KINETICS OF ACID CATALYZED DECOMPOSITION OF SUBSTITUTED 1,3-DIPHENYL-3-METHYLTRIAZENES

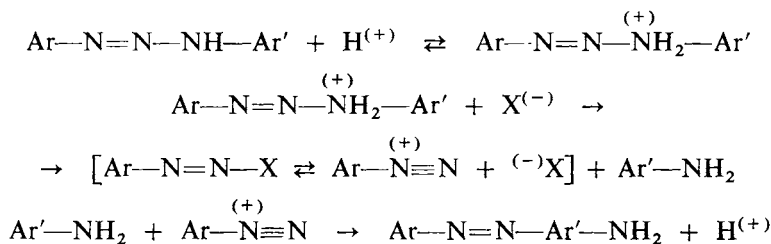Petr SVOBODA, Oldřich PYTELA and Miroslav VEČEŘA

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Kinetics of the acid catalyzed decomposition of fifteen 1-substituted-1,3-diphenyl-3-methyltriazenes have been studied in 40% aqueous ethanolic buffers at 25°C. The slope found for the dependence log k_{obs} vs pH of the buffer is not equal to unity, and a method of treating such experimental data is suggested. The reaction constant found ($\varrho = -3.70$) indicates that substituents have similar effects on both protonation and decomposition of the triazene chain.

Kinetics of the acid catalyzed decomposition of triazenes have been studied by several authors. Nietzki[1] gave the first experimental piece of evidence for the rearrangement to have an intermolecular course. Suizu and Yokozima found[2] that diazonium ion is formed in the course of the reaction. Hughes and Ingold[3,4] suggested the *A2* mechanism for the decomposition whose first step consists in the protonation of the triazene which is followed by decomposition into diazonium ion and aniline by attack of the nucleophile X according to Scheme 1.

$$\text{Ar—N=N—NH—Ar}' + \text{H}^{(+)} \rightleftarrows \text{Ar—N=N—}\overset{(+)}{\text{NH}_2}\text{—Ar}'$$

$$\text{Ar—N=N—}\overset{(+)}{\text{NH}_2}\text{—Ar}' + \text{X}^{(-)} \rightarrow$$

$$\rightarrow \left[\text{Ar—N=N—X} \rightleftarrows \text{Ar—}\overset{(+)}{\text{N}\equiv\text{N}} + {}^{(-)}\text{X} \right] + \text{Ar}'\text{—NH}_2$$

$$\text{Ar}'\text{—NH}_2 + \text{Ar—}\overset{(+)}{\text{N}\equiv\text{N}} \rightarrow \text{Ar—N=N—Ar}'\text{—NH}_2 + \text{H}^{(+)}$$

SCHEME 1

Kruglov et al.[5] and Beneš and coworkers[6] dealt with kinetic studies of this mechanism. In these studies no evidence was found in favour of the rapid protonation pre-equilibrium according to Scheme 1. Also studied were the kinetics of decomposition of 3-acyl- and 3-carbamoylderivatives of 1,3-diphenyltriazenes in water[7-10] and the solvent[11] and salt effects[12]. The hydrolysis of 3-(N-methylcarbamoyl)-1,3--diphenyltriazenes exhibits a break in the Hammett dependence for substituents

with $\sigma \geqq 0.7$, and this fact was explained by a change in the mechanism[7]. Large negative $\Delta S^{\neq}$ values were found for decomposition of 3-acetyl-1,3-diphenyltriazenes, which indicates participation of water molecules in the transition state[10]. This hypothesis was further supported by results of studies of the solvent and salt effects[11,12] on decomposition of these derivatives.

The kinetic studies of decomposition of 1-aryl-3-alkyl-triazenes carried out by Zvěřina and coworkers[13] and Isaacs and Rannala[14,15] postulated the $A1$ mechanism with a rapid pre-equilibrium for the decomposition of these derivatives. Jones and coworkers[16], on the contrary, suggested the $A - S_E2$ mechanism for the decomposition of alkylaryltriazenes in which the protonation of the substrate proceeds simultaneously with the decomposition of the triazene chain. Yamada[17] dealt with a study of decomposition of 1,3-diphenyl-3-methyltriazenes in 95% aqueous ethanol. The author postulated the decomposition of the protonated substrate (by the $A1$ mechanism) as the rate-limiting step.

On the whole it can be stated that the opinions of the decomposition mechanism of 1,3-diphenyltriazenes and their derivatives are considerably contradictory, and the problem is far from being fully solved. Participation of water in the transition state of the reaction has not yet been elucidated either.

The aim of this communication was to study the mechanism of the acid catalyzed decomposition of the triazene chain using substituted 1,3-diphenyl-3-methyltriazenes. Introduction of the methyl group into 1,3-diphenyltriazene chain prevents its prototropy, and thus it is possible to separately study the substituent effects in the benzene rings bound to 1 and 3 nitrogen atoms of the triazene chain.

EXPERIMENTAL

3-Methyl-1-(X-phenyl)-3-phenyltriazenes were prepared by reaction of substituted diazonium salts with N-methylaniline: 0·05 mol N-methylaniline was dissolved in 15 ml conc. HCl and 15 ml water. The mixture was boiled until dissolution of the hydrochloride formed, whereupon it was neutralized — while hot — with 20% sodium acetate solution. After cooling to 0°C, the diazonium salt solution was added with stirring. The mixture was stirred until the diazonium salt reacted (detection with disodium 3-hydroxynaphthalene-2,7-disulphonate). The yellow to orange solid formed was collected by suction, washed with water, and dried in air. The oily triazenes were extracted in benzene, the solution was dried with sodium sulphate, and benzene was distilled off in vacuum. The raw products were purified by recrystallization and column chromatography with alumina and tetrachloromethane as eluent. The yields, physical constants, and solvents used for the recrystallizations are summarized in Table I.

The kinetic measurements were carried out by the procedure described in ref.[8] using a Specord UV VIS and a VSU-2 spectrophotometers (Zeiss, Jena). The time dependence of the spectra measured during the decomposition showed no isosbestic points in most cases of the model compounds. Therefore, we added 10 µl 1 mol l^{-1} solution of 1,3-benzenediamine to the cell containing 10 ml 40% aqueous-ethanolic buffer. The diamine reacted faster than the aniline liberated with the diazonium ion formed, and so the isosbestic point of the time dependence of spectral records

TABLE I

Yields, physical properties, and elemental analyses of the substituted 3-methyl-1,3-diphenyl-triazenes $X—C_6H_4N=N—N(CH_3)C_6H_5$

Compound	X	Yield %	M.p. °C	Calculated/ /Found, %N	λ_{max} nm
I	H	90	oil[a]	19·89/20·13	343
II	4-CH_3O	86	59·5—60·1[b]	17·41/17·64	352
III	3-CH_3	98	61·0—61·5[c]	18·65/19·12	345
IV	4-CH_3	99	61·5—62·5[d]	18·65/18·71	347
V	3-F	70	oil	18·33/17·98	349
VI	4-F	98	43·5—46·0	18·33/17·99	343
VII	3-Cl	80	40·0—42·0	17·10/17·19	346
VIII	4-Cl	80	86·0—87·0[e]	17·10/16·98	347
IX	4-Br	98	88·0—89·0	14·48/14·34	349
X	3-CF_3	43	36·0—38·0	15·72/15·85	345
XI	4-CF_3	60	83·0—86·0[f]	15·72/15·85	345
XII	3-CN	95	56·0—58·0	23·71/22·70	347
XIII	4-CN	95	116·0—118·0[g]	23·71/23·49	357
XIV	3-NO_2	70	95·5—97·0	12·49/12·16	334
XV	4-NO_2	97	129·0—130·0	12·49/13·00	384

[a] M.p. (ref.[18]) — oil; [b] m.p. (ref.[19]) 59·8—60·2°C, (ref.[17]) 59·5—60·0°C, (ref.[20]) 61·0°C; [c] m.p. (ref.[17]) 63·5—64·5°C, (ref.[20]) 67°C; [d] m.p. (ref.[17]) 66—67°C, (ref.[19]) 67—67·8°C, (ref.[20]) 66·5 to 68°C; [e] m.p. (ref.[17]) 87—88°C, (ref.[19]) 86·7—88·1°C; [f] m.p. (ref.[19]) 86·0—86·9°C; [g] m.p. (ref.[17]) 120—120·5°C.

TABLE II

Dependence of the rate constant of decomposition of 1,3-diphenyl-3-methyltriazene on addition of 1,3-benzenediamine solution ($c = 1 \text{ mol } l^{-1}$) at 25°C in 40% ethanol at pH 4·79

Addition of the solution, μl	$10^3 k$ s^{-1}	$10^5 s_k$[a]
10	6·626	3·881
20	6·396	2·448
30	6·264	2·849
40	6·364	3·129
50	6·632	3·321
60	5·873	2·689
70	5·872	2·745
80	5·837	2·598

[a] s_k standard deviation of the rate constant.

of the decomposition was maintained. The kinetic measurements were evaluated according to an optimization program described elsewhere[21].

TABLE III

Rate constants of the acid catalyzed decomposition of substituted 1,3-diphenyl-3-methyltriazenes $I—XV$ at different pH values

pH	$10^3\ k, \text{s}^{-1}$	$10^5\ s_k$	pH	$10^3\ k, \text{s}^{-1}$	$10^5\ s_k$
		$I, \text{X} = \text{H}$			
2·63	497	206	4·24	19·2	14·1
2·63	482	158	4·24	19·1	11·4
2·63	481	86·1	4·36	12·9	7·33
2·80	325	123	4·36	13·0	9·05
2·80	330	86·0	4·45	14·2	11·8
2·80	333	72·2	4·45	16·9	6·53
2·92	264	66·9	4·53	10·2	3·71
2·92	260	47·2	4·53	12·4	5·52
2·92	261	100	4·60	6·46	5·89
3·15	164	81·6	4·60	6·83	3·20
3·15	165	100	4·74	5·31	2·97
3·15	169	49·9	4·74	6·44	13·4
3·31	121	39·6	4·79	4·67	3·29
3·31	122	38·6	4·79	4·91	2·89
3·31	123	32·0	4·84	4·67	2·22
3·50	79·1	44·9	4·84	4·67	2·17
3·85	37·1	16·7	5·09	2·42	1·43
3·85	40·2	21·5	5·09	2·44	1·94
3·92	32·1	19·8	5·56	0·987	0·517
3·92	31·7	12·5	5·56	0·942	0·523
3·92	32·5	14·1	6·09	0·265	0·242
			6·23	0·189	0·332
		$II, \text{X} = 4\text{-CH}_3\text{O}$			
2·63	3 333	9 739	3·61	535·3	227·9
2·63	3 920	5 311	3·92	256·0	57·86
2·80	2 755	2 240	4·24	126·1	64·14
2·80	2 728	2 294	4·45	75·37	136·6
2·80	2 745	2 470	4·74	40·07	14·32
2·92	2 167	1 727	4·84	32·61	6·498
2·92	2 159	1 223	5·09	18·39	5·272
3·15	1 394	1 410	5·58	7·234	3·583
3·15	1 395	507·7	6·09	2·353	1·205
3·31	925·2	316·3			

TABLE III
(*Continued*)

pH	$10^3 k, s^{-1}$	$10^5 s_k$	pH	$10^3 k, s^{-1}$	$10^5 s_k$
III, X = 3-CH$_3$			*IV*, X = 4-CH$_3$		
3·69	77·1	44·0	3·92	92·6	73·3
4·12	20·6	20·6	4·12	62·2	62·0
4·24	18·7	24·9	4·24	46·3	41·2
4·24	19·4	11·4	4·36	40·7	25·4
4·36	15·8	10·3	4·45	30·9	30·5
4·45	12·1	6·79	4·60	19·8	10·9
4·60	8·21	4·66	4·74	15·4	9·30
4·74	5·79	4·56	4·84	13·4	8·65
4·84	4·90	2·58	5·09	7·37	6·05
5·09	2·76	1·40	5·58	3·03	1·75
5·58	1·05	1·07	6·09	0·758	0·628
6·09	0·500	5·66	6·23	0·500	0·466
V, X = 3-F			*VI*, X = 4-F		
2·92	12·8	4·99	3·31	57·3	51·1
3·31	5·57	2·57	3·61	30·5	28·9
3·61	2·77	2·00	4·12	9·39	9·58
4·12	0·936	0·527	4·24	7·75	5·68
4·36	0·632	0·479	4·36	6·59	6·18
4·60	0·500	2·85	4·45	5·54	4·74
4·84	0·333	2·83	4·60	3·41	2·43
			4·74	2·44	2·65
			4·84	2·25	2·24
			5·09	1·16	0·915
			5·58	0·500	1·23
VII, X = 3-Cl			*VIII*, X = 4-Cl		
2·80	15·3	8·01	2·63	79·9	15·3
2·92	9·73	5·03	2·80	48·1	11·5
3·15	7·40	3·50	2·92	37·1	11·4
3·31	4·82	4·10	3·15	24·6	10·0
3·61	2·82	2·32	3·28	13·2	6·27
3·92	1·56	2·25	3·61	8·21	5·68
4·12	0·936	1·85	3·92	5·19	6·46
4·24	0·403	2·65	3·92	4·70	4·45
4·36	0·509	1·96	4·12	3·33	3·59
			4·24	2·03	0·406
			4·36	1·75	0·828
			4·45	1·51	1·03
			4·60	0·893	1·59
			4·74	0·867	0·689
			4·84	0·668	0·747
			5·09	0·500	0·313

TABLE III

(*Continued*)

pH	$10^3\,k,\,\text{s}^{-1}$	$10^5\,s_k$	pH	$10^3\,k,\,\text{s}^{-1}$	$10^5\,s_k$
	IX, X = 4-Br			*X*, X = 3-CF$_3$	
2·80	36·9	16·6	2·73	6·38	4·26
2·92	33·3	25·4	2·88	4·83	5·58
3·15	20·1	15·8	3·02	3·50	8·91
3·31	12·1	12·7	3·30	4·00	6·79
3·61	8·12	10·4	3·85	0·500	0·234
3·92	4·96	4·02	4·36	0·125	0·300
4·12	2·89	2·79			
4·24	1·55	2·87			
4·36	1·50	1·04			
4·45	1·25	0·844			
4·60	0·839	0·923			
4·74	0·545	0·888			
4·84	0·484	0·422			
5·09	0·294	0·315			
5·58	0·167	0·569			
	XI, X = 4-CF$_3$			*XII*, X = 3-CN	
2·80	3·67	3·07	2·73	1·71	0·697
2·92	2·73	1·77	2·88	1·39	0·508
3·15	2·33	5·35	3·31	0·500	1·41
3·31	1·35	0·714	3·61	0·560	8·35
3·31	1·49	2·15	3·85	0·176	0·294
3·61	0·866	0·980			
3·92	0·469	2·33			
4·12	0·374	1·23			
4·24	0·106	1·53			
4·36	0·169	1·50			
4·45	0·139	1·31			
	XIII, X = 4-CN			*XV*, X = 4-NO$_2$	
2·73	0·825	0·410	2·73	0·366	0·563
2·88	0·635	0·071			
3·31	0·500	0·79			
3·61	0·092	0·169			

RESULTS AND DISCUSSION

To exclude the possibility of influence of general base catalysis with 1,3-benzenedia-
mine, we examined the dependence of the rate constants of decomposition of 1,3-

diphenyl-3-methyltriazene on addition of $1 \text{ mol } l^{-1}$ solution of 1,3-benzenediamine. The results are given in Table II. The decomposition rate did not change in considerably broad range of addition of $1 \text{ mol } l^{-1}$ 1,3-benzenediamine. The rate constants of the acid catalyzed decomposition of compounds $I-XV$ are summarized in Table III for buffers of different pH. The values of the $\log k_I$ constants and the slope b of the pH profile were calculated from Eq. (1).

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

TABLE IV

The $\log k_I$ values and slopes b of the pH profiles determined from Eq. (1) by linear regression

Compound	$\log k_I$	$s(\log k_I)$	b	s_b	n^a	r^b
I	2·1025	0·0392	−0·914	0·010	42	−0·9978
II	3·0599	0·0238	−0·936	0·006	19	−0·9996
III	2·0605	0·1116	−0·896	0·024	12	−0·9965
IV	2·7878	0·0824	−0·968	0·017	12	−0·9985
V	0·5007	0·1266	−0·836	0·032	8	−0·9956
VI	1·8080	0·0782	−0·923	0·017	11	−0·9984
VII	0·6002	0·1021	−0·875	0·030	7	−0·9971
$VIII$	1·2144	0·0808	−0·907	0·020	16	−0·9986
IX	1·1849	0·1179	−0·919	0·031	11	−0·9949
X	0·6971	0·0831	−1·049	0·024	5	−0·9992
XI	−0·0499	0·1161	−0·842	0·032	10	−0·9943
XII	−0·2892	0·1166	−0·902	0·036	4	−0·9984
$XIII$	−0·0439	0·1713	−1·105	0·055	3	−0·9987

^{a} n number of points; ^{b} r the correlation coefficient of Eq. (1).

TABLE V

The t_{test} and t_{crit} values at the significance level $\alpha = 0.05$ for the slopes b of the relation (1)

Compound	t_{test}	n	t_{crit}	Compound	t_{test}	n	t_{crit}
I	8·835	42	2·021	$VIII$	4·579	16	2·145
II	10·590	19	2·110	IX	2·636	11	2·262
III	4·376	12	2·228	X	−2·008	5	3·182
IV	1·914	12	2·228	XI	4·949	10	2·306
V	5·099	8	2·447	XII	2·702	4	4·304
VI	4·404	11	2·262	$XIII$	−1·895	3	12·706
VII	4·189	7	2·571				

The values calculated are given in Table IV along with their statistical characteristics. For most of the compounds studied the slope b of the pH profile was not equal to but lower than unity. At the same time, the correlation coefficients of the relation (1) are quite high, $r \geqq 0.99$. So the relation (1) is fulfilled very well, the only exceptions being compounds X and $XIII$ for which the slope value found was greater than one.

To verify the non-unit slopes of the pH profiles, we tested the b values by the t-test. The test results are given in Table V along with the t_{crit} values at the significance

TABLE VI

The $\log' k_I$ and $\log k_I^i$ values calculated according to Eqs (3) and (4) and the $\log k_I$ values from Table IV

Compound	$\log k_I$	$\log k_I^i$	$\log' k_I$	$s(\log' k_I)$
I	2·103	2·426	2·442	0·0903
II	3·060	3·303	3·303	0·0748
III	2·061	2·495	2·544	0·0863
IV	2·788	2·892	2·944	0·0468
V	0·501	1·114	1·150	0·1318
VI	1·808	2·081	2·149	0·0595
VII	0·600	1·072	1·009	0·0877
$VIII$	1·214	1·566	1·581	0·0928
IX	1·185	1·497	1·518	0·1051
X	0·6971	0·6245	0·5949	0·1559
XI	−0·0499	0·5699	0·4947	0·1272
XII	−0·2899	0·0332	0·0803	0·1366
$XIII$	−0·0439	−0·2316	−0·2722	0·1929
XV	—	—	−0·7064	—

TABLE VII

The $\log k_o$ and ϱ values of the Hammett relation for decomposition of substituted 1,3-diphenyl-3--methyltriazenes

Constant	$\log k_o$	$s_{\log k_o}$	ϱ	s_ϱ	r	s
$\log k_I$	2·0250	0·0809	−3·51	0·22	−0·979	0·2278
$\log' k_I$	2·3663	0·0213	−3·70	0·05	−0·999	0·0604
$\log k_I^i$	2·3379	0·0245	−3·59	0·07	−0·998	0·0691

level of $\alpha = 0.05$. This condition is not fulfilled with compounds *IV*, *X*, *XII*, and *XIII* only. Hence, with most of the substrates studied, the non-unit slope (smaller than one) of the pH profile was confirmed.

The $\log k_I$ values obtained by linear regression from Eq. (*1*) are (with the non-unit slopes) loaded with great errors and give poor Hammett correlations, which leads to an error in determination of the reaction constant. Therefore, we evaluated the relations $\log k_{obs}$ vs pH also by means of Eqs (*3*) and (*4*).

$$\log' k_I = n^{-1} \sum_{i=1}^{n} (\log k_{obs} + pH)_i \tag{3}$$

$$\Delta \log k_I^{i+1} = \log k_I^i - \log k_I^{i+1} =$$

$$= (pH_2 - pH_1)^{-1} \left(\int_{pH_1}^{pH_2} \log k_{obs}^i - \int_{pH_1}^{pH_2} \log k_{obs}^{i+1} \right) \tag{4}$$

From Eq. (*3*) we obtain the mean value $\log k_I$ which corresponds best to the experimental values of the kinetic measurements. The relation (*4*) represents an analogy of the construction of the acidity function suggested by Pytela[22]. The $\log k_I^i$ values determined in this way respect best the relations between the individual pH profiles determined for the individual substrates. The basic $\log k_{obs}$ vs pH dependence used was that for 1-(4-methoxyphenyl)-3-phenyl-3-methyltriazene (*II*). Table VI gives the $\log' k_I$ and $\log k_I^i$ values found along with (for comparison) the $\log k_I$ values from Table IV.
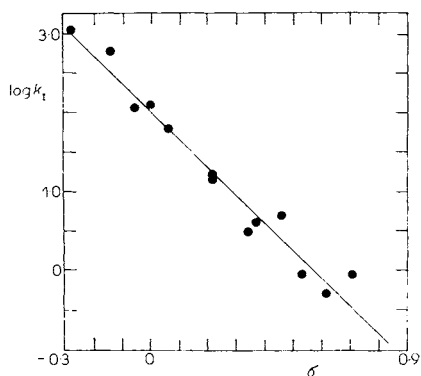

FIG. 1

The Hammett dependence of the $\log k_I$ values obtained from Eq. (*1*) for 3-methyl-1-(X-phenyl)-3-phenyltriazenes
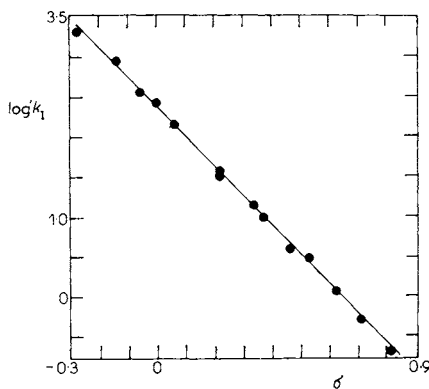
FIG. 2

The Hammett dependence of the $\log' k_I$ values obtained from Eq. (*3*) for 3-methyl-1-(X-phenyl)-3-phenyltriazenes

From Table VI it is seen that the $\log' k_I$ values are not significantly different from the $\log k_I^i$ values. The standard deviation $s(\log' k_I)$ is comparable with $s(\log k_I)$ (Table IV). The $\log' k_I$ values considerably differ from the $\log k_I$ values (Table IV) for the pH profiles with non-unit slope, being identical for the profiles with unit slopes.

The effects of the substituents in the phenyl ring bound to 1-nitrogen atom of the triazene chain were determined by linear regression of the $\log k_I$ values defined by Eqs (1), (3) and (4) with the substituent constants σ given in ref.[23]. The results are presented in Table VII and graphically represented in Figs 1 and 2 for $\log k_I$ and $\log' k_I$.

Table VII gives values of the correlation coefficients r, standard deviations s_ϱ and standard deviation s, wherefrom it follows that the Hammett dependences are fulfilled much better with the $\log' k_I$ and $\log k_I^i$ values than with the $\log k_I$ values determined by the linear regression. This fact is also documented by Figs 1 and 2. The best dependence is obtained with the $\log' k_I$ values. The respective reaction constant $\varrho = -3\cdot70$ agrees very well with that found by Yamada[17] in 95% aqueous ethanol $(\varrho = -3\cdot63)$.

The high value of the reaction constants indicates identical effect of substituents in the benzene ring at 1-nitrogen atom on both protonation of the triazene and stabilization of the diazonium cation formed. The reaction constant is then given by the sum of both the effects. These two effects make themselves felt equally in the $A - S_E2$ mechanism and in $A1$ and $A2$ mechanisms, so it is impossible to differentiate between these mechanisms on the basis of the ϱ constant value. The decision is also impossible on the basis of the decomposition pH profiles. The $A1$ and $A2$ mechanisms should exhibit a plateau in the pH profile at lower pH values. It is possible, however, that the plateau lies outside the region studied, and so it was not found.

The acid catalyzed decomposition of 1,3-diphenyltriazenes exhibits the value $\varrho = -2\cdot59$ in 20% aqueous ethanol at 20°C (ref.[6]). Comparison of the values $\log k_I = 4\cdot17$ for 1-phenyl-3-methyltriazene in water[13], $\log k_I = 3\cdot98$ for 1,3-diphenyltriazene in 20% ethanol[6], and $\log' k_I = 2\cdot44$ for 1,3-diphenyl-3-methyltriazene (Table VI) shows that substitution of both the hydrogen atoms at the 3-nitrogen atom of triazene chain by alkyl or aryl group results in a considerable retardation of the decomposition. This result can be explained by retardation of the proton transfer to the substrate and, hence, also by increase in the substituent effects on the reaction $(\varrho = -3\cdot70)$.

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