SUBSTITUENT EFFECT ON SOLVOLYSIS OF 3-ACETYL-1,3-DIPHENYLTRIAZENES

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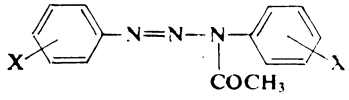
Eleven symmetrically disubstituted 3-acetyl-1,3-diphenyltriazenes have been synthetized by a new method. The solvolysis kinetics of the title compounds has been measured in 20% aqueous ethanol at several temperatures. The results are discussed from the point of view of temperature and substituent effects on the solvolysis rate constant of the 3-acetyl-1,3-diphenyltriazenes and conclusions are drawn about the reaction mechanism.

The 3-acetyl-1,3-diphenyltriazine derivatives *I* have not been much studied so far. Most data concern the non-substituted compound whose synthesis[1-9] and spectral properties[3] were described, as well as kinetics of its thermal decomposition[1,4,5], solvent effects[8] and salt effects[9] on its hydrolysis. Out of the derivatives of 3-acetyl--1,3-diphenyltriazene, the 4-methyl derivative[10] and various 4,4′ non-symmetrically disubstituted derivatives[4] are known. The compounds of this type have found industrial application as rubber additives which improved physico-mechanical properties[6]. 1-(4-Methylphenyl)-3-methyl-3-acetyltriazene was described[11] as antiparasitic agent.



I

In our previous papers[7-9,12,13] we suggested a mechanism of spontaneous solvolysis of this type of compounds. The aim of the present work is to verify the previous mechanistic suggestions by means of substituent effects and temperature dependences.

EXPERIMENTAL

The 1,3-diphenyltriazenes used in synthesis were prepared by the modified method according to ref.[14]. The corresponding substituted aniline (0·6 mol) was dissolved in 200 ml concentrated hydrochloric acid and 150 ml water. The solution was cooled to 0°C, and the suspension formed

was treated with solution of 41·4 g (0·6 mol) sodium nitrite in 200 ml water added drop by drop with stirring. 0·5 mol substituted aniline was mixed with 20 ml conc. hydrochloric acid and 125 ml water. The mixture was heated until dissolution of the hydrochloride formed and, while hot, treated with solution of 170 g anhydrous sodium acetate in 750 ml water, whereupon the mixture was cooled to 0°C, and the suspension formed was combined with the above diazonium salt solution. The mixture was stirred for further 2 h without cooling. The separated solid was washed with water and dried in air.

The parent 1,3-diphenyltriazene was acetylated according to ref.[1], whereas with the substituted derivatives this acetylation either failed or gave products of low purity.Therefore, we adopted the following procedure: 0·025 mol of the disubstituted triazene was dissolved in 150 ml toluene and treated with a sodium methoxide solution prepared from 0·7 g sodium and 20 ml methanol. All the methanol and about a half of the original amounts of toluene were removed by distillation. The resulting solution was cooled, and the separated salt was collected by suction with exclusion of air moisture, washed successively with toluene and hexane until the filtrate was pale yellow. The isolated salt was suspended in 50 ml hexane, 3 g freshly distilled acetic anhydride was added thereto, and the mixture was boiled on water bath 10 min. After cooling, the product was collected by suction, washed with hexane, and recrystallized from the same solvent. The whole synthesis necessitates perfectly dry solvents and exclusion of moisture. The yields and physical properties of the synthetized disubstituted 3-acetyl-1,3-diphenyltriazenes are given in Table I.

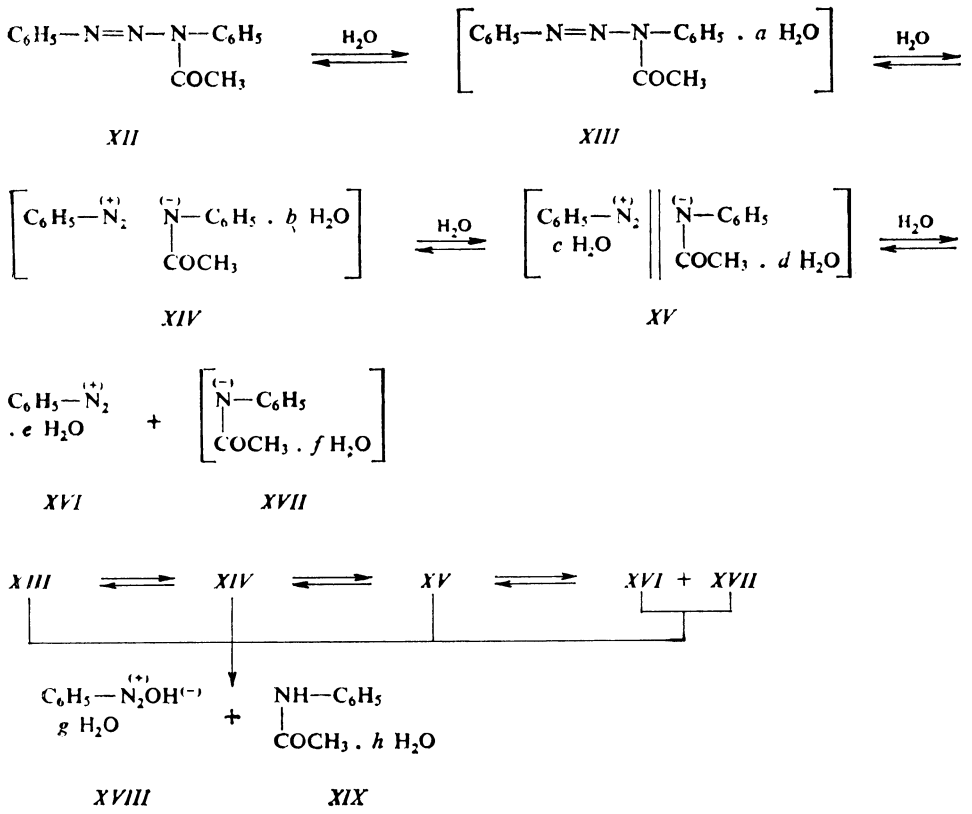
The kinetic measurements were carried out by the described method[5] in 20% (v/v) aqueous ethanol at the wavelength of the last absorption band using the Specord UV-VIS and VSU-2 apparatus (Zeiss, Jena). The experimental data were treated with the use of our own algorithms[13,15].

RESULTS AND DISCUSSION

Table II gives the solvolysis rate constants of the symmetrically disubstituted 3-acetyl--1,3-diphenyltriazenes in 20% (v/v) aqueous ethanol.

On the basis of previous studies[7–9,12,13], we suggested for the parent compound a mechanism analogous (except for the opposite charges) to the S_N1 mechanism (Scheme 1). The existence of the intimate, loose, and separated ionic pairs is deduced from the measurements of salt effects on this reaction[9], from participation of water in the transition state, and from solvent effects[8].

The treatment of the results given in Table II gave the values of activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ which are summarized in Table III. All the activation entropies are negative, which indicates that the transition state is less disordered than the starting substances due obviously to solvation of the charged fragments. When compared with the same quantity of analogous 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes (whose hydrolysis, however, was measured in water), the activation entropies of the 3-acetyl derivatives are smaller. As acetyl group has a greater ability to stabilize the anion formed (Scheme 1) than N-methylcarbamoyl group, and, hence, participation of solvent as a factor diminishing the transition state energy can be less distinct, the difference is probably due to transition to the aqueous-organic solvent, whose own order is less and enables better coordination of water molecules in the transition state.



SCHEME 1

Treatment[13] of the rate constants given in Table II (except for 4,4'-dinitro derivative) gave the isokinetic temperature $\beta = -4{\cdot}128 \cdot 10^3$ K, $n = 105$, $s_0 = 0{\cdot}064$, $s_{00} = 0{\cdot}072$, $\psi = 0{\cdot}094$ and three criteria[16,17] for statistical evaluation of the existence of the isokinetic temperature. According to these criteria the used set of straight lines are parallel ($F_3(10{\cdot}83) = 1{\cdot}66$; $F_{0{\cdot}95}(10{\cdot}83) = 1{\cdot}94$), *i.e.*, the reaction is isoenthalpic, although they intersect statistically in one point ($F_1(10{\cdot}83) = 0{\cdot}70$), *viz* even in the point $T^{-1} = 0$ ($T \to \infty$, $F_2(10{\cdot}83) = 0{\cdot}68$), hence, from this point of view the reaction is isoentropic, too. Comparison of the s_0 and s_{00} values indicates that scattering of the experimental values is comparable with that given by the opening of the determining family of lines, and, hence, the determination of the isokinetic temperature is meaningless under these conditions. According to the last criterion – the Exner test ψ (ref.[18]) – which tests the isokinetic relation as an approximative one, the isokinetic relation is fulfilled from "well" to "badly".

The activation parameters were used for calculation of he solvolysis rate constants

of substituted 3-acetyl-1,3-diphenyltriazenes at 25°C (Table II) which (except for the 4,4'-dinitro derivative) gave linear dependence (*1*) on the Hammett σ constants[19]:

$$\log k_{25} = -(3{\cdot}00 \pm 0{\cdot}05) - (2{\cdot}36 \pm 0{\cdot}12)\,\sigma \qquad (1)$$

$$n = 11, \quad s = 0{\cdot}114, R = 0{\cdot}989\,.$$

This dependence is represented graphically in Fig. 1. The 4,4'-dinitro derivative behaves anomalously as compared with the other compounds. The same situation has already been observed with the substituted 3-(N-methylcarbamoyl)-1,3-diphenyl-

TABLE I

Yields and physical properties of the disubstituted 3-acetyl-1,3-diphenyltriazenes X—C_6H_4—N=N—N($COCH_3$)—C_6H_4—X

X	M.p., °C (yield, %)	Formula (mol.mass)	Calculated/found % N	λ_{max}, nm
4-NO_2	126—130 (6·0)	$C_{14}H_{11}N_5O_5$ (329·3)	21·27 21·57	256
3-NO_2	140—143 (8·7)	$C_{14}H_{11}N_5O_5$ (329·3)	21·27 21·17	270
3-CN	119—123 (28)	$C_{16}H_{11}N_5O$ (289·3)	24·21 24·09	285
3-Br	86—87 (37)	$C_{14}H_{11}Br_2N_3O$ (397·1)	10·58 10·30	286
3-Cl	102—105 (25)	$C_{14}H_{11}Cl_2N_3O$ (308·2)	13·64 13·20	290
3-CH_3CO	115—120 (40)	$C_{18}H_{17}N_3O_3$ (323·4)	13·00 13·59	282
3-F	63—67 (33)	$C_{14}H_{11}F_2N_3O$ (275·3)	15·27 14·96	286
4-Br	123—129 (20)	$C_{14}H_{11}Br_2N_3O$ (397·1)	10·58 10·26	240
4-Cl	111—115 (56)	$C_{14}H_{11}Cl_2N_3O$ (308·2)	13·64 13·99	300
4-CH_3	97—99 (26)	$C_{16}H_{17}N_3O$ (267·3)	15·72 15·64	310
4-CH_3O	95—99 (38)	$C_{16}H_{17}N_3O_3$ (299·3)	14·04 13·83	312

TABLE II

The solvolysis rate constants of the disubstituted 3-acetyl-1,3-diphenyltriazenes $X—C_6H_4—N=N—N(COCH_3)—C_6H_4—X$

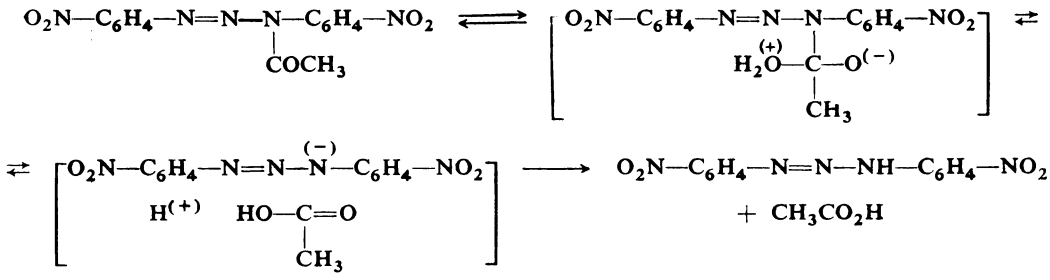
T, °C	X = 3-Br		X = 3-Cl		X = 3-F	
	10^4k, s^{-1}	10^5s_k, s^{-1}	10^4k, s^{-1}	10^5s_k, s^{-1}	10^4k, s^{-1}	10^5s_k, s^{-1}
35·0	5·18	1·21	5·83	1·97	5·18	0·93
40·0	9·41	2·42	8·78	8·03	9·65	1·10
40·0	10·2	0·62	8·03	1·90	8·91	0·53
45·0	13·9	3·13	11·8	1·77	15·5	5·23
50·0	26·8	3·68	18·8	3·17	32·9	13·6
50·0	28·7	1·32	21·9	1·47	24·5	2·00
55·0	36·3	13·0	38·9	6·66	45·4	3·58
55·0	48·3	22·1	41·2	2·13	—	—
60·0	54·8	10·2	59·7	2·17	65·1	0·12
60·0	87·6	17·9	75·4	9·71	—	—
	X = 3-NO_2		X = 3-CN		X = 3-CH_3CO	
35·0	0·50	0·085	0·67	0·079	5·40	3·40
40·0	1·21	0·206	1·25	0·104	10·3	0·72
40·0	1·18	0·089	1·82	0·325	11·5	1·06
45·0	2·82	0·198	2·66	1·45	20·7	11·0
50·0	3·41	0·198	3·95	0·712	31·0	11·0
50·0	4·00	0·367	4·91	0·649	29·2	3·26
55·0	6·27	0·824	7·04	0·790	47·5	8·26
55·0	5·90	0·399	8·97	0·919	50·1	3·53
60·0	8·61	1·14	9·41	1·94	68·3	9·29
60·0	10·7	0·758	13·8	3·59	80·1	6·89
	X = 4-Br		X = 4-Cl		X = 4-CH_3	
30·0	4·55	0·64	4·08	0·59	22·6	15·8
35·0	8·07	2·31	10·3	2·54	29·8	18·5
40·0	16·4	5·16	15·6	5·91	—	—
40·0	17·2	1·17	17·0	1·50	72·8	34·7
45·0	21·8	3·89	42·5	11·4	85·7	24·0
50·0	35·2	5·61	51·3	15·2	126	48·6
50·0	46·6	2·61	49·8	2·33	—	—
55·0	57·8	16·0	58·7	22·9	231	73·3
55·0	76·8	7·34	80·6	9·70	—	—
60·0	79·1	41·0	74·4	26·3	283	104
60·0	107	8·03	130	5·59	—	—

TABLE II
(*Continued*)

T, °C	X = H		X = 4-NO_2		X = 4-CH_3O	
	10^3k, s^{-1}	10^5s_k, s^{-1}	10^4k, s^{-1}	10^6s_k, s^{-1}	10^3k, s^{-1}	10^4s_k, s^{-1}
20·0	—	—	—	—	3·05	0·45
25·0	—	—	—	—	4·98	0·63
30·0	1·82	2·37	—	—	8·73	0·57
35·0	3·08	1·17	—	—	13·5	0·27
40·0	5·68	3·39	—	—	27·6	5·30
40·0	—	—	—	—	23·2	0·99
45·0	8·70	6·95	3·47	9·26	30·7	8·03
50·0	13·9	43·0	7·35	2·88	77·2	33·8
50·0	—	—	6·55	9·14	68·4	8·65
55·0	27·5	23·6	8·65	6·58	110	13·3
55·0	—	—	10·6	11·7	—	—
60·0	45·5[a]	40·4	10·6	26·9	167	62·3
60·0	—	—	17·4	53·1	—	—

[a] 62·5°C.

triazenes[12], where the break is explained by a change in the mechanism. Similarly, in the case of 3-acetyl-1,3-bis(3-nitrophenyl)triazene we can consider the reaction mechanism given in Scheme 2.



SCHEME 2

The nitro group will facilitate both the attack by water – nucleophile and splitting off of the leaving group, and in any case the expected reaction constant will be positive. From the available data, however, the rate-determining step cannot be decided.

The reaction constant ϱ determined for the substituents with $\sigma < 0{\cdot}7$ (Eq. (*1*)) confirms the previous conclusions[7-9,12,13] about mechanism of the spontaneous hydrolysis of 3-acetyl-1,3-diphenyltriazenes (Scheme 1). The substituents facilitating the transfer of the bond electrons between the nitrogen atoms 2 and 3 to the amide formed will affect unfavourably the formation of the diazonium salt and *vice versa*.

TABLE III

Activation enthalpies $\Delta H^{\neq}$, activation entropies $\Delta S^{\neq}$ and the extrapolated solvolysis rate constants of the disubstituted 3-acetyl-1,3-diphenyltriazenes X—C_6H_4—N=N—N($COCH_3$)—C_6H_4—X in 20% aqueous ethanol at 25°C

X	$H^{\neq}$, kJ mol^{-1}	$S^{\neq}$, J mol^{-1} K^{-1}	$10^4 k_{25}$, s^{-1}
4-NO_2	71·25 ± 13·02	−86·44 ± 39·87	0·621
3-NO_2	92·46 ± 5·36	−25·37 ± 16·67	0·185
3-CN	91·81 ± 6·02	−25·82 ± 18·71	0·228
3-Br	84·40 ± 4·99	−33·80 ± 15·49	1·73
3-Cl	84·04 ± 4·72	−35·85 ± 14·66	1·57
3-CH_3CO	83·72 ± 3·04	−34·86 ± 9·46	2·01
3-F	85·75 ± 4·04	−29·47 ± 12·62	1·69
4-Br	80·77 ± 4·09	−41·65 ± 12·79	2·92
4-Cl	85·47 ± 5·50	−25·68 ± 17·19	2·99
H	82·65 ± 2·37	−24·80 ± 7·46	10·4
4-CH_3	70·80 ± 5·0	−62·22 ± 15·75	13·7
4-CH_3O	80·08 ± 2·50	−20·34 ± 7·99	50·0

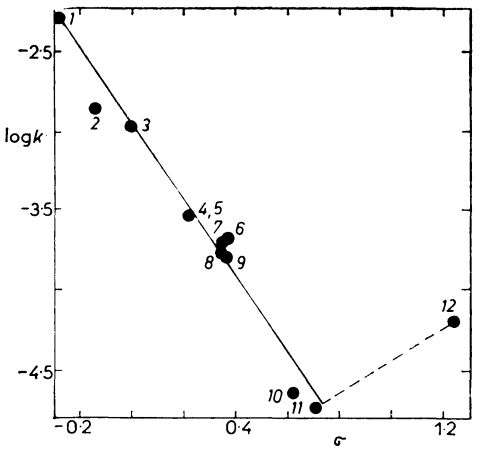


FIG. 1

The dependence of logarithms of the hydrolysis rate constants of disubstituted 3-acetyl-1,3-diphenyltriazenes in 20% aqueous ethanol at 25°C on the Hammett σ constant of the substituents *1* 4-CH_3O, *2* 4-CH_3, *3* H, *4* 4-Cl, *5* 4-Br, *6* 3-Br, *7* 3-CH_3CO, *8* 3-F, *9* 3-Cl, *10* 3-CN, *11* 3-NO_2, *12* 4-NO_2

The negative sign of ϱ indicates the dominant influence of substituent on the formation of the diazonium salt, whereas the transitory negative charge at the amide is sufficiently compensated by resonance with acetyl group and by the proton transfer from the solvent.

The reaction constant from Eq. (*1*) shows statistically significant agreement ($F(1{\cdot}22) = 0{\cdot}004$; $F_{0{\cdot}95}(1{\cdot}22) = 4{\cdot}30$) with the value found for the carbamoyl derivatives[12] in water ($\varrho = -2{\cdot}29$). If, however, the difference between the solvolyzing media (20% ethanol and water) is taken into account as well as the known "sensitizing" effect of addition of organic solvents to water[20], then the value of the solvolysis reaction constant of 3-acetyl-1,3-diphenyltriazenes can be expected to be somewhat smaller in water. This conclusion about lower substitution sensitivity stands in accordance with the higher hydrolytic reactivity of the acetyl derivatives as compared with the carbamoyl derivatives[7]. A logical consequence would be a further lowering of the substitution sensitivity in the case of the hydrolysis of the protonated diphenyltriazenes (the proton instead of acyl group). The ϱ value really found is $-5{\cdot}93$ (20°C, 20% aqueous ethanol)[14] and indicates that the dominant influence of substituent in the solvolysis of the parent 1,3-diphenyltriazenes is the influence on the protonation and not that on the splitting of the NN bond. There remains, however, still an open question whether the protonation of 1,3-diphenyltriazenes takes place in a pre-equilibrium or in the rate-limiting step simultaneously with the splitting of the bond in the triazine chain. The results of a study by Sinnott[21] indicate the synchronous process in the case of alkylaryltriazenes.

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