REACTIVITY OF PROTON AND GENERAL ACID WITH 1,3-BIS-(4-METHYLPHENYL)TRIAZENE IN AQUEOUS METHANOL

Oldřich Pytela[a]. Tatjana Nevěčná[b] and Jaromír Kaválek[a]

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

The effect of concentration of benzoic acid and composition of the binary solvent water–methano˙ on the rate of decomposition of 1,3-bis(4-methylphenyl)triazene has been studied. It has been found that both general acid catalysis by undissociated benzoic acid and catalysis by the proton are significant. The rate constant k_{HA} of general acid catalysis decreases monotonously with decreasing amount of water in the mixture due to preferred solvation of the activated complex as compared with the educts. The rate constant k_H of the catalysis by proton in its dependence on methanol concentration exhibits a minimum for 80% (by wt.) of methanol in the mixture. This phenomenon is caused by formation of the conjugated acid from more basic methanol and proton with simultaneous solvation by water and methanol; the particle thus formed is a weaker acid as compared with the complexes existing in water or in methanol. The k_H value is higher in methanol than in water due to preferred solvation of the educts as compared with that of the transition state.

As compared with individual solvents, solvent mixtures are substantially more complex from the standpoint of description of chemical and physical processes taking place therein. The interpretation of measured manifestations of most varied processes in mixed solvents is usually based — beside the structural properties of the solvent itself (see e.g. ref.[1]) — predominantly on an empirical description (for a survey see e.g. ref.[2]). The most widespread parametric scales are the Y scale by Grunwald and Winstein[3], the $E_T(30)$ scale by Reichardt in the modification by Langhals[4], and the scale by Kamlet and Taft[5–7]. With regard to the large number of mixed solvents it is advantageous to use a description by empirical function[2]; the procedure based on the additional Gibbs energy[8] proved to be relatively suitable.

A special standing among mixed solvents is assumed by mixtures water–organic solvent, particularly in connection with studies of behaviour of ions in these media. In this respect the most significant ion undoubtedly is the proton[9]. Neglecting the media formed by concentrated solutions of acids, one can study the behaviour of proton in a mixed aqueous-organic solvent preferably with the help of the following methods: dissociation of weak acids (e.g. refs[10–14]), electrochemistry[15], the Gibbs energy changes accompanying the proton transfer from a standard solvent (water)

into a mixed one[16,17], a reaction with suitably sensitive substrate. Such substrates undoubtedly include triazenes which are split into the respective diazonium salt and amine by action of the proton, a general acid, or its dimer. This reaction can be carried out practically in any solvent as we showed in earlier papers[18,19] of this series which also give a survey of reactions of triazene derivatives. Our studies[18–20] as well as those by other authors[21] show that the decomposition is subject to general acid catalysis and mechanistically represents an electrophilic substitution at nitrogen atom $(A-S_E 2)$. The mechanism involving protonation with subsequent decomposition of the protonated substrate in the rate-limiting step $(A-1)$ is not likely (even in aprotic solvents[19]) with respect to the reactivity of triazenes, although it continues to be mentioned in literature (ref.[22] and a survey in ref.[18]).

The aim of the present communication is to adopt 1,3-bis-(4-methylphenyl)triazene as a substrate labile to acids for measurements (and interpretation) of the activity of benzoic acid and of the proton formed by its dissociation in aqueous methanol.

EXPERIMENTAL

The synthesis of 1,3-bis(4-methylphenyl)triazene, drying of methanol, and kinetic measurements are described elsewhere[18]. The data obtained were treated statistically according to our own programs using a PC-AT. In the optimizations the objective function was constructed as a sum of squares of differences of logairthms.

RESULTS AND DISCUSSION

Like in the measurements with trichloroacetic acid[18] also the decomposition with benzoic acid exhibits a dependence of the observed rate constant k_{obs} on the analytical concentration c of the catalyst acid in a form corresponding to the participation of both general acid and the proton in the reaction. The dependence can be quantitatively described as follows

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

where k_{HA} and k_H are the catalytic constants in the reaction of the substrate with nondissociated acid and proton, respectively, and K_a is the dissociation constant of general acid. The constants k_{HA} and $k_H K_a^{1/2}$ are presented in Table I. The same table also gives the standard deviations s which in average vary about the value of 0·1 units of $\log k_{obs}$, which indicates a relatively good quality of interpretation of experimental data by Eq. (1). From the data of Table I it follows that both the rate constants mentioned decrease with decreasing water content in the mixed solvent, the decrease in k_{HA} being faster. In neat methanol the k_{HA} constant is statistically insignificant as compared with the $k_H K_a^{1/2}$ constant, which indicates that the substrate reacts only with the proton.

The decrease in the k_{HA} constant with decreasing content of water in the mixture was expected. Since the proton transfer from general acid to substrate is connected with creation of charges in the transition state, the latter is more solvated than the educts in any solvent. A transition from a better solvating solvent to a worse one is predominantly connected with a decrease in solvation of the activated complex, hence also with a marked deceleration of the reaction. The change in solvation ability can be due to both the change in relative permittivity of medium and that in quality of specific solvation at the molecular level. The latter case usually leads to nonlinear dependences on some characteristics reflecting the mixture composition[2,4,8]. In our case it is possible to find a very close dependence of logairthm of the k_{HA} rate constant on the volume fraction of solvent (x_{wt}) as follows:

$$\log k_{HA} = (3.09 \pm 0.13) - (4.97 \pm 0.21) x_{wt} , \tag{2}$$

$$n = 8, \quad s = 0.137, \quad r = 0.994 .$$

A markedly worse fit of the dependence is obtained with the application of molar fraction (x_{mol}):

$$\log k_{HA} = (2.49 \pm 0.12) - (4.86 \pm 0.33) x_{mol} , \tag{3}$$

$$n = 8, \quad s = 0.219, \quad r = 0.987 .$$

TABLE I

Weight concentraions of methanol in water (w/w, %) the concentration ranges of benzoic acid $(\Delta c, \text{ mol dm}^{-3})$, the number (n) of experimental rate constants determined in the solvent of the given composition, the catalytic constants $(k_{HA}$ and k_H, $\text{dm}^3 \text{ }^{-1} \text{ s}^{-1})$, and the residual standard deviations (s) in Eq. (1) (in logarithmic units)

w/w	Δc	n	k_{HA}	$k_H . 10^{-2}$	s
20	$7.5 . 10^{-4} - 2.5 . 10^{-2}$	22	148	15.3	0.1469
30	$2.1 . 10^{-4} - 3.5 . 10^{-2}$	39	29.6	14.4	0.1453
40	$6.0 . 10^{-4} - 5.2 . 10^{-2}$	31	12.9	7.59	0.0828
50	$6.0 . 10^{-4} - 5.6 . 10^{-2}$	28	6.03	4.03	0.1263
60	$1.0 . 10^{-3} - 1.6 . 10^{-1}$	32	1.04	3.21	0.0880
70	$6.0 . 10^{-4} - 4.5 . 10^{-1}$	40	0.269	3.19	0.0848
80	$1.2 . 10^{-3} - 8.2 . 10^{-1}$	36	0.179	2.17	0.0765
90	$5.6 . 10^{-3} - 1.3 . 10^{0}$	40	0.0413	3.19	0.2646
100	$5.7 . 10^{-2} - 2.2 . 10^{0}$	30	$-^a$	30.7	0.1439

^{a} Statistically insignificant (0.000 308).

A similarly significant dependence was also found with the Y parameter by Grunwald and Winstein[23]:

$$\log k_{HA} = -(1{\cdot}05 \pm 0{\cdot}10) + (1{\cdot}02 \pm 0{\cdot}06)\,Y, \tag{4}$$

$$n = 8, \quad s = 0{\cdot}185, \quad r = 0{\cdot}990.$$

In all the cases the statistically insignificant value of $\log k_{HA}$ for neat methanol was excluded from the regression. With respect to k_{HA} the mixed solvent studied behaves as an ideal mixture (in terms of the published theory[8] the additional Gibbs energy is statistically insignificant), the macroscopic quantity (volume of solvent components) and not the ratio of molecules being substantial. The m value found in the equation by Grunwald and Winstein[3] in unexpectedly high as compared with the value found for noncatalyzed solvolysis of acyltriazenes[24], and it indicates a rather charged transition state. As the k_{HA} constant reflects the situation in general catalysis, the dependence of $\log k_{HA}$ vs $\log K_a$ is also interesting in the sense of the Brönsted equation. This dependence (with the K_a values taken from refs[25,26]) reads as follows:

$$\log k_{HA} = (8{\cdot}78 \pm 0{\cdot}67) + (1{\cdot}50 \pm 0{\cdot}12) \log K_a, \tag{5}$$

$$n = 8, \quad s = 0{\cdot}252, \quad r = 0{\cdot}981.$$

As the regression coefficient in Eq. (5) is distinctly greater than one, the found decrease of k_{HA} with decreasing water concentration is connected with a more extensive solvation of the transition state during the proton transfer to the more basic nitrogen atom of triazene (compared with the solvation of the dissociation products after the proton transfer to the respective oxygen-containing solvent).

A somewhat more complicated situation is encountered with the reaction of the proton solvated in the given medium and the triazene substrate. The combined constant $k_H K_a^{1/2}$ decreases with decreasing water content, but after dividing it by the $K_a^{1/2}$ value (taken from refs[25,26]) we obtain the k_H constant which at first decreases and, after reaching the minimum at 80% (by wt.) methanol, it steeply increases to attain a value which is higher than that in water (Table I). If we only consider the reaction with the proton as an unsolvated particle, then the rate constant k_{HA} should increase on transition from water to methanol. The starting species are more solvated (the localized charge on the proton) than the transition state (the charge is delocalized), hence a transition to a less solvating solvent leads to a slight increase in the reaction rate. This process probably is significant at higher methanol concentration in the mixtures, and it has the consequence that the catalytic rate constant k_H is greater in methanol than in water. As, however, the proton is not free in the given medium, but is bound to a solvent molecule and further solvated[9,27,28], it behaves — in fact — as a new acid whose properties are continuously

or abruptly changed with solvent changes. In any case the main factor is the strength of the conjugated acid formed (which is indirectly proportional to the basicity of the host conjugated base and its solvation[27,28]). Due to the $+I$ effect of alkyl group, alcohols are usually more basic than water and the corresponding conjugated acids are weaker than H_3O^+. Alcohols theoretically also have a greater solvation ability (due to their higher basicity) for the conjugated acid formed. In fact, however, alcohols (due to the presence of bulky and nonpolarized alkyl group) stabilize charged particles substantially worse than water does, which can be seen from the standard molar Gibbs energies of the proton transfer from water to organic solvent (ΔG_t, refs[16,17]). The last paper cited studies the proton transfers from water to aqueous organic mixtures, and the dependence found between ΔG_t and composition of the binary solvents show minima about 60% (by weight) of the organic solvents (methoxyethanol, 1,2-dimethoxyethane). The same response to changes in solvent composition is also exhibited by the potential of glass electrode: the minimum for aqueous methanol was found between 60 and 70% (by weight) of methanol[29]. From the analysis given it follows that the proton in aqueous methanol is bound predominantly to the alcohol, and the conjugated acid formed is solvated by methanol and water: in the most stable arrangement probably by one molecule of methanol and two water molecules (molar ratio 1 : 1). The number of molecules in the solvate can be even greater (at the same molar ratio) but never smaller. If the concentration of proton––solvent adduct were linearly dependent on the molar concentration of solvent, no extremes could be observed but, instead, again only a linear dependence. If we turn back to the reaction studied, we can state that the decrease in the k_H rate constant with decreasing water content is unequivocally connected with formation of less strong conjugated acids in the solution. A small shift in position of the extreme (after recalculation to the same characteristics of composition, e.g. molar fraction) as compared with the data of the glass electrode potential[29] is due to a superposition of the manifestations of the conjugated acid and (probably) linear increase in k_H caused by different solvation of the educts and of the transition state.

REFERENCES

1. Franks F., Ines D. J. G.: Quart. Rev. 20, 1 (1966).
2. Pytela O.: Collect. Czech. Chem. Commun. 53, 1333 (1988).
3. Grunwald E., Winstein S.: J. Am. Chem. Soc. 70, 846 (1948).
4. Langhals H.: Angew. Chem., Int. Ed. 21, 724 (1982).
5. Krygowski T. M., Reichardt C., Wrona P. K., Wyszomirska C., Zielkowska U.: J. Chem. Res., Synop. 1983, 116.
6. Krygowski T. M., Wrona P. K., Zielkowska U., Reichardt C.: Tetrahedron 41, 4519 (1985).
7. Cheong W. J., Carr P. W.: Anal. Chem. 60, 820 (1988).
8. Pytela O., Ludwig M.: Collect. Czech. Chem. Commun. 53, 671 (1988).
9. Bell R. P.: The Proton in Chemistry. Chapman, London 1973.
10. Bates R. G.: J. Electroanal. Chem. 29, 1 (1971).

11. Kolthoff I. M., Chantooni M. K. in: *Treatise on Analytical Chemistry* (I. M. Kolthoff and P. I. Elving, Eds), Part 1, Vol. 2. Wiley, New York 1979.
12. Nummert V.: Org. React. (Tartu) *20*, 279 (1983).
13. Ludwig M., Pytela O., Večeřa M., Sb. Ved. Pr., Vys. Sk. Chemicko-technol., Pardubice *46*, 81 (1984).
14. Sadek H., Sidahmed M.: Z. Phys. Chem. (Leipzig) *270*, 929 (1989).
15. Bates R. G. in: *The Chemistry of Non-aqueous Solvents* (J. J. Lagowski, Ed.), Vol. 1, p. 97. Academic Press, New York 1966.
16. Glikberg S., Marcus Y.: J. Solution Chem. *12*, 255 (1983).
17. Ghosh S. K., Hazra D. K.: J. Chem. Soc., Perkin Trans. 2, *1989*, 1021.
18. Nevěčná T., Pytela O., Ludwig M., Kaválek J.: Collect. Czech. Chem. Commun. *55*, 147 (1990).
19. Pytela O., Nevěčná T., Ludwig M.: Collect. Czech. Chem. Commun. *55*, 156 (1990).
20. Pytela O., Svoboda P., Večeřa M.: Collect. Czech. Chem. Commun. *52*, 2492 (1987).
21. Jones C. C., Kelly M. A., Sinnott M. L., Smith P. J., Tzoztos G. T.: J. Chem. Soc., Perkin Trans. 2, *1982*, 1655.
22. Smith R. H., Wladkowski B. D., Mehl A. F., Cleveland M. J., Rudrow E. A., Chmurny G. N., Michejda C. J.: J. Org. Chem. *54*, 1036 (1989).
23. Fainberg A. H., Winstein S.: J. Am. Chem. Soc. *78*, 2770 (1956).
24. Pytela O., Svoboda P., Večeřa M.: Collect. Czech. Chem. Commun. *46*, 2091 (1981).
25. Voňáková Z., Štráfelda F.: Collect. Czech. Chem. Commun. *36*, 2993 (1971).
26. Exner O., Kalfus K.: Collect. Czech. Chem. Commun. *41*, 569 (1976).
27. Wels C. F.: Trans. Faraday Soc. *61*, 2194 (1965).
28. Wels C. F.: Trans. Faraday Soc. *62*, 2815 (1966).
29. Gelsema W. J., DeLigny C. L., Remijnse A. G., Blijleven H. A.: Rec. Trav. Chim. *85*, 647 (1966).

Translated by J. Panchartek.