
SOLVENT EFFECTS ON KINETICS AND MECHANISM OF ACID-CATALYZED DECOMPOSITION OF 1,3-BIS(4-METHYLPHENYL)-TRIAZENE II. REACTIONS IN APROTIC SOLVENTSOldřich PYTELA^a, Tatjana NEVĚČNÁ^b and Miroslav LUDWIG^a^a *Department of Organic Chemistry,
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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The effect of aprotic solvents (hexane, cyclohexane, dichloromethane, 1,2-dichloroethane, benzene, acetonitrile, acetone, 1,2-dimethoxyethane, ethyl acetate, dioxane) on kinetics and mechanism of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene has been studied with trichloroacetic acid as the acid catalyst. It has been found that beside the non-dissociated monomer of the acid also its dimer acts as the catalytic species. With regard to the results obtained in protic solvents (the catalysis by proton and general acid) three cases can be encountered of the dependence of observed rate constant on analytical concentration of the acid. The effect of solvents (inclusive of the protic ones) on the catalytic rate constant of the reaction with the non-dissociated monomer of acid is best interpreted by the equation suggested by Koppel and Palm and by the solvent scale suggested by us earlier. The solvent acidity and polarity have positive effect, whereas its basicity has negative effect. The catalytic rate constant of the reaction with the acid dimer decreases with increasing solvent basicity and polarity, due predominantly to the decrease in the equilibrium constant of dimerization.

In our previous communication¹ we evaluated the available knowledge about the mechanism and kinetics of acid-catalyzed decomposition of triazene derivatives. The most important was the finding of two forms of catalyst, namely the proton and the non-dissociated general acid (trichloroacetic acid was used). This indicates the existence of general catalysis in the decomposition of triazene derivatives in protic media, and this mechanism probably operates also in the proton catalysis.

The aim of this present communication is to extend the knowledge about the solvent effects on acid-catalyzed decomposition of triazene derivatives (using 1,3-bis(4-methylphenyl)triazene as a model substrate) in aprotic solvents with special regard to the mechanism of this reaction.

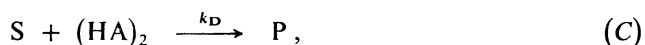
EXPERIMENTAL

The synthesis of the model triazene, kinetic experiments, and their treatment were described mainly in the previous report¹. The solvents were purified by known procedures².

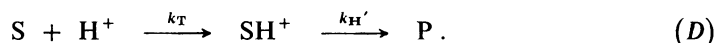
RESULTS AND DISCUSSION

The observed rate constants of acid-catalyzed decomposition of 1,3-bis(4-methylphenyl)triazene in 10 aprotic solvents are presented in Table I. As it was the case also with the kinetic measurements in alcoholic solvents¹ the dependences of the observed rate constant on analytical concentration of the catalyst trichloroacetic acid are not linear in all of the 10 solvents. A distinct increase of the observed rate constant corresponding to a higher order than the first order with respect to the acid concentration was observed in benzene, acetonitrile, acetone, 1,2-dimethoxyethane, ethyl acetate, and dioxane. A special behaviour is observed with benzene in which at low concentrations of acid ($c < 2.5 \cdot 10^{-3} \text{ mol dm}^{-3}$) the dependence exhibits an order in acid lower than 1, whereas at higher concentrations of acid ($c > 2.5 \cdot 10^{-3} \text{ mol dm}^{-3}$) a higher order with respect to acid is found. The aprotic non-polar solvents such as hexane, cyclohexane, dichloromethane, and 1,2-dichloroethane show linear dependences without statistically significant deviations. The non-linearity found by us was not observed with the application of benzoic acid as the catalyst³, and it is obviously due to properties of trichloroacetic acid in the given solvents. Trichloroacetic acid (as other organic acids) forms associates in aprotic solvents, mainly dimers^{4,5}. Thus a new particle appears in the reaction medium and can act as a catalyst or at least can affect concentrations of the other catalytic species.

Thus on the whole, the behaviour of the system of 1,3-bis(4-methylphenyl)triazene-trichloroacetic acid in solvents can be described by the following scheme



or we could admit an alternative specific catalysis, replacing Eq. (A) by Eq. (D)



In Eqs (A) through (D) S means the model substrate, HA represents the non-dissociated catalyst acid, $(HA)_2$ is its dimeric form, SH^+ means the protonated substrate, P stands for products, k_H , k_{HA} , k_D , and k_H' are the catalytic rate constants, and K_T is the equilibrium dissociation constant of the protonated substrate defined by the relation

$$K_T = [S][H^+]/[SH^+]. \quad (1)$$

TABLE I

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

$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$
Hexane							
0.022	4.08	0.031	5.48	0.032	5.78	0.038	5.91
0.038	5.91	0.053	8.31	0.064	10.8	0.080	12.3
0.080	12.1	0.085	13.1	0.085	13.0	0.085	13.4
0.11	14.4	0.11	14.4	0.14	20.8	0.14	20.6
0.15	21.0	0.15	21.6				
Cyclohexane							
0.0086	2.23	0.015	3.01	0.015	3.05	0.026	2.79
0.051	6.78	0.052	5.96	0.062	8.47	0.092	10.9
0.11	11.8	0.11	13.1	0.12	14.9	0.12	13.7
0.13	16.0	0.13	15.7	0.13	15.8	0.17	21.7
0.17	21.5	0.18	24.3	0.20	27.5	0.20	26.4
0.22	29.2	0.22	27.3	0.28	38.0		
Dichloromethane							
0.0041	0.0171	0.0089	0.0501	0.013	1.63	0.013	1.70
0.026	3.70	0.040	4.39	0.040	4.41	0.066	7.55
0.066	7.07	0.092	10.2	0.092	10.8	0.13	16.1
0.13	13.8	0.16	18.7	0.16	18.7	0.20	21.0
0.20	21.1						
1,2-Dichloroethane							
0.0019	0.311	0.0039	0.434	0.0078	0.677	0.0078	0.668
0.012	0.775	0.012	0.638	0.015	1.22	0.015	1.00
0.020	1.54	0.031	1.84	0.031	2.01	0.031	2.28
0.041	2.14	0.046	2.99	0.046	3.09	0.062	3.53
0.070	3.75	0.078	4.21	0.081	4.77	0.093	6.73
0.13	10.7	0.13	9.72	0.15	11.1	0.15	10.6
0.15	10.5	0.15	10.9	0.16	11.2	0.16	11.2
0.23	14.8	0.23	16.6	0.28	18.7	0.28	19.0
Benzene							
0.010	0.297	0.021	0.560	0.022	0.441	0.037	0.672
0.040	0.763	0.059	1.15	0.062	1.28	0.097	1.52
0.097	1.51	0.10	1.82	0.10	1.82	0.22	2.65
0.22	2.52	0.27	2.93	0.27	2.81	0.28	2.83
0.28	2.83	0.37	4.03	0.45	5.57	0.45	5.31
0.54	5.48	0.63	6.70	0.63	6.78	0.65	7.29
0.65	6.92	0.72	8.25	0.80	9.37	0.82	9.63
0.90	11.5	1.4	20.4				

TABLE I
(Continued)

$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$	$c \cdot 10^2$	$k \cdot 10^2$
Acetonitrile							
0.049	0.235	0.073	0.443	0.098	0.630	0.12	0.83
0.25	1.76	0.47	3.88	0.47	3.82	0.70	5.81
0.70	5.81	0.94	8.17	0.94	8.05	1.2	10.6
1.2	9.80	1.2	9.77	1.6	15.0	1.7	16.0
2.4	22.2	2.4	22.2				
Acetone							
0.50	0.115	0.50	0.141	0.92	0.250	0.92	0.247
1.7	0.504	1.7	0.546	2.4	0.910	2.4	0.889
3.2	1.53	3.2	1.49	6.1	3.70	6.1	3.84
9.2	6.66	9.2	6.64	12	10.3	12	10.7
12	10.2	15	13.2	15	14.1	19	18.1
19	18.1	21	20.4	21	21.0	22	21.5
22	21.2						
1,2-Dimethoxymethane							
0.56	0.0263	1.2	0.0383	2.6	0.107	5.4	0.379
8.1	0.734	11	0.900	11	0.840	11	0.855
16	1.43	16	1.48	21	2.36	21	2.50
25	3.16	25	3.10	29	4.00	29	4.66
33	5.47	33	5.32	40	7.05	40	7.41
47	9.60	47	9.86	50	11.9	50	11.6
57	14.0	57	14.5				
Ethyl acetate							
0.40	0.0250	0.74	0.0792	1.8	0.187	1.8	0.201
2.1	0.225	2.8	0.309	2.8	0.293	3.2	0.355
3.2	0.441	5.0	0.621	6.9	0.929	7.0	1.13
8.4	1.42	9.2	1.78	9.2	1.72	10	2.17
10	2.06	12	2.94	14	3.77	16	5.12
20	8.25						
Dioxane							
0.13	0.00121	0.32	0.00229	0.53	0.00250	0.77	0.00638
1.1	0.00901	2.2	0.0270	4.3	0.0341	6.2	0.0799
8.3	0.110	11	0.148	11	0.150	16	0.285
21	0.427	21	0.443	28	0.714	30	0.839
42	1.46	42	1.44	51	2.33	51	2.22

The equilibrium constants between the individual forms of trichloroacetic acid are defined by the relations

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] = [\text{H}^+]^2/[\text{HA}], \quad (2)$$

$$K_D = [(\text{HA})_2]/[\text{HA}]^2, \quad (3)$$

where K_a and K_D are the dissociation and dimerization constants, respectively, of trichloroacetic acid in the given medium.

Generally, three cases may occur which will be manifested by different types of dependences of the observed rate constant k on the analytical concentration of acid c .

1) The concentrations of the catalytic forms of acid are related as follows: $[(\text{HA})_2] \ll [\text{H}^+] < [\text{HA}]$. If the catalytic constant k_H is large enough, the observed dependence has the form of Eq. (4)

$$k = k_H K_a^{1/2} c^{1/2} + k_{\text{HAC}}, \quad (4)$$

where k_H is defined in Scheme (A) or represents the quotient k'_H/K_T in the case of validity of Scheme (D) (see the discussion in the previous paper¹). Only the proton and non-dissociated acid will be catalytically active, and this situation will preferably be encountered in protic solvents¹ where the formation of hydrogen bonds with solvent will be more favourable as compared with the dimer. Partially this situation can also be expected in dilute solutions of acid in aprotic solvents where the concentration of monomer is higher. Obviously this is the case of benzene as the solvent (vide supra). The combined constant $k_H K_a^{1/2}$ determined from the data of Table I up to the concentration $c < 2.5 \cdot 10^{-3} \text{ mol dm}^{-3}$ is $4.0 \cdot 10^{-1}$. As the dissociation constant K_a is very small in benzene, the catalytic constant k_H must be large, perhaps in the region of the diffusion-controlled reactions. This fact favours the general acid catalysis with proton in the sense of discussion in the previous paper¹. From another standpoint the existence of free protons in solvents such as benzene is surprising, on the other hand, however, it can be detected only by means of sufficiently sensitive reactions such as the decomposition studied by us.

2) Another possible relation is $[\text{H}^+] \ll [(\text{HA})_2] < [\text{HA}]$. The non-dissociated acid is still the predominant particle, but the dimer begins to be catalytically significant, too. In this case the dependence of the observed rate constant on the acid concentration reads as follows

$$k = k_{\text{HAC}} + k_D K_D c^2. \quad (5)$$

This dependence can be expected in the media which at least partially stabilize the monomer of acid and thus contribute to increase its concentration in the medium.

This requirement is met by the solvents containing a free electron pair able to form a hydrogen bond with the acid, e.g. ethers, esters, ketones, and some other compounds. Obviously, the role of electron donors can also be played by the π electron systems of aromatics as shown by the results obtained from the measurements in benzene. The catalytic rate constants k_{HA} and the combined constant $k_D K_D$ for the solvents used are summarized in Table II. The evaluation of activity of the dimer in comparison with the monomer of acid is complicated by the dimerization equilibrium constant K_D . As obviously also higher associates are formed in the solution

TABLE II

The catalytic rate constants of Eqs (5) and (6) for the decomposition of 1,3-bis(4-methylphenyl)-triazene catalyzed with trichloroacetic acid in aprotic solvents and their statistical characteristics inclusive of the residual standard deviation s

Solvent	$k_{HA} \cdot 10^2$ ($s \cdot 10^2$) ^a	$k_D K_D$ (s) ^a	$k_D \cdot 10^2$ (s) ^a	$s \cdot 10^3$
Hexane	—	—	2.95 (4.24)	8.36
Cyclohexane	—	—	2.57 (3.34)	11.4
Dichloromethane	—	—	2.22 (3.53)	7.78
1,2-Dichloroethane	—	—	1.42 (2.20)	7.39
Benzene	875 ^b (44.7)	$3.66 \cdot 10^2$ ($4.80 \cdot 10^1$)	—	4.73
Acetonitrile	801 (23.0)	$5.55 \cdot 10^1$ ($1.20 \cdot 10^1$)	—	3.68
Acetone	59.3 (3.63)	1.84 ($1.95 \cdot 10^{-1}$)	—	5.40
1,2-Dimethoxyethane	3.41 (0.596)	$3.82 \cdot 10^{-1}$ ($1.31 \cdot 10^{-2}$)	—	2.58
Ethyl acetate	1.55 (0.844)	1.94 ($5.89 \cdot 10^{-2}$)	—	1.15
Dioxane	0.388 (0.133)	$7.79 \cdot 10^{-2}$ ($3.12 \cdot 10^{-3}$)	—	0.401

^a The standard deviation of the respective quantity. ^b From the data subtracted was the effect of the dependence (4) — see the text.

(although in minor concentrations), the K_D value is somewhat depending on the concentration of acid⁴. The K_D value of trichloroacetic acid is available only in benzene^{4,5}. Taking the mean value of $K_D(\text{benzene}) = 10$, we obtain $k_D(\text{benzene}) = 3.7 \cdot 10^1$. Hence the dimer is a somewhat stronger catalyst than the monomer, which agrees with the idea of the assistance of a second molecule of acid in the proton transfer in the transition state.

3) The last possible relation is $[\text{H}^+] < [\text{HA}] \ll [(\text{HA})_2]$. In this case the dimer predominates in the reaction medium and, at the same time, is a stronger catalyst than HA. Other forms of the catalyst do not make themselves felt catalytically, and the dependence of the observed rate constant on the concentration of acid reads as follows

$$k = 0.5k_{DC} \quad (6)$$

This is a situation typical of the solvents unable of formation of hydrogen bonds with the acid catalyst, i.e. solvents of the sort of aliphatic hydrocarbons and halogen derivatives. The catalytic rate constants k_D determined from Eq. (6) are summarized in Table II. The above-estimated k_D constant in benzene is in good accordance with them.

Another source of information about the system studied is provided by the quantitative description of solvent effect by means of empirical equations. The equation with a single empirical parameter $E_T(30)$ (the parametrization from ref.⁶) could interpret the values of catalytic constant k_{HA} found for 6 solvents from Table II and 7 alcohols from the previous communication¹ only with the correlation coefficient $r = 0.766$. A similar result ($r = 0.774$) was obtained from the application of the equation by Swain et al.⁷, the ACITY parameter only being statistically significant. Better results were obtained with application of the equation by Kamlet, Abboud and Taft (the parametrization according to these authors⁸):

$$\log k_{\text{HA}} = (9.39 \pm 7.17) \cdot 10^{-1} + (5.97 \pm 1.15) \alpha - (5.39 \pm 1.84) \beta$$

$$s = 0.800, \quad R = 0.914, \quad n = 9. \quad (7)$$

Out of the equations used currently at present, the empirical equation by Koppel and Palm⁹ proved to be the best one in application to the given data:

$$\log k_{\text{HA}} = - (6.71 \pm 9.18) \cdot 10^{-1} + (7.07 \pm 2.48) Y +$$

$$+ (2.75 \pm 0.54) \cdot 10^{-1} E - (1.88 \pm 0.41) \cdot 10^{-2} B$$

$$s = 0.589, \quad R = 0.957, \quad n = 9. \quad (8)$$

However, the overall best results were obtained by application of the new statistical

scale of solvent parameters¹⁰:

$$\begin{aligned} \log k_{\text{HA}} = & - (6.45 \pm 1.18) + (9.68 \pm 1.07) PA - (8.33 \pm 1.45) PB + \\ & + (1.54 \pm 0.28) \cdot 10^1 PP \end{aligned} \quad (9)$$

$s = 0.462, \quad R = 0.974, \quad n = 9.$

As it can be seen from the empirical equations (7) and (8) obtained with application of the scales with the defined origin in vacuum, the quantity $\log k_{\text{HA}}$ for vacuum has statistically significant zero value. Hence the reaction would proceed more slowly in this medium than in protic solvents and little basic aprotic solvents but – on the contrary – faster than in basic aprotic solvents such as ethers, esters, and ketones. All the empirical correlation relations given indicate a positive effect of solvent acidity and negative effect of solvent basicity. Therefrom it follows that in the transition state of the reaction the solvent stabilizes (by its acidity) the conjugated base formed from the general acid HA. On the other hand, an increased basicity results in increased solvation of the general acid HA before the reaction and, hence, in the activation energy increased by this additional solvation energy. The results concerning the solvent polarity are contradictory. Whereas in the cases of less successful empirical correlation equations the respective parameter dropped out as insignificant (the BASITY parameter in the equation by Swain et al.⁷ describes also predominantly the polarity¹¹), it appears as statistically significant in Eqs (8) and (9). In Eq. (9), which adopts standardized parameters, the *PP* parameter describing polarity/polarizability represents the greatest contribution (even though with the smallest partial correlation coefficient) to interpretation of the dependence. Polarity makes itself felt undoubtedly in the reaction, any increased stabilization of a more polar transition state (as compared with the reactants) leading to acceleration of the reaction. The conclusions given do not quite agree with the results obtained in the study³ of solvent effect on decomposition of 1-(4-methylphenyl)-3-methyltriazene with benzoic acid. Although the correlations with currently employed parameter scales were relatively close, the only important property of solvent was its basicity (ref.¹¹, the process No. 284). Applications of the parameters by Pytela¹⁰ were less close, however, the solvent polarity appeared as an additional parameter. These differences are probably due to the acid employed (the acidity difference between trichloroacetic and benzoic acids in water is greater than three orders of magnitude), the different solvent set investigated (the absence of acidity effects from the data by Isaacs and Rannala³ is caused by the selection of aprotic solvents), and partially also the substrate used.

The small number of catalytic rate constants k_{D} and/or $k_{\text{D}}K_{\text{D}}$ (Table II) does not allow to carry out a quantitative evaluation of solvent effect by means of multi-parameter correlation equations. Application of $E_{\text{T}}(30)$ parameters⁶ and ACITY,

BASITY (ref.⁷) did not lead to a statistically significant dependence. Qualitatively it can be stated that in the case of k_D constant an increase in solvent polarity and basicity results in the decreased k_D value. The dominant manifestation of solvent is the decrease of K_D constant (see Eq. (3)) and, hence, also of the dimer concentration. The solvent effect on the combined constant $k_D K_D$ is more complex. Obviously, the same effect as in the previous case makes itself felt, but the differences are larger, and the two effects are not equally significant in all the solvents.

In conclusion it can be stated that simple derivatives of triazene are very sensitive substrates with regard to the presence of substances able to provide protons, it making no matter whether the proton is free or bound in a general acid or its dimer. The fastest reaction takes place with the proton, a somewhat slower one with the non-dissociated acid itself, and several orders slower one with the acid dimer. The reactions with acids and probably also with the proton go by the mechanism of general acid catalysis.

REFERENCES

1. Nevěčná T., Pytela O., Ludwig M., Kaválek J.: *Collect. Czech. Chem. Commun.* **55**, 147 (1990).
2. Šafařík L., Stránský Z.: *Odměrná analýza v organických rozpouštědlech*. SNTL, Prague 1982.
3. Isaacs N. S., Rannala E.: *J. Chem. Soc., Perkin Trans. 2*, **1974**, 902.
4. Bulmer J. T., Shurvell H. F.: *J. Phys. Chem.* **77**, 256 (1973).
5. Bulmer J. T., Shurvell H. F.: *Can. J. Chem.* **53**, 1251 (1975).
6. Reichardt C., Harbusch-Görnert E.: *Liebigs Ann. Chem.* **1983**, 721.
7. Swain C. G., Swain M. S., Powel A. L., Alunni S.: *J. Am. Chem. Soc.* **105**, 502 (1983).
8. Kamlet M. J., Abboud J.-L. M., Abraham M. H., Taft R. W.: *J. Org. Chem.* **48**, 2877 (1983).
9. Palm V. A.: *Osnovy kolichestvennoi teorii organicheskikh reaktivii*. Khimiya, Leningrad 1977.
10. Pytela O.: *Collect. Czech. Chem. Commun.* **54**, 136 (1989).
11. Pytela O.: *Collect. Czech. Chem. Commun.* **53**, 1333 (1988).

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