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Thermometric Studies of the Kinetics of the Reactions of Substituted Benzenediazonium Salts with 1-(4′-Sulphophenyl)-3-methylpyrazolin-5-one under Real Production Conditions

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ABSTRACT

The majority of azo coupling reactions have so far been studied by means of spectrophotometric methods. However, with respect to high absorption coefficients of azo dyestuffs these reactions must be carried out in very dilute solutions. The present paper deals with a kinetic study of azo coupling reactions of substituted benzenediazonium salts with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one under real production conditions. The method of direct injection enthalpimetry (DIE) has been used for this study. The rate constants of the reactions studied have been determined and correlated by means of the Hammett equation. The applicability of the DIE method to the study of azo coupling reactions under real production conditions has been demonstrated on the reaction of 4-chlorobenzenediazonium cation with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one. At the concentration used, the azo dyestuff formed is precipitated, and can be distinctly observed in the temperature–time curve.

1 INTRODUCTION

The azo coupling reaction is the basis of the industrial production of synthetic dyestuffs. In connection with the attempts at producing the dyestuffs in a non-traditional way, i.e. carrying out the azo coupling reaction at higher temperatures, in heterogeneous media with emulsifiers and with application of continuous production equipment, it is necessary to

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determine the rate constant values under conditions as close as possible to the real conditions of production. The problem is unusually complex, since most industrially important azo coupling reactions produce water-insoluble dyestuffs, which complicates the application of classical methods. Velich *et al.*,[1] suggested thermometry and potentiometry for use in studies of the azo coupling kinetics in real reaction media. The thermometric method consists of direct injection enthalpimetry (DIE) which can be modified in such a way that the diazonium salt is injected into the reaction medium with the coupling component, the initial concentration ratio of the two components being 1:1. The applicability of this method to studies of azo coupling reaction kinetics has been investigated by Velich *et al.*[1,2] and Smékal *et al.*[3] The potentiometric method is based on the analysis of the currentless potential–time curves obtained with the use of a gold indicator electrode with periodically restored surface. The applicability of this method to studies of diazotization and azo coupling reactions has been studied by Dlask.[1,4]

The problem of azo coupling reactions in multi-phase reaction systems was investigated by Růžička *et al.*,[5] who showed that addition of a suitable emulsifier to the systems in which either the reactants or the products (dyestuffs) are of limited solubility in the reaction medium can create a considerable reaction surface which is formed by the interface between the heterogeneous phase (the coupling component) and the homogeneous phase (the diazonium salt solution). Such an emulsion reaction system is favourable for the optimum course of the azo coupling reaction.

The reaction kinetics of substituted benzenediazonium salts with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one have been discussed by Dobáš *et al.*,[6] who examined the effects of pH, ionic strength and substituents on the azo coupling rate constant and determined the corresponding reaction constants of the Hammett equation. The measurements were carried out spectrophotometrically at extremely low concentrations.

The aim of this present paper is to determine the reaction rate constants of some substituted benzenediazonium salts with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one at pH 4, ionic strength $I = 1$, and concentrations about 10^{-3} mol litre^{-1}, and to derive therefrom the value of the reaction constant of the Hammett equation. The reaction was studied in more detail with 4-chlorobenzenediazonium salt, since in this case the azo dyestuff formed is precipitated under the conditions mentioned.

2 RESULTS AND DISCUSSION

The azo coupling reactions of substituted benzenediazonium salts with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one were studied in an isoperibolic twin reaction calorimeter (an improved version of the calorimeter described elsewhere)[7] with an on-line Sharp MZ-80K computer. A program (THERKIN-c) has been written (Dittrich, F. & Velich, V., unpublished) to control the calorimeter, read the temperature–time experimental data, and calculate the azo coupling rate constants. The reactions were carried out in a volume of 100 cm^3 at 25°C, pH 4, $I = 1$, initial concentration of both reactants $9{\cdot}615 \times 10^{-4}$ mol dm^{-3} (for benzenediazonium and 3- and 4-chlorobenzenediazonium chlorides) or $1{\cdot}442 \times 10^{-3}$ mol dm^{-3} (for 3- and 4-methoxy- and 3- and 4-methyl-benzenediazonium chlorides). The results are given in Table 1.

The recorded temperature–time curves exhibit a uniform increase of temperature with time; Fig. 1 gives the record for benzenediazonium chloride. The temperature is expressed by the output voltage of a resistance bridge which is proportional to the temperature. The rate constant k and the temperature ΔT_∞ of the reaction mixture at the time $t = \infty$ were calculated by the method of non-linear regression (Dittrich, F. & Velich, V., unpublished). The expression optimized was that valid for a bimolecular reaction of second order at identical initial concentrations of both reactants ($[A]_0 = [B]_0$):[8]

$$\Delta T_\infty / \Delta T = 1 + (k[A]_0 t)^{-1} \qquad (1)$$

where $\Delta T = T - T_0$, $\Delta T_\infty = T_\infty - T_0$, T_0, T and T_∞ being the temperatures of the reaction mixture at the times $t = 0$, t and ∞, respectively, and k is the rate

TABLE 1

The Rate Constants of Azo Coupling Reactions of Substituted Benzenediazonium Chlorides with 1-(4'-Sulphophenyl)-3-methylpyrazolin-5-one in Acetate Buffer at pH 4, Ionic Strength $I = 1$, Temperature $T = 25$°C

Substituent	*Initial concentrations of reaction components* (c. $10^4 \times mol\,dm^{-3}$)	*Rate constants,* $k(dm^3\,mol^{-1}\,s^{-1})$
3-Cl	9·615	76·52 ± 1·51
4-Cl	9·615	22·60 ± 2·87[a]
H	9·615	6·07 ± 0·14
3-CH_3	14·423	4·85 ± 0·26
4-CH_3	14·423	2·17 ± 0·17
3-OCH_3	14·423	13·09 ± 0·52
4-OCH_3	14·423	0·69 ± 0·09

[a] The rate constant was determined with the addition of the emulsifer.

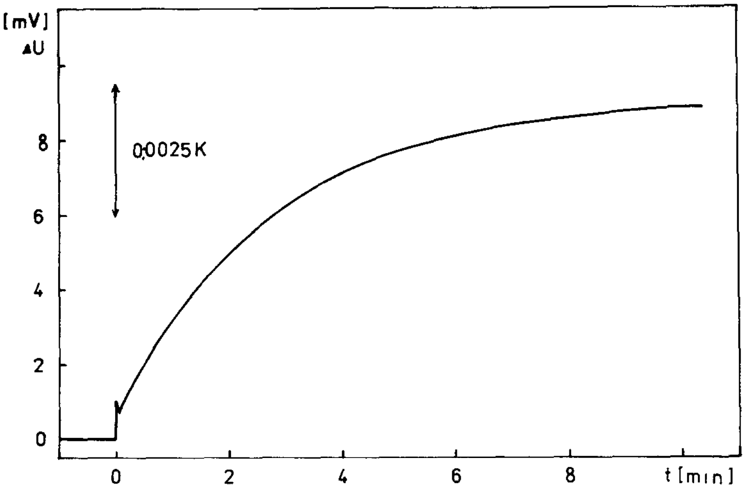

Fig. 1. The temperature–time dependence of the reaction of benzenediazonium with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one; $T = 25°C$, $pH = 4$, $I = 1$, $c = 9{\cdot}615 \times 10^{-4}$ mol dm^{-3}. The calculated values: $\Delta T_{\infty} = 11{\cdot}856 \pm 0{\cdot}1126$ mV, $k = 6{\cdot}4422 \pm 0{\cdot}1483$ dm^{3} mol^{-1} s^{-1}, $r = 1{\cdot}0068$.

constant of the second-order reaction [dm^{3} mol^{-1} s^{-1}]. For the optimization procedure eqn (1) was modified to the following form:

$$f(j) = P(1)/(1 + 1/[P(2) * x(j) * [A]_0]) \tag{2}$$

where $f(j) = \Delta T$, $x(j) = t$, $P(1) = \Delta T_{\infty}$, $P(2) = k$. From the results obtained (Table 1) the following Hammett correlation was calculated:

$$\log k = 3{\cdot}67\,(\pm 0{\cdot}02) + 3{\cdot}08\,(\pm 0{\cdot}12)\sigma \tag{3}$$

(number of data $n = 7$, correlation coefficient $r = 0{\cdot}9960$, standard deviation $\sigma = 0{\cdot}447 \times 10^{-2}$).

In the azo coupling reactions with 3- and 4-chlorobenzenediazonium chlorides the azo dyestuffs formed are precipitated during the reaction, particularly with the latter diazonium salt. Růžička *et al.*[5] dealt with the azo coupling reactions taking place under real reaction conditions (i.e. those used in dyestuffs production). Under these conditions, the reactions are influenced by the existence of heterogeneous systems and are complicated by diffusion, nucleation, growth of crystal nuclei, and, finally, precipitation of the dyestuffs formed, these dyestuffs being predominantly insoluble in the reaction medium. It has been shown that the azo coupling kinetics can be studied by thermometry or potentiometry under these conditions, if there exists a sufficiently large interfacial area between the reactants. This reaction surface is formed by the interfacial area between the diazonium salt solution and the coupling component, which can be insoluble. A sufficiently large reaction surface can be created by addition of suitable emulsifiers to the standard solution of the coupling component. Velich *et al.*[1,2] and Růžička *et al.*[5] have previously shown that measurements of the azo coupling kinetics taking place at a sufficiently large interfacial area (where the physical factors affecting the rate of chemical reactions do not predominate over the chemical ones) can provide satisfactory results which do not lack basic physical meaning. The kinetics of the chemical process can be approximated in these cases by the mathematical model valid for reactions taking place in homogeneous phases. In the case of the reaction of 4-chlorobenzenediazonium chloride with the coupling component, the emulsifier Slovasol EL (CHZWP Nováky, Czechoslovakia), in an amount of 5% by wt, was added to the basic solution of the coupling component, and the solution was thoroughly mixed before pipetting. (The emulsifier used is produced by oxyethylation of oleic acid with about the same amount of oxirane.) The temperature–time dependence recorded in this reaction is given in Fig. 2. Obviously, this dependence is more complex than that obtained with benzenediazonium chloride (Fig. 1). The overall temperature–time dependence is a result of superposition of two processes: the azo coupling reaction itself (part A) and precipitation of the dyestuff formed (part C).

This form of thermometry was used for precipitation reactions, for the first time in the case of precipitation reactions of Na_2SO_3 with $MgCl_2$ in aqueous medium giving $MgSO_3 . 6H_2O$ (Janošová, M., Velich, V. & Söhnel, O., unpublished). The temperature–time dependence obtained for this reaction

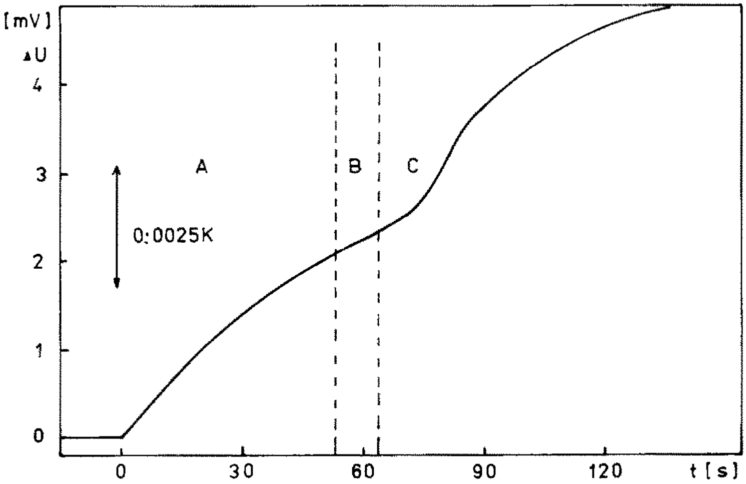

Fig. 2. The temperature–time dependence of the reaction of 4-chlorobenzenediazonium with 1-(4′-sulphophenyl)-3-methylpyrazolin-5-one; $T = 25°C$, $pH = 4$, $I = 1$, $c = 9{\cdot}615 \times 10^{-4}\,mol\,dm^{-3}$.

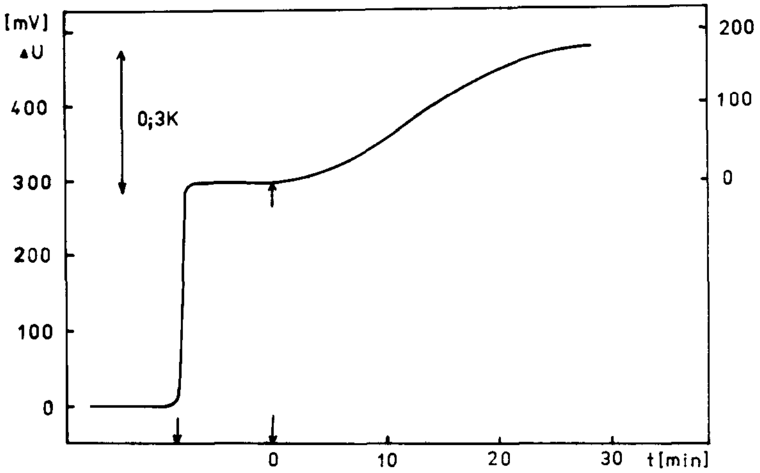

Fig. 3. The temperature–time dependence of the reaction of Na_2SO_3 with $MgCl_2$ in aqueous medium; $T = 25°C$, $c = 0{\cdot}25\ \mathrm{mol\,dm^{-3}}$. The beginning of precipitation of $MgSO_3 . 6H_2O$ is denoted by two arrows. The calculated values: $\Delta T_\infty = 209{\cdot}896 \pm 2{\cdot}834\ \mathrm{mV}$, $k_{exp} = 0{\cdot}0637 \pm 0{\cdot}0018\ \mathrm{min^{-1}}$, $r = 0{\cdot}9999$.

is presented in Fig. 3. It can be seen that the reaction proper is practically instantaneous, being followed by the precipitation induction period of various times (this involves nucleation, growth of crystal nuclei, and finally precipitation of the reaction product from the supersaturated solution). This process is connected with liberation of reaction heat which causes the temperature of the reaction mixture to increase. The temperature–time dependence corresponding to the precipitation of $MgSO_3 . 6H_2O$ can be approximated by the kinetic model of the first order. It must be realized, of course, that the constant calculated is of an experimental nature, involving other quantities (diffusion coefficient, etc.) in addition to the rate constant. For the kinetic model of the first-order reaction, the expression of the temperature–time dependence is as follows:[8]

$$\ln(1 - \Delta T/\Delta T_\infty) = -k_{exp}t \qquad (4)$$

Again it is possible to calculate ΔT_∞ and k_{exp} from this relationship by the method of non-linear regression.

In the case of the reaction of 4-chlorobenzenediazonium chloride with the coupling component in an emulsion medium (Fig. 2) we attempted to describe the temperature–time dependence as a sum of two expressions describing the chemical process proper and the subsequent precipitation. It was presumed that the chemical process (part A in Fig. 2) obeyed eqn (1). The precipitation process (part C in Fig. 2) is characterized by a distinct S-shaped course of the temperature–time dependence, which could indicate an autocatalytic reaction with the following mechanism:

$$\mathrm{A} + \mathrm{B} \rightarrow 2\,\mathrm{B} \tag{5}$$

On the basis of this mechanism we obtain the following expression in the concentration–time form:

$$k_{\mathrm{exp}}t([\mathrm{B}]_0 + [\mathrm{A}]_0) = \ln \frac{[\mathrm{A}]_0\,([\mathrm{B}]_0 + x)}{[\mathrm{B}]_0([\mathrm{A}]_0 + x)} \tag{6}$$

where x denotes the so-called reacted amount, and k_{exp} is the so-called experimental constant of precipitation. For the temperature–time dependence, eqn (6) can be modified to give eqn (7),

$$\frac{\Delta T}{\Delta T_\infty} = \frac{1 - \exp\{-k_{\mathrm{exp}}t([\mathrm{B}]_0 + [\mathrm{A}]_0)\}}{1 + \dfrac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\exp\{-k_{\mathrm{exp}}t([\mathrm{B}]_0 + [\mathrm{A}]_0)\}} \tag{7}$$

TABLE 2

The Values of Parameters Calculated by the Optimization Program[7] from the Data Read during the Reaction of 4-Chlorobenzenediazonium with 1-(4′-Sulphophenyl)-3-methylpyrazolin-5-one (Fig. 2)

Azo coupling (A in Fig. 2)
$k = 21{\cdot}95 \pm 1{\cdot}94\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$
$\Delta T_\infty = 5{\cdot}32 \pm 0{\cdot}19\ \mathrm{mV}$
Residual square sum function: 0·011
$r = 0{\cdot}9986$

Precipitation (C in Fig. 2)
$k_{\mathrm{exp}} = 99{\cdot}86 \pm 1{\cdot}83\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$
$\Delta T_\infty = 2{\cdot}10 \pm 0{\cdot}02\ \mathrm{mV}$
$([\mathrm{A}]_0 + [\mathrm{B}]_0) = 1{\cdot}082 \times 10^{-3} \pm 5{\cdot}287 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$
$[\mathrm{A}]_0/[\mathrm{B}]_0 = 5{\cdot}39 \pm 0{\cdot}84$
Residual square sum function: 0·004
$r = 0{\cdot}9996$

Optimization of the whole process
$\Delta T_\infty^{\mathrm{A}} = 5{\cdot}20 \pm 0{\cdot}06\ \mathrm{mV}$
$\Delta T_\infty^{\mathrm{C}} = 1{\cdot}57 \pm 0{\cdot}05\ \mathrm{mV}$
The beginning of precipitation $t = 54{\cdot}47 \pm 2{\cdot}76\ \mathrm{s}$
$([\mathrm{A}]_0 + [\mathrm{B}]_0) = 1{\cdot}156 \times 10^{-3} \pm 8{\cdot}751 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$
$[\mathrm{A}]_0/[\mathrm{B}]_0 = 38{\cdot}23 \pm 5{\cdot}86$
Residual square sum function: 0·103
$r = 0{\cdot}9998$

and for the calculation of k_{exp} and T_{∞} by the optimization procedure, eqn (7) is rewritten in the form of eqn (8):

$$f(j)=\frac{P(1)*[1-\exp(-P(2)*x(j)*P(3))]}{[1-P(4)\exp(-P(2)*x(j)*P(3))]} \tag{8}$$

where $f(j)=\Delta T$, $x(j)=t$, $P(1)=\Delta T_{\infty}$, $P(2)=k_{\mathrm{exp}}$, $P(3)=([\mathrm{A}]_0+[\mathrm{B}]_0)$, $P(4)=[\mathrm{A}]_0/[\mathrm{B}]_0$.

At first, the two processes were optimized separately, an additional parameter ($P(5)$) being introduced with respect to the uncertainty of determination of the time $t=0$ (especially that of the precipitation process); this parameter expresses the correction for the determination of the precise commencement of the precipitation process. Thereafter, the whole curve given in Fig. 2 was optimized as the sum of eqns (1) and (7), the k and k_{exp} constants calculated from the optimization of the two processes being introduced into eqns (1) and (7). The results are presented in Table 2. The values of the correlation coefficients r in all the three calculations indicate a close fit of the experimental curves and calculated values. The example given shows that it is possible to apply thermometry to investigation of reactions in real reaction media taking place at the interfacial area. It is possible to determine the induction periods of precipitation, reaction heats of both the physical and chemical processes taking place, and the rate constants of these physical and chemical processes.

3 EXPERIMENTAL

3.1 Reagents

1-(4′-Sulphophenyl)-3-methylpyrazolin-5-one, pure (VCHZ Synthesia, Pardubice-Semtín, Czechoslovakia) was purified by repeated crystallization from hot water and filtration through charcoal. Its purity was checked by elemental analysis.

The hydrochlorides of 3- and 4-chloroaniline, 3- and 4-methylaniline, 3- and 4-methoxyaniline and aniline were prepared from the respective anilines (pure, VCHZ-Synthesia, Pardubice-Semtín, Czechoslovakia) and purified by repeated crystallizations from water. Their purity was checked by elemental analysis.

The other reagents used were of p.a. purity grade (Lachema, Brno, Czechoslovakia).

3.2 Preparation of stock solutions

The buffer of pH 4, $I=1$, was prepared by mixing 236·45 cm^3 99% acetic acid, 73·8 g anhydrous sodium acetate, 301·92 g potassium chloride, and water up to the volume of 5 litres. The pH was checked with a Radelkis OP 211/1 pH-meter (Hungary). The stock solution of 0·01 M-1-(4'-sulphophenyl)-3-methylpyrazolin-5-one in the above buffer of pH 4 was prepared either without emulsifier or with addition of the emulsifier Slovasol EL (CHZWP) Nováky, Czechoslovakia) in an amount of 5% by wt with respect to the coupling component. (The emulsifier is oxyethylated oleic acid containing about 50% ethylene oxide.) The stock solutions of aniline hydrochlorides were prepared by mixing the calculated amount of the respective hydrochloride with 3·2 cm^3 conc. HCl and water up to a volume of 100 cm^3. The final concentrations were: 0·3 M-HCl, 0·025 M-$ArNH_3Cl$ (Ar = phenyl, 3- and 4-chlorophenyl), 0·037 M-$ArNH_3Cl$ (Ar = 3- and 4-methylphenyl and 3- and 4-methoxyphenyl).

The diazonium salt solutions were prepared by placing 34 cm^3 of the respective aniline hydrochloride solution into a 50-cm^3 calibrated flask, cooling to 5°C, and adding of a 1·5 molar excess sodium nitrite. The mixture was shaken and left to stand $\frac{1}{2}$ h at this temperature. Excess nitrous acid was then removed by addition of urea (potassium iodide–starch paper test) and the volume was completed with water.

3.3 Thermometric measurements

The reactions were followed in an isoperibolic twin reaction calorimeter which was an improved version of the calorimeter described by Velich *et al.*[7] The reaction and the reference vessels of 200 cm^3 volume were charged with 100 cm^3 of the reaction and reference solutions, respectively, and kept at the desired temperature for at least 30 min. Then they were transferred into the calorimeter thermostated at the same temperature. The THERKIN-c program (Dittrich, F. & Velich, V., unpublished) was started in the attached computer to evaluate the pre-reaction process and, after reaching the criterion chosen (the parameter chosen was that of the slope of the temperature–time dependence of the pre-reaction process), the computer gave the signal to start the reaction. The diazonium solution (4 cm^3) was added to both the reaction and the reference vessels from pipettes whose outlets reached under the surface of the liquids in the vessels. In the reaction vessel the azo coupling reaction took place and its course was followed by recording the temperature–time dependence in digital form (pairs of temperature–time values were read at chosen time intervals and stored in the computer memory) and in analogue form (by means of a parallel line recorder attached to the digital voltmeter). When the reaction was complete, the azo coupling rate constant and the temperature of the final phase of the reaction were calculated by means of the Levenberg–Marquardt optimization procedure, which forms a part of the THERKIN-c program (Dittrich, F. & Velich, V., unpublished).

4 CONCLUSIONS

This present communication confirms the presumption that thermometry is a very suitable method for investigation of the kinetics of azo coupling reactions in real reaction media, especially in such cases when the azo dyestuffs produced, or even the starting reactants, show limited solubility in the reaction medium. The temperature–time dependences found experimentally in the investigation of these azo coupling reactions can also contribute to elucidation of the kinetics of the growth of the crystalline phase of the dyestuffs produced.

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