SOLVOLYSIS KINETICS AND MECHANISM OF SUBSTITUTED 3-ACETYL-1,3-DIPHENYLTRIAZENES IN ACID MEDIUM; KINETIC ACIDITY FUNCTION

Oldřich Pytela, Martin Kaska, Miroslav Ludwig and Miroslav Večeřa

Department of Organic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

The decomposition kinetics has been measured of fourteen 3-acetyl-1,3-bis(subst.phenyl)triazenes in 40% (v/v) ethanol and sulphuric acid. The kinetic acidity function and catalytic rate constants have been determined from the rate constants observed. Mechanism has been suggested for the general acid-catalyzed solvolysis from comparison of the course of the kinetic acidity function and H_0 function and from the reaction constant of the Hammett equation.

The solvolysis kinetics and mechanism of 3-acetyl-1,3-diphenyltriazenes $(X-C_6H_4-$ $-N=N-N(COCH_3)-C_6H_4-X)$ has already been dealt with in several papers[1-4], but only the spontaneous solvolysis was studied in more detail[4] and the presence of water was proved in the activated complex of its rate-limiting step. The activation entropy of the acid-catalyzed hydrolysis of 3-acetyl-1,3-diphenyltriazene is positive[1], which indicates the operation of the mechanism of acid-catalyzed hydrolysis of amides. The same conclusion was made in the case of acid-catalyzed solvolysis of the cognate substituted 3-carbamoyl-1,3-diphenyltraizenes[5]. The proton-induced splitting of triazene chain of the title substrates can proceed according to the mechanisms of general or specific acid catalysis. The general acid-catalyzed decomposition was found in solvolyses of 1-aryl-3-alkyltriazenes[6] and is usually denoted as A-S$_E$2. The mechanism of specific acid-catalyzed decomposition can be monomolecular, *e.g.* in the decomposition of 1,3-diphenyl-3-methyltriazenes[7] or 1-aryl-3-alkyl-triazenes[8-10], or bimolecular with participation of water as a nucleophile, as it is the case with the spontaneous solvolysis of 3-N-methylcarbamoyl-1,3-diphenyl-triazenes[11].

A piece of information on the mechanism of reactions in strongly acidic media is provided by the kinetic acidity function[12-15], because a comparison of the courses of the kinetic acidity function and the acidity function constructed from equilibrium processes gives a valuable indication of the role of water in the reaction mechanism[15]. Another advantage of the kinetic acidity function lies in the possibility of obtaining the catalytic rate constants whose values depend on the acidity function characterizing

the protonating medium, and, moreover, most dependences of log k_{obs} on the acidity function values do not have a unit slope[3].

The aim of this present communication is to suggest a mechanism of acid-catalyzed solvolysis of 3-acetyl-1,3-diphenyltriazene with application of the Hammett relation and kinetic acidity function.

EXPERIMENTAL

Syntheses and properties of the X-substituted 3-acetyl-1,3-diphenyltriazenes were described in the previous paper[4]. The same procedure was used to complete the series by the 4-acetyl and 4-cyano derivatives with the following results: X = 4-CH$_3$CO; yield 38·1%; m.p. 105—107°C; % N calculated/found 14·04/14·21, X = 4-CN; yield 11·5%; m.p. 209—212°C; % N calculated/ /found 24·21/24·36.

The standard procedure was applied[4] in the kinetic measurements of the decomposition in the medium of 40% (v/v) ethanol and 0·01 to 4·9 mol dm^{-3} sulphuric acid at 25·0 ± 0·1°C. The wavelengths used for the 4-acetyl and 4-cyano derivatives were 325 and 308 nm, respectively. The sulphuric acid concentration was determined titrimetrically immediately after finishing the experiment. The kinetic data were evaluated by the procedure given in ref.[16] using a Sinclair ZX 81 microcomputer. The kinetic acidity function and catalytic rate constants were calculated by the KINAC program[15] on an EC 1033 computer.

RESULTS AND DISCUSSION

From 283 values of the rate constants observed for the individual substitution derivatives (16 to 26 measurements for each derivative) the kinetic acidity function H_K was constructed for 40% (v/v) ethanol and the sulphuric acid concentration range from 0·01 to 4·9 mol dm^{-3}. The acidity function obtained increases monotonously and can be described by an orthogonal polynomial $(z = \log c(H_2SO_4)$, c in mol . . dm$^{-3})$ in the following form:

$$H_K = 2{\cdot}0798338z + 1{\cdot}1418569z^2 + 1{\cdot}11774047z^3 + 1{\cdot}3595110z^4 +$$
$$+ \; 0{\cdot}86574399z^5 + 0{\cdot}19337551z^6 . \tag{1}$$

A comparison of the kinetic acidity function H_K of solvolysis of 3-acetyl-1,3-diphenyltriazenes with the acidity function H_0 by Paul and Long[17] is presented in Fig. 1. In analogy to 3-hydroxy-1,3-diphenyltriazenes[15] measured in the same medium, the H_K function is shifted downward as compared with the straight line $H_K = H_0$, which is obviously due to the addition of the organic solvent. However, as low as from $H_0 = 0$ we can observe an upward deviation of the H_K function, and from the values of $H_0 = 1$ the kinetic acidity function has a higher value than H_0. This phenomenon can be interpreted as a consequence of changed water activity, as it is shown in Eq. (2).

$$H_K = -(0.434 \pm 0.025) + (1.063 \pm 0.028) H_0 - (4.439 \pm 0.564) \log a \, (H_2O)$$

$$n = 41 \,, \quad s = 0.299 \,, \quad R = 0.9983 \tag{2}$$

As the proton represents the most solvated particle in the given medium, its activity will be most affected by any change in the water activity due to partial or even complete desolvation during formation of the activated complex. The regression coefficient of the term $\log a(H_2O)$ has a value which indicates a loss (the acidity function increases with decreasing water activity) of four to five water molecules during the formation of the activated complex. This value fully agrees with the number of water molecules in the solvation sphere of the proton[18,19] (most probably four). Therefrom it can be concluded that the proton is almost completely desolvated in the activated complex and, hence, the proton–substrate bond is formed to a considerable extent.

The effect of an acidfying medium on the protonation of substrate expressed by the coefficient of H_0 is identical with the model of primary aromatic amines[17] or also diphenylamines[20]. This finding supports the idea of the protonation at nitrogen atom 3 of the triazene chain.

When constructing the kinetic acidity function we obtained the catalytic rate constants which are summarized in Table I. The dependence of logarithms of the catalytic rate constants on the substituent constants of the Hammett relation (the values taken from ref.[21]) can be described by Eq. (*3*).

$$\log k_H = -(1.404 \pm 0.082) - (3.547 \pm 0.177) \sigma_{Ex} \tag{3}$$

$$n = 14 \,, \quad s = 0.206 \,, \quad R = 0.985$$

The analysis of differences between experimental values of the dependent variable and the values calculated from the regression showed that some of the substitution
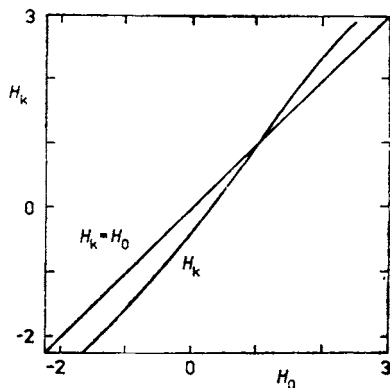

Fig. 1

Comparison of the kinetic acidity function H_K of solvolysis of 3-acetyltriazenes in sulphuric acid and 40% (v/v) ethanol with the standard acidity function H_0

derivatives $(4\text{-OCH}_3, 4\text{-CN}, 3\text{-NO}_2, 4\text{-NO}_2)$ exhibit a distinct deviation from the linear dependence. Almost the same result is obtained if the substituent constants used are those obtained from the measurement of dissociation constants of substituted benzoic acids in water[22].

$$\log k_H = -(1\cdot420 \pm 0\cdot086) - (3\cdot539 \pm 0\cdot187)\,\sigma_W \qquad (4)$$
$$n = 14, \quad s = 0\cdot218, \quad R = 0\cdot984$$

A distinct improvement is achieved by application of the substituent constants determined from the measurements of dissociation of substituted benzoic acids in water and in six organic solvents (methanol, ethanol, acetonitrile, acetone, dimethylformamide, sulpholane) (σ_{F7}) or only in the organic solvents (σ_{F6}) (ref.[22]).

$$\log k_H = -(1\cdot254 \pm 0\cdot066) - (3\cdot790 \pm 0\cdot143)\,\sigma_{F7} \qquad (5)$$
$$n = 14, \quad s = 0\cdot157, \quad R = 0\cdot992$$

$$\log k_H = -(1\cdot280 \pm 0\cdot064) - (3\cdot888 \pm 0\cdot143)\,\sigma_{F6} \qquad (6)$$
$$n = 14, \quad s = 0\cdot153, \quad R = 0\cdot992$$

Comparison of Eqs (3), (4) and (5), (6) supports the hypothesis about the solvent effect on the substituent constant of the Hammett equation which was suggested in our earlier paper[22].

Irrespective of the substituent constant set used, the reaction constant has a negative value comparable with those of the cognate triazene derivatives: 3-(N-methyl-carbamoyl)-1,3-diphenyltriazenes; water; 25°C; $\varrho = -3\cdot193$ (ref.[5]), 1,3-diphenyltriazenes; 20% ethanol; 20°C; $\varrho = -5\cdot932$ (ref.[23]). Disregarding the reaction condi-

TABLE I
Catalytic rate constant of solvolysis of substituted 3-acetyl-1,3-diphenyltriazenes XC_6H_4N=$=N-N(COCH_3)C_6H_4X$ in 40% (v/v) ethanol and sulphuric acid obtained from the kinetic acidity function. In brackets given is the number of k_{obs} for the corresponding derivative

X	k_H	X	k_H
4-OCH$_3$ (16)	$5\cdot69 \cdot 10^{-1}$	3-Cl (21)	$1\cdot24 \cdot 10^{-3}$
4-CH$_3$ (20)	$1\cdot88 \cdot 10^{-1}$	3-Br (21)	$1\cdot19 \cdot 10^{-3}$
H (18)	$4\cdot86 \cdot 10^{-2}$	4-COCH$_3$ (22)	$1\cdot15 \cdot 10^{-3}$
4-Cl (26)	$5\cdot27 \cdot 10^{-3}$	3-CN (17)	$1\cdot27 \cdot 10^{-4}$
4-Br (22)	$4\cdot49 \cdot 10^{-3}$	4-CN (19)	$2\cdot03 \cdot 10^{-4}$
3-F (21)	$1\cdot58 \cdot 10^{-3}$	3-NO$_2$ (17)	$1\cdot31 \cdot 10^{-4}$
3-COCH$_3$ (22)	$1\cdot82 \cdot 10^{-3}$	4-NO$_2$ (21)	$1\cdot20 \cdot 10^{-4}$

tions, we can consider the substituent effect on stabilization of the diazonium cation formed according to the equation

$$X—C_6H_4—N=N—NR—C_6H_4—X + H^+ \rightarrow$$

$$\rightarrow X—C_6H_4—N_2^+ + RNH—C_6H_4—X$$
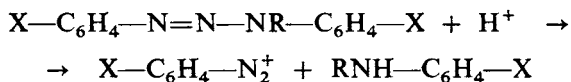
to be identical in all the triazene derivatives given. The replacement of the hydrogen atom in 1,3-diphenyltriazene by an acyl group results in a distinct lowering of the absolute value of the reaction constant which cannot be explained by the change in reaction conditions and is greater with acetyl than with N-methylcarbamoyl group. The differences exhibited are due to a higher electron-acceptor ability of the acyl as compared with hydrogen atom, which facilitates the splitting of the N(2)—N(3) bond.

REFERENCES

1. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *45*, 1269 (1980).
2. Pytela O., Svoboda P., Večeřa M.: Collect. Czech. Chem. Commun. *46*, 2091 (1981).
3. Ludwig M., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *46*, 3104 (1981).
4. Pytela O., Pilný M., Večeřa M.: Collect. Czech. Chem. Commun. *49*, 1173 (1984).
5. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *45*, 2108 (1980).
6. Jones C. C., Kely M. A., Sinnott M. L., Smith P. J., Tzotzos G. T.: J. Chem. Soc., Perkin Trans. 2, *1982*, 1655.
7. Yamada T.: Bull. Chem. Soc. Japan *42*, 3565 (1961).
8. Zvěřina V., Remeš M., Diviš J., Marhold J., Matrka M.: Collect. Czech. Chem. Commun. *38*, 251 (1973).
9. Isaacs N. S., Rannala E.: J. Chem Soc., Perkin Trans. 2, *1974*, 899.
10. Isaacs N. S., Rannala E.: J. Chem. Soc., Perkin Trans. 2, *1974*, 902.
11. Pytela O., Večeřa M., Vetešník P.: Collect. Czech. Chem. Commun. *46*, 898 (1981).
12. Greig C. C., Johnson D. C., Rose A., Taylor P. G.: J. Org. Chem. *44*, 745 (1979).
13. Johnson D. C., Rose S., Taylor P. G.: J. Org. Chem. *44*, 753 (1979).
14. Graham W. L. E., Johnson C. D.: J. Chem. Soc., Perkin Trans. 2, *1982*, 1025.
15. Pytela O., Štumrová S., Ludwig M., Večeřa M.: Collect. Czech. Chem. Commun. *51*, 564 (1986).
16. Pytela O., Večeřa M., Vetešník P.: Chem. Listy *73*, 745 (1979).
17. Paul M. A., Long F.: Chem. Rev. *57*, 1 (1957).
18. Bell R. P.: *The Proton in Chemistry*. Chapman and Hall, London 1973.
19. Gutmann V.: *The Donor–Acceptor Approach to Molecular Interactions*. Plenum Press, New York 1978.
20. Pytela O., Vetešník P.: Collect. Czech. Chem. Commun. *48*, 2368 (1983).
21. Exner O.: *Korelační vztahy v organické chemii*. Published by SNTL/ALFA — Nakladatelství technické literatury, Prague 1981.
22. Pytela O., Ludwig M., Večeřa M.: Collect. Czech. Chem. Commun. *51*, 2143 (1986).
23. Beneš J., Beránek V., Zimprich J., Vetešník P.: Collect. Czech. Chem. Commun. *42*, 702 (1977).

Translated by J. Panchartek.