AZO COUPLING KINETICS OF SUBSTITUTED PYRAZOLINE-5-ONES AND THEIR AMPHOTERIC CHARACTER

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Nine 3'- and 4'-substituted 1-phenyl-3-aminopyrazoline-5-ones have been prepared, and their ionization properties have been measured in 20% (by vol.) ethanol and correlated with the substituent constants. In spectrophotometric measurements no influence of prototropic tautomerism was observed, in potentiometric titration the influence of the tautomeric changes probably makes itself felt. The determined rate constants of azo coupling of the series of nine substituted 1-phenyl-3-aminopyrazoline-5-ones and twelve 1-phenyl-3-methylpyrazoline-5-ones were correlated with the Hammett constants. The influence of substituents in benzene ring at the position 1 on the reactivity of the methylene group at the position 4 of pyrazolinone ring is only slight and equal in the both studied series of the compounds.

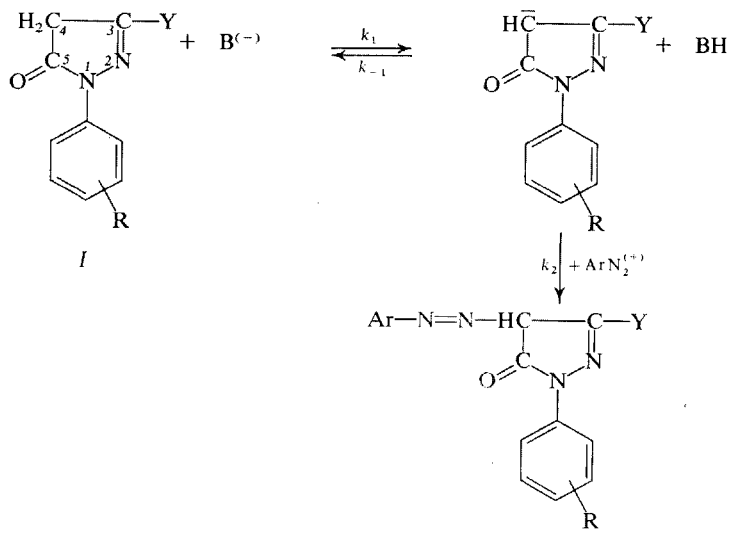
For the reactions used in dyestuff chemistry and color photography it is important to know the reactivity of the methylene group at 4-position of pyrazolinone ring (*I*). For the sake of simplicity we give the structure *I* in spite of that there exist extensive literature[1-9] dealing with influence of substituents and medium on the position of the double bond in pyrazolinone ring. Substituent effects on reactivity of the methylene group of pyrazoline-5-ones have not yet been studied. Some time ago we investigated the azo coupling kinetics with substituted 1-phenyl-3-methylpyrazoline-5-ones[10] from the point of view of substitution of the reagent. Mechanism of azo coupling of pyrazoline-5-ones is similar to that of the reaction of diazonium salts with phenols[11] and can be represented by Scheme 1. The Scheme is simplified by considering neither the tautomerism of pyrazoline-5-one nor that of the azo dyestuff formed. The azo coupling rate is given by Eq. (*1*) where k_2 is the bimolecular rate constant independent of pH, k_s is the stoichiometric

$$v = k_2[II]\,[ArN_2^+] = k_s[ArN_2^+]\,[I]_{anal} \qquad (1)$$

constant of the bimolecular reaction, and $[II]$ is concentration of pyrazolinone anion. The concentration $[I]_{anal}$ includes the concentrations of pyrazoline-5-one and its anion, and in neutral and alkaline regions it equals the analytical concentration of pyrazoline-5-one given by weighing (pH 4 to 14). $[ArN_2^+]$ is analytical concentration of the diazonium salt. Provided the excess of pyrazoline-5-one is at least ten fold, Eq. (*2*) can be used, and the bimolecular rate constant can be calculated from Eq. (*3*) where K_a^I is dissociation constant of pyrazoline-5-one.

$$v = k'[ArN_2^+]\,, \qquad (2)$$

$$k_2 = k'/[II] = k'(K_a^I + [H^+])/K_a^I[I]_{anal}\,. \qquad (3)$$



I *II*

SCHEME 1

In contrast to phenols, pyrazoline-5-ones are protonated in less acidic region (pH 1 to 2), and if the measurements are carried out in this region, the concentration $[I]_{anal}$ of the pyrazoline-5-one must be corrected with the use of Eq. (*4*) where K_a^{II} is the ionization constant of protonation

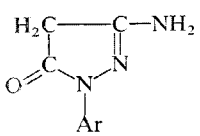
$$[I]_{anal} = K_a^{II} \cdot C_{anal}/([H^+] + K_a^{II}), \qquad (4)$$

of pyrazoline-5-one, $[I]_{anal}$ stands for the total concentration of non-protonated pyrazoline-5-one, and C_{anal} is the analytical concentration of pyrazoline-5-one given by the weighing and including all the forms of the pyrazoline-5-one molecule present in the solution, *i.e.* the protonated form, too.

The aim of this work was, first of all, the determination of the influence of substituents of pyrazolone ring on the methylene group at 4-position. For this purpose two series of 1-phenylpyrazoline-5-ones (*I*, Y = CH_3 and Y = NH_2; the tautomerism being not considered) substituted in the 1-phenyl group were chosen.

Kinetic measurements necessitate the knowledge of ionization constants K_a^I and K_a^{II}. These constants are known for substituted 1-phenyl-3-methylpyrazoline-5-ones[1,2]; 1-phenyl-3-amino-pyrazoline-5-ones can exist in five tautomeric forms (*III* to *VII*) according to the medium in which they are present. Although this point was given considerable attention in literature, the results of the individual authors do not always agree with one another. Acid–base equilibria can be represented generally by Eq. (*A*) where PyH, Py^-, PyH_2^+ and PyH_3^{2+} stand for neutral 3-amino-pyrazoline-5-one molecule, its anion, its mono-protonated and di-protonated forms, respectively.

$$PyH_3^{2+} \underset{+H^+}{\overset{K_a^{III}}{\rightleftharpoons}} PyH_2^+ \underset{+H^+}{\overset{K_a^{II}}{\rightleftharpoons}} PyH \underset{+H^+}{\overset{K_a^{I}}{\rightleftharpoons}} Py^- \qquad (A)$$



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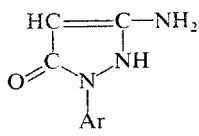

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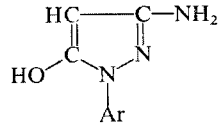

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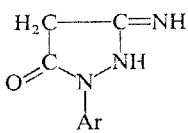

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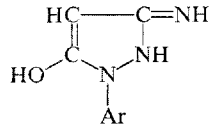


VII

Hence the second aim of the present paper was determination of the ionization constants K_a^I, K_a^{II} or also K_a^{III} and their possible correlation with the Hammett σ constants. Also we were interested in the ionization constants measurements as potential criterion for decision which of the tautomeric structures is predominant in the given medium.

EXPERIMENTAL

Preparation of Pyrazoline-5-ones

1-Phenyl-3-methylpyrazoline-5-ones were prepared by condensation of the respective hydrazines with ethyl acetoacetate in usual way, and their purity was checked by known methods[13]. 1-Phenyl--3-aminopyrazoline-5-ones were prepared by condensation of the respective hydrazines with ethyl malonate monoimido ester and crystallized from ethanol, methanol or mixture of the solvents $CHCl_3$—CH_3OH (1 : 2) until constant melting point, and their purity was checked by paper chromatography (Whatman No 3 impregnated with 20% solution of formamide in acetone; eluent system $CHCl_3$, pyridine, n-heptane 39 : 1 : 10).

Ionization Constants of 3-Aminopyrazoline-5-ones in 20% (by vol) Ethanol

Potentiometric titration. The measurements were carried out by the method described in literature[12] using tetramethylammonium hydroxide instead of KOH, which makes it possible to obtain relatively well developed titration curves.

Spectrophotometric determination of pK_a^I. The measurement was carried out by the method described for 3-methylpyrazoline-5-ones with the use of fresh solutions temperated at 20°C and buffers tris(hydroxymethyl)aminomethane–HCl (ref.[14]) with constant ionic strength 0·01. For the substituent R = CO_2CH_3 it was not possible to obtain constant spectra of the anion and, therefore, the basic equilibrium relation for pK_a was transformed into the form Eq. (*5*) where E_{PyH} and

$$E = K_a^I(E - E_{PyH})/[H^+] + E_{Py^-} \qquad (5)$$

E_{Py} — stand for the extinctions of the neutral molecule and anion of pyrazoline-5-ones, respectively; E is the extinction of the equilibrium mixture.

Spectrophotometric determination of pK_a^{II}. The measurement was carried out in the same way as that for pK_a^{I} of the 4′-CO_2CH_3 derivative, because the difference between the first and the second protonation was 2 to 3 pK units, and it was not possible to determine the accurate extinctions of the monoprotonated form of pyrazoline-5-one. Again the basic equilibrium relation for pK_a was transformed to the intercept form (Eq. (6)) with the use of which pK_a^{II} and extinction

$$E = K_a^{II}(E_{PyH} - E)/C_{H_2SO_4} + E_{PyH_2^+} \qquad (6)$$

of the mono-protonated molecule were calculated. In Eq. (6) E_{PyH} and $E_{PyH_2^+}$ denote the extinctions of the respective forms of pyrazoline-5-ones, E stands for extinction of the equilibrium mixture and $C_{H_2SO_4}$ is the known sulphuric acid concentration (mol/l). All the other important conditions of a correct measurement (measurements at constant spectra, the same way of preparation of a comparison and a sample solution, titration procedure, substitution of $-H_0$ for $C_{H_2SO_4}$ according to literature) were respected as in the studies[12] of 3-methylpyrazoline-5-ones.

Spectrophotometric determination of pK_a^{III}. The measurement procedure was substantially the same as that of pK_a^{II}, and also the calculation was carried out with the use of the intercept form of the equation of ionization constant which here has the form Eq. (7). For the value $E_{PyH_2^+}$ the calculation results from pK_a^{II} determination were used and the precise concentration was taken

$$E = K_a^{III}(E_{PyH_2^+} - E)/H_0' + E_{PyH_3^{2+}} \qquad (7)$$

into account. The both ionization constants were determined at the same wavelength. The measured $E_{PyH_2^+}$ could not be used for calculation, because the spectra measured in highly concentrated sulphuric acid could not secure the required grade of accuracy. The sulphuric acid concentration was determined by titration, and the function H_0' (ref.[15]) was used. Suitability of this procedure will be discussed.

Kinetic Measurements

Preparation of azo dyestuffs. The azo dyestuffs were prepared by usual methods[16] from three 3-methylpyrazoline-5-ones (4′-OCH_3, H, and 4′-NO_2) and one 3-aminopyrazoline-5-one. Sulphanilic acid was chosen for better solubility of the formed dyestuffs. The compounds melted with decomposition above 300°C, therefore their purity was checked by chromatography on Silufol with mixture ethanol–benzene 1 : 3 and on paper with propanol–ammonia 2 : 1.

Spectra of all the prepared azo dyestuffs were identical with those obtained in kinetic experiments and those obtained by direct mixing of the components in cells. Therefore, the rest of the dyestuffs were not isolated.

Measurements. All the kinetic experiments were carried out at 20°C in 20% (by vol.) aqueous ethanol, the respective buffers having constant ionic strength 0·5. The solution volume change after injection of diazo component was not taken into account. In the case of slower reactions ($\tau_{1/2}$ about two minutes) the time increase of extinction was followed directly with a spectrophotometer Unicam SP 800 at the wavelength of the maximum extinction of the dyestuff formed. Such amounts were weighed that the final dyestuff concentration in the cell was $2 \cdot 10^{-5}$ mol/l and the reactions took pseudomonomolecular course. The constant k' was then calculated

from Eq. (*8*) where E_t and and E_∞ are extinctions of the formed dyestuff at the time t and $t = \infty$,

$$k't = 2{\cdot}303 \log (E_\infty/(E_\infty - E_t)) \qquad (8)$$

respectively. At least nine E_t values measured within the reaction half-life were used for calculation. For quicker reactions ($\tau_{1/2}$ about 0·5 min) the amounts chosen were the same as above. The reaction mixture was vigorously stirred, and at definite time intervals the reaction was stopped by addition of 20 ml 2·5N-HCl. The samples were adjusted at 50 ml volume by addition of redistilled water, and the extinctions were measured with the use of a spectrophotometer VSU-1 (Zeiss, Jena). The k' constants were calculated according to Eq. (*8*), too.

RESULTS AND DISCUSSION

Ionization Constants of Substituted 1-Phenyl-3-aminopyrazoline-5-ones

Deprotonation. In contrast to the substituted 1-phenyl-3-methylpyrazoline-5-ones, electronic spectra of 1-phenyl-3-aminopyrazoline-5-ones are suitable for pK_a measurements also in neutral and alkaline regions. The pK_a^I values of 1-phenyl-3-aminopyrazoline-5-ones were determined both by the potentiometric and the spectrophotometric method, however, the results obtained from the two methods were different. Correlation with the Hammett σ constants was good in the both series of measurements giving Eqs (*9*) and (*10*).

$$pK_a^I \text{(potentiometrically)} = (-2{\cdot}47 \pm 0{\cdot}09)\,\sigma + (9{\cdot}22 \pm 0{\cdot}05) \qquad (9)$$

$$r = -0{\cdot}991,\ n = 9$$

$$pK_a^I \text{(spectrophotometrically)} = (-1{\cdot}26 \pm 0{\cdot}13)\,\sigma + (9{\cdot}24 \pm 0{\cdot}05) \qquad (10)$$

$$r = -0{\cdot}964,\ n = 9\,.$$

Table I gives the results for individual substituents. For explanation of deprotonation of 3-aminopyrazoline-5-ones a number of factors must be considered which were described in literature[6,9,17]. Therefore, the constancy and reversibility of the spectra of all the forms of molecules of these derivatives were checked, and it was found that the spectra of the extreme forms are not changed, however, spectra of the equilibrium mixtures changed on heating. Here it was impossible to prove complete reversibility, which is due especially to possible tautomeric changes. However, heating is necessary for dissolution of the samples for potentiometric titration with respect to their bad solubility at higher concentrations.

Although the Hammett correlation was good for the potentiometric determination, too, the following discussion of structure and kinetic calculations are based on the spectrophotometric results where the constancy of spectra was sufficiently proved, and accuracy of measurements was secured.

The results show that 3-aminopyrazoline-5-ones are, in accord with what could be expected, weaker acids than the corresponding 3-methyl analogs by 2 pK units (Table II). Since the ϱ constant values are similar in the both series of pyrazoline-5-ones (−0·953 and −1·26 for 3-methyl and 3-amino derivatives, respectively),

TABLE I

Values of Ionization Constants of Substituted 1-Phenyl-3-aminopyrazoline-5-ones in 20% (by vol.) Ethanol at 20°C

No	R	M.p., °C	$pK_a^{I,a}$	$pK_a^{I,b}$	$pK_a^{II,a}$	$pK_a^{II,b}$
1	4′-CH_3	183	9·58 ± 0·02	9·39 ± 0·03	0·87 ± 0·02	−2·34 ± 0·10
2	3′-CH_3	177–78	9·36 ± 0·01	9·35 ± 0·04	0·86 ± 0·01	−2·22 ± 0·26
3	H	220–21	9·27 ± 0·01	9·29 ± 0·05	0·63 ± 0·09	−2·31 ± 0·23
4	4′-Cl	173–74	8·92 ± 0·01	9·03 ± 0·03	0·37 ± 0·02	−2·24 ± 0·09
5	4′-Br	155	8·62 ± 0·04	8·94 ± 0·06	0·44 ± 0·05	−2·38 ± 0·09
6	3′-Cl	208	8·11 ± 0·05	8·94 ± 0·05	0·36 ± 0·02	−2·13 ± 0·09
7	4′-$COOCH_3$	210	8·15 ± 0·09	8·46 ± 0·01	0·25 ± 0·05	−2·26 ± 0·07
8	3′-NO_2	141–42	7·46 ± 0·05	8·41 ± 0·04	0·05 ± 0·02	−2·33 ± 0·11
9	4′-NO_2	258–59	7·28 ± 0·09	8·28 ± 0·07	−0·07 ± 0·04	−2·26 ± 0·09

[a] Potentiometric determination. [b] Spectrophotometric determination. Basis of the acidity function: 3-nitroaniline, pK_a = 2·29 ± 0·05 in 20% (by vol.) ethanol at 20°C.

TABLE II

Numerical Values of the Hammett Indicator Diagrams for Calculation of pK_a^{II} and Difference in Acid–Base Properties between 1-Phenyl-3-methyl- and 1-Phenyl-3-aminopyrazoline-5-ones

Compound	Slope[a]	r	$\Delta pK_a^{I,b}$	$\Delta pK_a^{II,c}$
1	1·00 ± 0·03	0·996	1·94	−0·93
2	0·99 ± 0·01	0·999	1·96	−0·85
3	1·03 ± 0·04	0·995	1·90	−0·74
4	1·04 ± 0·03	0·998	2·00	−0·90
5	1·07 ± 0·03	0·997	2·00	−1·01
6	1·02 ± 0·04	0·996	1·99	−0·92
7	1·04 ± 0·04	0·997	1·65	−0·77
8	1·00 ± 0·02	0·999	1·67	−0·77
9	1·01 ± 0·04	0·996	1·63	−0·75

[a] For 3-nitroaniline slope 0·915, s = 0·033, r = 0·997; [b] $\Delta pK_a^I = pK_a^I(3\text{-}NH_2) - pK_a^I(3\text{-}CH_3)$; [c] $\Delta pK_a^{II} = pK_a^{II}(3\text{-}NH_2) - pK_a^{II}(3\text{-}CH_3)$.

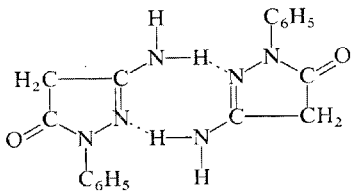
we suppose that also here the proton is split from 2-position, as it was proved in our previous work[12].

The first protonation. In acid medium the proton is added to the substituted 1-phenyl-3-aminopyrazoline-5-ones according to Eq. (*A*). The ionization constants pK_a^{II} (Table I) were obtained spectrophotometrically and correlated with the Hammett σ constants (Eq. (*11*)).

$$pK_a^{II} = (-0{\cdot}965 \pm 0{\cdot}06)\,\sigma + (0{\cdot}687 \pm 0{\cdot}03); \quad r = -0{\cdot}983\,, \quad n = 9 \qquad (11)$$

Table II gives a summary of the slopes of the dependence of log ($[BH_2^+]/[BH]$) on sulphuric acid concentration obtained by the least squares method. From the values found it follows that all the substances can be considered to be the Hammett indicators. The ϱ constant values of the first protonation of 3-amino- and 3-methylpyrazoline-5-ones are similar, too ($-0{\cdot}965$ and $-1{\cdot}21$, respectively), and, hence, it can be deduced that the both processes are the same, *i.e.* the proton is added at 2-position of the pyrazolinone ring.

Low values of the protonation constants of 3-aminopyrazoline-5-ones were expected, because generally amino group of heterocyclic amines is less basic than hetero nitrogen[17,18]. There still remains a question why 3-aminopyrazoline-5-ones are weaker bases than 3-methylpyrazoline-5-ones, whereas the reverse should be true (in spite of the low values of dissociation constants), and the proton loss confirms it, too. Generally, the basicity decrease against expectations in the case of nitrogen heterocyclic rings is due to formation of various types of hydrogen bonds at the nitrogen atom at which the protonation occurs (8-aminoquinoxaline, 1-aminoacridine, pyrazole[19]); *e.g.* structures *VIII* and *IX* can be suggested for 1-phenyl-3-aminopyrazoline-5-ones. Structure of a dimer was also considered[9] on the basis of IR and NMR spectra, its form was, however, different. The present way seems more natural to us, and it could explain also the difficult protonation at 2-nitrogen atom as compared with 3-methylpyrazoline-5-ones.



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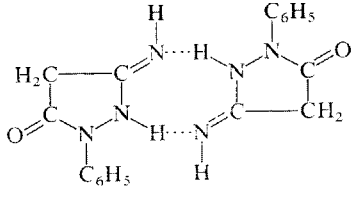

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The second protonation. Spectra of pyrazoline-5-ones indicate a further acid–base process. However, the mono-protonated pyrazolinone molecule is a very weak base, and the measurements must be carried out in solutions of concentrated sulphuric

acid. Accurate calculation of the ionization constant K_a^{III} (Eq. (*A*)) would necessitate the knowledge of the course of H'_+ function in the solutions H_2SO_4–H_2O + 20% (by vol.) ethanol containing high concentrations of sulphuric acid. Eq. (7) uses the H'_0 function instead of H'_+. For aqueous concentrated solutions of sulphuric acid the both functions H_0 and H_+ were studied[20], and their identity was proved in the concentration ranges 30–55% and 75–95% H_2SO_4. As the H'_+ function course is not known for aqueous ethanolic solutions, and it was not easy to determine it in our case, we can only presume a similar course of the both functions H'_0 and H'_+ and use their mutual substitution in calculation. After carrying out this change it is clear that the given relation and results do not express the real process. The calculated values of constants (Table I) serve as a prove of a further acid–base process and as a value giving the sulphuric acid concentration at which the ratio $[BH_2^+]/[BH_3^{2+}]$ equals unity. The practically constant values indicate that the process takes place at a reaction centre quite distant from benzene ring. Since the protonation of carbonyl oxygen takes place in much more acidic media, and, besides that, no similar process was observed with 3-methylpyrazoline-5-ones, it is obvious that the protonation occurs at the amino group.

KINETIC MEASUREMENTS

The kinetic measurements were based on the presumption (taken from ref.[10] and similar investigations of other coupling components *e.g.* phenols) that azo coupling with undissociated resp protonated form is so slow compared with the deprotonated form (the difference being more than 9 orders of magnitude), that it can be neglected in the experiments carried out; the same presumption was made with respect to decomposition of diazonium salt during coupling.

Under the mentioned conditions the dependence of the bimolecular rate constant on the Hammett σ constants is expressed by Eqs (*12*) and (*13*) for the substituted 1-phenyl-3-methylpyrazoline-5-ones and 1-phenyl-3-aminopyrazoline-5-ones, respectively (Table III). The σ values are taken from ref.[21].

$$\log k_2 = (-0{\cdot}655 \pm 0{\cdot}067)\,\sigma + (6{\cdot}917 \pm 0{\cdot}029)\,; \quad r = 0{\cdot}955\,, \quad n = 11\,, \qquad (12)$$

$$\log k_2 = (-0{\cdot}646 \pm 0{\cdot}058)\,\sigma + (7{\cdot}650 \pm 0{\cdot}024)\,; \quad r = 0{\cdot}972\,, \quad n = 9\,. \qquad (13)$$

The kinetic measurement results agree with the presumed mechanism (bimolecular electrophilic substitution) as far as sign and magnitude of the ϱ constant are concerned. Due to practical reasons the kinetics were studied at pH 3·73 and 4·48 in the case of 1-phenyl-3-methylpyrazoline-5-one and 1-phenyl-3-aminopyrazoline-5-one, respectively. Under these conditions the reaction could be easily followed and no complications were encountered due to possible N-coupling in the case of 1-(4′-aminophenyl)-3-methylpyrazoline-5-one and substituted 1-phenyl-3-amino-

pyrazoline-5-ones. The value of 1-(4′-aminophenyl)-3-methylpyrazoline-5-one was not included in correlation, because here the amino group is protonated, and real concentration of pyrazolinone anion is controlled not only by the dissociation constant K_a^I. The velocity is higher than it should be according to calculations, because the amonium cation withdraws electrons (−I effect) from the reaction centre whereby the dissociation of the pyrazolinone is facilitated.

The pH dependence of the stoichiometric rate constant k_s of the azo coupling served for verification of constancy of the bimolecular rate constant k_2. In the both series of compounds, *i.e.* 1-phenyl-3-methylpyrazoline-5-ones and 1-phenyl-3-aminopyrazoline-5-ones (Tables IV and V, respectively), a deviation is observed in media of low pH value. The protonation of pyrazolinone ring cannot be the reason, because it takes place first at pH 2·5 to 2·6. Decomposition of diazonium salt is more probable. The problem could not be solved with the used experimental method. The reaction was very slow at pH below 3, so that E_∞ had to be measured after 24 hours from the reaction start. The stoichiometric rate constant of the two series differ by almost one order of magnitude, the methylene group of 1-phenyl-3-methylpyrazoline-5-one being ten times more reactive. The real reason of the different reactivity at the given pH is the value of ionization constant. If we compare the rate constants k_2, which are the real measure of reactivity of the methylene group, the effect of ionization con-

TABLE III

Influence of Substituents of Benzene Ring of 1-Phenylpyrazoline-5-ones on Reactivity of Methylene Group

R	σ	3-Methyl k_2, l mol^{-1} min^{-1} $\times 10^{-6}$	3-Amino k_2, l mol^{-1} min^{-1} $\times 10^{-7}$
4′-NH_2	−0·66	36·736	—
4′-OCH_3	−0·26	14·010	—
4′-CH_3	−0·14	8·773	5·624
3′-CH_3	−0·10	10·260	5·453
H	0	9·640	4·165
4′-Cl	0·22	5·332	3·241
4′-Br	0·23	4·671	2·634
3′-Cl	0·39	4·869	3·192
4′-$COOCH_3$	0·43	4·044	1·238
4′-CN	0·69	2·382	—
3′-NO_2	0·70	4·008	1·429
4′-NO_2	0·80	2·513	1·373

stant being eliminated, then the reverse is true: 1-phenyl-3-aminopyrazoline-5-ones are almost 10× more reactive. Whereas amino group decreases the acidity of the compound, it increases its ability for electrophilic substitution.

TABLE IV

pH Dependence of Stoichiometric Rate Constant k_s (l mol^{-1} min^{-1}) of Azo Coupling of 1-Phenyl-3-methylpyrazoline-5-one .

pH	k', min^{-1}	$c \cdot 10^{4,a}$	$k_2 \cdot 10^{-6,b}$	$k_s \cdot 10^{-2}$
2·21	0·037 ± 0·005	3·894	14·309	0·9016
2·48	0·074 ± 0·001	4·791	12·418	1·5275
2·71	0·148 ± 0·003	5·487	12·707	2·6545
2·91	0·277 ± 0·008	6·065	13·722	4·5994
3·24	0·154 ± 0·002	2·434	8·785	6·2087
3·42	0·267 ± 0·009	2·451	9·974	10·667
3·61	0·357 ± 0·006	2·475	8·557	14·128
3·73	0·486 ± 0·012	2·292	9·640	15·998
4·47	3·236 ± 0·207	2·498	10·701	148·960
5·08	12·220 ± 0·658	2·504	10·370	506·990

[a] In mol/l. [b] In l/mol min.

TABLE V

pH Dependence of Stoichiometric Rate Constant k_s (l mol^{-1} min^{-1}) of 1-Phenyl-3-aminopyrazolin-5-one

pH	k', min^{-1}	$c \cdot 10^{4,a}$	$k_2 \cdot 10^{-7,b}$	k_s
3·065	0·0146 ± 0·002	2·498	9·421	5·87
3·275	0·0205 ± 0·002	2·489	8·129	8·224
3·615	0·0318 ± 0·002	2·499	5·748	$1·272 \cdot 10^2$
3·775	0·0430 ± 0·006	2·498	5·382	$1·721 \cdot 10^2$
4·09	0·0704 ± 0·004	2·502	4·265	$0·281 \cdot 10^3$
4·22	0·1053 ± 0·006	2·491	4·751	$0·422 \cdot 10^3$
4·52	0·2347 ± 0·014	2·475	5·342	$0·948 \cdot 10^3$
4·76	0·4045 ± 0·006	2·575	5·089	$1·570 \cdot 10^3$
4·83	0·5267 ± 0·012	2·554	5·674	$2·061 \cdot 10^3$
5·19	1·0205 ± 0·056	2·499	5·796	$4·083 \cdot 10^3$
5·39	1·9316 ± 0·154	2·503	5·852	$7·714 \cdot 10^3$

[a] In mol/l. [b] In l/mol min.

Correlation of the stoichiometric rate constants k_s with the σ constants is possible, if the dependence of log k_s on pH is linear, which is fulfilled for $K_a^I \gg [H^+]$. The Eqs (*14*) and (*15*) resulted for 1-phenyl-3-methylpyrazoline-5-ones and 1-phenyl-3-aminopyrazoline-5-ones, respectively.

$$\log k_s = (0{\cdot}300 \pm 0{\cdot}041)\,\sigma + (3{\cdot}339 \pm 0{\cdot}018)\,; \quad r = 0{\cdot}925\,, \quad n = 11\,, \qquad (14)$$

$$\log k_s = (0{\cdot}532 \pm 0{\cdot}039)\,\sigma + (2{\cdot}859 \pm 0{\cdot}0165)\,; \quad r = 0{\cdot}981\,, \quad n = 9\,. \qquad (15)$$

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