A MATHEMATICAL MODELLING OF ACID CATALYZED DECOMPOSITION OF 3-METHYL-1,3-DIPHENYLTRIAZENE

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The effect of acids on the decomposition of 3-methyl-1,3-diphenyltriazene has been studied in aqueous ethanol (40% (v/v) ethanol). The dependences found between the rate constant and acid concentration have been analyzed by means of non-linear regression using models including the specific and general catalysis and formation of associates between the substrate and the buffer components. The substrate has been found to form electrostatic associates with the conjugated base of acid. The complex formed is decomposed with the assistance of the proton or a general acid in the rate-limiting step to form the product. The Brönsted coefficient $\alpha = 0{\cdot}81$ has been found. Investigation of the activation parameters supports the earlier conclusions, indicating a dependence between the reaction mechanism and composition of the aqueous organic solvent.

Two previous communications dealt with the acid-catalyzed decomposition of 3-methyl-1,3-diphenyltriazenes[1,2], one of them[1] analyzing the substituent effects in 1-phenyl group and the other examining the effect of substitution in the 3-phenyl group and disubstitution[2] as well as sensitivity to the leaving group. In accordance with some conclusions of other authors (an analysis of possible mechanisms is presented in the first part[1] of this series), the most probable decomposition mechanism suggested involves the proton transfer and splitting of nitrogen–nitrogen bond of the triazene chain in the rate-limiting step (the so-called A-S_E2 mechanism).

The aim of this work is a study of general acid catalysis and activation parameters as a source of further information for suggestion of a probable mechanism. On the basis of the definition of general catalysis, the term acid is used in this work to denote a compound which can transfer its proton to the reaction centre of the substrate in the rate-limiting step.

EXPERIMENTAL

The technique of measurements and evaluation of kinetic experiments were described in the previous communication[1]. The effect of temperature on the rate constant was studied in the temperature region from 25°C to 55°C at 4 temperature values for 5 selected substituted derivatives at pH 3·56. Three kinetic runs were measured at each temperature which was measured in the cell and maintained with the accuracy of ±0·1°C.

The kinetic measurements of general acid catalysis in decomposition of 3-methyl-1,3-diphenyltriazenes were carried out in 40% (v/v) ethanolic-aqueous buffers prepared from chloroacetic, formic, and succinic acids and potassium hydroxide for 5 different analytical concentrations of the acids (about 0·2, 0·1, 0·05, 0·025, and 0·0125 mol l^{-1}) and 2 different pH values. The ionic strength of the buffers was adjusted at $I = 0·2$ mol l^{-1} by addition of sodium chloride. The precise analytical concentration of general acid in a buffer was determined (along with the pK value) by titration with a sodium hydroxide solution using an RTS 622 apparatus (Radiometer, Copenhagen). The same apparatus was also used to determine pH; the standard buffers for 40% ethanol were taken from ref.[3].

RESULTS AND DISCUSSION

Table I presents the rate constants obtained by evaluation of the kinetic experiments for various pH values and analytical concentrations of acids. The analysis of the dependences shows that the case studied is not a simple type of general catalysis but represents a type involving an additional formation of a complex between the sub-

TABLE I

The dependence of decomposition rate constants of 3-methyl-1,3-diphenyltriazene on the total analytical concentration of the general acid

Chloroacetic acid			Formic acid			Succinic acid		
pH	$10^2 c_{HA}$ mol dm^{-3}	$10^2 k$ s^{-1}	pH	$10^2 c_{HA}$ mol dm^{-3}	$10^2 k$ s^{-1}	pH	$10^2 c_{HA}$ mol dm^{-3}	$10^2 k$ s^{-1}
3·89	21·2	10·4	4·15	15·8	5·95	4·25	22·9	3·83
3·89	21·2	9·80	4·15	15·8	6·12	4·25	22·9	4·12
3·87	11·0	9·58	4·15	8·30	5·74	4·25	10·6	3·71
3·87	11·0	9·81	4·15	8·30	5·65	4·25	10·6	3·53
3·86	5·64	9·37	4·15	3·80	5·52	4·25	5·54	3·46
3·86	5·64	9·04	4·15	3·80	5·43	4·24	2·95	3·00
3·87	2·82	8·49	4·16	2·05	5·14	4·33	1·59	2·77
3·87	2·82	8·74	4·16	2·05	5·12	4·33	1·59	3·00
3·91	1·41	7·90	4·19	1·10	4·27	4·80	25·9	1·25
3·91	1·41	7·59	4·19	1·10	4·60	4·80	25·9	1·19
—	—	—	4·76	20·8	1·58	4·80	13·2	1·13
—	—	—	4·76	20·8	1·52	4·80	6·72	1·11
—	—	—	4·73	10·5	1·45	4·80	6·72	1·12
—	—	—	4·73	10·5	1·46	4·80	3·40	1·07
—	—	—	4·72	5·13	1·35	4·80	3·40	1·10
—	—	—	4·74	2·68	1·33	4·82	1·75	0·97
—	—	—	4·74	2·68	1·32	4·82	1·75	0·98
—	—	—	4·75	1·28	1·22	—	—	—
—	—	—	4·75	1·28	1·20	—	—	—

strate and components formed from the acid at the given pH. The shape of the curve reminds of the special salt effect observed in the acetolysis of threo-3-*p*-anisyl-2-butyl-*p*-bromobenzenesulphonate in the presence of lithium perchlorate[4]. Although the previous studies[5] showed a positive salt effect in the hydrolysis of 3-acyl derivatives of 1,3-diphenyltriazene, the acceleration of the reaction was smaller and depended on the salt type. Nevertheless, the study[5] of the salt effects indicated a possibility of existence of ionic pairs and, hence, a possibility of formation of various associates. The association of the components of the acid, which is responsible for the effect observed, can take several ways. If a complex is formed with the substrate, we can presume *e.g.* the addition of the acid molecule (HA) or its conjugated base (A^-) with formation of the conjugated base. If the complex is formed with the already protonated substrate, it is only possible to presume the addition of the conjugated base of the acid or addition of the acid molecule with liberation of the proton. The possible combinations are presented in Eqs (*A*)–(*F*), where S denotes 3-methyl-1,3-diphenyltriazene.

$$S + HA \rightleftharpoons SHA \tag{A}$$

$$S + A^- \rightleftharpoons SA^- \tag{B}$$

$$S + HA \rightleftharpoons SA^- + H^+ \tag{C}$$

$$S + HA \rightleftharpoons SH^+ + A^- \tag{D}$$

$$SH^+ + A^- \rightleftharpoons SHA \tag{E}$$

$$SH^+ + HA \rightleftharpoons SHA + H^+ \tag{F}$$

The schemes given in Eqs (*A*), (*E*), and (*F*) are kinetically indistinguishable, and the same is true of (*B*) and (*C*). Scheme (*D*) does not describe the "saturation" effect. The complexes formed can be decomposed in several ways: spontaneously, with the assistance of acid, or with the proton participation. The possible combinations are presented in Eqs (*G*)–(*L*).

$$SHA \rightarrow P \tag{G}$$

$$SHA + HA \rightarrow P \tag{H}$$

$$SHA + H^+ \rightarrow P \tag{I}$$

$$SA^- \rightarrow P \tag{J}$$

$$SA^- + HA \rightarrow P \tag{K}$$

$$SA^- + H^+ \rightarrow P \tag{L}$$

The spontaneous decompositions (*G*) and, especially, (*J*) can be considered little probable; in addition, the analysis of the expression for the observed rate constant indicates the independence of the pH of medium at high acid concentrations, which contradicts the experimental results. Moreover, it is obvious that if the decomposition types (*H*) and (*K*) are operating, they are accompanied by (*I*) and (*L*), because the proton is a stronger acid than HA.

Last but not least, the fact must be considered that the decomposition depends on the proton concentration (the first power), which – in the case given – can be described by the kinetically indistinguishable schemes (*M*) and (*N*)–(*O*).

$$\mathrm{S} + \mathrm{H}^+ \rightarrow \mathrm{P} \tag{M}$$

$$\mathrm{S} + \mathrm{H}^+ \rightleftharpoons \mathrm{SH}^+ \tag{N}$$

$$\mathrm{SH}^+ \rightarrow \mathrm{P} \tag{O}$$

From the analysis it follows that the model of the acid catalyzed decomposition of 3-methyl-1,3-diphenyltriazenes with participation of an acid must involve the equations (*M*) or (*N*) and (*O*) and further the decompositions type (*I*), (*K*), or (*H*), (*I*), or (*K*), (*L*) preceded by the equilibria (*A*)–(*F*).

If the individual pathways are described with the corresponding equilibrium and rate constants, the reaction rate being limited by the rate of the slowest step, all the reaction steps until the rate-limiting step are considered as rapid equilibria, and if all actual concentrations of compounds (denoted by square brackets) are expressed by means of the overall analytical concentrations (denoted as c_i), then the expressions can be obtained for the observed rate constants. In principle, two equations can be derived for description of the dependence of the observed rate constant on the concentration of the reacting components (a, b, c, d are constants with different meaning, see below).

$$k_{\mathrm{obs}} = (a[\mathrm{HA}]\, c_{\mathrm{H}^+} + b[\mathrm{HA}]^2 + cdc_{\mathrm{H}^+})/(d + [\mathrm{HA}]) \tag{1}$$

$$k_{\mathrm{obs}} = (a[\mathrm{HA}]\, c_{\mathrm{H}^+} + b[\mathrm{HA}]^2 + cd(c_{\mathrm{H}^+})^2)/(dc_{\mathrm{H}^+} + [\mathrm{HA}]) \tag{2}$$

The actual concentration of the non-dissociated component HA is given by the expression:

$$[\mathrm{HA}] = c_{\mathrm{HA}}c_{\mathrm{H}^+}/(K_{\mathrm{HA}} + c_{\mathrm{H}^+})\,, \tag{3}$$

where c_{HA} represents the analytical concentration of the acid, and K_{HA} means its dissociation constant defined as follows:

$$K_{\mathrm{HA}} = c_{\mathrm{H}^+}[\mathrm{A}^-]/[\mathrm{HA}]\,. \tag{4}$$

The non-linear regression of the experimental data (with application of the rate constants of Table I and ref.[1]) according to Eqs (*1*) and (*2*) with application of Eq. (*3*) and experimental dissociation constants (pK_{HA}: chloroacetic acid 3·49, formic acid 4·12, succinic acid to the first degree 4·93) gave the overall standard deviations listed in Table II. Application of the published[6] pK_{HA} values of chloroacetic acid (3·69), formic acid (4·35), and succinic acid (4·97) gave only slightly different results. Table II shows that the difference in the standard deviations for all the experimental series (succinic acid) with the models (*1*) and (*2*) is not always unambiguous. Nevertheless, the model (*1*) clearly leads to a negative value of the *d* parameter, whereas the model (*2*) only gives positive values of the parameters. The regression parameters of the model (*2*) are also summarized in Table II for three general acids used. The statistical characteristics show an excellent agreement with the experimental data within their accuracy.

The regression model (*2*), which appears to be most suitable on the basis of the experimental data used, represents four kinetically indistinguishable mechanisms involving the pre-equilibrium (*B*) or (*C*) and decompositions (*K*), (*L*), and (*M*) or (*N*), (*O*). As the system of the reagents exhibits the general catalysis, we consider the proton participation in the rate limiting step according to Eq. (*M*) to be more probable, the substrate reacting in the form of a complex with basic components of the solvents. This conclusion is supported by the values of the parameters *a* and *c* in Eq. (*2*). If the bond to the proton is formed in the rate-limiting step, then *a* represents the rate constant of the reaction of the proton with the complex substrate – conjugated base, and *c* represents the rate constant of the reaction of the proton with the complex substrate–basic component of the solvent. The roughly double value of the *a* parameter as compared with *c* represents a reasonable relation. If the protonation of the substrate takes place in the pre-equilibrium, then the *c* parameter represents the ratio of the rate constant of decomposition of the protonated substrate

TABLE II

The overall standard deviations (*s*) (Eqs (*1*) and (*2*)) and the regression parameters (*a*, *b*, *c*, *d*) of the model (*2*) obtained by non-linear regression for the individual experimental series

Quantity	Chloroacetic acid	Formic acid	Succinic acid
$s(1)$	$1{\cdot}8353 \,.\, 10^{-2}$	$1{\cdot}1533 \,.\, 10^{-2}$	$1{\cdot}6883 \,.\, 10^{-3}$
$s(2)$	$1{\cdot}9953 \,.\, 10^{-3}$	$2{\cdot}0345 \,.\, 10^{-3}$	$1{\cdot}7663 \,.\, 10^{-3}$
$a(2)$	$6{\cdot}3430 \,.\, 10^{2}$	$7{\cdot}9796 \,.\, 10^{2}$	$6{\cdot}2056 \,.\, 10^{2}$
$b(2)$	$3{\cdot}2760 \,.\, 10^{-1}$	$5{\cdot}1600 \,.\, 10^{-2}$	$2{\cdot}2761 \,.\, 10^{-2}$
$c(2)$	$2{\cdot}7022 \,.\, 10^{2}$	$2{\cdot}8746 \,.\, 10^{2}$	$5{\cdot}3584 \,.\, 10^{1}$
$d(2)$	$1{\cdot}6767 \,.\, 10^{0}$	$2{\cdot}2127 \,.\, 10^{1}$	$5{\cdot}3584 \,.\, 10^{1}$

and the constant of dissociation of the protonated substrate into its components. The dissociation constant is inaccessible experimentally, but it must be high (up to pH of about 2·6 there is no curvature in the pH profile[1]), perhaps higher than that for diphenylamine (pK 0·64; ref.[7]). The rate constant of the decomposition according to Eq. (*O*) would be at least comparable with or rather greater than that of the generally proton-catalyzed decomposition of the substrate–base complex. Although this result is not excluded, it seems to be less probable in comparison with the reasons for the proton transfer in the rate-limiting step (see also refs[1,2]).

It is impossible to suggest a probable way of formation of the SA^- complex from the kinetic data, it is even possible that the reactions of the substrate with the conjugated base (Eq. (*B*)) and with the acid molecule (Eq. (*C*)) proceed side by side. In both the cases the a parameter of Eq. (*2*) (Table II) means the rate constant of decomposition of the SA^- complex with the proton assistance in the rate-limiting step, the b parameter means the rate constant of the decomposition of the SA^- complex with catalysis of the acid HA, and the meaning of the c parameter has already been discussed. If the pre-equilibrium (*C*) makes itself felt, then the d parameter means the equilibrium constant of the decomposition of the complex into the products.

The values of Table II indicate increasing instability of the complex with decreasing acidity of the general acid and, hence, increasing basicity of the conjugated base. This result can be interpreted by the base and substrate forming a merely electrostatic associate which depends only on the charge and not on the basicity or nucleophilicity of the acid anion. With decreasing strength of the acid the base shows increasing tendency to bind the proton and, hence, the complex shows increasing tendency to decomposition. In the case of formation of the complex according to Eq. (*B*) the d parameter is given by the product of the equilibrium constant of decomposition of the complex and dissociation constant of the acid, *i.e.* for the chloroacetic, formic, and succinic acids it is $5{\cdot}39 \,.\, 10^{-4}$, $1{\cdot}7 \,.\, 10^{-3}$, and $6{\cdot}33 \,.\, 10^{-4}$, resp. These values roughly reflect sterical requirements of the bases at relative independence of the basicity of the conjugated bases, the reasons being the same as in the previous case. This section can be concluded by the statement that the substrate exists in the solution in the form of ionic pairs (as already suggested[5]), the anions of general acid (by their electrostatic action) facilitating the formation of the diazonium ion and, hence, the splitting of the bond between nitrogen atoms in the triazene chain. Obviously, this effect is more distinct than the salt effect due to anions of strong mineral acids. At the same time, this explains the non-unit slopes found in the study of pH effects on the decomposition of 3-methyl-1,3-diphenyltriazenes[1,2], because at higher pH the reaction solution contains a greater amount of negatively charged components. This leads to a small (as compared with the pH effect) but perceptible increase of the rate constant and, hence, decrease of the slope of the dependence of log k_{obs} on pH.

As already stated above, the *b* parameter of Eq. (2) represents the rate constant of general acid catalyzed decomposition of the base–substrate complex. A statistical estimate of the Brönsted coefficient $\alpha = 0{\cdot}81$ can be obtained from the dependence of logarithm of this constant on logarithm of the dissociation constant of the acid. This value indicates a large extent of the proton transfer to the substrate in the transition state of the rate-limiting step. A somewhat lower value ($\alpha = 0{\cdot}71$) was

TABLE III

The temperature dependence of the decomposition rate constant of derivatives of 3-methyl-1,3-diphenyltriazene (X^1—C_6H_4—N=N—N(CH_3)—C_6H_4—X^2) in aqueous 40% (v/v) ethanol at pH 3·56

T °C	10^3k, s^{-1}				
	I, X = H	*II*, X^1 = 4-CH_3	*III*, X^1 = 4-Cl	*IV*, X^2 = 4-CH_3	*V*, X^2 = 4-Cl
25·0	1·28	4·88	20·6	3·07	45·7
25·0	1·97	4·46	18·1	2·79	49·3
25·0	1·34	3·89	16·6	2·71	51·4
35·0	2·69	10·3	61·6	7·11	131
35·0	2·67	11·0	74·2	7·04	138
35·0	2·79	10·9	79·8	6·96	113
45·0	10·8	19·0	104	12·5	249
45·0	10·7	19·1	117	12·2	242
45·0	10·2	24·3	111	12·7	249
55·0	12·2	51·2	296	25·4	448
55·0	12·8	50·9	225	25·9	433
55·0	14·2	54·3	226	24·6	439

TABLE IV

The activation enthalpy $\Delta H^{\ddagger}$ and entropy values $\Delta S^{\ddagger}$ of the acid-catalyzed decomposition of 3-methyl-1,3-diphenyltriazene derivatives X^1—C_6H_4—N=N—N(CH_3)—C_6H_4—X^2 in aqueous 40% (v/v) ethanol at pH 3·56

Derivative	X^1	X^2	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
I	H	H	63·64 ± 5·73	−86·60 ± 18·44
II	4-CH_3	H	65·73 ± 3·02	−69·63 ± 9·71
III	4-Cl	H	69·18 ± 5·84	−83·42 ± 18·69
IV	H	4-CH_3	54·01 ± 3·29	−111·82 ± 10·52
V	H	4-Cl	59·64 ± 3·96	−107·99 ± 12·66

found in the study[8] of the acid-catalyzed decomposition of 1-phenyl-3-propyltriazene in water. Also the isotope effect found[9] in the decomposition of methylaryltriazenes in non-aqueous media catalyzed with benzoic acid supports the existence of general acid catalysis (k_H/k_D = 2·47).

Table III presents the rate constants obtained from kinetic experiments of the acid-catalyzed decomposition of five substituted derivatives of 3-methyl-1,3-diphenyltriazene at various temperatures. The activation enthalpies and entropies calculated therefrom are given in Table IV. From Table IV it is seen that the activation entropies are markedly negative. This finding disagrees with the results obtained[10] for the decomposition of some 3-methyl-1,3-diphenyltriazenes in 95% methanol: The activation entropies found in these cases are in the range from 5·0 to 23·7 J mol^{-1}. . K^{-1}. As the negative entropy values found by us correspond well with the idea of formation of the associates observed in the studies of general acid catalysis, the positive activation entropies indicate a change of the mechanism or of the way of solvation of the transition state in the rate-limiting step. It is possible that the decreasing solvation stabilization of both the diazonium ion formed and the proton will cause an almost complete proton transfer to the substrate in the transition state and/or a formation of the protonated substrate as the intermediate (a charge in the mechanism). As the proton represents the most highly solvated particle in the system, the processes described will make themselves felt by a release of the proton solvation entropy and/or an entropy increase due to the decomposition. This hypothesis is supported by the above-mentioned increase in the Brönsted coefficient α found if the reaction is transferred from water to 40% ethanol.

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