SOLVENT EFFECTS ON KINETICS AND MECHANISM OF ACID-
-CATALYZED DECOMPOSITION OF 1,3-BIS(4-METHYLPHENYL)-
TRIAZENE I. REACTIONS IN ALCOHOLS

Taťjana NEVĚČNÁ[a], Oldřich PYTELA[b], Miroslav LUDWIG[b] and Jaromír KAVÁLEK[b]

[a] Department of Inorganic and Physical Chemistry,
Palacký University, 771 46 Olomouc and
[b] Department of Organic Chemistry, Institute of Chemical Technology, 532 10 Pardubice

Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The effect of protic solvents (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, cyclohexanol) has been studied on the kinetics and mechanism of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene, using trichloroacetic acid as the acid catalyst. Both the non-dissociated acid and the proton have been found to be catalytically active. The mechanism of splitting of the triazene substrate with the non-dissociated acid involves the general acid catalysis. Comparison of the catalytic rate constants of the two acid catalysts and effect of solvents on these values indicate that the general acid catalysis probably also operates in the reaction of the substrate with proton.

The triazenes of the general formula I in which R^1 most often is aryl, R^2 is aryl or alkyl, and X is hydrogen, alkyl, acyl, or even hydroxyl group are split very easily in acid media[1-25].

$$\overset{1}{R^1}—\overset{2}{N}=\overset{3}{N}—N—R^2$$
$$|$$
$$X$$
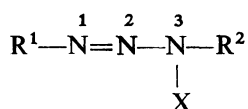
I

The products involve diazonium salts and complementary compounds having the bond to N-2 replaced by a bond to hydrogen. The triazene molecule is interesting in that the proton can be attached to any of the three nitrogen atoms, as it follows from the distribution of electron density determined by X-ray diffraction analysis of two crystalline modifications of 1,3-diphenyltriazene[26,27] and 4-nitrodiphenyltriazene[28]. Quantum-chemical calculations showed roughly the same probability of protonation at N-1 and N-3 (ref.[29]), other authors[30] even prefer the N-1 position. The rupture of triazene chain, of course, only occurs after the interaction of proton

with N-3 centre, whereas the protonations at the two remaining centres can only represent side equilibria. The interaction of N-3 centre with proton can lead either to a protonated intermediate which is subsequently decomposed into the products (specific catalysis) or to a simultaneous formation of bond between the proton and the attacked N-3 centre and bond splitting between N-2 and N-3 (general catalysis). In both cases the proton can be one solvated by the solvent or one transferred from general acid during the interaction.

In literature there is no unique opinion about the mechanism of acid catalysis. Older reports (e.g. refs[1,5-9]) prefer the idea of specific catalysis by the mechanism of A1 type. This mechanism is postulated also by some recent studies[17,19,22] mainly based on solvent kinetic isotope effects. On the other hand, there exists experimental evidence in support of the hypothesis of general acid catalysis (by the proton or general acid) via the mechanism denoted as A-S_E2 (ref.[16]). This evidence involves — first of all — the existence of salt effect with the acyl derivatives of triazenes[15] ($R^1 = R^2 = C_6H_5$, X = $COCH_3$, $CONHCH_3$) which indicates the existence of ion pairs and, hence, easy cleavage of the bond between N-2 and N-3. The bimolecular nature of the reaction is preferred according to the criterion based on the isokinetic temperature[14]. A mathematical modelling of the decomposition mechanism of 3-methyl-1,3-diphenyltriazene in buffer media composed of general acids led to the idea of both proton-catalyzed splitting and the general acid-catalyzed one by the A-S_E2 mechanism[24]. A significant piece of evidence is provided by the course of kinetic acidity function H_K constructed on the basis of substituted derivatives of 3-acetyl-1,3-diphenyltriazene in sulfuric acid and 40% ethanol which clearly deviates from the H_0 acidity function at higher concentrations of acid. As the proton is the most highly solvated particle in the given medium, its higher reactivity at higher concentrations of acid supports the mechanism of bimolecular electrophilic substitution at the N-3 centre of triazene chain. This simultaneously excludes the alternative reaction at the carbonyl of acetyl group via possible mechanism of A_{Ac}2 type. The interpretation of substituent effects in 3-methyl-1,3-diphenyltriazenes with the use of the Hammett equation did not bring univocal results[20,23]. The evaluation of other dependence on pH of the leaving diazonium cation gave a β_{1g} value indicating that the bond between N-2 and N-3 is half split in the transition state[23]. The activation entropy determined for some disubstituted derivatives of 3-methyl-1,3-diphenyl-triazene at pH 3·56 in 40% aqueous ethanol was markedly negative[24]. Hence on the basis of available results the bimolecular mechanism A-S_E2 appears more likely for the acid-catalyzed decomposition of triazenes.

Although the acid-catalyzed decomposition of triazene derivatives is dealt with in a number of reports, only one of them deals with the solvent effect[8] but does not cover protic solvents. The aim of this present communication is to fill in this gap and study the kinetics of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)-triazene in various alcohols with subsequent interpretation of the results obtained

with regard to solvent effects and the reaction mechanism. The choice of model substrate followed the criteria of minimization of consecutive reactions (azo coupling in the aromatic ring) and of good solubility. Trichloroacetic acid was selected as the catalyst because of its high acidity and solubility in various solvents.

EXPERIMENTAL

1,3-Bis(4-methylphenyl)triazene was prepared by the procedure described in a previous communication[18].

The solvents were dried by the procedure given in ref.[31], the molecular sieve 3A (Fluka AG) being used for the last drying. The water content determined by Fischer's titration method[32]: methanol 0·02%, ethanol 0·05%, 1-propanol 0·02%, 2-propanol 0·01%, 1-butanol 0·01%, 2-butanol 0·03%, cyclohexanol 0·09%. No acidic nor basic admixtures were found by known methods[31].

Trichloroacetic acid was dried by long-term standing over phosphorus pentoxide in vacuum.

Kinetic Measurements. A solution of trichloroacetic acid in the given solvent was thermo-statted at $25·0 \pm 0·1°C$ in a cell of an SP8-100 spectrophotometer (Pye Unicam Cambridge). A solution (4—6 μl) of 1,3-bis(4-methylphenyl)triazene in the given solvent was added into the cell by means of a syringe (Hamilton Bonaduz AG), and the solution was mixed. The absorbance decrease was followed at the wavelength of 354 — 358 nm (the absorbance maximum) for a period of at least 3 half-lives. The rate constants above $0·2 \text{ s}^{-1}$ were obtained by the stopped-flow technique using a Durrum D 150 apparatus.

Treatment of Results. The kinetic curves were evaluated with a PMD 85-2 microcomputer (Tesla) using our own program according to an algorithm described earlier[33]. Further statistical treatment of the rate constants observed was carried out on a PC-AT computer using our own programs.

RESULTS AND DISCUSSION

The observed rate constants of acid-catalyzed decomposition of 1,3-bis(4-methyl-phenyl)triazene in the individual alcohols at various concentrations of trichloro-acetic acid are presented in Table I. The graphical representation of this dependence shows a non-linear course, the increase in the rate constant with increasing acid concentration being gradually smaller in all the solvents studied. The regression analysis using a number of regression functions provided two variables as the most suitable for interpretation, viz. the concentration of trichloroacetic acid and its second square root. The only explanation of this finding is an independent catalysis by two particles: the non-dissociated trichloroacetic acid (HA) and the proton (H^+) released by dissociation from acid. As the non-catalyzed decomposition was not observed, the dependence of the observed rate constant (k) of decomposition on the concentration (c) of the acid catalyst can be described by Eq. (1)

$$k = k_{HA}c + k_H K_a^{1/2} c^{1/2} , \qquad (1)$$

TABLE I

The observed rate constants (k in s^{-1}) of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene at various concentrations of trichloroacetic acid (c in mol dm^{-3}) in the given alcoholic solvents at 25°C

$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$
			Methanol				
0·030	7·70	0·030	7·45	0·073	13·3	0·073	12·8
0·073	12·4	0·095	16·1	0·095	16·5	0·12	19·3
0·12	20·4	0·15	23·1	0·15	21·7	0·18	25·7
0·18	26·7	0·18	26·7	0·22	28·9	0·25	30·1
0·25	31·5	0·29	34·7	0·29	36·5	0·37	43·3
0·37	40·8	0·49	53·3	0·49	49·5	0·60	57·8
0·60	55·5	0·60	60·3				
			Ethanol				
0·012	0·317	0·012	0·357	0·025	0·409	0·050	0·696
0·050	0·743	0·088	1·19	0·088	1·21	0·13	1·50
0·13	1·59	0·18	2·06	0·18	2·14	0·19	1·73
0·19	1·82	0·22	2·50	0·22	2·48	0·22	2·55
0·25	2·31	0·25	2·57	0·28	2·96	0·28	2·99
0·30	2·89	0·30	2·77	0·40	3·47	0·40	3·65
0·60	4·95	0·60	5·13	0·60	5·33	0·70	5·33
0·70	5·78	0•70	5·55	0·99	6·93	0·99	7·70
			1-Propanol				
0·10	0·422	0·16	0·685	0·16	0·675	0·27	1·30
0·27	1·08	0·50	1·79	0·50	1·67	0·70	2·04
0·70	2·10	0·70	2·17	0·72	2·06	0·82	2·69
0·84	2·24	0·84	2·31	0·84	2·39	0·92	2·57
1·0	2·69	1·2	3·01	1·6	3·85	1·6	3·65
1·6	3·47	2·0	4·36	2·0	4·21	2·1	4·95
2·1	4·78	2·6	5·33	2·6	5·55	2·6	5·13
3·2	6·93	3·2	7·30				
			2-Propanol				
0·11	0·271	0·11	0·330	0·18	0·408	0·36	0·751
0·36	0·651	0·50	0·749	0·50	0·742	0·94	1·08
0·94	0·959	1·3	1·30	1·3	1·38	1·8	1·49
1·8	1·48	2·7	2·24	2·7	2·16	2·7	2·24
2·7	2·10	3·4	2·47	3·4	2·21	3·6	2·77
3·6	2·72	3·6	2·67	5·5	3·85	5·5	3·65
7·0	5·33	7·0	4·78	7·0	4·57	9·1	6·03
12	6·93	12	7·70				

TABLE I
(Continued)

$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$	$c \cdot 10^2$	$k \cdot 10$
			1-Butanol				
0·11	0·272	0·11	0·331	0·17	0·385	0·17	0·398
0·67	1·02	0·67	1·05	1·6	2·04	1·6	2·04
1·9	2·30	1·9	2·51	2·0	2·57	2·0	2·67
2·7	3·47	2·7	3·15	2·7	3·30	3·2	3·32
3·2	3·55	4·0	4·08	4·0	4·33	6·0	6·30
6·0	5·78	8·5	7·70	8·5	7·53	13	10·8
13	11·6						
			2-Butanol				
0·31	0·158	0·31	0·144	0·61	0·226	0·61	0·264
1·3	0·53	1·3	0·564	1·3	0·610	2·3	0·878
2·3	0·840	3·8	0·990	3·8	1·07	3·8	1·02
4·4	1·39	4·4	1·42	4·7	1·33	4·7	1·36
4·7	1·24	5·7	1·54	5·7	1·48	5·7	1·44
5·7	1·39	6·8	1·93	6·8	1·83	7·7	1·98
7·7	1·82	7·7	1·63	7·7	1·73	9·5	2·31
9·5	2·24	9·8	2·42	9·8	2·55	15·0	3·30
18	3·85	18	4·07	26	5·33	26	4·62
26	4·95						
0·017	0·00834	0·035	0·0105	0·060	0·0147	0·12	0·0251
0·18	0·0234	0·45	0·0790	0·63	0·116	0·93	0·149
0·99	0·187	1·4	0·231	1·6	0·249	2·5	0·375
3·4	0·449						

where k_{HA} and k_H are the catalytic rate constants and K_a is the dissociation constant of trichloroacetic acid in the given solvent. The catalytic rate constants determined by the regression using Eq. (1) are summarized in Table II. The residual standard deviations in Table II indicate a high validity of the regression model used.

As there exists no absolute acidity scale, it is difficult to obtain significant values of dissociation constant of trichloroacetic acid in the solvents used and, hence, also significant catalytic constants. Nevertheless, the pK_a values published[34] (methanol 4·9, ethanol 5·7, 1-butanol 6·3) allow at least approximative estimates of the catalytic constant k_H to be made: methanol $1·1 \cdot 10^4$, ethanol $1·9 \cdot 10^3$, 1-butanol $1·2 \cdot 10^3$. From the trend of these values it can be presumed that the value will be still greater in water (undoubtedly differing in the order of magnitude). Hence the general

catalysis appears more likely. If we accept the hypothesis of specific catalysis, then the calculated rate constant k_H represents the quotient of the rate constant of decomposition of the protonated substrate into products and its dissociation constant. The value of dissociation constant can be determined only from the break in the dependence of log k vs pH, which would simultaneously represent univocal evidence in support of specific catalysis. However, this phenomenon has not been observed yet. From the comparison with the dissociation constant of diphenylamine in water[35] it follows that the dissociation constant of the presumed protonated substrate in water will be in the region of acidity function, i.e. great. The rate constant of decomposition into products can then be higher (by as much as several orders of magnitude) than the k_H value given. These high values throw doubt upon the model of specific catalysis, of course, without excluding it. If the k_H value found expresses the rate of general catalysis with the proton, then the increase by two orders of magnitude as compared with the k_{HA} constant is small. This indicates a small extent of bond formation between the substrate and catalyst in the transition state and corresponds to high reactivity of the proton.

The interpretation of the catalytic rate constants of Table II from the standpoint of solvent effect was carried out only with the individual empirical and semiempirical parameters due to the small number of solvents. The univocally closest correlation for the k_{HA} constant was obtained with the ACITY parameter by Swain et al.[36]

$$\log k_{HA} = -(7.02 \pm 0.52) + (1.30 \pm 0.08)\ 10^1\ \text{ACITY} \qquad (2)$$

$$s = 0.100, \quad r = 0.994, \quad n = 5.$$

TABLE II

The catalytic rate constants of Eq. (*1*) for the acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene (trichloroacetic acid in various alcoholic solvents) and the respective statistical characteristics (*s* residual standard deviation)

Solvent	k_{HA}	$s_k \cdot 10$	$k_H K_a^{1/2} \cdot 10$	$s_{kK} \cdot 10^2$	$s \cdot 10^4$
Methanol	471	338	395	206	180
Ethanol	47.3	29.8	27.2	22.0	3.84
1-Propanol	13.4	10.7	13.2	14.9	5.14
2-Propanol	4.63	2.60	5.65	6.62	3.73
1-Butanol	6.25	2.63	8.82	6.99	4.07
2-Butanol	1.29	0.747	3.32	2.80	2.17
Cyclohexanol	1.02	0.931	0.640	1.33	0.0157

Also the $E_T(30)$ parameter by Dimroth and Reichardt[37] gave a close correlation

$$\log k_{HA} = = (1.44 \pm 0.10) + (3.07 \pm 0.20) \cdot 10^{-1} E_T(30) \qquad (3)$$

$$s = 0.148, \quad r = 0.989, \quad n = 7,$$

all the measured k_{HA} values being included. Relatively close are also the correlations with the parameters π^* $(r = 0.987)$ and α $(r = 0.985)$ by Kamlet, Abboud and Taft[38]. On the other hand, the dependence on the β parameter by the same authors is not statistically significant. The correlation with the B parameter from the equation by Koppel and Palm is only little close $(r = 0.866)$. These results indicate the solvent participation in the transition state of the reaction investigated, in particular the stabilization of the conjugated base formed from the acid catalyst (a positive effect of the solvent acidity) and electrostatic stabilization of the transition state which is more polar than the reactants. The solvent basicity plays only a little part in the activation energy (the desolvation energy contribution during formation of the transition state). These results fully agree with the mechanism of general acid catalysis.

The interpretation of solvent effects on the combined constant $k_H K_a^{1/2}$ is somewhat more complicated. As in the above case the best correlation is obtained with the ACITY parameter[36]

$$\log k_H K_a^{1/2} = -(7.17 \pm 0.33) + (1.16 \pm 0.05) \cdot 10^1 \text{ ACITY} \qquad (4)$$

$$s = 0.064, \quad r = 0.997, \quad n = 5.$$

Very good correlations are also obtained with the E and α parameters

$$\log k_H K_a^{1/2} = -(3.10 \pm 0.42) + (3.10 \pm 0.36) \cdot 10^{-1} E \qquad (5)$$

$$s = 0.166, \quad r = 0.987, \quad n = 4,$$

$$\log k_H K_a^{1/2} = -(7.96 \pm 0.86) + (1.02 \pm 0.11) \cdot 10^1 \alpha \qquad (6)$$

$$s = 0.148, \quad r = 0.984, \quad n = 5.$$

Less close are the dependences on the parameters π^* $(r = 0.967)$, $(r = 0.957)$, $E_T(30)$ $(r = 0.967)$. On the other hand, the basicity plays here a more significant part than in the case of k_{HA} as it can be seen from the correlations with the parameters B $(r = -0.933)$ and β $(r = -0.960)$. The positive effects of solvent acidity indicate a stabilization of the conjugated base of the acid and, hence, increase of the concentration of the proton catalyst in the medium. The positive effect of polarity in the case of combined constant $k_H K_a^{1/2}$ is due to the increase of dissociation constant and, hence, the proton concentration in the reaction medium. The increased proton

solvation as compared with the non-dissociated acid is reflected in a negative effect of basicity. A qualitative idea about the behaviour of the k_H constant alone can be obtained from the above-given values. As this constant decreases with decreasing polarity and acidity and, at the same time, with increasing basicity of solvent, the first two properties of solvents affect positively the reactivity, whereas the basicity has a negative influence. The contributions of the individual effects, however, cannot be evaluated.

REFERENCES

1. Shine H. Y.: in *Aromatic Rearrangements*, p. 212. Elsevier, Amsterdam 1967.
2. Suizu K., Yokozima N.: J. Soc. Chem. Ind. Jpn. *19*, 32 (1926).
3. Hughes E. D., Ingold C. K.: Quart. Rev., Chem. Soc. *6*, 34 (1952).
4. Yamada T.: Bull. Chem. Soc. Jpn. *42*, 3565 (1961).
5. Kruglov V. K., Erskov A. P., Charcharov A. A.: Reakts. Sposobnost Organ. Soedin. *2*, 9 (1965).
6. Zvěřina V., Remeš M., Diviš J., Marhold J., Matrka M.: Collect. Czech. Chem. Commun. *38*, 251 (1973).
7. Isaacs N. S., Rannala E.: J. Chem. Soc., Perkin Trans. 2, *1974*, 899.
8. Isaacs N. S., Rannala E.: J. Chem. Soc., Perkin Trans. 2, *1974*, 902.
9. Beneš J., Beránek V., Zimprich J., Vetešník P.: Collect. Czech. Chem. Commun. *42*, 702 (1977).
10. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *45*, 1269 (1980).
11. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *45*, 2108 (1980).
12. Jones C. C., Kelly M. A., Sinnott M. L., Smith P. J.: J. Chem. Soc., Chem. Commun. *1980*, 322.
13. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *46*, 898 (1981).
14. Pytela O., Svoboda P., Večeřa M.: Collect. Czech. Chem. Commun. *46*, 2091 (1981).
15. Ludwig M., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *46*, 3104 (1981).
16. Jones C. C., Kelly M. A., Sinnott M. L., Smith P. J., Tzotzos G. T.: J. Chem. Soc., Perkin Trans. 2, *1982*, 1655.
17. Sieh D. H., Michejda C.: J. Am. Chem. Soc. *103*, 442 (1982).
18. Pytela O., Pilný M., Večeřa M.: Collect. Czech. Chem. Commun. *49*, 1173 (1984).
19. Smith R. H., Denlinger C. L., Kupper R., Koepke S. R., Michejda C. J.: J. Am. Chem. Soc. *106*, 1056 (1984).
20. Pytela O., Štumrová S., Ludwig M., Večeřa M.: Collect. Czech. Chem. Commun. *51*, 564 (1986).
21. Svoboda P., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *51*, 553 (1986).
22. Smith R. H., Denlinger C. L., Kupper R., Mehl A. F., Michejda C. J.: J. Am. Chem. Soc. *108*, 3726 (1986).
23. Svoboda P., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *52*, 2217 (1987).
24. Pytela O., Svoboda P., Večeřa M.: Collect. Czech. Chem. Commun. *52*, 2492 (1987).
25. Iley J., Moreira R., Rosa E.: J. Chem. Soc., Perkin Trans. 2, *1987*, 1503.
26. Gladkova V. F., Kondrashev Yu. D.: Kristallografiya *16*, 929 (1971).
27. Gladkova V. F., Kondrashev Yu. D.: Kristallografiya *17*, 33 (1972).
28. Kondrashev Yu. D.: Zh. Strukt. Khim. *15*, 517 (1974).
29. Schmiedekamp A., Smith R. H., Michejda C. J.: J. Org. Chem. *53*, 3433 (1988).

30. Nduen M. T., Hoesch L.: Helv. Chim. Acta *69*, 1627 (1986).
31. Šafařík L., Stránský Z.: *Odměrná analýza v organických rozpouštědlech.* SNTL, Prague 1982.
32. Fischer K.: Angew. Chem. *48*, 394 (1935).
33. Pytela O., Večeřa M., Vetešník P.: Chem. Listy *73*, 754 (1979).
34. Izmailov N. A., Izmailova V. N.: Zh. Fiz. Khim. *29*, 1050 (1955).
35. Pytela O., Vetešník P.: Collect. Czech. Chem. Commun. *48*, 2368 (1983).
36. Swain C. G., Swain M. S., Powel A. L., Alunni S.: J. Am. Chem. Soc. *105*, 502 (1983).
37. Reichardt C., Harbusch-Görnert E.: Liebigs Ann. Chem. *1983*, 721.
38. Kamlet M. J., Abboud J.-L. M., Abraham M. H., Taft R. W.: J. Org. Chem. *48*, 2877 (1983).
39. Palm V. A.: *Osnovy kolichestvennoi teorii organicheskikh reaktsii.* Khimiya, Leningrad 1977.

Translated by J. Panchartek.