KINETICS AND MECHANISM OF ACID CATALYZED DECOMPOSITION OF SUBSTITUTED 1,3-DIPHENYLTRIAZENES

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The kinetics of acid catalyzed decomposition of 3-substituted and 1,3-disubstituted 1,3-diphenyl-3-methyltriazenes have been studied in 40% aqueous ethanolic buffers at 25°C. The reaction constant for substitution of the phenyl ring at the 3 position of the triazene chain has been determined and the reaction constants of the protonation and bond splitting between the nitrogen atoms 2 and 3 have been estimated. By the covariance analysis it has been found that the standard constants of the Hammett relation are better than the constants determined in the media of organic solvents. Also estimated were the values of the slope β_{1g} of the linear relation between the rate constants and the equilibrium between the diazonium salt and diazotate. The A-S_E2 mechanism is suggested as probable, the bond between nitrogen atoms of triazene chain being more than half split in the transition state and the nitrogen–proton bond formation being more advanced than the nitrogen–nitrogen bond splitting.

This work forms a continuation of the previous communication[1] which dealt with kinetics and mechanism of the acid catalyzed decomposition of 1-substituted 1,3-diphenyl-3-methyltriazenes. From the substituent effects it was impossible to differentiate between the alternative mechanisms A1 (the protonated substrate formed in a rapid pre-equilibrium is split into products in the rate-limiting step) and A-S_E2 (the rate-limiting step involves both the proton transfer on the substrate and the bond splitting between the nitrogen atoms 2 and 3 of the triazene chain). Both the mechanisms were suggested in literature as it was already mentioned in the previous analysis[1].

The aims of the present communication are a statistical evaluation of validity of the Hammett equation for the acid catalyzed decomposition of substituted 1,3-diphenyl-3-methyltriazenes with application of various sets of the substituent constants, and, on the basis of comparison of the reaction constants for substitution in 1- and 3-phenyl rings, an estimation of the most probable reaction mechanism.

EXPERIMENTAL

The 1-phenyl-3-(X-phenyl)-3-methyltriazenes and 1-(X^1-phenyl)-3-(X^2-phenyl)-3-methyltriazenes were prepared by the reaction of substituted N-methylanilines with the respective benzene-

diazonium salt by the procedure described earlier[1]. Yields, physical properties, and elemental analyses of the compounds prepared are given in Table I. The substituted N-methylanilines were prepared from the respective acetanilides by the following procedure: 250 ml benzene, 20 g sodium hydroxide dissolved in 50 ml water, and 2·5 g benzyltriethylammonium chloride were added to 0·1 mol substituted acetanilide, and the mixture was intensively shaken 30 min.Thereafter, 11·5 ml (0·125 mol) dimethyl sulphate was added, and the mixture was shaken 2 h. The benzene layer was separated and washed successively with 250 ml water, 250 ml 20% hydrochloric acid, and three 150 ml portions of water. The raw product obtained by evaporation of benzene was recrystallized from cyclohexanol. Raw N-methylaniline was obtained by hydrolysis of N-methylacetanilide in aqueous–ethanolic hydrogen chloride (100 ml 50% aqueous ethanol and 20 ml conc. hydrochloric acid per 0·1 mol anilide; 1 h).

The kinetic measurements were carried out in the same way as in our previous work[1]. The results were treated by means of an EC 1033 computer and an IQ-151 microcomputer with application of our own programs.

RESULTS AND DISCUSSION

Table II contains the rate constants of acid catalyzed decomposition of substituted 1,3-diphenyl-3-methyltriazenes $X^1C_6H_4N{=}N{-}N(CH_3)C_6H_4X^2$ in 40% (v/v) aqueous–ethanolic buffers of various pH values at 25°C. The pH dependences of rate constants were submitted to the linear regression treatment to obtain the $\log k_I$ and b values (the same symbols as in ref.[1]) according to Eq. (1)

$$\log k_{obs} = \log k_I - b\,pH\,. \qquad (1)$$

TABLE I

Yields, physical properties, and results of elemental analyses of substituted 3-methyl-1,3-diphenyltriazenes $X^1{-}C_6H_4{-}N{=}N{-}N(CH_3){-}C_6H_4{-}X^2$

Compound	X^1	X^2	Yield %	M.p. °C	Calc. found % N	λ_{max} nm
I	H	3-CH$_3$	75	oil	18·65/18·50	346
II	H	4-CH$_3$	68	28—30	19·65/18·42	345
III	H	4-Cl	55	30—32	17·10/17·21	358
IV	H	3-NO$_2$	53	97—98·5	12·49/12·31	337
V	4-CH$_3$O	3-NO$_2$	68	105—106	19·57/19·03	351
VI	4-F	4-Br	72	84·5—85	13·64/13·26	347
VII	4-F	3-NO$_2$	70	104—106	23·13/23·38	339
VIII	4-CH$_3$O	4-CH$_3$	38	103—104	16·46/16·75	349

Table III gives the parameters calculated along with the statistical characteristics. In contrast to the X^1-substituted derivatives[1], the slopes for the X^2-substituted and X^1,X^2-disubstituted 1,3-diphenyl-3-methyltriazenes do not exhibit a statistically significant difference from 1. The $\log k_1'$ values calculated from the relation

$$\log k_1' = n^{-1} \sum_{i=1}^{n} (\log k_{obs} + pH)_i \tag{2}$$

show a smaller standard deviation as can be seen from Table IV.

The calculated catalytic constants of Tables III and IV along with those of ref.[1] were used to determine the parameters of the extended Hammett equation

$$\log k_1 = (2.089 \pm 0.077) - (3.391 \pm 0.199)\,\sigma_1 -$$
$$- (1.948 \pm 0.247)\,\sigma_2 \tag{3}$$
$$n = 22, \quad s = 0.276, \quad R = 0.971$$

$$\log k_1' = (2.242 \pm 0.065) - (3.444 \pm 0.173)\,\sigma_1 -$$
$$- (2.153 \pm 0.211)\,\sigma_2 \tag{4}$$
$$n = 22, \quad s = 0.244, \quad R = 0.978.$$

The substituent constants by Exner[2] were used in the calculation.

The way given for calculation of the reaction constants is applicable but not quite correct statistically. Moreover, it does not allow a verification of validity of the Hammett equation. In the calculation starting directly from the values of observed rate constants according to the formulas

$$\log k_{obs} = \log k_{00} + b\,pH + \varrho_{10}\sigma_1 + \varrho_{02}\sigma_2 \tag{5}$$

or

$$(\log k_{obs} + pH) = \log k_{00}' + \varrho_{10}'\sigma_1 + \varrho_{02}'\sigma_2, \tag{6}$$

it is possible to apply the covariance analysis to determine the extent of the explained variance. At the same time, Eq. (6) is an unambiguous regression model, because the independent variables are non-random. Application of Eqs (5) and (6) to the data of Table II of this report and Table III of the previous report[1] gave the following dependences:

$$\log k_{obs} = (2.080 \pm 0.035) - (0.934 \pm 0.008)\,pH -$$
$$- (3.565 \pm 0.029)\,\sigma_1 - (2.164 \pm 0.038)\,\sigma_2 \tag{7}$$
$$n = 229, \quad s = 0.102, \quad R = 0.995$$

and

$$(\log k_{obs} + pH) = (2.357 \pm 0.008) - (3.641 \pm 0.031)\,\sigma_1 -$$
$$- (2.276 \pm 0.039)\,\sigma_2 \qquad (8)$$
$$n = 229, \quad s = 0.115, \quad R = 0.993.$$

The reaction constants obtained by all the methods given are comparable; application of Eqs (5) and (6) leads to more accurate and undoubtedly also more correct results.

Validity of the regression relation applied to the experimental data can be examined by means of the covariance analysis. The overall dispersion variance can be divided into the part explained by the regression model (S_V), the part describing the error of specification of the regression model (lack of fit) (S_S), and the residual pure error, given by the experimental error (S_R). Comparison of the dispersion variances S_S

TABLE II

The rate constants of acid-catalyzed decomposition of substituted 1,3-diphenyl-3-methyltriazenes $I-VIII$ in buffers with various pH values (40% (v/v) C_2H_5OH/H_2O, 25°C)

pH	$10^3 k$, s^{-1}	$10^5 s_k{}^a$	pH	$10^3 k$, s^{-1}	$10^5 s_k{}^a$
I, $X^1 = H$; $X^2 = 3\text{-}CH_3$			II, $X^1 = H$; $X^2 = 4\text{-}CH_3$		
3.30	138	85.7	3.61	95.9	17.9
3.30	130	101	4.12	24.9	13.8
3.61	57.1	29.4	4.24	23.9	11.5
3.85	31.4	15.2	4.36	19.6	5.88
3.85	30.2	19.9	4.45	14.9	6.98
4.24	14.6	7.36	4.60	12.0	6.75
4.36	12.0	7.57	4.74	8.19	2.66
4.45	10.9	8.20	4.84	6.01	7.89
4.60	6.93	4.19	5.09	3.57	2.44
4.74	2.55	1.47	5.58	1.17	3.60
4.84	3.96	2.31	6.09	0.284	0.445
5.09	2.07	3.57	—	—	—
5.58	0.664	3.34	—	—	—
III, $X^1 = H$; $X^2 = 4\text{-}Cl$					
2.73	128	96.9	3.61	17.4	15.2
2.88	100	46.1	3.85	8.97	11.6
3.31	33.8	24.0	4.12	5.72	5.02

TABLE II

(*Continued*)

pH	$10^3 k, \text{s}^{-1}$	$10^5 s_k{}^a$		pH	$10^3 k, \text{s}^{-1}$	$10^5 s_k{}^a$
	IV, $X^1 = \text{H}$; $X^2 = 3\text{-NO}_2$				V, $X^1 = 4\text{-CH}_3\text{O}$; $X^2 = 3\text{-NO}_2$	
2·73	13·9	7·98		2·73	112	117
2·88	8·23	3·38		2·88	69·5	54·4
3·02	5·94	3·03		3·02	52·5	28·9
3·30	3·26	2·12		3·30	36·6	21·5
3·61	1·45	1·03		—	—	—
3·85	1·00	1·57		—	—	—
4·36	0·293	0·164		—	—	—
4·45	0·200	0·234		—	—	—
	VI, $X^1 = 4\text{-F}$; $X^2 = 4\text{-Br}$				VII, $X^1 = 4\text{-F}$; $X^2 = 3\text{-NO}_2$	
2·73	42·7	54·2		2·73	5·05	12·0
2·88	34·1	44·9		2·88	3·38	8·66
3·02	16·1	45·3		3·02	2·47	5·88
3·30	10·2	35·2		3·30	1·39	4·24
		$VIII$, $X^1 = 4\text{-CH}_3\text{O}$; $X^2 = 4\text{-CH}_3$				
4·74	83·2	64·1		5·58	18·8	11·0
4·74	81·6	64·2		6·09	4·83	4·11
4·84	70·6	44·2		5·23	2·90	1·62
5·09	45·9	16·3		6·60	1·40	1·09

^{a} The standard deviation of the rate constant k.

TABLE III

The values of $\log k_I$ and slopes of pH profiles b determined according to Eq. (*1*)

Compound	$\log k_I$	$s(\log k_I)$	b	s_b	n	R
I	2·4159	0·1607	−1·006	0·037	14	−0·993
II	2·4315	0·1163	−0·958	0·025	10	−0·997
III	1·8704	0·0014	−1·006	0·027	6	−0·999
IV	0·8226	0·0929	−1·001	0·027	7	−0·998
V	1·7771	0·4049	−0·824	0·135	4	−0·974
VI	1·2520	0·6145	−1·151	0·206	4	−0·970
VII	0·3312	0·1486	−0·969	0·050	4	−0·997
$VIII$	3·5587	0·1874	−0·968	0·039	4	−0·996

and S_R enables testing of the validity of the model according to the criterion

$$F(m - k - 1, n - m) = (n - m) S_S[(m - k - 1) S_R]^{-1}, \qquad (9)$$

where n means the number of experimental points, m is number of classes with the same values of the independent variable, and k is the number of regressors. The regression relation (7) explains 98·965 of the original variance, $S_S = 2\cdot225$, $S_R = 9\cdot946 \cdot 10^{-2}$, and $F(178,47) = 5\cdot906$. As this value is larger than the critical one, it must be stated that Eq. (7) insufficiently explains the experimental data used. The same conclusion is reached by the analysis using Eq. (8): $S_S = 1\cdot259$, $S_R = 1\cdot732$, and $F(18,208) = 8\cdot396$. No improvement is achieved even with application of the substituent constants calculated from the measurements of dissociation of benzoic acids in organic solvents[3] (set σ_{F6}) as it is documented by the standard deviations $s = 0\cdot142$ and $0\cdot153$ for Eqs (5) and (6), respectively. Obviously, aqueous methanol is closer to water (the standard substituent constants) than to the selected organic solvents of ref.[3] (set σ_{F6}) in its character of affecting the substituents. The attempt at interpretation of the experimental data by the Yukawa–Tsuno equation using σ_p^+ constants for the 1-phenyl substituents results in a slight improvement ($s = 0\cdot101$), but the respective regression coefficient is statistically insignificant.

The failure of Eqs (5) and (6) in interpretation of substituent effects from the statistical point of view can be explained in two ways. In the first case the validity of the Hammett equation is given by the substituent constant set used, hence in the correlations with the universal set of substituent constants the validity region of the substitution model is broader from the physical point of view than from the matematical-statistical point of view. In the opposite case other factors make themselves felt besides the substituent effects, these factors being hidden e.g. in the kinetic model used for evaluation of the rate constants.

If we resign ourselves to leaving the statistical viewpoint, and if we take into account that the Hammett equation is an approximative relation which is usually

TABLE IV
The values of log k_I' and their standard deviations determined from Eq. (2)

Compound	log k_I'	s (log k_I')	Compound	log k_I'	s (log k_I')
I	2·3896	0·0850	V	1·7764	0·0631
II	2·6171	0·0495	VI	1·3271	0·0794
III	1·8485	0·0291	VII	0·4231	0·0186
IV	0·8094	0·0403	VIII	3·7339	0·0903

fulfilled with an accuracy of about 0·06 units of $\log k$ (ref.[2]), we can accept the accuracy in the individual substituent series $(s(X^1) = 0.0604$, ref.[1]; $s(X^2) = 0.0645$ for the relation type (6)). A mere combination without disubstitution in the two nuclei causes, at the same time, an increase in the value of the overall standard deviation to $s = 0.108$ (the relation type (6)). The application of Eq. (5) leads to similar conclusions. Obviously, the source of larger standard deviation lies in non-additivity of substituent effects in the two phenyl groups of 1,3-diphenyl-3-methyltriazenes. Regardless of the way of calculation of the reaction constants for substituents in the 1- and 3-phenyl groups, the overall reaction constant $(\varrho_1 + \varrho_2) \approx -5.9$ agrees well with the value $\varrho = -5.932$ found for 1,3-diphenyltriazenes in 20% ethanol at 20°C (ref.[4]). Hence, the presence of methyl group at the N(3) atom has no distinct effect on the charge distribution during the reaction. The reaction constant ϱ_1 agrees fully with the results obtained for the acid-catalyzed decomposition of 1,3-diphenyl-3-methyltriazenes in 95% aqueous ethanol at 30°C $(\varrho = -3.63)$ (ref.[5]). Both the value and sign of the reaction constant ϱ_2 stand in accordance with those of the acid-catalyzed hydrolysis of 3-(N-subst. phenylcarbamoyl)-1,3-diphenyltriazenes[6] (water, 25°C, $\varrho = -0.730$).

The reaction constants ϱ_1 and ϱ_2 reflect (without considering any particular mechanism) two phenomena — the protonation of substrate at the nitrogen 3 and splitting of the bond between the nitrogen atoms 2 and 3. Whereas the protonation contributions into the reaction constants will be negative, ϱ_{P1} being slightly smaller than ϱ_{P2} (roughly 2/3 according to ref.[7]), the contributions reflecting the N(2)—N(3) bond splitting will have opposite signs and will be roughly the same $(\varrho_{S1} = \varrho_{S2})$. Presuming validity of the relation $\varrho_{P2} \approx 1.5\varrho_{P1}$, we can obtain, by simple calculation, the values $\varrho_{P1} \approx 2.53$, $\varrho_{P2} = 3.37$ and $-\varrho_{S1} = \varrho_{S2} = 1.24$. The estimates of the protonation reaction constants agree well with the values found for the protonation of anilines[2]. On the other hand, the estimate of ϱ_S has a small value and indicates partial N(2)—N(3) bond splitting in the transition state of the rate-limiting step. The reaction studied can be treated as an electrophilic substitution at nitrogen atom, the bond formation to the electrophile being more advanced than the bond splitting to the leaving group in the transition state.

If the diazonium ion is considered as the leaving group, then the sensitivity to leaving group can be estimated from the substituent effects on the equilibria with hydroxyl ion[8,9]. In our case the results will be somewhat deformed due to the reaction of diazonium ion with two hydroxyl ions. As the substituents will affect the equilibrium diazonium salt–diazonium hydroxide in the same sense as the equilibrium diazonium hydroxide–diazotate, it can be expected that the calculated value of slope of the linear dependence β_{lg} will be somewhat smaller just due to operation of the latter equilibrium. The dependence of catalytic constants of 8 derivatives substituted in the 1-phenyl ring[1] on the pK values of the equilibrium diazonium salt–diazotate[10] can be described by the equation

$$\log k_1 = (4{\cdot}712 \pm 0{\cdot}074) + (0{\cdot}520 \pm 0{\cdot}010)\,\mathrm{p}K \qquad (9)$$
$$n = 8, \quad s = 0{\cdot}065, \quad R = 0{\cdot}999 \,.$$

Hence the N(2)—N(3) bond is more than half split in the transition state. Roughly the same result was also obtained by Jones et al.[11] who found $\beta_{\mathrm{lg}} = 0{\cdot}6$ for the acid-catalyzed decomposition of 1-phenyl-3-propyltriazene.

In conclusion it can be stated that the acid-catalyzed decomposition of 1,3-diphenyl--3-methyltriazenes goes by the A-S_E2 mechanism, the proton–nitrogen bond formation being more advanced than the nitrogen–nitrogen bond splitting of the triazene chain in the transition state. The nitrogen–nitrogen bond splitting itself is more than half finished in the transition state.

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