

KINETIC ACIDITY FUNCTION AND SOLVOLYSIS OF 3-HYDROXY-1,3-DIPHENYLTRIAZENES

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Ten 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes have been synthesized, and kinetics of their solvolysis have been measured in 40% (v/v) ethanol and sulphuric acid. The concept of kinetic acidity function has been generalized, its construction has been suggested, and the procedure has been applied to the solvolysis of 3-hydroxy-1,3-diphenyltriazenes. The kinetic acidity function found has been confronted with the H_0 acidity function. The substituent effects have been evaluated with respect to mechanism of the acid catalyzed solvolysis.

The concept of acidity function was introduced by Hammett and Deyrup¹ who denoted it H . In this concept the acidity function represents an extrapolation of pH scale to media exhibiting non-ideal behaviour of components of the protonating or deprotonating medium and substrate. Definition of the acidity function is based on the equilibrium constant of the dissociation process

$$K = \frac{a_B a_{H^+}}{a_{BH^+}} = \frac{[B][H^+]}{[BH^+]} \cdot \frac{f_B \cdot f_{H^+}}{f_{BH^+}} \quad (1)$$

Taking the logarithms we obtain after modification

$$pK = \log \frac{[BH^+]}{[B]} - \log [H^+] - \log \frac{f_B f_{H^+}}{f_{BH^+}} = \log I + H, \quad (2)$$

where the symbol I denotes the measurable concentration ratio of the protonated to the non-protonated forms, and the symbol H denotes the acidity function. Using Eq. (2) and a series of structurally similar indicators (with constant ratio f_B/f_{BH^+} at a given concentration of acid) it is possible to construct the dependence of H function on the acid concentration. A difficulty consists in that the H function depends on the indicator. Several authors^{2,3} tried to remedy this fault by introduction of a general acidity function, so *e.g.* Cox and Yates³ in the following form:

$$pK = \log I - \log [H^+] - m^* X, \quad (3)$$

where m^* expresses sensitivity of the substrate (indicator) to the protonation, and X is a quantity only depending on the protonating acid and its concentration.

The whole derivation is only applied to acid–base equilibrium processes, but kinetic measurements are carried out, too, in non-ideal media of concentrated acids and bases. In this case it is usual to plot logarithm of the rate constants against a suitable acidity function. Troubles are encountered, if we must work with media whose acidity functions are not known. Therefore, several years ago Johnson and coworkers^{4–6} suggested the concept of kinetic acidity function. Their definition, however, is problematic in solving the connection with the pH scale. We tried to remove this drawback in the following way.

Basic idea of construction and, at the same time, applicability of acidity functions, generally, is that the indicators used (be it in equilibrium or in reaction) behave equally to the acidifying medium, *i.e.* that the ratio of activity coefficients is the same for all indicators at a given acid concentration. If the observed rate constant (k_{obs}) can be expressed as a product of catalytic rate constant k (which even can be composed of rate and equilibrium constants), the proton activity, and activity coefficients of the reacting components expressed summarily as f_s (they depend on the mechanism), it can be written

$$k_{\text{obs}} = ka_{\text{H}^+}f_s = k[\text{H}^+]f_{\text{H}^+}f_s. \quad (4)$$

Taking the logarithms we obtain after modification

$$\log k = \log k_{\text{obs}} - \log [\text{H}^+] - \log f_{\text{H}^+}f_s = \log k_{\text{obs}} + H_{\text{K}} \quad (5)$$

which is analogous to Eq. (2), the measurable quantity being k_{obs} . Similarly it is possible to express kinetic analogue of Eq. (3)

$$\log k = \log k_{\text{obs}} - \log [\text{H}^+] - m_{\text{K}}^* X_{\text{K}}. \quad (6)$$

Two points are decisive for construction of the kinetic acidity function. First it is necessary that the above-mentioned condition were fulfilled, *viz.* the constant ratio of the activity coefficients of the components taking part in the process until the rate-limiting step (inclusive of all indicators – substrates). At these conditions general procedure of construction of the acidity function⁷ can be used which is based on the relation (see Eq. (5))

$$\log k^{i+1} = \log k^i - \log k^{i+1} = \left(\int_{c_1}^{c_2} \log k_{\text{obs}}^i - \int_{c_1}^{c_2} \log k_{\text{obs}}^{i+1} \right) / (c_2 - c_1), \quad (7)$$

where c_1 and c_2 denote concentrations of the acid used between which the two indicators – substrates were measured.

The other point consists in the connection of the kinetic acidity function with the pH scale. For ideal medium it is

$$H_K = \text{pH} . \quad (8)$$

Introduction from Eq. (8) into Eq. (5) gives

$$\log k = \log k_{\text{obs}} + \text{pH} . \quad (9)$$

Thus it is sufficient to measure the kinetics with the substrate reacting in the region of pH scale. For the general construction according to Eq. (5) to be possible, it is necessary to define a hypothetical substrate to which the whole construction will be referred. It is most advantageous to postulate for this substrate

$$\log k^0 = 0 , \quad (10)$$

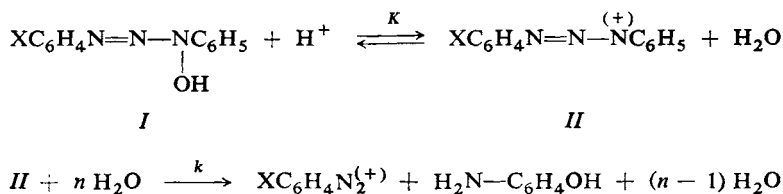
wherefrom introduction into Eq. (9) gives

$$\log k_{\text{obs}}^0 = -\text{pH} . \quad (11)$$

Practically this means to measure pH of diluted solutions of the protonating acid.

The above-given theory and construction of the acidity function was applied to acid catalyzed solvolysis of 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes *I* in 40% ethanol. The aim was to obtain the kinetic acidity function in 40% ethanol and sulphuric acid (no suitable acidity function has been found in literature), to compare it with the standard H_0 function in water, and, last but not least, to determine the catalytic constants and evaluate their dependence on substitution with regard to the reaction mechanism.

In the previous communication⁸ analogous models were dealt with involving the 3-alkyl derivatives and non-substituted 3-hydroxy-1,3-diphenyltriazene. On the basis of analysis of the dependences of k_{obs} on sulphuric acid concentration a mechanism was suggested which can also be presumed with the substrates *I* investigated (Scheme 1).



SCHEME 1

It is possible to derive the following dependence of the observed rate constant on the proton activity and water activity:

$$k_{\text{obs}} = kK a_{\text{H}^+} a_{\text{H}_2\text{O}}^n f_{\text{II}} / (a_{\text{H}_2\text{O}} f_{\text{II}} + K a_{\text{H}^+} f_{\text{I}}). \quad (12)$$

The dependence (12) has a somewhat more complicated form than that presumed for kinetic acidity function. First of all, in construction of H_K with the k_{obs} constant according to Eq. (12), logarithm of water activity will be involved in H_K . If the exponent n at the water activity is the same for all the substrates at a given water activity (acid concentration), then this fact represents no fault in the construction according to Eq. (7). If n is not the same, then its change will make itself felt with the individual substrates through an additional term Δn which will change values of the catalytic constants. The involvement itself of the water activity in the H_K term changes somewhat the meaning of this term in the sense of classical definition of the acidity function.

The denominator of expression (12) presents a more serious problem for construction as well as definition of the kinetic acidity function in this particular case. The reason lies in that the equilibrium constant (in the sense of the definition used here) is not a function of medium but only a function of the substrate. Consequently, the parts of kinetic acidity function obtained with different substrates need not generally link up. The construction of kinetic acidity function is only justified in a medium for which it is $K a_{\text{H}^+} f_{\text{I}} \ll a_{\text{H}_2\text{O}} f_{\text{II}}$, i.e. in the region in which the substrate is not protonated to a greater extent. Then Eq. (12) is simplified to

$$k_{\text{obs}} = kK a_{\text{H}^+} a_{\text{H}_2\text{O}}^{n-1} f_{\text{I}} \quad (13)$$

and the kinetic acidity function can be both constructed and defined with the above-mentioned restriction concerning the water activity.

EXPERIMENTAL

*Synthesis of phenylhydroxylamine*⁹: 49.2 g (0.4 mol) nitrobenzene was emulsified in 800 ml water and 25 g ammonium chloride. The mixture was stirred and treated with 62 g zinc powder during 25 min whereby the temperature increased to 65°C. After addition of zinc the mixture was stirred 50 min, the solution was filtered, and the residue was washed with hot water. The filtrate was cooled at 0°C and saturated with sodium chloride. The precipitated hydroxylamine was collected by suction and immediately used in subsequent reaction. Yield 40 g.

Synthesis of 1-(X-phenyl)-3-phenyl-3-hydroxytriazenes: 0.4 mol substituted aniline was diazotized in 140 ml concentrated hydrochloric acid and 100 ml water by addition of a solution of 28 g sodium nitrite in 140 ml water. The diazonium salt formed was added to 40 g phenylhydroxylamine suspended in 200 ml water. The mixture was stirred 2 h, the precipitate was collected by suction and dried in air. The solvents used for crystallizations, physical properties, and elemental analyses are given in Table I.

Kinetic measurements: 8 ml sulphuric acid solution in 40% (v/v) ethanol was tempered in a cell compartment of a Specord UV VIS spectrophotometer (Zeiss, Jena) at $25.0 \pm 0.1^\circ\text{C}$. Then $2.5 \mu\text{l}$ 0.2 mol l^{-1} solution of the substrate in dioxane was injected into the cell, and the content of the cell was mixed. The kinetics was followed up to 2–3 half-lives at the wavelength of the longest-wave maximum (Table I). Immediately after the reaction the sulphuric acid concentration in the reaction mixture was determined titrimetrically. The kinetic measurements were evaluated according to ref.¹⁵.

Construction of the kinetic acidity function: In the sulphuric acid concentration range from 0.012 to 0.139 mol l^{-1} pH was measured with the system glass–calomel electrodes using an RTS 622 apparatus (Radiometer, Copenhagen). These values were taken as basis for the construction of the acidity function according to Eq. (11). The remaining part of the kinetic acidity function was constructed with the help of the observed rate constants measured according to Eqs (5) and

TABLE I

The solvents used for recrystallization, physical properties, and elemental analyses of 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes $\text{XC}_6\text{H}_4\text{N}=\text{N}-\text{N}(\text{OH})\text{C}_6\text{H}_5$

X	Solvent Yield, %	M.p. exp., °C M.p. ret., °C	Formula (Mol. mass)	Calculated Found	%N	λ nm
H	hexane 63	126–127 125 ^a , 126 ^b , 127 ^c	$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$ (213.2)	— —	—	355
4-CH ₃ O	cyclohexane 56	114–116 105 ^d	$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2$ (243.2)	17.27 16.89	—	350
4-CH ₃	heptane 58	135–137 —	$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$ (227.5)	18.47 18.64	—	355
3-CH ₃ O	cyclohexane 56	112–114 —	$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2$ (243.2)	17.27 16.93	—	351
4-Cl	hexane 46	160–161 148 ^a	$\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}$ (247.7)	16.97 16.51	—	352
4-Br	hexane 67	162–164 154 ^a	$\text{C}_{12}\text{H}_{10}\text{BrN}_3\text{O}$ (292.1)	14.38 14.25	—	351
3-Cl	hexane 49	160–162 —	$\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}$ (247.7)	16.97 17.21	—	350
3-Br	hexane 54	157–159 —	$\text{C}_{12}\text{H}_{10}\text{BrN}_3\text{O}$ (292.1)	14.38 14.59	—	345
3-NO ₂	ethanol 65	191–192 —	$\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_3$ (258.2)	21.69 21.35	—	362
4-NO ₂	ethanol 49	188–189 —	$\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_3$ (258.2)	21.69 21.62	—	375

^a Ref.¹⁰; ^b ref.¹¹; ^c refs^{12,13}; ^d ref.¹⁴.

(7). The calculation was carried out according to the program KINAC which represents a modified version of the program ACID⁷.

RESULTS AND DISCUSSION

Dependence of the observed rate constants on concentration of sulphuric acid has an increasing character in contrast to the earlier-studied 3-hydroxy-1-phenyl-3-alkyl(phenyl)triazenes in aqueous sulphuric acid where the same dependence was cone-shaped with the peak at the sulphuric acid concentration of 4–10 mol l⁻¹. The kinetic measurements carried out in this work fall in the acid concentration region where the substrate is not significantly protonated, and, therefore, the observed rate constant can be interpreted according to Eq. (13). This presumption is confirmed by a very good linking of the curves of corresponding substrates after application of the construction procedure (the KINAC program, Fig. 1). The resulting kinetic acidity function can be described by an orthogonal polynomial ($z = \log c_{\text{H}_2\text{SO}_4}$, c in mol l⁻¹) in the following form:

$$H_K = -0.08056719 + 0.61852958z + 0.09594239z^2 + 0.29510650z^3 + \\ + 0.06794214z^4 - 0.06706820z^5 - 0.01725295z^6 + \\ + 0.00373056z^7 + 0.00097481z^8. \quad (14)$$

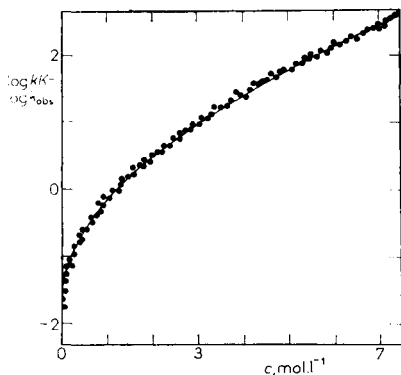


FIG. 1

Dependence of the difference ($\log kK - \log k_{\text{obs}}$) of solvolysis of 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes (in 40% (v/v) ethanol at 25°C) on concentration of sulphuric acid

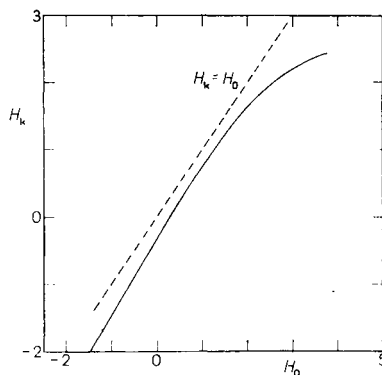


FIG. 2

Dependence of kinetic acidity function (constructed on 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes in sulphuric acid and 40% (v/v) ethanol) on H_0

As available literature describes no acidity function in 40% (v/v) ethanol and sulphuric acid, a direct comparison is impossible. Therefore, we chose for the basis the standard H_0 function by Paul and Long¹⁶. As shown in Fig. 2, dependence of the kinetic acidity function H_K constructed by us on the H_0 function is not linear, and, in addition to it, it is shifted downwards as compared with the straight line $H_K = H_0$. The shift agrees with the presumption that addition of organic solvent suppresses dissociation of the acid, and, hence, sulphuric acid represents a weaker acid in 40% (v/v) ethanol than in water. A distinct deviation of the dependence from the straight line $H_K = H_0$ in downward direction can be observed from about 4 mol l^{-1} sulphuric acid. This fact is an obvious consequence of involvement of the water activity (following from the reaction mechanism) in the H_K function. In addition, the water activity begins to decrease markedly in this acid concentration region. This decomposition of the H_K function can be expressed by the equation

$$H_K = -(0.36 \pm 0.01) + (1.23 \pm 0.02) H_0 - (2.72 \pm 0.18) \log a_{\text{H}_2\text{O}}. \quad (15)$$

TABLE II

Catalytic rate constants of solvolysis of 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes in sulphuric acid and 40% (v/v) ethanol at 25°C (in brackets given is the number of k_{obs} for each substrate)

X	H (10)	4-CH ₃ O (19)	4-CH ₃ (18)	3-CH ₃ O (26)	4-Cl (20)
k	$3.98 \cdot 10^{-3}$	$5.89 \cdot 10^{-2}$	$1.07 \cdot 10^{-2}$	$8.51 \cdot 10^{-4}$	$2.95 \cdot 10^{-4}$
X	4-Br (22)	3-Cl (21)	3-Br (24)	3-NO ₂ (23)	4-NO ₂ (14)
k	$3.47 \cdot 10^{-4}$	$8.32 \cdot 10^{-5}$	$1.12 \cdot 10^{-4}$	$1.12 \cdot 10^{-5}$	$1.86 \cdot 10^{-5}$

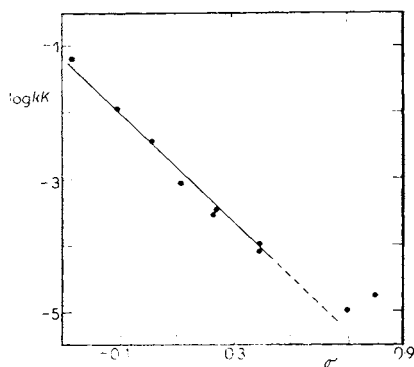


FIG. 3

Dependence of the catalytic constants kK of solvolysis of 3-hydroxy-1-(X-phenyl)-3-phenyltriazenes in sulphuric acid and 40% (v/v) ethanol at 25°C on the Hammett substituent constants

According to Eq. (13) the coefficient at the term $\log a_{\text{H}_2\text{O}}$ represents an estimate of the number of water molecules in the transition state.

During construction of the kinetic acidity function we also determined the catalytic constants in the form of product kK (Table II). Their dependence on the Hammett σ substituent constants is given in Fig. 3, wherefrom it can be seen that the catalytic constants of both the nitro derivatives markedly deviate from the usual linear dependence (the 4-isomer more than the 3-isomer). These deviations are explained usually by a change in the rate-limiting step or in mechanism. In the case studied the second alternative seems more likely, because formation of nitrenium cation (Scheme 1) from the substrates containing electron-acceptor substituents will be at least difficult if not impossible. The higher value of catalytic composed constant found with the 4-nitro derivative (as compared with the 3-isomer) indicates a mechanism with participation of a nucleophile and without a pre-equilibrium producing cationic forms. It is interesting that no anomalies can be observed in construction of the acidity function, and the parts corresponding to the individual substrates (inclusive of the nitro derivatives) link up very well (Fig. 2).

The linear regression of $\log kK$ from Table II (except the nitro derivatives) on the Hammett σ constants¹⁷ gives the equation

$$\log kK = -(1.312 \pm 0.087) - (4.335 \pm 0.378) \sigma. \quad (16)$$
$$n = 8 \quad s = 0.231 \quad r = 0.990$$

The large value of the reaction constant ρ supports the hypothesis about the reaction mechanism with participation of the nitrenium cation as the intermediate (Scheme 1). As the reaction constant is composed of two contributions, the ρ value of the nucleophilic attack being presumably positive or small negative (formation of the diazonium salt), the reaction constant of the pre-equilibrium has rather large negative value. For comparison, *e.g.* the value found¹⁸ for acid catalyzed decomposition of 3-methyl-1-(X-phenyl)-3-phenyltriazenes in 40% ethanol is $\rho = -3.68$, for symmetrically disubstituted 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes in water^{19,20} $\rho = -3.19 (\sum \sigma)$.

All the facts given confirm correctness of the choice of mechanism of acid decomposition of 3-hydroxytriazenes in the previous communication⁸ and also its validity for substituted 3-hydroxy-1,3-diphenyltriazenes.

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