KINETICS OF REACTION
OF 5-PHENYL-1,3,4-THIADIAZOL-2-DIAZONIUM ION WITH WATER

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5-Phenyl-1,3,4-thiadiazol-2-diazonium ion (*I*) is transformed into 2-amino-5-phenyl-1,3,4 thia-diazol (*II*) in diluted mineral acids. The reaction rate measured in solutions of diluted sulphuric acid reaches its maximum at concentrations of 2 to $2.5\text{M-H}_2\text{SO}_4$. The reaction intermediate is 5-phenyl-1,3,4-thiadiazol-2-diazo hydroxide (*III*). The rate-limiting step in formation of *III* consists in base-catalyzed reaction of the diazonium ion *I* with water; it is 4.3 times slower in $0.1\text{M-D}_2\text{SO}_4$ than in $0.1\text{M-H}_2\text{SO}_4$. Ratio of the rate constants of the transformation of the diazo hydroxide *III* into the diazonium ion *I* and into the amine *II* increases rapidly with increasing sulphuric acid concentration.

Five-membered heterocyclic amines containing at least two heteroatoms in the cycle give diazonium salts of extraordinary reactivity on reaction with nitrous acid. Many of them react even in diluted mineral acids with water to give the corresponding diazo hydroxide or the isomeric nitrosamine which could be isolated in several cases[1]. In this respect they differ from carbocyclic aromatic diazonium ions which do not react with hydroxyl ions until at higher pH values when they give the corresponding diazo hydroxides which are immediately transformed into diazotates. A great number of diazonium salts prepared from primary heterocyclic amines are described along with a number of different substitution and coupling reactions of these salts[1]. However, mechanistic data and rate and equilibrium constants of these reactions are rare.

The aim of this paper is to give rate and equilibrium constants of reaction of water with the 5-phenyl-1,3,4-thiadiazol-2-diazonium ion (*I*) which belongs among the most reactive diazonium ions[2].

EXPERIMENTAL

2-Amino-5-phenyl-1,3,4-thiadiazol (II) was prepared according to ref.[3] with the yield 62%, m.p. 227.5—229°C, ref.[3] m.p. 224°C.

Diazotization of the compound II was carried out in 85% phosphoric acid at 0°C (ref.[2]). The obtained solution of 5-phenyl-1,3,4-thiadiazol-2-diazonium ion (*I*) was diluted with $10\text{M-H}_2\text{SO}_4$,

to the concentration $1 \cdot 10^{-1}$ or $5 \cdot 10^{-2}$M (according to the further use) and kept in the dark at temperatures below 0°C.

5-Phenyl-1,3,4-thiadiazol-2-diazotate (IV): 5 ml of fresh diazonium salt *I* solution (0·005 mol amine *II* in 30 ml 85% phosphoric acid) was added drop by drop (within 2 min) in 25 ml cooled 2M-NaOH with stirring. After cooling to 0°C the separated sodium hydrogen phosphate hydrate was filtered off, and the filtrate was purified with charcoal. The phosphate concentration in the final solution was below 0·2M in all the cases. The diazotate prepared in this way was kept in the dark at 0°C. The obtained diazotate solution did not change during 14 days (according to spectral records).

Dissociation constants of the amine *II* and diazo hydroxide *III* were determined spectrophoto-metrically[4,5] by measuring the absorbance in chloroacetate (*II*) and formate buffers (*III*) using a VSU-2P spectrophotometer (Zeiss, Jena) at the wavelengths 322 and 240 nm, respectively. Absorbances of the protonated form were measured in 0·2M-HCl (for the diazo hydroxide *III* it was determined by extrapolation of the measured values to zero time), those of the non-protonat-ed form were measured in phosphate buffer at pH 6·5. The found pK_a values are 2·80 and 3·24 for the amine *II* and the compound *III*, respectively.

Determination of rate constants of transformation of the ion I *into amine* II *and nitrous acid*: One drop of the diluted diazonium salt solution was added (from a burette cooled with ice) to 1 ml diluted acid of known concentration in a quartz cell. At suitable time intervals the ab-sorbance decrease at the wavelength 397 nm was measured at 25°C using the VSU-2P spectro-photometer. The rate constants k_{obs} were calculated from Eq. (*1*) where A_t and A are the ab-sorbances measured at the time *t* and after 7—8 halflives, respectively. The same procedure was used in the cases where the diazotate *IV* solution was added instead of the diazonium salt.

$$t \cdot k_{obs} = -2 \cdot 303 \log (A_t - A) + \text{const} . \qquad (1)$$

Measurement of rate constants of transformation of the diazo hydroxide *III* to the ion *I*: 0·1 ml 0·1M solution of sodium salt of 1·8-dihydroxy-3,6-naphthalenedisulphonic acid (*V*) was added to 1·9 ml diluted mineral acid or chloroacetate buffer. In solutions of diluted hydrochloric acid ([HCl] < 0·5M) and chloroacetate buffers the ionic strength was adjusted to 0·5 by addition of po-tassium chloride. One drop of the diazotate *IV* was added to this solution and absorbance increase at 530 nm (the absorbance maximum of the dyestuff formed) was followed. The observed con-stants were evaluated according to Eq. (*1*).

Measurement of rate constants of transformation of the diazonium ion I *into the diazo hydroxide III.* One drop of the diazonium salt solution was added to 8 ml diluted acid with stirring. At vari-ous time intervals (0·4 to 4 s) from the moment of incidence of the drop 2 ml 0·05M disulphonic acid *V* was injected in the reaction mixture. After 2—3 s 0·5M sodium acetate was added in such amount (0 to 5 ml) to make the final pH about 3·5. Then absorbance of these solutions was measured at λ 530 nm. The rate constants k_1 were evaluated from Eq. (*1*).

Determination of relative velocities of transformation of the diazohydroxide III *into the ion* I *and amine* II. 0·5 ml 0·1M acid *V* was added to 9·5 ml diluted sulphuric acid of known concentra-tion, whereupon 0·2 ml diazotate *IV* was added with stirring. The absorbance was measured at 530 nm. From the value measured the absorbance of blank test was subtracted corresponding to the disulphonic acid *V* and its nitrosation product. At the same time solution of azo dyestuff was prepared by addition of the diazonium salt *I* to a roughly double concentration of the di-sulphonic acid *V* in 9·5 ml 0·1M-H_2SO_4. After suitable dilution 0·7 ml of this azo dyestuff solu-tion was pipetted into 9·5 ml diluted sulphuric acid and its absorbance was measured. By com-

parison of the corresponding absorbances of the azo dyestuff and the corrected absorbance in the reaction of the diazotate with 0·1M disulphonic acid V in the same medium we calculated relative amount of the azo dyestuff (or diazonium salt) formed from the diazotate IV. Difference in the absorbance values was considered equivalent to the amount of the amine formed. As both formation of the diazonium ion and that of the amine take pseudomonomolecular course, the concentration ratio of the both components formed corresponds to the ratio of their pseudomonomolecular rate constants k_{-1}/k_2.

RESULTS AND DISCUSSION

In media of diluted mineral acids the diazo hydroxide III, formed by reaction of the diazonium ion I with water, is transformed practically quantitatively into the amine II. The reaction course is given in Scheme 1. The reaction proceeds as pseudomonomolecular, and its k_{obs} increases linearly with increasing proton concentration at first, then the increase is slowed down and reaches the maximum at 2 to 2·5M-H_2SO_4, whereupon it decreases again (Table I). The amine II was the only reaction product practically even in the cases where the diazotate IV was added to the acid instead of the diazonium ion I. However, in the latter case the reaction clearly has two phases. In the first much faster step the diazo hydroxide III (formed by acidification of the diazotate ion IV) is transformed simultaneously to the diazonium ion I and amine II. In the second step, which makes itself felt kinetically after reaching the maximum concentration of the diazonium ion I, the reaction proceeds in the same way as that after addition of the diazonium ion I in diluted mineral acid. The constants k_{obs} have, within experimental error, the same value (Table I). At low acid concentrations the diazonium salt I is mainly formed in the first step, but with increasing acid concentration relative amount of the amine II rapidly increases. The dependence of log . (k_2/k_{-1}) for higher concentrations of sulphuric acid is given in Fig. 1. The values for 0·1M, 0·5M and 1M-H_2SO_4 were calculated from the measured kinetical data.
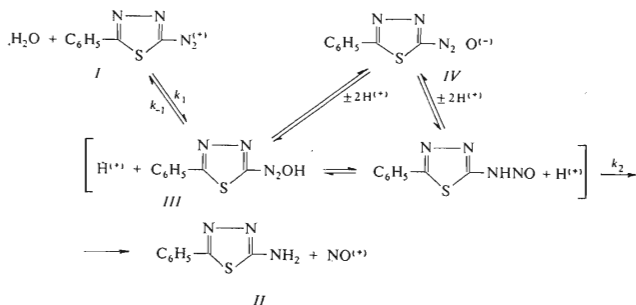
SCHEME 1

In the overall reaction (Scheme 1) three reactions are kinetically significant: transformation of the diazonium ion *I* into the diazo hydroxide *III* and acid-catalyzed transformation of the diazonium hydroxide either back to the diazonium ion or further to the amine *II* and nitrous acid. Generally this reaction can be expressed in Eq. (*A*).

$$I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} III \overset{k_2}{\longrightarrow} II . \qquad (A)$$

The way of determination of individual constants was different for three concentration ranges of sulphuric acid: *a*) At $[H_2SO_4] \geqslant 3.5M$ concentration of the diazo hydroxide *III* is much smaller than that of the diazonium ion, and Eq. (*2*) can be used for k_{obs}.

$$k_{obs} = k_1 k_2/(k_{-1} + k_2) . \qquad (2)$$

Value of the ratio $k_2/(k_{-1} + k_2)$ was calculated from the determined ratios k_2/k_{-1} (Table I). The proper k_{-1} and k_2 values cannot be determined in this sulphuric acid concentration range, since transformation of *III* to *I* and *II* is too rapid. Also the diazonium hydroxide *III* concentration is inaccessible by direct measurement, because it is too low. *b*) In the concentration range 1M to 3.5M-H_2SO_4 the concentrations of the compounds *I* and *III* are comparable. The system rapidly passes into the steady state (in a time shorter than that which is necessary for taking the first absorbance record, *i.e.* 9 to 12 s) which is characterized by practically constant ratio
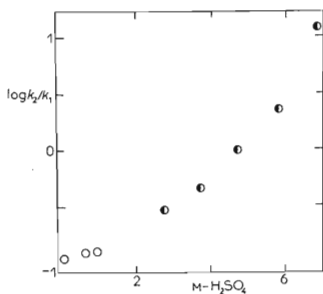

FIG. 1

Dependence of $\log(k_2/k_1)$ on Molarity of Sulphuric Acid
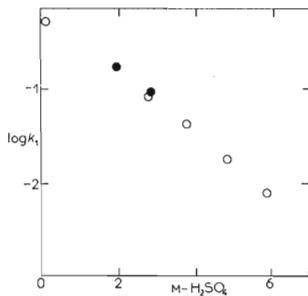   Values: ○ calculated; ◉ measured.

FIG. 2

Dependence of $\log k_1$ (s^{-1}) on Molarity of Sulphuric Acid
    Values: ● calculated; ○ measured.

TABLE I

Values of Rate Constants (s^{-1}) of the Reactions $I \rightarrow II$ (k_{obs}); $I + H_2O \rightarrow III$ (k_1) and Reverse Reaction (k_{-1}); $III \rightarrow II$ (k_2) and Ratio $[III]/[I]$ in Steady State in Diluted Sulphuric Acid at 25°C

M-H_2SO_4	$10^2 \cdot k_{obs}$	k_2/k_{-1}	$[III]/[I]$	$10^2 \cdot k_2$	$10^2 \cdot k_{-1}$	$10^2 \cdot k_1$	$K' = k_1/k_{-1}$
0·10	0·06	0·12[a]	—	0·07	0·57	65[b]	114[c]
0·53[d]	0·43	0·14[e]	14·9	0·46	3·3	50	15·1
0·91[d]	0·8	0·15[e]	5·26	0·97	6·7	36	5·40
1·47	1·5	0·165[f]	1·59	2·6	15·7	27	1·70
1·93	1·8	0·175	0·63	4·65	26·7	18·5	0·71
2·40	1·98	0·20[f]	0·23	10·7	53·5	14	0·27
2·86	1·7	0·235	0·09	20·6	87·5	10	0·11
3·35	1·46	0·32[f]	0·03	50·0	160	6·2	0·04
3·79	1·13	0·47	—	—	—	3·5	—
4·83	0·85	1·0	—	—	—	1·7	—
5·86	0·63	2·3	—	—	—	0·9	—
6·8	0·38	11·0	—	—	—	0·4	—

[a] Calculated from the measured values k_2 and k_{-1}; [b] the value k_1 found experimentally; [c] the K value calculated from k_1/k_{-1}; [d] the k values were calculated by the both methods (for $[H_2SO_4] \leqq 1$M also by the method for 1 to 3·5M-H_2SO_4) and agree within experimental error; [e] determined by the both methods; [f] approximative values.

$[III]/[I]$. Further reaction takes pseudomonomolecular course, and k_{obs} is defined[6] by Eq. (3).

$$k_{obs} = \tfrac{1}{2}\left(k_1 + k_{-1} + k_2 \pm \left((k_1 + k_{-1} + k_2)^2 - 4k_1k_2\right)^{1/2}\right). \qquad (3)$$

The ratio $[III]/[I]$ was obtained (in the measurements of k_{obs}) from the absorbance values extrapolated to zero time and from the found absorbance values of the diazo hydroxide III and diazonium ion I at the same wavelength. From the found ratio $[III]/[I]$ and k_{obs} the k_2 values were calculated according to Eq. (4), and the k_{-1} values were obtained from the measured ratio k_2/k_{-1} (Table I).

$$v \;= k_{obs}([I] + [III]) = k_2[III],$$
$$k_2 = k_{obs}[III]/([I] + [III]) = k_{obs}(1 + [I]/[III]). \qquad (4)$$

For 2M and 3M-H_2SO_4 the values k_1 were calculated by iteration procedure from the values k_2, k_{-1}, k_{obs} and Eq. (3). The ratio k_1/k_{-1} gives the value of ratio of equilibrium concentrations $[I]_{eq}$ and $[III]_{eq}$ (the quantity K' in Table I). c) At $[H_2SO_4] \ll 1$M it is $k_1 > k_{-1} > k_2$. The Eq. (A) can be kinetically solved as a rapid pre-equilibrium with subsequent rate-limiting step (5), wherefrom Eq. (6) follows for k_2.

$$k_{obs} = k_1k_2/(k_1 + k_{-1}), \qquad (5)$$

$$k_2 \;= k_{obs}(1 + k_{-1}/k_1). \qquad (6)$$

The rate constant k_1 was measured directly for 0·1M-H_2SO_4 (0·65 l mol^{-1} s^{-1}) and for 0·1M-HCl (0·58 l mol^{-1} s^{-1}). The other k_1 values were read from the graph in Fig. 2. For determination of k_{-1} rate of the reaction (B) was measured in 0·1M- -1M-H_2SO_4 and HCl.

$$IV + 2\,H^+ \;\rightleftharpoons\; III + H^+ \begin{array}{c} \xrightarrow{k_{-1}} I \xrightarrow{+v} \text{azo dyestuff} \\[1ex] \xrightarrow{k_2} II + NO^+ \end{array} \qquad (B)$$

Under the reaction conditions used the formed diazonium ion I is transformed into the corresponding azo compound practically immediately and quantitatively, so that the observed rate constant $k_{obs} = k_{-1} + k_2$.

In chloroacetate buffers ($[HA] : [A^-] = 1 : 1, 2 : 1, 3 : 1$) the k_{obs} value (reaction (B)) increased linearly with the chloroacetic acid concentration, hence the reaction is subject to general acid catalysis. Rate constant of the chloroacetic acid-catalyzed transformation of the diazo hydroxide III into the diazonium ion I $k_{HA} = 2·52 \pm \pm 0·03$ l mol^{-1} s^{-1} was calculated from the slope of the dependence k_{obs} vs con-

centration of chloroacetic acid. If also the formation of the amine *II* is subject to general acid catalysis, then the found rate constant k_{HA} is equal to the sum of the rate constants of general-acid-catalyzed formation of the diazonium ion and formation of amine.

The reaction of the diazonium ion *I* with water giving the diazo hydroxide *III* can be expressed by Eq. (*C*).

$$ArN_2 + (n + 1) H_2O \rightleftarrows ArN_2OH + H^+.n\,H_2O . \qquad (C)$$
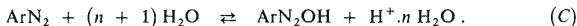
This reaction resembles that of carbenium ion with water giving alcohol. Dependence of $\log([III]/[I])$ on H_R function[7,8] is linear with the slope 0.9 ± 0.1.

As the transformation of the diazo hydroxide *III* into the diazonium ion *I* is subject to general acid catalysis, the reverse reaction must be subject to general base catalysis. For the reactions in diluted mineral acids water molecule acts as the catalyst, for those in buffers the basic buffer component A^- is also active, so that the activated complex has the structure *VI* and *VII*, respectively.

$$VI \qquad\qquad\qquad VII$$
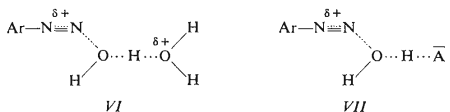
The hydroxonium ion formed in the activated complex *VI* is solvated by further water molecules, but their number is smaller than that after the end of the reaction (mainly for sterical reasons). With increasing concentration of sulphuric acid activity of water decreases and, consequently, k_1 decreases, too. The dependence $\log k_1$ *vs* $\log a_{H_2O}$ is not linear, its slope being decreased from the value 7 in $2M\text{-}H_2SO_4$ to about 3 in $6M\text{-}H_2SO_4$.

The reaction of the diazonium ion *I* with water is reversed by the proton-catalyzed splitting off of hydroxyl group from *III*. The latter reaction must go through the same activated complex, which means that in the activated complex a part of the water molecules are bound which solvated the proton before beginning of the reaction. In very dilute acid solutions the reaction rate is directly proportional to the proton concentration. In medium of mildly diluted sulphuric acid the rate increases faster than the proton concentration, but the change of $\log k_{-1}$ (which predominantly involves the proton-catalyzed reaction in this medium) is smaller than that of $\log([III]/[I])$, and slope of the dependence $\log k_{-1}$ *vs* H_r is about -0.5 for $1M$ to $3M\text{-}H_2SO_4$.

From analogy with substituted benzenediazonium ions[9] it can be supposed that the diazo hydroxide *III* formed in reaction of the diazonium ion with water is a *syn*-isomer which is rapidly transformed into the *anti*-isomer, the ratio *anti/syn* being 10^2 to 10^3. Therefrom it should follow

that rate constants of transformation of the *syn*-isomer to the diazonium ion are in fact higher by $2-3$ orders of magnitude than the values k_{-1} given in Table I, and that the values $[III]/[I]$ in Table I give the concentration ratio of the *anti*-diazo hydroxide to the diazonium ion I.

General base and acid catalysis in reactions $I \rightarrow III$ and $III \rightarrow I$, respectively, was confirmed by measurements in D_2O using either $0 \cdot 1M\text{-}D_2SO_4$ (the reactions in the both directions) or chloroacetate buffers (the reaction $III \rightarrow I$). The rate constants ratio k_{H_2O}/k_{D_2O} was $4 \cdot 3$ for formation of the diazo hydroxide, and it was $1 \cdot 3$ and $2 \cdot 8$ for the reaction $III \rightarrow I$ in $0 \cdot 1M\text{-}D_2SO_4$ and buffer, respectively.

The kinetic isotope effects involve the secondary isotope effect of the hydrogens not reacting in the rate-limiting step and the primary isotope effect of the proton transferred in the activated complex[10], Eq. (7). From the found value $\alpha = 0 \cdot 2$

$$k_{H_2O}/k_{D_2O} = (k_H/k_D)_{sec} \cdot (k_H/k_D)_{prim} \qquad (7)$$

of acid-catalyzed transformation of substituted benzenediazo hydroxides into diazonium ions[11], from the relation between α value and the proton transfer[12], and from the value of the isotope fraction factor[10] $1 = 0 \cdot 69$ it follows that secondary isotope effects are $1 \cdot 9$ and $0 \cdot 6$ for reactions $I \rightarrow III$ and $III \rightarrow I$, respectively, in $0 \cdot 1M$ sulphuric acid. Hence the respective values of the primary isotope effect are $2 \cdot 3$ and $2 \cdot 2$. In reactions carried out in buffer water molecule is not directly involved, so that the found value $2 \cdot 8$ is due predominantly to the primary isotope effect. The relatively low value of the primary isotope effect is typical of the reactions involving a proton transfer concerted with a bond change between two "heavy atoms"[10]. The rate constant k_2 of formation of the amine from the diazohydroxide III involves the tautomeric equilibrium diazohydroxide–nitrosamine, protonation of the nitrosamine, and possibly also decomposition of the protonated nitrosamine to the products (as the rate-limiting step). Nitrosation of aromatic amines is catalyzed by chloride ions, *i.e.* also the reverse reaction (formation of amines from nitrosamines) must be catalyzed in the same way, which was confirmed in the case of N-methylnitrosoaniline[13]. Formation of the amine from the ion I is practically equally fast both in hydrochloric and perchloric acids ($0 \cdot 5M$ as well as $1M$), which contradicts the chloride ion catalysis.

The Cl⁻ ion catalysis was disproved also in denitrosation of N-1-butyl-N-nitroso-acetamide[14] and N-methyl-N-nitrosotoluene-*p*-sulphonamide[15], which was explained by the rate-limiting protonation of nitrogen (possibly with partial splitting of the N—N bond in the activated complex), because the denitrosation was $1 \cdot 5$ times faster in diluted H_2SO_4 than in D_2SO_4. In the case of the diazo hydroxide III another explanation is possible that the formed protonated nitrosamine is so much reactive that nucleophile (Cl⁻ or H_2O) plays no (or a slight) part in the activated complex of splitting off of NO⁺. The ratio k_2/k_{-1} increases rapidly with increasing sulphuric acid concentration (Table I). Hence it follows that the activated complex of the rate-limiting step of formation of the amine II from the diazo hydroxide III is less solvated

with water than is the activated complex of formation of the ion *I*. Its structure will be similar to that of the protonated nitrosamine with partially split N—N bond and with an only partial positive charge at the NH_2 group.

The rapid and almost quantitative decomposition of the ion *I* in dilute mineral acid sharply contrasts with behaviour of benzenediazonium ion and other aromatic diazonium ions where this reaction proceeds to a slight extent only.[16] In this case the decisive factor consists in that the decomposition goes through the nitrosamine the concentration of which is slight in solutions of usual aromatic diazonium ions. In sufficiently acidic medium almost all the formed amine *II* is protonated ($pK_a = 2.8$), so that the reaction proceeds practically quantitatively. At lower proton concentrations ($pH > 1$) concentration of the non-protonated amine markedly increases. The reverse reaction *II* + HONO → *III* is increasingly significant, so that after the end of the reaction (after the equilibrium is established) the mixture contains considerable amounts of diazo hydroxide. After addition of mineral acid the reaction proceeds until completion.

High reactivity of diazonium ion stands in apparent discrepancy with high basicity of the amine *II*. The reason is in that the protonation takes place at nitrogen atom of the heterocycle, the cation formed being stabilized by resonance with amino group. Basicity of NH_2 group is very low.

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