MODELLING OF HYDROLYSIS MECHANISM OF 3-HYDROXYTRIAZENES IN STRONGLY ACIDIC MEDIUM

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Four derivatives of 3-hydroxy-1-phenyl-3-alkyltriazene have been synthetized and their hydrolytic stability has been measured in sulphuric acid medium (0·2–16 mol l^{-1}). The rate constant has been found to increase with increasing concentration of sulphuric acid at first, but, on the contrary, at higher concentrations it decreases. Twelve kinetic schemes of acid catalysis have been suggested and evaluated, and a probable mechanism of decomposition has been suggested which involves nitrenium ion as an intermediate.

Hydroxytriazenes C_6H_5—N=N—N(OH)—R (or Ar) are prepared by coupling of diazonium salts with alkyl- or arylhydroxylamines. They were tested as insecticides and caricides[1,2], and their herbicidal activity was also proved[3]. They tend to form stable complexes with heavy metals and were suggested for analytical proof and determination of these ions[4–11]. Formation of the complexes is connected with the existence of intramolecular hydrogen bond between the hydroxyl hydrogen atom and nitrogen atom 1, which is also dealt with in literature[12]. Several reports [13–18] deal with reactivity of hydroxytriazene derivatives, none of them, however, describes hydrolytic stability of these compounds in acid medium (though this information is indispensable for analytic applications) and mechanism of acid catalyzed decomposition.

This paper forms a continuation in the series dealing with hydrolytic decomposition of triazene derivatives, and its aim is elucidation of the role played by water in the mechanism of acid catalyzed hydrolysis and of mechanism of this process in the case of 3-hydroxytriazene derivatives.

EXPERIMENTAL

Syntheses: 0·6 mol nitroalkane (nitrobenzene) was emulsified in 95 ml water and treated with 12 g ammonium chloride. The mixture was stirred, and 36·6 g zinc powder was added thereto within 15–20 min whereby the temperature increased to 40–50°C. When the reaction was finished, the mixture was heated to 50–60°C, and the suspension of unreacted zinc and the zinc oxide formed was collected by suction and washed with hot water. The filtrate was treated with a solution of 366 g anhydrous sodium acetate in 550 ml water and cooled to 0°C. Aniline (0·2 mol) was dissolved in 70 ml conc. hydrochloric acid and 50 ml water. The solution was cooled to 0 °C, and a solution of 14 g sodium nitrite in 70 ml water was added dropwise with stirring and cooling. The diazonium salt prepared was added to the stirred solution of alkyl(aryl)hydroxylamine, and the mixture was stirred 1 h. The separated solid was collected by suction, washed with water, and dried in air. The raw product was reprecipitated from methanolic solution by addition of water and repeatedly crystallized from hexane. Pure 3-hydroxy-1-phenyl-3-alkyltriazenes are colourless, whereas 3-hydroxy-1,3-diphenyltriazene forms pale yellow crystals. The yields related to the starting nitro compound are given in Table I.

Kinetic measurements: Sulphuric acid of required concentration (8 ml) was temperated at 25·0 ± 0·1°C in a cell of a Specord UV-VIS apparatus (Zeiss Jena), and 2—5 μl solution of the compound (0·2 mol l^{-1}) in dioxane was added with a syringe, whereupon the content of the cell was mixed. The absorbance decrease was followed at 305 nm for 2—3 half-lives. The rate constants were evaluated according to the known program[19].

Treatment of results: The dependence of the observed rate constants on medium was interpreted by 12 regression models whose parameters were optimized by the least squares method.

RESULTS AND DISCUSSION

Logarithms of the rate constants (Table II) plotted against the H_0 acidity function gave the dependence given in Fig. 1 for 3-hydroxy-1,3-diphenyltriazene and 3-hydroxy-1-phenyl-3-methyltriazene. In the given case the dependence found can be explained by three possible reasons. The first one consists in participation of water molecule (molecules) in the transition state of the rate-limiting step. Decrease in water activity with increasing concentration of sulphuric acid would result in a decrease of the rate constant. The second explanation considers the existence of a side equilibrium which has a steeper acidity function than the pre-equilibrium leading to the decomposition. The last alternative is based on a possibility of protonation to the second degree, the protonation to the first degree increasing the concentra-

TABLE I

Yields and physical properties of 3-hydroxy-1-phenyl-3-subst.-triazenes

Compound	Substituent	Yield, %	M.p., °C	M.p., °C, (ref.)
I	—CH_3	22	66—67	69, (16—18)
II	—CH_2—CH_3	10	45—47	44·5, (16—18)
III	—$(CH_2)_2$—CH_3	7	62—63	61, (16—18)
IV	—$CH(CH_3)_2$	10	52—54	—[a]
V	—C_6H_5	36	127—128	127—128, (16, 18) 126, (14) 127, (17)

[a] Calculated: 60·31% C, 7·31% H, 23·45% N; found: 60·53% C, 7·59% H, 23·10% N.

tion of the activated form of substrate, whereas that to the second degree prevents the decomposition.

If these ideas are applied to the substrates studied, a scheme of probable reaction mechanisms is obtained (Scheme 1), the diprotonation of triazene chain, however, being considered unlikely.

TABLE II

Dependence of logarithm of observed rate constants on concentration of sulphuric acid (c, mol . l^{-1}) at 25°C

c	$-\log k_{obs}$	c	$-\log k_{obs}$	c	$-\log k_{obs}$	c	$-\log k_{obs}$
			Compound *I*				
1·98	3·319	3·60	2·455	7·35	1·270	11·10	1·000
2·10	3·201	3·74	2·381	8·54	1·110	11·97	1·264
2·33	3·094	3·93	2·279	8·54	1·130	12·35	1·447
2·37	2·975	4·20	2·160	8·54	1·100	12·78	1·648
2·54	2·926	4·56	2·009	9·38	1·009	13·40	1·934
2·85	2·773	5·09	1·824	9·38	0·940	14·10	2·262
3·04	2·678	5·70	1·591	9·38	1·009	14·70	2·533
3·21	2·610	6·50	1·491	10·82	0·914	15·30	2·714
3·40	2·522	7·35	1·502	11·10	1·050	15·76	2·833
			Compound *II*				
2·75	3·088	6·50	1·634	11·97	1·391	13·40	2·054
3·25	2·801	7·35	1·508	11·97	1·400	13·40	2·120
3·67	2·689	8·54	1·320	12·35	1·569	14·10	2·413
4·15	2·429	9·38	1·193	12·35	1·620	14·70	2·648
4·62	2·301	11·10	1·219	12·78	1·790	15·30	2·846
5·50	1·948	11·10	1·210	12·78	1·780		
			Compound *III*				
2·75	3·256	6·50	1·829	10·82	1·380	13·40	2·374
3·25	2·983	7·35	1·595	11·10	1·448	14·10	2·667
3·67	2·811	8·54	1·506	11·97	1·673	14·70	2·941
4·15	2·607	9·38	1·365	12·35	1·870	15·30	3·119
5·50	2·065	10·82	1·359	12·78	2·044		
			Compound *IV*				
2·57	2·154	5·50	1·920	10·82	1·242	14·10	2·485
2·75	3·063	6·50	1·633	11·10	1·345	14·20	2·706
3·25	2·838	7·35	1·468	11·97	1·548	15·30	2·894
3·67	2·606	8·54	1·339	12·78	1·858		
4·15	2·410	9·38	1·247	13·40	2·144		

TABLE II
(*Continued*)

c	$-\log k_{obs}$	c	$-\log k_{obs}$	c	$-\log k_{obs}$	c	$-\log k_{obs}$
			Compound *V*				
0·19	3·057	0·75	2·384	1·58	1·987	3·67	1·182
0·22	2·967	0·92	2·277	1·68	1·920	3·67	1·210
0·24	2·963	0·92	2·210	1·68	1·950	4·15	1·051
0·25	2·850	1·01	2·253	1·77	1·882	9·61	1·144
0·28	2·846	1·12	2·198	1·88	1·840	10·18	1·319
0·29	2·854	1·12	2·180	2·04	1·775	11·05	1·581
0·34	2·752	1·12	2·120	2·24	1·705	11·49	1·784
0·39	2·685	1·21	2·120	2·39	1·628	12·04	2·155
0·44	2·642	1·21	2·123	2·57	1·557	12·83	2·382
0·49	2·564	1·21	2·120	2·57	1·610	13·17	2·547
0·54	2·540	1·30	2·062	2·75	1·498	13·45	2·951
0·59	2·532	1·30	2·050	2·75	1·560	14·11	3·249
0·63	2·457	1·30	2·080	3·25	1·356		
0·67	2·454	1·39	2·017	3·25	1·370		
0·69	2·465	1·49	1·990	3·25	1·110		

Obviously, Scheme 1 cannot be verified as a whole by the experimental data obtained, as there are many rate and equilibrium constants involved therein. Therefore, only selected reaction sequences leading from the starting substances to the

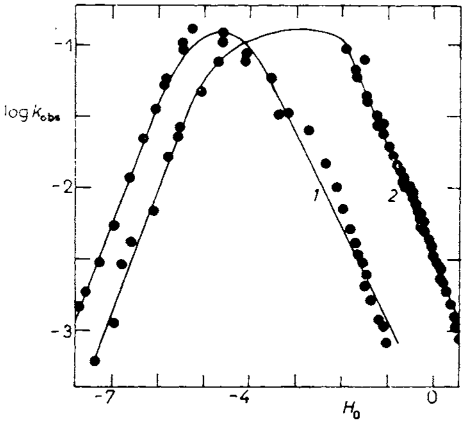
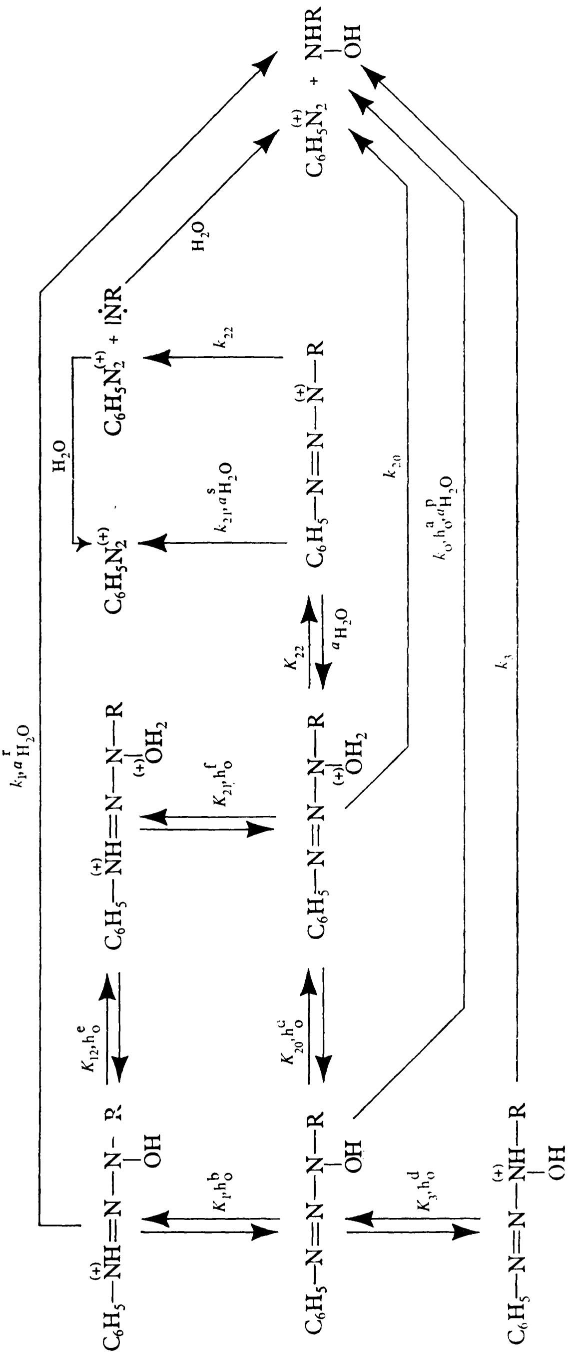


FIG. 1

Dependence of logarithm of the observed rate constant of hydrolysis of 3-hydroxy-1-phenyl-3-methyltriazene (*1*) and 3-hydroxy-1,3-diphenyltriazene (*2*) on the acidity function H_0 for sulphuric acid; the points are interlaced with the curve calculated for the seventh model


C6H5—NH(+)=NH—N—R | OH
C6H5—NH(+)=NH—N—R | (+)OH2
C6H5N2(+)
C6H5N2(+) + |N̈R
H2O
C6H5—N=N—N—R | OH
C6H5—N=N—N—R | (+)OH2
C6H5—N=N—N(+)—R
C6H5N2(+) + NHR | OH
C6H5—N=N—NH(+)—R | OH
k1, r aH2O
H2O
K12, he o
K1, hb o
K3, hd o
K20, hc o
K21, hf o
K22 aH2O
k21, s aH2O
k22
k20
k0, a ho, p aH2O
k3

SCHEME 1

products were verified with involvement of 6 parameters at the most. Only considered were those mechanisms which gave the diazonium salt as one of the products, because the diazonium salt was proved by coupling with 2-naphthalenamine after dilution of the reaction mixture. Table III presents the selected mechanisms with the theoretical dependences of the observed rate constant on the H_0 acidity function and on water activity. The first mechanism describes a case in which the proton behaves as a general acid, and the proton transfer takes place in the rate-limiting step, which is similar to the situation of diaryl- and arylalkyltriazenes[20,21]. The second mechanism is characterized by a protonation pre-equilibrium at the 1 nitrogen atom, the proton being transferred to the 3 nitrogen atom in the rate-limiting step with participation of a water molecule, which is accompanied by the decomposition. The third mechanism is analogous to the previous one, a simultaneous competitive protonation at the hydroxyl oxygen atom being considered. The fourth mechanism can be described by the protonation pre-equilibrium at the hydroxyl oxygen atom, the proton being transferred to the 3 nitrogen atom in the rate-limiting step (an analogy to the second mechanism). The same kinetic picture is obtained, if splitting off of water represents the rate-limiting step. From the expression for the observed rate constant it is obvious that it does not describe the experimental dependence

TABLE III

Elementary mechanisms and theoretical forms of the dependence of k_{obs} on h_o ($= \log(-H_o)$) and a_{H_2O} for acid catalyzed decomposition of 3-hydroxytriazenes

No	Reaction steps	k_{obs}
1	k_o	$k_o h_o^a a_{H_2O}^p$
2	K_1, k_1	$k_1 a_{H_2O}^r h_o^b/(K_1 + h_o^b)$
3	K_1, K_{20}, k_1	$k_1 K_2 a_{H_2O}^r h_o^b/(K_1 K_2 + K_2 h_o^b + K_1 h_o^c)$
4	K_{20}, k_{20}	$k_{20} h_o^c/(K_2 + h_o^c)$
5	K_{20}, K_{21}, k_{20}	$k_{20} . K_{21} h_o^c/(K_{20} K_{21} + K_{21} h_o^c + h_o^c h_o^f)$
6	K_{20}, K_{22}, k_{21}	$k_{21} . K_{22} h_o^c a_{H_2O}^s/(K_{22} h_o^c + K_{20} a_{H_2O} + h_o^c a_{H_2O})$
7	$(K_{20} + K_{22}), k_{21}$	$k_{21} . K_A . h_o^c a_{H_2O}^s/(K_A h_o^c + a_{H_2O})$; $K_A \doteq K_{22}/K_{20}$
8	K_{20}, K_{22}, k_{22}	$k_{22} . K_{22} h_o^c/(K_{22} h_o^c + K_{20} a_{H_2O} + h_o^c a_{H_2O})$
9	$(K_{20} + K_{22}), k_o$	$k_o . K_A . h_o^a a_{H_2O}/(K_A h_o^c + a_{H_2O})$; $K_A \doteq K_{22}/K_{20}$
10	K_{20}, K_{22}, k_{20}	$k_{20} . h_o^c a_{H_2O}/(K_{22} h_o^c + K_{20} a_{H_2O} + h_o^c a_{H_2O})$
11	K_3, k_3	$k_3 h_o^d/(K_3 + h_o^d)$
12	K_1, K_3, k_3	$k_3 K_1 h_o^d/(K_1 K_3 + K_3 h_o^a + K_1 h_o^d)$

found. The fifth mechanism is obtained by extending the previous sequence with a side equilibrium describing another protonation at the 1 nitrogen atom. The sixth mechanism presumes formation of the nitrenium cation as an intermediate which reacts with water (as a nucleophile) at another position of the molecule in the rate-limiting step. The seventh mechanism represents a simplified version of the previous one, as it presumes a negligible concentration of the substrate protonated at the hydroxyl oxygen atom as compared with the other possible forms. The eighth mechanism presumes decomposition of the nitrenium ion in the rate-limiting step without participation of water. After deriving the expression for the observed rate constant it is obvious that this mechanism will not be able to explain the experimental facts. The ninth mechanism describes the case in which the decomposition of the substrate connected with the proton transfer to the 3 nitrogen atom in the rate-limiting step and subsequent decomposition is combined with a side equilibrium lowering the actual concentration of the reacting form. The tenth mechanism presumes a decomposition of the substrate protonated at the hydroxyl oxygen atom connected with a side equilibrium producing the nitrenium ion. The eleventh mechanism corresponds to the "classic" mechanism given for acid catalyzed decomposition of triazenes[22,23]. Table III shows, however, that the expression for the observed rate constant disagrees with experiment. The last of the mechanisms suggested presumes decomposition of the substrate protonated at the 3 nitrogen atom (similar to the previous case), but it also considers the side equilibrium *e.g.* protonation at the 1 nitrogen atom, but the same expression is also obtained for the protonation at the hydroxyl oxygen atom.

The given survey shows that the mechanisms 1, 2, 3, 6, 7 explain the rate constants observed in strongly acidic medium by decreased water activity in the transition state of the rate-limiting step, the mechanisms 3, 5, 9, 12 consider the existence of a side equilibrium with a steeper acidity function, and the mechanism 5 explains the dependence found by the protonation to the second degree. Table IV presents the standard deviations of non-linear regression of the dependences of log k_{obs} *vs* h_0 and a_{H_2O} for selected mechanisms from Table III. From Table IV it is obvious that there is no distinct difference in the standard deviation between the mechanisms considered, hence in all the cases the experimental points fit well the respective model curve. Another test of validity of the models consists in statistical significance of the parameters. In this respect the model No 6 fails, since it is much too complex for a description of the experimental dependence, considerable intercorrelation of the parameters taking place, which means that the parameters are statistically insignificant (the standard deviations exceed the parameter value by its multiple). In addition, negative values of equilibrium constants appear in this model. Similar situation is encountered with the model No 10. The other models have the standard deviations smaller than or at least comparable with the values of parameters (the latter case applies to the models with several parameters).

A decision about the most probable model can be made on the basis of chemical interpretation. The model No 1 is simple and elegant, but it presumes the presence of 3 water molecules in the transition state (p : *I* = 2·75, *II* = 2·73, *III* = 2·83, *IV* = 2·70, *V* = 3·43). At the same time, the proton itself represents the most highly solvated particle in the reaction mixture, and formation of the activated complex would rather be accompanied by liberation of water molecules (desolvation of the proton). Besides that, this model presumes the fastest proton transfer to the substrate with phenyl (10^4k_0: *I* = 8·44, *II* = 4·74, *III* = 3·14, *IV* = 5·46, *V* = 3·95), which is not likely, because the 3 nitrogen atom of the derivative *V* has the lowest electron density due to electron delocalization to the nucleus, the possibility of stabilization of the transition state being the lowest here, too. From the point of view of the model, this case is interesting, because the product of the proton activity and water activity forms a part of numerator in some other models (Table III) and can considerably affect both the values and significance of further parameters of the model. The second model cannot be accepted due mainly to that it presumes an about one hundred fold better protonation of the aryl derivative as compared with the alkyl derivatives ($10^{-4}K_1$: *I* = 2·08, *II* = 3·12, *III* = 2·51, *IV* = 1·51, *V* = 0·0481, K_1 means the dissociation constant), which is unlikely, because the nucleus of the aryl derivative cannot take part in stabilization of the cation. The above-mentioned conclusions, however, presume identical decomposition mechanism with all the derivatives. A similar situation is encountered also with the mechanisms Nos 5 and 6. The dissociation constant K_{21} of the fifth mechanism is – according to ex-

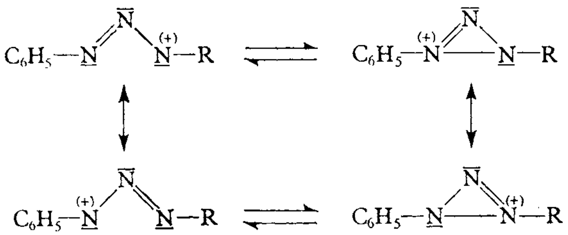
TABLE IV

Root mean square deviations 10^2 s for optimization of the dependence $\log k_{obs} = \log f(h_o, a_{H_2O})$ expressed according to Table III for the derivatives *I*–*V*

No	*I*	*II*	*III*	*IV*	*V*	Number of parameters
1	2·21	3·60	2·44	2·71	5·50	3
2	1·97	2·86	2·68	1·83	5·60	4
3	1·35	2·18	1·21	1·76	3·12	6
5	2·07	2·50	1·83	1·91	4·20	5
6	2·41	3·19	2·70	1·85	6·16	5
7	2·82	3·61	4·09	2·05	8·02	4
9	3·19	4·18	4·11	2·44	8·39	4
10	4·49	5·85	4·11	6·67	7·66	4
12	2·07	2·50	1·83	1·91	4·20	5
N[a]	36	23	19	18	57	

[a] Number of experimental points.

pectation – great, but it lies at the significance limit $(10^{-5}(K_{21} \pm s_{K_{21}})$: $I = (8{\cdot}88 \pm 11{\cdot}07)$, $II = (5{\cdot}91 \pm 6{\cdot}65)$, $III = (4{\cdot}46 \pm 5{\cdot}67)$, $IV = (4{\cdot}65 \pm 5{\cdot}66)$, $V = (0{\cdot}311 \pm 0{\cdot}215))$, the dissociation constant K_{20} exhibits an unexplainable relation between the aryl and alkyl derivatives $(10^{-2}K_{20}: I = 9{\cdot}55, II = 7{\cdot}66, III = 8{\cdot}06, IV = 7{\cdot}87, V = 0{\cdot}371)$. Neglecting of the K_{21} constant in the mechanism No 5 leads to mechanism No 4 (Table III), the latter being unable to explain the experimental data. In the sixth mechanism the equilibrium constants K_{22} of formation of the nitrenium cation lie near the significance limit $(10^{2}(K_{22} \pm s_{K_{22}})$: $I = (5{\cdot}02 \pm 5{\cdot}21)$, $II = (7{\cdot}79 \pm 7{\cdot}83)$, $III = (9{\cdot}83 \pm 11{\cdot}80)$, $IV = (5{\cdot}32 \pm 5{\cdot}83)$, $V = (7{\cdot}70 \pm 9{\cdot}51))$, which is, however, due to large intercorrelation with the K_{20} constant. Relations of alkyl and aryl derivatives for this constant are unexpected, too $(10^{-3}K_{20}: I = 1{\cdot}90, II = 2{\cdot}52, III = 2{\cdot}61, IV = 1{\cdot}71, V = 0{\cdot}148)$. Simplification of the seventh model (smaller number of constants) gives, after the optimizing, the parameters values agreeing with the reaction chemism (Table V). The nitrenium cation formed can be stabilized according to Scheme 2, after rehybridization and delocalization of positive charge, which is more extensive for R = C_6H_5 in accordance with the calculation result (Table V). The existence of nitrenium ions in the mechanism



SCHEME 2

TABLE V
Rate and equilibrium constants in the seventh model

Compound	$k_{21} \pm s_{K_{21}}$	$10^4(K_A \pm s_{KA})$	$10(c \pm s_c)$	$(s \pm s_s)$
I	2·09 ± 0·66	1·10 ± 0·36	6·92 ± 0·27	1·10 ± 0·07
II	2·24 ± 0·56	0·844 ± 0·241	6·51 ± 0·26	1·19 ± 0·06
III	1·17 ± 0·32	0·990 ± 0·307	6·73 ± 0·32	1·19 ± 0·06
IV	1·03 ± 0·31	1·50 ± 0·49	6·77 ± 0·33	1·07 ± 0·06
V	1·64 ± 0·28	20·9 ± 3·5	8·34 ± 0·14	1·50 ± 0·04

suggested is real[24,25], as the mechanism represents an analogue of the Beckmann rearrangement which presumes their formation in some cases. The nitrenium ions are also formed as intermediates in decomposition of N-chloroamines. The reaction of nitrenium ion with water in the rate-limiting step is apparently surprising, because the nitrenium ion is a very reactive particle. In fact, low activity of water distinctly shifts the equilibrium in favour of formation of the nitrenium ion and, at the same time, lowers the rate of its decomposition, due to which the nitrenium ion can even be accumulated in the reaction mixture for some period of time. Decomposition of the nitrenium ion is connected with participation of water as the nucleophilic reagent. As the positive charge is delocalized over the whole molecule, the position of attack can only be presumed. The most likely attack leading to irreversible decomposition into products takes place at 2 and 4 positions of the benzene ring (rings in case of derivative *V*) or at α carbon atom in the alkyl derivatives. Due to high reactivity of the nitrenium ion we can expect small reactivity differences with different substituents; the more stable phenyl derivative should react somewhat more slowly than the alkyl derivatives, and/or sterical effects should make themselves felt. These conclusions about mechanism in this model are practically confirmed by experimental data (Table V).

The low slope of the acidity function found as compared with the H_0 function (the *c* parameter in Table V) indicates a strong interaction of the protonated centre with the medium and strenghtens the presumption about the protonation at hydroxyl oxygen atom. Number of water molecules in the transition state (the *s* parameter in Table V) corresponds to the indispensable one water molecule needed for the reaction, the value $s = 1{\cdot}5$ for the phenyl derivative *V* indicates partial solvation during the reaction, the solvation of this derivative taking place in media of higher water activity than that usual for less reactive alkyl derivatives.

On the whole, the seventh mechanism discussed can be denoted as likely, although it is impossible to estimate unambiguously the decomposition products which can involve, besides the benzene-diazonium ion, also aminophenol, various alcohols, as well as products of possible rearrangements. The reaction products cannot be determined experimentally, because the sulphuric acid used is considerably concentrated, and the starting substrates are soluble in the given medium up to concentrations of spectral measurements only.

The ninth mechanism involving decomposition of the substrate with proton transfer to the 3 nitrogen atom in the rate-limiting step and with the side equilibrium giving the non-reactive nitrene is real even though less likely as compared with the previous mechanism. First of all we find a relation of rate constants which is difficult to explain (k_0: $I = 2{\cdot}04$, $II = 5{\cdot}65$, $III = 2{\cdot}85$, $IV = 1{\cdot}12$, $V = 9{\cdot}89$), which, in addition, exhibit quite considerable standard deviations. Order of the equilibrium constants agrees with chemical ideas (10^5K_A: $I = 11{\cdot}2$, $II = 3{\cdot}73$, $III = 4{\cdot}51$, $IV = 13{\cdot}8$, $V = 33{\cdot}9$). Slopes of the acidity function found (a: $I = 0{\cdot}69$, $II = 0{\cdot}61$, $III = 0{\cdot}63$,

$IV = 0.67$, $V = 0.80$; c: $I = 0.71$, $II = 0.73$, $III = 0.75$, $IV = 0.70$, $V = 1.06$) correspond to the mechanism and indicate a distinct interaction of the protonated centre with the medium.

The twelfth mechanism gives the K_1 and K_3 constants which are not likely with respect to possibility of protonation of the aryl and alkyl derivatives (10^8K_1: $I = 8.48$, $II = 4.55$, $III = 3.60$, $IV = 3.66$, $V = 115$; 10^2K_3: $I = 9.55$, $II = 7.65$, $III = 8.06$, $IV = 7.86$, $V = 3.71$).

The discussion presented shows that the most probable mechanisms are those involving formation of the nitrenium ion in the triazene chain (Nos 7 and 9).

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