

**KINETICS AND MECHANISM OF DECOMPOSITION  
OF 1,3-BIS(4-METHYLPHENYL)TRIAZENE  
CATALYZED WITH SUBSTITUTED BENZOIC ACIDS  
IN 25% AQUEOUS METHANOL – GENERAL OR SPECIFIC CATALYSIS?**

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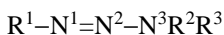
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The kinetics of decomposition of 1,3-bis(4-methylphenyl)triazene catalyzed with 13 substituted benzoic acids of various concentrations have been measured in 25 vol.% aqueous methanol at 25.0 °C. The rate constants observed (297 data) have been used as values of independent variable in a series of models of the catalyzed decomposition. For the catalytic particles were considered the undissociated acid, its conjugated base, and the proton in both the specific and general catalyses. Some models presumed formation of reactive or nonreactive complexes of the individual reactants. The substituent effect is described by the Hammett equation. The statistically best model in which the observed rate constant is a superposition of a term describing the dependence on proton concentration and a term describing the dependence on the product of concentrations of proton and conjugated base is valid with the presumption of complete proton transfer from the catalyst acid to substrate, which has been proved. The behaviour of 4-dimethylamino, 4-amino, and 3-amino derivatives is anomalous (lower catalytic activity as compared with benzoic acid). This supports the presumed participation of conjugated base in the title process.

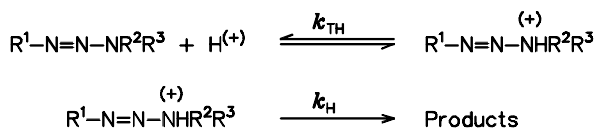
Triazene derivatives of general formula *I*



*I*

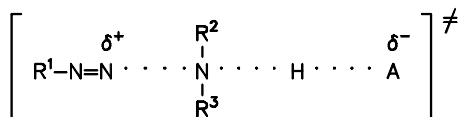
are interesting for their biological activity<sup>1,2</sup> and high substituent (R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup>)-dependent sensitivity to electrophiles such as metal ions<sup>3</sup>, diazonium salts<sup>4</sup> and especially the proton<sup>5-23</sup>. Being well soluble, triazenes can be submitted to acid-catalyzed decomposition in a wide variety of solvents from alkanes to aqueous-organic mixtures. This also enables applications of triazenes as indicators of acid-base behaviour of organic acids

in nonaqueous solvents<sup>5,6</sup>. On the other hand, the solvent used, due to preferred solvation of the proton, affects the mechanism of acid-catalyzed decomposition of triazene derivatives, hence several mechanisms can operate. Even if the discussion is restricted to the alkyl and aryl derivatives, literature gives arguments for two basic mechanism at least, viz. specific catalysis<sup>7-15</sup> (A1) and general acid catalysis<sup>5,6,6-23</sup> (A-S<sub>E</sub>2). The mechanism involving specific acid catalysis presumes the protonation of N<sup>3</sup> atom of triazene chain in a fast pre-equilibrium and the decomposition of the intermediate formed in a subsequent rate-limiting step (Scheme 1). On the other hand, the mechanism of general acid catalysis involves simultaneous proton transfer to N<sup>3</sup> atom and



SCHEME 1

splitting of N<sup>2</sup>-N<sup>3</sup> bond (Scheme 2). In both cases the products include the corresponding diazonium salts and amines, i.e. components from which triazenes can be prepared. Generally speaking, the two mechanisms mentioned represent limit cases, and any real reaction course can well be realized involving a certain extent of proton transfer to N<sup>3</sup> atom and another extent of N<sup>2</sup>-N<sup>3</sup> bond splitting. The data published so far suggest that 3-alkyltriazenes (having rather basic N<sup>3</sup> atom) more likely undergo the decomposition by a mechanism close to Scheme 1 in aqueous medium<sup>13-15</sup>. A mechanism involving slow proton transfer from the catalyst acid to substrate and subsequent fast decomposition to products<sup>12</sup> can be considered highly unlikely.



SCHEME 2

In the case of 1,3-diaryltriazenes, which represent the subject of our studies<sup>5,6,19,20,23</sup>, the interpretation of experiments carried out so far rather indicates general acid catalysis. In this case probably the N<sup>3</sup> atom is very little basic, which can be supported by the following consideration. In the first approximation, the structure of 1,3-diphenyltriazene can be derived from that of diphenylamine with an azo group inserted be-

tween nitrogen atom and phenyl group. The basicity of diphenylamine in water is expressed<sup>24</sup> by the value  $pK_a = 0.643$ . The lowering of basicity due to the insertion of azo group can be estimated from the difference of dissociation constants of 1,3-diphenyltriazene<sup>11</sup> ( $pK_a = 13.26$ , 20% ethanol) and diphenylamine<sup>25</sup> ( $pK_a = 22.4$ , dimethyl sulfoxide–water) which, irrespective of the solvent change, is about 9 pK units. From this consideration it is possible to assess the value of  $pK_a \approx -8$  for protonated 1,3-diphenyltriazene. The experimentally determined<sup>11</sup> sum of logarithm of rate constant of decomposition of protonated substrate and its  $pK_a$  is 4.55, hence the rate constant  $k_H$  in Scheme 1 shifts to the region of diffusion-controlled reactions. Therefrom it follows that the formation of protonated intermediate is little likely or, if it is formed, it is decomposed very quickly. Relatively significant arguments in support of the role of general acid and its dimer as proton donors in the A-S<sub>E</sub>2 mechanism were found<sup>5,6</sup> in the decomposition of 1,3-bis(4-methylphenyl)triazene (*I*,  $R^1 = R^2 = 4\text{-CH}_3\text{C}_6\text{H}_4$ ,  $R^3 = \text{H}$ ) in media of organic solvents with trichloroacetic acid. Studies of decomposition of the same substrate with benzoic acid in aqueous-methanolic solvents<sup>22</sup> confirmed the participation of both types of catalysis. The rate of one of them depends on square root of analytical concentration of catalyst acid and it probably corresponds to the catalysis by the proton. The rate of the second catalysis type was directly proportional to the analytical concentration of catalyst acid and this observation was interpreted by general acid catalysis with benzoic acid. The extent of operation of the two catalysis types depends distinctly on the composition of mixed solvent. The rate constant of the catalysis by general acid was always smaller and decreased monotonously with increasing amount of methanol. The rate constant of the corresponding catalysis by the proton has its lowest value in 80% aqueous methanol, which corresponds to the most efficient solvation and hence also deactivation of the proton by solvent. Such an effect could not be observed in the specific acid catalysis.

Our previous study<sup>23</sup> dealt with the decomposition of 1-phenyl-3,3-dialkyltriazenes with bulky pivalic acid in 40 vol.% ethanol and stated a formation of nonreactive adducts between the substrate and catalyst acid, hence only the reaction with proton led to the decomposition. Such effects were observed neither in the reaction with benzoic acid in aqueous methanol<sup>22</sup> and organic solvents<sup>17</sup> nor in that with trichloroacetic acid in a series of 17 individual organic solvents (from cyclohexane to methanol)<sup>5,6</sup>. This indicates that, in addition, the reaction course at the molecular level depends on the strength and steric capabilities of the catalyst acid involved in the rate-limiting step. The role of catalyst acid was also investigated with the help of the kinetic isotope effect. Its value  $k(\text{C}_6\text{H}_5\text{COOH})/k(\text{C}_6\text{H}_5\text{COOD}) = 2.47$  for the decomposition of 1,3-bis(4-methylphenyl)triazene in chloroform<sup>16</sup> clearly indicates the general specific catalysis. On the other hand, the inverse solvent effect  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 0.37$  found in aqueous buffers was interpreted<sup>14</sup> in favour of specific acid catalysis. A study of substituent effects of catalyst benzoic acid upon the decomposition of 1,3-bis(4-methylphe-

nyl)triazene in chloroform<sup>16</sup> gave the value of  $\rho = 1.14$ , i.e. smaller than usual  $\rho$  values in nonaqueous solvents<sup>26</sup>. A similar later study of decomposition of 1-aryl-3-alkyldi-phenyltriazenes with arylacetic acids in acetone<sup>21</sup> gave the value of  $\rho = 0.35$ , i.e. again smaller than that in water ( $\rho = 0.562$ , ref.<sup>27</sup>) and other solvents<sup>28</sup>. Both the papers mentioned indicate that the proton is not completely transferred to the triazene in the transition state of reaction.

A special, not yet quite elucidated effect consists in the role of nucleophiles and/or bases in the acid catalyzed decomposition of triazenes. If the cases involving an attack by nucleophile at an aliphatic carbon atom bound to the triazene chain<sup>14,29</sup> are excluded, there still exist a number of arguments<sup>14,20,30</sup> in favour of participation of nucleophile and/or base in the process of decomposition of triazene. In protic solvents the role of nucleophile is played probably by the solvent molecule and, in general, by the anion of catalyst acid. Most probably, the participation of nucleophiles/bases consists in formation of ion pairs with the diazonium salt formed, and that of solvent consists in solvation of the ions and ion pairs formed. In the case of anions, also the salt effect can be operating.

With regard to the above-mentioned discrepancies concerning the acid catalyzed decomposition of triazene derivatives, the aim of the present paper is to continue the previous studies<sup>5,6,20,22,23</sup> and adopt substituent effects to investigate the role of general acid in the decomposition of 1,3-diaryltriazenes in a protic solvent. For the model substance we have used the well-tried 1,3-bis(4-methylphenyl)triazene<sup>5,6,22</sup>, for the catalyst we have chosen substituted benzoic acids<sup>16,22</sup>, and for medium – 25 vol.% aqueous methanol in which two types of acid catalysis can unambiguously be observed<sup>22</sup>.

## EXPERIMENTAL

The synthesis of 1,3-bis(4-methylphenyl)triazene, purification of methanol, and the procedure of treatment of kinetic measurements are described elsewhere<sup>5</sup>. The substituted benzoic acids were used in the purity described in ref.<sup>26</sup>. The kinetic measurements were carried out in 25 vol.% aqueous methanol at  $25 \pm 0.1$  °C.

The mathematical-statistical treatment of the results was carried out using our own programs; when optimizing the models suggested we minimized the sum of squares of differences of natural logarithms of experimental and predicted rate constant  $k_{\text{obs}}$ . All the data of Table I were treated simultaneously as a single set. The models were evaluated according to the physico-chemical meaning of the optimized parameters and according to the quality of fit of experimental data with the regression model using the residual standard deviation  $s$  (recalculated to the  $\log k_{\text{obs}}$  units) and the Akaike information criterion (AIC) defined by the relation:

$$\text{AIC} = n \ln [S_R/(n - p)] + 2p, \quad (1)$$

where  $n$  is number of experimental data,  $p$  is number of parameters in regression model, and  $S_R$  is the residual sum of squares. The AIC value is the smaller the better the model reflects the experimental data. The proton concentration  $[\text{H}^+]$  in  $\text{mol dm}^{-3}$  was calculated from the relation (2)

$$[\text{H}^+] = 0.5 [-K_a + (K_a^2 + 4K_a c_{\text{CHA}})^{1/2}] , \quad (2)$$

where  $K_a$  is the dissociation constant ( $\text{mol dm}^{-3}$ ) of general acid (here substituted benzoic acid), and  $c_{\text{CHA}}$  ( $\text{mol dm}^{-3}$ ) is its analytical concentration in solution. The dissociation constants  $K_a$  of benzoic acids were calculated from the Hammett equation using the formula (3)

$$K_a = K_a^0 \cdot 10^{\rho\sigma} , \quad (3)$$

the value of dissociation constant of the nonsubstituted benzoic acid in the given medium ( $\text{p}K_a = -4.862$ ) being taken from literature<sup>31</sup>. For the substituent constants we adopted the values given by Exner<sup>32</sup>, and the reaction constant  $\rho$  was the parameter being optimized. The actual concentration of undissociated acid  $[\text{HA}]$  in  $\text{mol dm}^{-3}$  was calculated from the relation (4)

$$[\text{HA}] = c_{\text{CHA}} - [\text{H}^+] . \quad (4)$$

## RESULTS AND DISCUSSION

Table I presents the rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) of decomposition of 1,3-bis(4-methylphenyl)triazene with substituted benzoic acids of various concentrations. The reaction mechanism was suggested on the basis of the procedure of chemometrical analysis of probable models of acid catalysis. For the probable chemical reactions and chemical equilibria we took the interactions with proton, general acid, and its conjugated base. The concentrations of the individual particles were calculated from the relations given in Experimental. In the course of calculations, the analysis of residuals showed that three derivatives of benzoic acid (3-NH<sub>2</sub>, 4-NH<sub>2</sub>, 4-N(CH<sub>3</sub>)<sub>2</sub>) behaved anomalously as catalysts, and therefore they were excluded from further calculations. The behaviour mentioned is probably due to the existence of these compounds in the form of dipolar ions, hence here the catalytic acid is N-acid instead of O-acid.

*Model 1.* The specific acid catalysis (Scheme 1) is described by the relation for the observed rate constant  $k_{\text{obs}}$  in the form

$$k_{\text{obs}} = k_{\text{H}} K_{\text{TH}} [\text{H}^+] / (1 + K_{\text{TH}} [\text{H}^+] ) , \quad (5)$$

where  $k_{\text{H}}$  ( $\text{s}^{-1}$ ) is the catalytic rate constant and  $K_{\text{TH}}$  ( $\text{dm}^3 \text{mol}^{-1}$ ) is the equilibrium constant. The optimization of this model showed unambiguously a redundancy of the model in the data, viz. due to the very high  $K_{\text{TH}}$  value (see the analysis), the  $k_{\text{H}}$  and  $K_{\text{TH}}$  values were strongly intercorrelated and hence statistically insignificant. The residual standard deviation was  $s = 1.153 \cdot 10^{-2}$ , AIC = -781.

TABLE I

Observed rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) of decomposition of 1,3-bis(4-methylphenyl)triazene with substituted benzoic acids ( $\text{X}-\text{C}_6\text{H}_4\text{COOH}$ ) of concentration  $c$  in aqueous methanol (25 vol.%) at 25.0 °C

$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$
X = 4-N(CH <sub>3</sub> ) <sub>2</sub>							
0.095	1.16	0.095	1.16	0.095	1.00	0.086	1.04
0.086	1.01	0.086	1.07	0.076	1.02	0.076	1.02
0.076	0.990	0.076	0.976	0.072	0.889	0.072	0.866
0.072	0.825						
X = 4-NH <sub>2</sub>							
2.5	6.67	2.5	6.80	2.5	6.67	2.5	6.54
2.0	6.30	2.0	6.60	2.0	6.30	2.0	6.30
1.5	6.03	1.5	6.08	1.5	6.25	1.5	6.30
1.0	5.42	1.0	5.46	1.0	5.59	1.0	5.78
1.0	5.78	0.75	5.25	0.75	4.95	0.75	5.02
0.52	4.28	0.52	4.62	0.52	4.44	0.52	4.47
0.25	3.30	0.25	3.47	0.25	3.30	0.25	3.08
0.15	3.01	0.15	2.77	0.15	3.01	0.15	2.83
0.10	2.31	0.10	2.20	0.075	2.01	0.075	2.10
0.075	2.04						
X = 3-NH <sub>2</sub>							
0.50	3.85	0.50	4.08	0.50	3.96	0.41	3.75
0.41	3.56	0.41	3.65	0.30	3.47	0.30	3.38
0.30	3.47	0.25	3.30	0.25	3.30	0.21	3.15
0.21	3.15	0.21	3.01	0.16	2.95	0.16	2.89
0.16	2.89	0.16	2.95	0.10	2.57	0.10	2.57
0.10	2.62	0.10	2.67	0.075	2.31	0.075	2.39
0.075	2.31	0.075	2.39				
X = 4-OH							
2.5	19.3	2.5	18.7	2.0	16.5	2.0	15.7
1.4	13.3	1.4	14.4	1.4	13.9	1.0	12.0
1.0	11.6	1.0	12.4	0.75	11.2	0.75	10.7
0.52	8.66	0.52	8.66	0.25	5.55	0.25	5.33
0.15	4.08	0.15	3.96	0.10	3.65	0.10	3.47
0.10	3.30	0.075	3.01	0.075	3.01	0.075	3.15
X = 4-OCH <sub>3</sub>							
0.20	4.56	0.20	4.47	0.20	4.62	0.20	4.33
0.17	4.33	0.17	4.08	0.17	4.56	0.15	3.96
0.15	4.03	0.13	3.85	0.13	3.81	0.11	3.37
0.11	3.22	0.082	2.77	0.082	2.77		

TABLE I  
(Continued)

$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$
X = 4-CH <sub>3</sub>							
0.50	10.8	0.50	11.0	0.45	10.7	0.45	10.2
0.45	10.2	0.45	9.90	0.40	9.0	0.40	9.12
0.40	8.66	0.30	7.88	0.30	7.79	0.30	7.70
0.25	7.07	0.25	6.93	0.25	6.80	0.20	5.78
0.20	6.09	0.20	6.42	0.15	5.13	0.15	4.78
0.15	5.55	0.15	5.33	0.15	5.33	0.100	4.47
0.10	4.33	0.10	4.20				
X = 3-CH <sub>3</sub>							
1.4	23.1	1.4	23.1	1.4	23.5	1.4	22.4
1.2	20.4	1.2	21.0	1.0	18.7	1.0	18.7
1.0	19.2	0.92	18.2	0.92	17.3	0.92	18.2
0.92	16.9	0.73	14.4	0.73	13.9	0.73	13.9
0.73	13.9	0.51	9.50	0.51	9.90	0.51	10.0
0.38	8.45	0.38	8.66	0.38	8.66	0.25	6.03
0.25	6.42	0.15	4.33	0.15	4.20	0.15	4.62
0.076	2.01	0.076	2.07	0.076	2.10	0.076	2.13
X = H							
2.5	36.5	2.5	37.5	2.5	39.6	2.0	32.2
2.0	30.1	2.0	31.5	2.0	31.5	1.7	27.7
1.7	26.7	1.7	28.9	1.0	19.3	1.0	18.2
1.0	18.2	0.5	12.4	0.5	12.4	0.50	12.8
0.25	8.66	0.25	7.53	0.25	8.66	0.13	5.78
0.13	5.78	0.13	5.55	0.075	4.21	0.075	4.47
0.075	3.96						
X = 3-CH <sub>3</sub> O							
1.5	27.7	1.5	28.9	1.5	29.5	1.3	27.7
1.3	25.7	1.1	23.9	1.1	24.3	1.1	25.2
0.79	20.4	0.79	20.7	0.79	20.7	0.64	17.3
0.64	17.8	0.64	17.3	0.53	15.4	0.53	14.7
0.53	16.5	0.39	12.0	0.39	12.8	0.39	13.9
0.39	13.8	0.26	9.63	0.26	10.5	0.26	9.37
0.26	10.2	0.16	7.22	0.16	6.67	0.16	7.22
0.078	5.55	0.078	5.78				

TABLE I  
(Continued)

$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$	$c \cdot 10^2$	$k_{\text{obs}} \cdot 10$
X = 4-Cl							
0.14	6.30	0.14	6.42	0.14	5.78	0.14	5.64
0.12	5.59	0.12	5.59	0.10	5.10	0.10	4.95
0.10	5.33	0.070	3.85	0.070	3.85		
X = 3-Cl							
0.32	17.3	0.32	17.8	0.32	17.3	0.26	14.4
0.26	14.4	0.26	14.1	0.21	12.4	0.21	12.4
0.21	12.3	0.16	9.90	0.16	10.2	0.16	10.8
0.11	8.16	0.11	8.06	0.11	8.06	0.080	6.30
0.080	6.08	0.080	6.42	0.080	6.67		
X = 3-NO <sub>2</sub>							
1.8	86.6	1.8	86.6	1.3	69.3	1.3	69.3
1.3	69.3	0.98	57.8	0.98	57.8	0.87	53.3
0.87	55.5	0.87	55.5	0.49	40.8	0.49	38.5
0.25	24.8	0.25	23.1	0.25	23.1	0.15	19.8
0.15	19.3	0.10	13.1	0.10	14.1	0.10	13.6
0.10	14.7	0.075	13.3	0.075	12.8	0.075	12.6
X = 4-NO <sub>2</sub>							
0.18	17.8	0.18	17.8	0.18	16.9	0.16	16.9
0.16	16.5	0.16	16.5	0.13	14.7	0.13	15.4
0.13	15.9	0.094	12.6	0.094	12.8	0.094	11.6
0.072	9.37	0.072	9.90	0.072	10.7		

*Model 2.* The general acid catalysis (Scheme 2) is expressed by the relation for observed rate constant  $k_{\text{obs}}$  in the form

$$k_{\text{obs}} = k_{\text{HA}}^0 \cdot 10^{\rho_{\text{HA}} \sigma} [\text{HA}] , \quad (6)$$

a dependence of the catalytic rate constant  $k_{\text{HA}}$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) upon the strength of general acid being presumed. The optimization results did not confirm this presumption (this parameter was statistically insignificant), and, in addition to it, the optimized reaction constant in Eq. (3) assumes an unexpected value of  $\rho = 0.681$ . Since the global



statistical characteristics  $s = 7.735 \cdot 10^{-2}$  and  $AIC = -368$  do not show any high-quality fit of experimental data with the regression model either, this model can be considered to be unsuitable and the respective process described by it to be improbable.

*Model 3.* Simultaneous acid catalysis with the proton and general acid (Scheme 2, the proton and general acid playing the role of HA). This model, which proved very satisfactory several times in the past<sup>5,22</sup>, can be described by Eq. (7), where  $k'_H = k_H K_{TH}$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) represents a combined catalytic constant.

$$k_{\text{obs}} = k'_H[\text{H}^+] + k_{\text{HA}}^0 \cdot 10^{\rho_{\text{HA}}\sigma}[\text{HA}] \quad (7)$$

From the statistical point of view, all the parameters are significant, and the global statistical characteristics are favourable as compared with the previous models, since  $s = 5.190 \cdot 10^{-3}$ ,  $AIC = -953$ . The rate constant  $k'_H$  has the value of  $3.86 \cdot 10^3$ , whereas the rate constant  $k_{\text{HA}}$  is smaller, as expected, namely  $5.67 \cdot 10^1$ . For the reaction constant of dissociation of the catalyst acid we found  $\rho = 1.02$ , for the reaction constant  $\rho_{\text{HA}} = 1.06$ . The latter value is surprising, since it indicates that the catalyst acid is completely dissociated in the transition state, which contradicts the principle of general catalysis. One of possible interpretations is presented in the following model.

*Model 4.* Using the definition of dissociation constant, we can replace the value of  $[\text{HA}]$  as in Eq. (8).

$$[\text{HA}] = [\text{H}^+][\text{A}^-]/K_a = [\text{H}^+][\text{A}^-] \cdot 10^{-\rho\sigma}K_a^0 \quad (8)$$

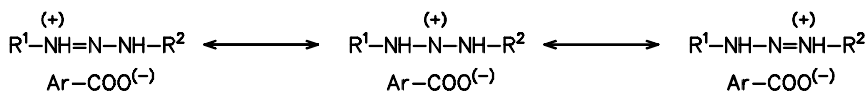
With the already proved presumption of  $\rho_{\text{HA}} = \rho$  we can introduce the above relation into Eq. (7) to obtain Eq. (9)

$$k_{\text{obs}} = k'_H[\text{H}^+] + k_{\text{H,A}}[\text{H}^+][\text{A}^-] , \quad (9)$$

where  $k_{\text{H,A}}$  ( $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ ) represents the catalytic rate constant of decomposition of triazene with simultaneous catalyses by the proton and conjugated base of respective acid. At the experimental conditions used it is also  $[\text{H}^+] = [\text{A}^-]$ , hence the reaction could be of the second order in the proton. The optimization of parameters according to Eq. (9) gave the following results:  $k'_H = 3.86 \cdot 10^3$ ,  $K_{\text{H,A}} = 4.17 \cdot 10^6$ , and  $\rho = 1.03$ ,  $s = 5.168 \cdot 10^{-3}$ ,  $AIC = -956$ . These results are slightly better than those of the previous model, but this is only due to the smaller number of parameters optimized, since the residual sum of squares is identical with that of *Model 4*. As an additional regression function we verified the relation (9) extended by the dependence of the rate constant

$k_{H,A}$  upon substituents, however the corresponding reaction constant was statistically insignificant.

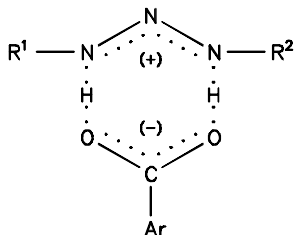
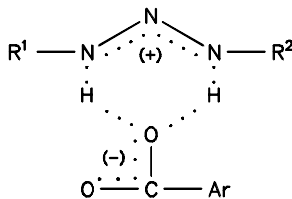
From the values of rate constants found, the reaction of the second order in the proton can almost certainly be excluded. In principle, triazene has three centres of protonation, but from both the resonance structures and quantum-chemical calculations<sup>33,34</sup> it follows that the protonation can only take place at N<sup>1</sup> and N<sup>3</sup> atoms, preferably at N<sup>1</sup> (ref.<sup>33</sup>). Addition of a second proton is unlikely and it would lead to a lower value of the rate constant  $k_{H,A}$  since the diazonium salt could not be formed without splitting off of a proton. On the other hand, the presence of a base in solution can accelerate the splitting of protonated substrate by stabilization of the diazonium salt. As a termolecular reaction cannot be expected, the reaction probably proceeds in two steps. One of the variants is the specific acid catalysis (Scheme 1) where the second step is accelerated by the nucleophilic attack of conjugated base on N<sup>2</sup> atom. In this case the rate constant  $k_{H,A}$  is a product of the equilibrium constant  $K_{TH}$  and the proper constant of base catalyzed decomposition of protonated substrate  $K_{H(A)}$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ). As the found value is  $k_{H,A} = 4.17 \cdot 10^6$  and the basicity of triazenes is low, the rate constant  $k_{H(A)}$  must be very high. Another possibility consists in the protonation of the more basic N<sup>1</sup> atom giving the complex *II* which is stabilized by resonance and by coordination with the conjugated base (see Scheme 3).



SCHEME 3

*II*

The rate-limiting step of decomposition would consist in an intramolecular proton transfer from one outside nitrogen atom to the other with simultaneous splitting of the triazene chain. The measurements show that this transfer connected with tautomerism is relatively slow in protic solvents<sup>15</sup> (in the sense of frequency of such an event). Another possibility consists in an incomplete proton transfer to N<sup>1</sup> atom with formation of complexes whose structure could be described by the formulas *III* and *IV*. Probability of formation of such groupings is supported by the existence of associates<sup>33,35-37</sup>, however, their decomposition obviously does not take place<sup>23</sup>.

*III**IV*

*Model 5.* The specific acid catalysis with the assistance by the conjugated base in rate-limiting step is described by Eq. (10)

$$k_{\text{obs}} = k_{\text{H(A)}}K_{\text{TH}}[\text{H}^+][\text{A}^-]/(1 + K_{\text{TH}}[\text{H}^+]) , \quad (10)$$

where  $k_{\text{H(A)}}$  is the above-defined constant of base catalyzed decomposition of protonated substrate. This model is connected with the discussion of *Models 1* and *4*. The optimization gave the following values:  $k_{\text{H(A)}} = 6.19 \cdot 10^3$ ,  $K_{\text{TH}} = 2.00 \cdot 10^4$ ,  $\rho = 1.04$ ,  $s = 7.80 \cdot 10^{-3}$ ,  $\text{AIC} = -866$ . The statistical significance of this model is lower than that of the most successful *Model 4*. The value of equilibrium constant  $K_{\text{TH}}$  is much too high, because in this case a decrease of pH below about 4 would have to lead to a lowering of slope of pH profile, which however stands in contrast with the experiments carried out so far<sup>11-14,18,19</sup>. An extension of the numerator of the expression (10) by the term  $k'_{\text{H}}[\text{H}^+]$  led to an improvement in the fit of experimental data with the regression model, but the constants  $K_{\text{TH}}$  and  $k_{\text{H(A)}}$  became statistically insignificant being mutually intercorrelated.

*Model 6.* This model describes the operation of side equilibrium between triazene and general acid giving a nonreactive complex. In our earlier paper<sup>23</sup> we suggested Eq. (11) as the most suitable model for the reaction of 1-phenyl-3,3-dialkyltriazenes with bulky pivalic acid

$$k_{\text{obs}} = k'_{\text{H}}[\text{H}^+]/(1 + K_{\text{K}}[\text{HA}]^2) , \quad (11)$$

where  $K_{\text{K}}$  ( $\text{dm}^6 \text{mol}^{-2}$ ) is the equilibrium constant of formation of complex. The treatment of data of Table I adopting this formula gave a close fit ( $s = 8.66 \cdot 10^{-3}$ ,  $\text{AIC} = -849$ ), but the  $K_{\text{K}}$  constant had a statistically significant negative value. A modification of Eq. (11) in the sense of *Model 4* gives Eqs (12) and (13):

$$k_{\text{obs}} = k_{\text{H(A)}}[\text{H}^+][\text{A}^-]/(1 + K_{\text{K}}[\text{HA}]^2) \quad (12)$$

$$k_{\text{obs}} = k_{\text{H(A)}}[\text{H}^+][\text{A}^-]/(1 + K'_{\text{K}}[\text{HA}]) . \quad (13)$$

The optimization gave the following results for Eqs (12) and (13), respectively:  $s = 2.929 \cdot 10^{-2}$  and  $1.216 \cdot 10^{-2}$ ,  $\text{AIC} = -597$  and  $-770$ . The more successful relation (13) was extended in its numerator by the term  $k'_{\text{H}}[\text{H}^+]$ , however the optimization

showed the equilibrium constant  $K'_K$  to be statistically insignificant, which means a reduction to *Model 4*. Hence any significant formation of nonreactive complexes could be proved in the system studied.

## CONCLUSIONS

Although a number of other models were investigated, none of them reached the quality of the above-given ones. From Discussion it follows that *Model 4* appears to be the most suitable: it describes the mechanism of acid catalyzed decomposition of diaryltriazenes as one involving the protonation of substrate in a rapid pre-equilibrium followed by decomposition of the complex formed. The intermediate with the proton bound to N<sup>1</sup> atom is more stable and is formed in higher concentration. On the other hand, the intermediate with protonated N<sup>3</sup> atom is less stable and is formed in very low concentration, but it is more reactive. The solvent isotope effect found with 1,3-dialkyltriazenes<sup>14</sup> more likely indicates the second variant. Irrespective of the protonation centre, the present communication gives an important conclusion: the observed dependence on the concentration of general acid need not necessarily be connected with general acid catalysis, but it can represent a manifestation of participation of the nucleophile/base in the overall process of acid catalyzed decomposition in polar protic solvents<sup>14,20</sup>. Since the two ways of catalysis cannot be differentiated on the basis of concentration dependences, the dependence on concentration of general acid does not represent an unambiguous proof in favour of general acid catalysis<sup>14</sup>, which was presumed earlier<sup>5,23</sup>. However, general acid catalysis most probably makes itself felt in the decomposition of triazenes, particularly so in aprotic and little polar solvents<sup>6,22</sup>. Decreasing solvent polarity is inevitably connected with decreased stabilization of any polar structures during the reaction, and the importance of general acid catalysis involving the less polar transition state is increased<sup>22</sup>.

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