 2

Dependence of logarithm of experimental rate constants  $k_{\text{exp}}$  ( $\text{s}^{-1}$ ) of hydrolyses of compounds *I* (○), *II* (●), *III* (◐), *IV* (◑), and *V* (◒) in water–tetrahydrofuran mixture (1 : 1 by vol.) at 25°C on the  $H_0$  acidity function<sup>23</sup>

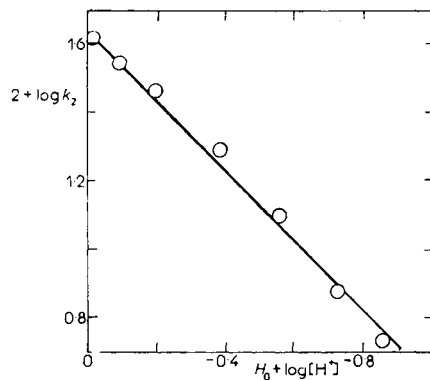


FIG. 3

Dependence of logarithm of the rate constants  $k_1$  ( $\text{s}^{-1}$ ) calculated from Eq. (2) for hydrolysis of compound *V* in water–tetrahydrofuran mixture (1 : 1 by vol.) at 25°C on the acidity of medium expressed by the  $(H_0 + \log [H^+])$  value<sup>24–26</sup>

$-\log(\gamma_{H^+}\gamma_S/\gamma_{SH})$ , respectively<sup>24-26</sup>. The dependence of  $\log k_1$  on  $(H_0 + \log [H^+])$  is presented in Fig. 3 for the methoxy derivative *V*. The  $k_1$  rate constants were obtained from  $k_{exp}$  by a correction for the proportion of the non-protonated form according to Eq. (2)

$$k_{exp} = k_1 h_0 / (h_0 + K_A), \quad (2)$$

where  $h_0$  means the negative antilogarithm of  $H_0$ , and  $K_A$  is the dissociation constant of the protonated substrate ( $K_A = 10^{-1.3}$ ). The 1.3 value is the  $H_0$  function at which the substrate is half protonated, and it corresponds to the proton concentration of  $0.37 \text{ mol l}^{-1}$ . The great difference between  $[H^+]$  and the negative value of antilogarithm of  $H_0$  is caused by the fact that the determination of  $H_0$  was based on diluted aqueous solution of hydrochloric acid<sup>23</sup>. The  $k_1$  value extrapolated to the zero value of the  $(H_0 + \log [H^+])$  function (all the activity coefficients are equal to one) is  $0.425 \text{ s}^{-1}$ , and it represents the  $k_1$  rate constant value in diluted solutions of hydrogen chloride in the water-tetrahydrofuran (1 : 1 by vol) medium.

At the proton concentration as low as  $0.5 \text{ mol l}^{-1}$  there already occurs a considerable decrease in  $k_1$ , but the dependence of  $k_{exp}$  on  $H_0$  for the nitro compounds *II* and *III* is linear even at the highest hydrochloric acid concentration used ( $1 \text{ mol} \cdot \text{l}^{-1}$ ). The applied  $H_0$  function was determined by the measurement of dissociation constant of 4-nitroaniline<sup>21</sup> (the Hammett indicator). The protonated substances *I-IV* are less solvated than the substituted anilines (a single acidic hydrogen only, and the charge partially dispersed by electron delocalization). The corresponding acidity function is steeper, hence at higher proton concentrations the concentration of the protonated form increases faster than it should increase according to the  $H_0$  function used. At the same time, however, the  $k_1$  rate constant is decreased. Both these factors are operating in the case of the nitro compounds *II* and *III*, and their effects on  $k_{exp}$  are obviously comparable. The result is a linear dependence of  $\log k_{exp}$  on  $H_0$ .

The application of improper acidity function to the determination of the  $k_1$  rate constant and of  $pK_A$  of the methoxy derivative *V* introduces a relatively small error. The difference between the two acidity functions becomes more distinct only at higher proton concentrations (when the substrate is predominantly in its protonated form). The correction for the dissociation degree is small then, and therefrom it follows that the error in the correction is still smaller. As there is linear interdependence between the individual  $(H_X + \log [H^+])$  functions<sup>26</sup>, the type of the function used has no effect on the extrapolated  $k_1$  value (Fig. 3).

At the lowest proton concentrations used it is

$$k_{exp} = (k_1/K_A) [H^+]. \quad (3)$$

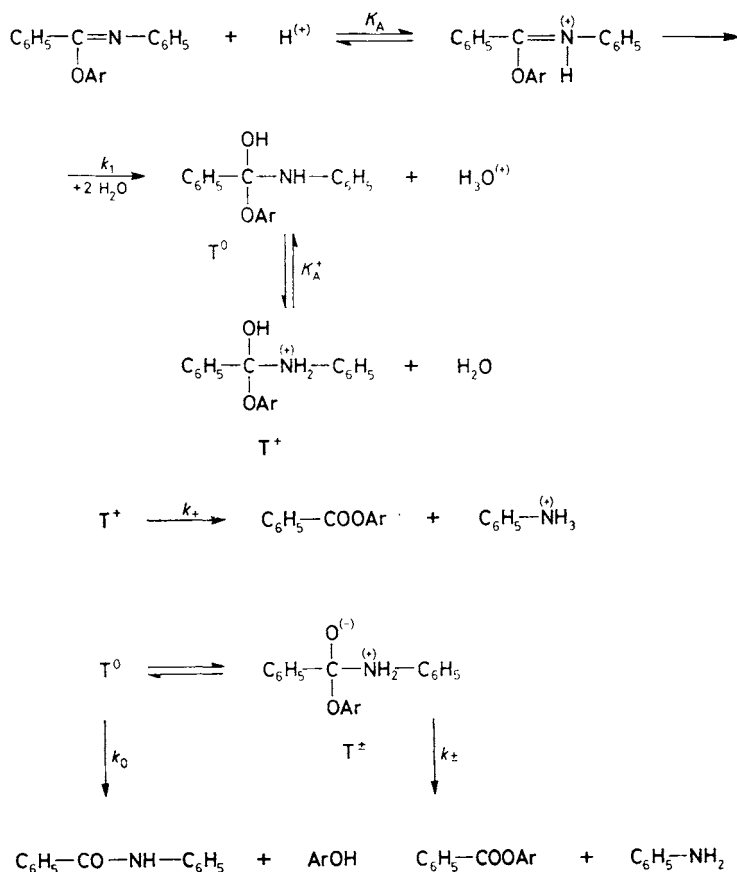
The  $k_1/K_A$  value depends on  $\sigma$  constants according to Eq. (4).

$$\log(k_1/K_A) = -0.7\sigma + \text{const.} \quad (4)$$

At the highest proton concentrations  $k_{\text{exp}} \approx k_1$  for the compounds I and IV. The effect of substituents is reversed in this case. A rough estimate gives  $\rho \approx 0.5$ . The small difference in the  $k_1$  values shows that the O—Ar bond is not yet split in the activated complex. From Eq. (5) it is possible to assess the  $\rho(K_A)$  value 1 to 1.5.

$$\rho(K_A) = \rho(k_1) - \rho(k_1/K_A) \quad (5)$$

The reaction mechanism is given in Scheme 4.



SCHEME 4



The product-determining steps follow the rate-determining step of the hydrolysis. No direct connection is between the effect of medium on the rate constant and that on the reaction product composition. The reaction products are either benzanilide and the substituted phenol or aniline and the substituted phenyl benzoate. Tables II and III present relative amounts of aniline in the reaction product for different proton concentrations. From the dependence of the relative aniline content in the reaction product on the hydrochloric acid concentration it is obvious that the extrapolation to zero concentration of the proton (when the reaction mixture does not contain the protonated intermediate) indicates a practically zero content of aniline in the reaction mixture (Fig. 4). Therefore it follows that the reaction *via* the dipolar ion  $T^{\pm}$  is only slightly significant or insignificant at all, although the hydrolysis of N-alkylimidoesters in neutral or mildly acidic media takes predominantly this pathway<sup>7</sup>. The equilibrium constant of the transformation of the neutral intermediate  $T^0$  to the dipolar ion  $T^{\pm}$  is at least by four orders of magnitude smaller for N-arylimidoesters than for N-alkylimidoesters. The rate constants of decomposition of the dipolar ion  $T^{\pm}$  are so large that they are not practically affected by the substitution of alkyl

TABLE II

Aniline content (mol%) in products (aniline + benzanilide) of hydrolysis of compound I in water-tetrahydrofurane mixture (1 : 1 by vol.) at various hydrogen chloride concentrations  $c_{\text{HCl}}$  ( $\text{mol l}^{-1}$ )

| $10^3 \cdot c_{\text{HCl}}$       | 4.89 | 4.91 | 6.10 | 7.30 | 9.68 | 9.78 | 19.6 | 36.8 | 61.0 | 79.0 | 97.0 | 100 |
|-----------------------------------|------|------|------|------|------|------|------|------|------|------|------|-----|
| $\text{C}_6\text{H}_5\text{NH}_2$ | 30   | 37   | 36   | 43   | 49   | 62   | 74   | 79   | 88   | 91   | 87   | 92  |

TABLE III

Aniline content (mol%) in reaction products (aniline + benzanilide) of hydrolyses of compounds II, III, and IV in aqueous methanol and tetrahydrofurane (1 : 1 by vol.) at various hydrogen chloride concentrations  $c_{\text{HCl}}$  ( $\text{mol l}^{-1}$ )

| $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ |     |    | $\text{C}_4\text{H}_8\text{O}-\text{H}_2\text{O}$ |     |    | $10^3 \cdot c_{\text{HCl}}$ |
|---|-----|----|---|-----|----|-----------------------------|
| II  | III | IV | II  | III | IV |                             |
| 72  | 68  | 88 | 4   | 6   | 26 | 19.6                        |
| 78  | —   | —  | —   | —   | —  | 36.8                        |
| 77  | —   | —  | —   | —   | —  | 61.0                        |
| —   | —   | —  | 8   | —   | —  | 96.8                        |
| —   | —   | —  | 10  | 15  | 58 | 120                         |

by aryl group<sup>13</sup>. Moreover, the splitting off of aryloxy group from the neutral intermediate  $T^0$  is by several orders faster than that of alkyloxy group. Hence it follows that the pathway through the dipolar ion  $T^\pm$  is practically insignificant for these compounds. The rates of formation of phenol and aniline are defined by Eqs (6) and (7), resp. The relative amount of aniline in the reaction product is given by Eq. (8), where  $a = k_+/K_A^+k_0$ .

$$v_{OH} = k_0[T^0] \quad (6)$$

$$v_{NH_2} = k_+[T^+] = k_+[H^+][T^0]/K_A^+ \quad (7)$$

$$\frac{v_{NH_2}}{v_{NH_2} + v_{OH}} = \frac{k_+[H^+]}{k_+[H^+] + k_0K_A^+} = \frac{a[H^+]}{a[H^+] + 1} \quad (8)$$

The theoretical curve for compound *I* is given in Fig. 4 and it was calculated for  $a = 110$  ( $a^{-1}$  means the proton concentration in the product, if it contains equal amounts of aniline and phenol). By analogy with literature data<sup>22</sup> it is possible to consider the dissociation constant to be  $K_A^+ = 10$ . In this case  $k_+ = k_0 \cdot 10^3$ , which means that the protonated intermediate  $T^+$  is decomposed faster than the neutral one (by about three orders of magnitude). The  $k_0$  value increases rapidly and the dissociation constant  $K_A^+$  less rapidly with increasing  $\sigma$  value of the substituent. The  $k_+$  constant somewhat decreases. The result is a preferable splitting of the neutral intermediate  $T^0$  to the substituted phenol and benzanilide (Tables II and III).

#### Solvolyses in Water–Methanol Medium

The solvolysis kinetics were measured with compounds *II–V*. The dependence of logarithm of the absorbance change on time was linear in the whole range, although one of the products is the methoxy derivative *V*. The absorbance change in the

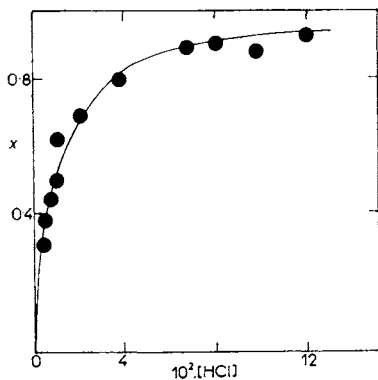


FIG. 4

Dependence of the aniline content expressed by the molar fraction (●) (in its mixture with benzanilide) in the hydrolysis products of compound *I* in water–tetrahydrofuran mixture (1:1 by vol.) on molar concentration of hydrogen chloride. The curve was calculated from Eq. (8) for  $a = 110$

solvolytic of compound *V* is much smaller at the wavelengths used as compared with the absorbance change in the solvolyses of compounds *II–IV*, and the solvolysis rate constant of the methoxy derivative *V* is greater. Hence the initial deviation from linearity due to this consecutive reaction is negligible.

The  $k_{\text{exp}}$  rate constants measured at various hydrochloric acid concentrations are given in Table IV. The dependences of  $k_{\text{exp}}$  on the hydrochloric acid concentration

TABLE IV

Experimental<sup>a</sup> constants  $k_{\text{exp}}$  ( $\text{s}^{-1}$ ) of solvolyses of compounds *II–V* in water–methanol mixture (1 : 1 by vol.) at 25°C at various hydrogen chloride concentrations  $c_{\text{HCl}}$  ( $\text{mol l}^{-1}$ )

| $10^2 \cdot c_{\text{HCl}}$ | $10^2 \cdot k_{\text{exp}}$ |            |           |          |
|-----------------------------|-----------------------------|------------|-----------|----------|
|                             | <i>II</i>                   | <i>III</i> | <i>IV</i> | <i>V</i> |
| 0.1                         | —                           | —          | 0.45      | 0.96     |
| 0.2                         | 0.39                        | 0.46       | 0.85      | 1.68     |
| 0.5                         | —                           | 1.02       | 1.69      | 3.34     |
| 1.0                         | —                           | —          | 3.20      | 5.04     |
| 2.0                         | 3.75                        | 3.75       | 5.33      | 6.89     |
| 3.0                         | —                           | —          | 6.60      | 7.31     |
| 5.0                         | 7.11                        | 6.93       | 8.94      | 8.15     |
| 10                          | —                           | 8.93       | 9.24      | 8.40     |
| 20                          | —                           | —          | —         | 8.66     |
| 50                          | —                           | —          | —         | 7.70     |
| 100                         | —                           | —          | —         | 5.33     |
| 150                         | —                           | —          | —         | 4.20     |
| 200                         | —                           | —          | —         | 3.01     |
| 250                         | —                           | —          | —         | 2.24     |

<sup>a</sup> Measured at  $\lambda_{\text{anal}}$  (nm): *II* (358), *III* (312), *IV* (250), *V* (250).

TABLE V

The acidity dissociation constants  $K_{\text{A}}$  and rate constants  $k_1$  ( $\text{s}^{-1}$ ) of solvolyses of compounds *III–V* in water–methanol mixture (1 : 1 by vol.) at 25°C calculated according to Eq. (1)

| Compound   | $10^2 \cdot k_1$ | $10^2 \cdot K_{\text{A}}$ | $\text{p}K_{\text{A}}$ |
|------------|------------------|---------------------------|------------------------|
| <i>III</i> | 14.0             | 6.0                       | 1.22                   |
| <i>IV</i>  | 12.5             | 2.75                      | 1.56                   |
| <i>V</i>   | 8.9              | 0.8                       | 2.1                    |

(up to  $0.1 \text{ mol l}^{-1}$ ) and Eq. (1) were used for calculation of the  $K_A$  dissociation constants of the protonated substrates and of the  $k_1$  rate constant (in this case it represents a sum of the rate constants of the reaction of the protonated substrate with water and methanol): they are given in Table V.

For the methoxy derivative *V* we measured the solvolysis rate constant up to the hydrochloric acid concentration of  $2.5 \text{ mol l}^{-1}$ . At the proton concentrations above  $0.2 \text{ mol l}^{-1}$ , practically all the substrate is present in the protonated form. Again the  $k_{\text{exp}}$  decrease is caused by the effect of medium on  $k_1$ . The change in  $k_1$  with the acidity of medium is similar to that in  $k_1$  of the hydrolysis in aqueous tetrahydrofuran. The overall decrease of  $k_1$  is, however, somewhat smaller, which can be due to the fact that, in the water-methanol medium, the methanol molecules also can participate in the solvation of the proton being split off.

The  $k_1$  constant is a sum of the rate constants of the attack of the protonated substance by water and methanol. In the case of the attack by methanol the methoxy derivative *V* is produced which gives aniline and aryl benzoate on hydrolysis, which was confirmed by the solvolysis of the pure compound *V*. The aniline content in the reaction products was 95–98%. The reaction with water gives (as it is the case in aqueous tetrahydrofuran, too) the neutral intermediate  $T^0$  (Scheme 4) which is decomposed to phenol and benzanilide, and the protonated intermediate  $T^+$  which produces aniline and aryl benzoate. Table III presents the aniline content (in mole %) in the reaction products of solvolyses of compounds *II–IV*. At the lowest proton concentrations, when the acid-catalyzed splitting into aniline and phenyl benzoate is insignificant for the nitro compounds *II* and *III*, the amount of aniline in the reaction products is 70 mole %. Hence it follows that, in the reaction of the protonated substrates with the solvent molecules, 70% of the substance reacts with methanol and 30% with water. In the water-methanol mixture the molar ratio of the components is 2.3 : 1. Hence methanol is 5.4 times more reactive than water in the reaction with the protonated substrate in the given medium.

Reactions of a large number of carbocations with nucleophilic reagents exhibit no or only a small change in selectivity, so that the nucleophilic reactivity can be defined<sup>27,28</sup> in these cases by a simple equation (9) in which  $k_{\text{H}_2\text{O}}$  means

$$\log(k_n/k_{\text{H}_2\text{O}}) = N^+ \quad (9)$$

the rate constant of the reaction of the cation with water in water;  $k_n$  is the rate constant of the reaction of the same cation with the given nucleophile, and  $N^+$  is a parameter characteristic for the nucleophile in the given medium and independent of the nature of the cation. The rate constants of the reactions involving solvent as the reagent are given in  $\text{s}^{-1}$  units. The  $N^+$  value for methanol (in methanol) is 0.5 (ref.<sup>28</sup>). From our results (in 50 vol. % aqueous methanol) it follows  $N^+ = 0.4$ .

## REFERENCES

1. Martin R. B., Hedrick R. I., Parcell A.: *J. Org. Chem.* **29**, 3197 (1964).
2. Cunningham B. A., Schmir G. L.: *J. Am. Chem. Soc.* **89**, 917 (1967).
3. Jencks W. P., Gilchrist M.: *J. Am. Chem. Soc.* **90**, 2622 (1968).
4. Blackburn G. M., Jencks W. P.: *J. Am. Chem. Soc.* **90**, 2638 (1968).
5. Schmir G. L.: *J. Am. Chem. Soc.* **90**, 3478 (1968).
6. Okuyama T., Pletcher T. C., Sahn D. J., Schmir G. L.: *J. Am. Chem. Soc.* **95**, 1253 (1973).
7. Satterthwait A. C., Jencks W. P.: *J. Am. Chem. Soc.* **96**, 7018 and 7031 (1974).
8. Schmir G. L., Cunningham B. A.: *J. Am. Chem. Soc.* **87**, 5692 (1965).
9. Chaturvedi R. K., Schmir G. L.: *J. Am. Chem. Soc.* **90**, 4413 (1968).
10. Pletcher T. C., Koehler S., Cordes E. H.: *J. Am. Chem. Soc.* **90**, 7072 (1968).
11. Kandel M., Cordes E. H.: *J. Org. Chem.* **32**, 3061 (1967).
12. McClelland R., Potter J. P.: *Can. J. Chem.* **58**, 2318 (1980).
13. Smith V. F., Schmir G. L.: *J. Am. Chem. Soc.* **97**, 3171 (1975).
14. Deslongchamps P., Dube S., Lebreux C., Patterson D. R., Taillefer J.: *Can. J. Chem.* **53**, 2791 (1975).
15. Caswell M., Schmir G. L.: *J. Am. Chem. Soc.* **101**, 7323 (1979).
16. Ref.<sup>7</sup>, p. 7041.
17. Yin-Nan Lee, Schmir G. L.: *J. Am. Chem. Soc.* **101**, 6277 (1979).
18. Braun J., Pinkernelle W.: *Chem. Ber.* **67**, 1218 (1934).
19. Wheeler O. H., Roman F., Santiago M. V., Quiles F.: *Can. J. Chem.* **47**, 503 (1969).
20. Wiberg K. B., Rowland B. T.: *J. Am. Chem. Soc.* **77**, 2205 (1955).
21. Rowe J. E.: *Synthesis* **1980**, 114.
22. McClelland A. R., Patel G.: *J. Am. Chem. Soc.* **103**, 6908 (1981).
23. Torck B., Hellin M., Coussemant F.: *Bull. Soc. Chim. Fr.* **1962**, 1657.
24. Bunnett J. F., Olsen F. P.: *Can. J. Chem.* **44**, 1899 (1966).
25. Cox R. A., Yates K.: *Can. J. Chem.* **61**, 2225 (1983).
26. Marziano N. C., Traverso P. G., Tomasin A., Passerini R. C.: *J. Chem. Soc., Perkin Trans. 2*, **1977**, 309.
27. Ritchie C. D.: *Acc. Chem. Res.* **5**, 348 (1972).
28. Ritchie C. D., Virtanen P. O.: *J. Am. Chem. Soc.* **94**, 1589 and 4966 (1972).

Translated by J. Panchartek.