KINETICS AND MECHANISM OF ACID-CATALYZED DECOMPOSITION OF 1,3-BIS(4-METHYLPHENYL)TRIAZENE IN HEXANE–ORGANIC ACID MEDIUM

Miroslav LUDWIG and Miriam KABICKOVA

Department of Organic Chemistry,
University of Pardubice, 532 10 Pardubice, Czech Republic

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The kinetics of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene have been studied in mixtures of hexane and organic acid of various ratios using acetic, isovaleric, and pivalic acids as the catalysts. In all the cases, a monotonously increasing dependence of the observed rate constant upon mol fraction of the acid has been found. The results obtained are discussed with the help of the classic third- and fourth-order functions by Margules and the respective kinetic model. The main catalyzing particle appears to be the dimer of the respective acid, the reaction probably going via a complex formed by two molecules of acid and one molecule of the triazene.

Key words: Triazene; Kinetics; Mechanism; Acid-catalyzed decomposition.

The mechanism of acid-catalyzed decomposition of substituted triazenes $R'N^1{=}N^2{-}N^3R''R'''$ in various media was studied in a number of papers[1–22]. The decomposition produces the respective diazonium salts and additional compounds with the bond to N^2 replaced by a bond to hydrogen. The splitting of triazene chain probably starts with protonation of N^3 atom (ref.[5]), the protonation of other nitrogen atoms – though possible – being involved in side equilibria. As for mechanism type of the reaction studied, it can represent a specific acid catalysis involving a rapid protonation pre-equilibrium of the substrate and subsequent decomposition to the products, or a general acid catalysis involving simultaneous formation of $H{-}N^3$ bond and splitting of $N^2{-}N^3$ bond. The catalysis type probably depends on the nature of substituents on the triazene skeleton. As for the reaction molecularity, some papers prefer the monomolecular mechanism of specific acid catalysis, A1 (refs[1–5,12,14]) while other experiments rather indicate the bimolecular mechanism type $A\text{-}S_E2$ with general acid catalysis[11,17,19–22]. In addition, the decomposition of 1-phenyl-3,3-dialkyltriazenes in aqueous ethanol with catalysis by pivalic acid[22] was affected by the existence of complexes between the triazene and nondissociated acid. This shows that the real mechanism is quite complex.

Studies[19–21] of effect of medium on the decomposition of 1,3-bis(4-methylphenyl)-triazene catalyzed by trichloroacetic acid in amphiprotic and aprotic solvents showed three types of dependences between the observed rate constant and concentration of catalyst acid (Cl_3CCO_2H). The fastest reaction was that with the proton, slower was that with the nondissociated acid, and the slowest that with the acid dimer. The reaction rates in the individual media depended upon the form of acid predominating in the given medium, the reaction proceeding as general-acid-catalyzed with nondissociated acid, proton, and acid dimer as well.

The aim of the present paper is to extend the problem investigated by the decomposition of 1,3-bis(4-methylphenyl)triazene in the medium of aprotic solvent plus carboxylic acid, the latter playing also the role of catalyst in this case. Acetic, isovaleric, and pivalic acids have been chosen for the catalysts.

EXPERIMENTAL

1,3-Bis(4-methylphenyl)triazene was prepared in a known way[13]. The kinetic measurements were carried out on a UV/VIS HP 8452a and Specord M40 apparatus. The respective mixture (solution) hexane–carboxylic acid was kept at 25.0 ± 0.1 °C in a quartz cell, and a solution of triazene in dioxane (ca 5 μl 0.001 mol dm^{-3}) was added by means of a Hamilton syringe. The absorbance decrease at the maximum (356 nm) was monitored for at least three half-lives.

RESULTS AND DISCUSSION

The observed rate constants, k_{obs}, of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene in mixtures of carboxylic acids and hexane are given in Table I, Figs 1 and 2 giving the results (experimental results shown as points) for the mixtures of hexane with acetic acid and with isovaleric acid, respectively. In all the cases the increasing content of catalyzing acid results in monotonous increase in k_{obs}. When describing the dependences found, one must take into account (beside the effect of concentration of catalyzing acid) also the overall change of properties of the medium in which the reaction takes place. However, no parameters quantifying the solvent proper-

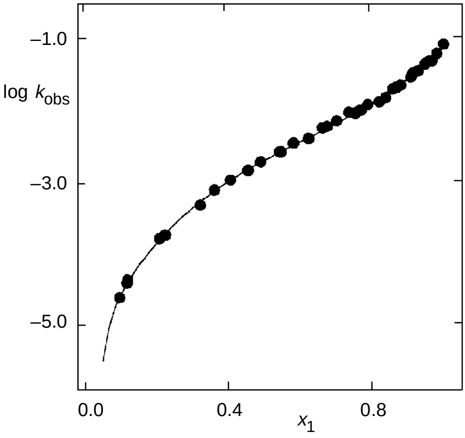

FIG. 1
Dependence of log k_{obs} of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene on composition of hexane–acetic acid mixture (x mole fraction of acid, the curve corresponds to the optimized model (*21*))

ties are available for description of mixed solvents of the type studied. Nevertheless, it is possible to adopt a theoretical description of effect of binary solvent mixtures on the processes taking place in solution. Such a description can be based, e.g., on the proportional relation between the Gibbs energy change of the process investigated and the Gibbs energy change of solvent for transfer of reacting components from the pure sol-

TABLE I
Observed rate constants (k_{obs} in s^{-1}) of decomposition of 1,3-bis(4-methylphenyl)triazene catalyzed by acetic, isovaleric, and pivalic acids (c_{HA} in mol dm^{-3}) in hexane

c_{HA}	$k_{obs} . 10^4$	c_{HA}	$k_{obs} . 10^4$	c_{HA}	$k_{obs} . 10^4$
		Acetic acid			
0.80	0.246	0.98	0.392	1.00	0.437
1.83	1.65	2.00	1.85	3.03	4.91
3.48	7.90	4.05	11.0	4.71	15.0
5.21	19.8	6.00	27.4	6.08	27.4
6.63	36.4	7.36	41.9	8.08	59.4
8.33	62.7	8.88	74.8	9.63	98.4
10.03	95.5	10.15	100	10.41	107
10.86	126	11.66	138	12.14	159
12.71	210	12.96	216	13.29	236
14.16	307	14.36	348	14.85	377
15.47	470	15.85	508	16.16	518
16.71	657	17.47	891	17.47	893
		Isovaleric acid			
0.56	0.150	0.82	0.170	1.10	0.251
1.36	0.321	1.56	0.370	1.73	0.381
2.29	0.529	2.85	0.731	3.30	1.02
3.69	1.27	4.35	1.84	5.00	2.70
5.27	3.00	6.23	4.91	7.14	7.00
8.08	9.32	9.17	12.0	9.17	12.2
9.17	12.2	9.17	12.0		
		Pivalic acid			
0.20	0.410	0.54	1.00	0.81	2.12
0.94	3.19	1.01	3.62	1.03	3.79
1.14	4.38	1.25	5.21	1.36	6.33
1.50	7.60				

vent into the mixed solvent[23]. The Gibbs energy change is described by so-called classic function by Margules[24], van Laar–Wohl[25] or van Laar–Null[26], which was confirmed by a description of 151 processes (p*K*, IR, UV-VIS, NMR, log *K* and others), the Margules 4th order function (Eq. (*1*)) being the most suitable for description of a quantity proportional to the Gibbs energy change (in our case the logarithm of rate constant, log k_{obs}). From among other functions of approximately the same quality having one parameter less we have used the Margules 3rd order function (Eq. (*2*)).

$$\log k_{obs} = x_1 \log k_1 + x_2 \log k_2 + x_1 x_2 (x_1 A_{21} + x_2 A_{12} + x_1 x_2 D_{12}) \tag{1}$$

$$\log k_{obs} = x_1 \log k_1 + x_2 \log k_2 + x_1 x_2 (x_1 A_{21} + x_2 A_{12}) \ , \tag{2}$$

where k_1 and k_2 are the rate constants in pure media 1 and 2, respectively, x are mole fractions describing the composition of mixture (x_1 = 1 and x_2 = 0 for pure hexane), *A* and *D* are the optimized parameters. The descriptions given, however, do not reflect the fact that the acid is not only a component of the medium but also a catalyst. In addition to the description of this relation it is also necessary to describe the likely processes in acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene in mixtures of hexane plus carboxylic acid. With regard to low polarity of hexane, acetic acid, and isovaleric acid[27,28] (relative permittivity ε_r(hexane) = 1.91, ε_r(acetic acid) = 6.15, ε_r(isovaleric acid) = 2.60) these substances show low ability to solvate both the dissociated and the nondissociated acid. Hence, associates of homo- and heteroconjugation type are formed in the solution (Eqs (*3*)–(*6*)). The associates between triazene (T) and nondissociated acid (HA) were discussed in our previous paper[22].

$$\mathrm{HA} + \mathrm{HA} \rightleftharpoons \mathrm{D}, \quad K_D = [\mathrm{D}]/[\mathrm{HA}]^2 \tag{3}$$

$$\mathrm{T} + \mathrm{HA} \rightleftharpoons \mathrm{KT_1}, \quad K_1 = [\mathrm{KT_1}]/[\mathrm{T}][\mathrm{HA}] \tag{4}$$

$$\mathrm{KT_1} + \mathrm{HA} \rightleftharpoons \mathrm{KT_2}, \quad K_2 = [\mathrm{KT_2}]/K_1[\mathrm{T}][\mathrm{HA}]^2 \tag{5}$$

$$\cdot$$

$$\cdot$$

$$\mathrm{KT}_{n-1} + \mathrm{HA} \rightleftharpoons \mathrm{KT}_n, \quad K_n = [\mathrm{KT}_n]/K_K[\mathrm{T}][\mathrm{HA}]^n \ ,$$

$$K_K = K_1 K_2 \ldots K_{n-1} \ . \tag{6}$$

The decomposition of triazene can be connected with its reactions with nondissociated acid (Eq. (*7*)), dimer of catalyzing acid (Eq. (*8*)), proton (Eq. (*9*)) or with decomposition of associates $KT_1 \ldots KT_n$ (Eqs (*10*)–(*12*)).

$$T + HA \longrightarrow P, k_{HA} \tag{7}$$

$$T + D \longrightarrow P, k_D \tag{8}$$

$$T + H^+ \longrightarrow P, k_{H^+} \tag{9}$$

$$KT_1 \longrightarrow P, k_1 \tag{10}$$

$$KT_2 \longrightarrow P, k_2 \tag{11}$$

$$\begin{array}{c} \cdot \\ \cdot \end{array}$$

$$KT_n \longrightarrow P, k_n \quad . \tag{12}$$

Analytical concentrations of catalyzing acid and of triazene can be expressed by Eqs (*13*) and (*14*), respectively.

$$c_{HA} = [HA] + [D] + [H^+] + [KT_1] + [KT_2] + \ldots + [KT_n] \tag{13}$$

$$c_T = [T] + [KT_1] + [KT_2] + \ldots + [KT_n] \quad . \tag{14}$$

The dissociation constant $K_{HA} = [H^+]^2/[HA]$. From the value $pK_{HA} = 4.76$ for acetic acid in water[29] and from the polarity of all the media used it can be concluded that the catalyzing acids will not be appreciably dissociated. The autoprotolytic constant of acetic acid[29], $pK_{SH} = \lim [CH_3COO^-][CH_3COOH_2^+] = 14.45$, indicates also a low extent of autoprotolysis in the acid itself. A similar situation can be expected with the other acids, too, even though not all the necessary data are available here. When assembling the kinetic equations we must adopt certain simplifications using the findings of refs[19–21]. Equation (*13*) can be modified to the expression $c_{HA} = 2[D]$ since the concentrations of other components can be neglected as compared to the dimer concentration in the media studied[20]. The analytical concentration of triazene, c_T, will probably involve predominantly the triazene itself, since the acid molecules will prefer formation of dimers. Hence, Eq. (*14*) can be simplified to the expression c_T = [T]. Using these simplified equations and the expression for velocity $v = k_{obs}c_T$, one can derive Eqs (*15*)–(*20*) for the isolated processes expressed by Eqs (*7*)–(*12*), respectively.

For process (*7*):

$$k_{obs} = (2K_D)^{-0.5}\, k_{HA}c_{HA}^{0.5} \quad . \tag{15}$$

For process (*8*):

$$k_{obs} = 0.5\, k_D c_{HA} \quad . \tag{16}$$

For process (*9*):

$$k_{obs} = (2K_D)^{-0.25}\, K_{HA}^{0.5}\, k_{H^+}\, c_{HA}^{0.25} \quad . \tag{17}$$

For process (*10*):

$$k_{obs} = (2K_D)^{-0.5}\, k_1\, K_1\, c_{HA}^{0.5} \quad . \tag{18}$$

For process (*11*):

$$k_{obs} = 0.5\, K_1\, K_2\, k_2\, c_{HA} \quad . \tag{19}$$

For process (*12*):

$$k_{obs} = 0.5\, K_1\, K_2 \,\ldots\, K_n\, k_n\, c_{HA}^{n/2} \quad . \tag{20}$$

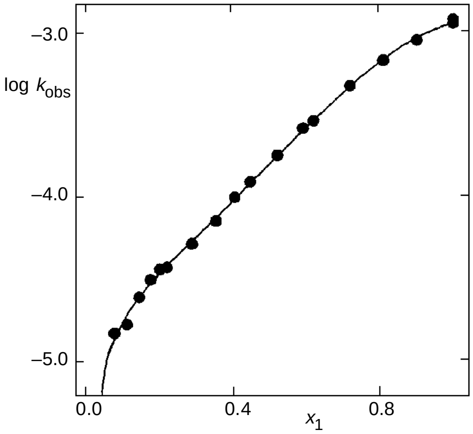

FIG. 2
Dependence of log k_{obs} of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene on composition of hexane–isovaleric acid mixture (*x* mole fraction of acid, the curve corresponds to the optimized model (*21*))

The equations thus obtained can generally be expressed by k_{obs} = const c_{HA}^{p} (or $\log k_{obs} = \log(\text{const}) + p \log c_{HA}$), where p can assume the values of 0.25, 0.5, 1, 1.5, …, $n/2$ and const is proportional to the corresponding rate constant, i.e., can be expressed by some expression type (*1*) or (*2*). From the papers published earlier (particularly ref.[20]) it follows that, in media of low polarity, the nondissociated acid and proton are practically insignificant as catalysts, and the complexes KT_3 and higher seem not very likely either. Hence only the expressions (*16*), (*18*) and (*19*) (the processes (*16*) and (*19*) being kinetically indistinguishable) are left from Eqs (*15*)–(*20*). Hence the observed rate constant, k_{obs}, can be proportional to the concentration of catalyst acid or to its second square root or to a combination of both the functions. Combination of the equations describing the classic Margules functions with the expressions describing the dependence of k_{obs} on the acid concentration c_{HA} leads to the relations (*21*)–(*24*):

for the Margules third-order function, k_{obs} proportional to c_{HA}

$$\log k_{obs} = x_1 \log k_h + x_2 \log k_k + x_1 x_2 (x_1 A_{21} + x_2 A_{12}) + \log c_{HA} \,, \qquad (21)$$

for the Margules third-order function, k_{obs} proportional to $c_{HA}^{0.5}$

$$\log k_{obs} = x_1 \log k_h + x_2 \log k_k + x_1 x_2 (x_1 A_{21} + x_2 A_{12}) + 0.5 \log c_{HA} \,, \qquad (22)$$

for the Margules fourth-order function, k_{obs} proportional to c_{HA}

$$\log k_{obs} = x_1 \log k_h + x_2 \log k_k + x_1 x_2 (x_1 A_{21} + x_2 A_{12} + x_1 x_2 D_{12}) + \log c_{HA} \,, \qquad (23)$$

for the Margules fourth-order function, k_{obs} proportional to $c_{HA}^{0.5}$

$$\log k_{obs} = x_1 \log k_h + x_2 \log k_k + x_1 x_2 (x_1 A_{21} + x_2 A_{12} + x_1 x_2 D_{12}) + 0.5 \log c_{HA} \,. \qquad (24)$$

The constants k_h and/or k_k rather express the constants proportional to the respective catalytic rate constants for pure solvents. The experimental data obtained for acetic acid were used for testing of models (*21*)–(*24*). The results of nonlinear regression are summarized in Table II and depicted by Fig. 1. The values of Akaik information criterion AIC (ref.[30]) show that the most suitable model is (*21*) suggested on the basis of Eqs (*16*) and (*19*) describing the processes (*8*) and (*9*). The result indicates the mechanism of general acid catalysis with the dimer (D) of nondissociated acid as the catalytic particle or a similar mechanism involving previous formation of complex (TD) of triazene and dimer or complex (KT2) of triazene and two molecules of nondissociated acid. The two models cannot be distinguished. The results obtained with isovaleric acid (Fig. 2, Table II) also confirm the suitability of this model for the dependences studied. The data for pivalic acid cannot be discussed from these points of view because the measurements could not be carried out in the region of insolubility of the acid in hexane.

The results obtained confirm the acid dimer to be the predominant catalyst of decomposition of the triazene in little polar media. The mechanism may also involve the formation of complexes of triazene and two molecules of nondissociated acid. If we compare the rate constants of decomposition of the triazene studied at identical concentrations of the catalyst acid, we will find the order: pivalic acid > acetic acid > isovaleric acid over the whole range studied. Evidently, this order is identical neither with the order of pK_{HA} values of the catalyst acids[31]: 4.76, 4.77, and 5.05 for acetic, isovaleric, and pivalic acids, respectively, nor with that of sterical demands of alkyl groups bound to the carboxyl group (1,1-dimethylethyl, 2-methylpropyl, methyl), nor with that of relative permittivities of the acids (see above), which shows that it results from simultaneous operation of all these effects.

TABLE II
Results of treatment of data of Table I by nonlinear regression according to the models (*21*)–(*24*)

Model	$\log k_h$ (s)	$\log k_k$ (s)	A_{21} (s)	A_{12} (s)	D_{12} (s)	AIC	RSS
			Acetic acid				
(*21*)	–5.024	–2.331	3.370	–1.253	–	–0.51	25.27
	(1.108)	(0.398)	(6.999)	(3.652)			
(*22*)	–5.226	–1.705	4.417	–1.050	–	2.33	27.33
	(1.153)	(0.414)	(7.729)	(3.799)			
(*23*)	–4.883	–2.312	1.755	–1.956	3.532	2.70	23.86
	(2.022)	(0.455)	(20.63)	(9.208)	(42.53)		
(*24*)	–5.136	–1.693	3.392	–1.497	2.243	4.22	26.40
	(2.127)	(0.479)	(21.70)	(9.686)	(44.74)		
			Isovaleric acid				
(*21*)	–4.520	–3.883	–2.144	0.531	–	12.90	20.44
	(1.385)	(0.547)	(9.895)	(5.991)			
(*22*)	–4.754	–3.398	0.809	0.757	–	12.92	22.63
	(1.457)	(0.576)	(10.40)	(6.302)			
(*23*)	–4.490	–3.881	–2.520	0.310	–1.045	15.92	20.17
	(2.303)	(0.579)	(25.10)	(14.81)	(62.39)		
(*24*)	–4.728	–3.400	–0.375	1.006	–1.154	18.49	22.94
	(2.456)	(0.612)	(26.75)	(15.79)	(66.53)		

s Standard deviation, RSS residual sum of squares.

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