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Determination of thermal and kinetic data of the diazotisation of 6-bromo-2,4-dinitroaniline with nitrosylsulphuric acid

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Abstract

In the diazotisation of 6-bromo-2,4-dinitroaniline (BDNA) with nitrosylsulphuric acid in sulphuric acid, the water content of the reaction mass increases during the reaction, leading to an acceleration of the rate. The thermal and kinetic data of the diazotisation of BDNA were recorded by reaction calorimetry.

1. INTRODUCTION

Extensive studies have been conducted on the process safety of diazotisation reactions. The diazotisation of 6-bromo-2,4-dinitroaniline (BDNA) in sulphuric acid solvent can be carried out with varying water contents. From a large number of publications on diazotisation reactions, it is known that the water content of the medium exercises a strong catalytic influence on the reaction rate.

In studies by Ridd [1], three areas have been identified in which the reaction rate changes greatly, depending on the acidity of the medium. In these instances, the reaction rate is regarded as a function of pH. Where the medium is even more acidic, the Hammet acidity scale is used. Hammet defines a function h_0 as a measure of the ability of a solution to convert basic neutral molecules into their conjugate acid; h_0 is a useful quantitative measure of the relative proton-donor properties of solutions of high dielectric constant and high acidity. The quantity H_0 is defined as the negative logarithm of h_0, $H_0 = -\log h_0$. Typical H_0 values are -5.54 for 70% H_2SO_4 and -10.6 for 100% H_2SO_4 [2].

The shape and slope of the curve of the logarithm of reaction rate plotted as a function of acidity have contributed to the determination of the reaction path. Regardless of the range in which it takes place, a diazotisation reaction is always a multi-step reaction. The mechanism with

the multi-step reactions shown in eqn. (1), where the addition of the NO^+ ion to aniline is considered to be the rate-determining step, is valid only in the low-acidity range:

$$RNH_2 \rightarrow RN^+H_2NO \rightarrow RNHNO \rightarrow RN{:}NOH \rightarrow RN_2^+ \quad (1)$$

A different step in the reaction can become rate-determining, depending on the acidity range. Within all possible intermediate reactions, there are two important individual processes that have opposing effects on the reaction rate as acidity increases. In the acidity range investigated, the equilibrium for the protonation of aniline is completely on the right side

$$RNH_2 + H^+ \rightarrow RN^+H_3 \quad (2)$$

Thus the concentration of free amine decreases with decreasing concentration of the H^+ ion, or, at higher acidities, with decreasing Hammet acidity function h_0. In contrast, the concentration of the NO^+ ion increases sharply as acidity rises

$$ONOH + H^+ \rightarrow NO^+ + H_2O \quad (3)$$

By analogy, with nitrosylsulphuric acid

$$ONOSO_3H + H^+ \rightarrow NO^+ + OSO_3H_2 \quad (3a)$$

The superimposition of several concentration relations is essentially responsible for the fact that the reaction rate shows strong variation with acidity. The use of solvents of high acidity, as in our studies, renders the reaction mechanism more complex. It is found that the reaction rate increases more strongly with increasing water content, i.e. decreasing acidity, than would at first be expected in consideration of the equilibrium shift eqn. (2). If it is assumed that the reaction of NO^+ with RNH_2 is rate-determining, then this fact, along with equilibrium (2), should result in a linear relationship with a slope of 1 between the acidity function H_0 and $\log k$ [3]. But because larger slopes are always found, Challis and Ridd [4] have proposed the mechanism

$$RHN_3^+ + NO^+ \rightarrow RNH_2NO + H^+ \quad (4)$$

$$RNH_2NO^+ \rightarrow RN_2^+ + H_2O \quad (5)$$

with a slow, rate-determining proton transfer to the solvent, which is more difficult at higher acidities.

However, the reaction order does not change in the range of medium and high acidity in which simplified diazotisation can be interpreted as a bimolecular reaction; reaction rate = k_2 [amine][nitrosylsulphuric acid].

2. EXPERIMENTAL

Reaction calorimetry is widely used for the development and optimisation of chemical processes and it is also a useful tool for assuring safe process performance. The experiments were performed in a Mettler RC1 calorimeter. Thermal, kinetic, heat transport and material data can be determined as a function of dosage or temperature profiles.

In practice, a direct measurement of the instantaneous heat-power transfered, which is caused by chemical or physical processes, as a function of the process time is useful. The calorimetric principle employed in the RC1 is the heat-flux principle. It is based on continuous measurement of the temperature difference $T_r - t_j$ between the reactor contents and the heat-transfer oil in the reactor jacket. The temperature difference is the driving force of the heat transport. Furthermore, the heat flow depends on the overall heat transport coefficient U and on the heat exchange area A. The product UA is determined by calorimetric calibration. These three factors form the basic equation

$$Q_r/\text{watt} = UA(T_r - T_j)$$

3. RESULTS

3.1. *Determination of the mixing heat on the addition of nitrosylsulphuric acid to sulphuric acid*

In a semi-batch process, two reaction stages can be distinguished: the addition stage and the post-reaction stage. At the end of the addition stage, as a rule at the stoichiometric point, the prevailing conditions are batch conditions. The nitrosylsulphuric acid accumulated in the reaction mixture and the unconsumed BDNA react to completion. Heat is released in both stages and is registered as a signal. But an additional effect must be taken into account during the addition stage.

The mixing or dilution heat, which is generated if nitrosylsulphuric acid (NSA) is added to the BDNA dissolved in sulphuric acid, contributes to the total heat during the addition stage. In order to determine this contribution, nitrosylsulphuric acid (NSA) was added to sulphuric acid containing no BDNA under other identical conditions. This measurement does not provide an exact record of this contribution of the mixing heat over the addition period, because during the reaction one additional mole of water is formed for each mole of educt, so that the medium is again being constantly diluted. Nevertheless, this separate measurement yields a sufficiently accurate indication of the magnitude of this heat contribution. The heat

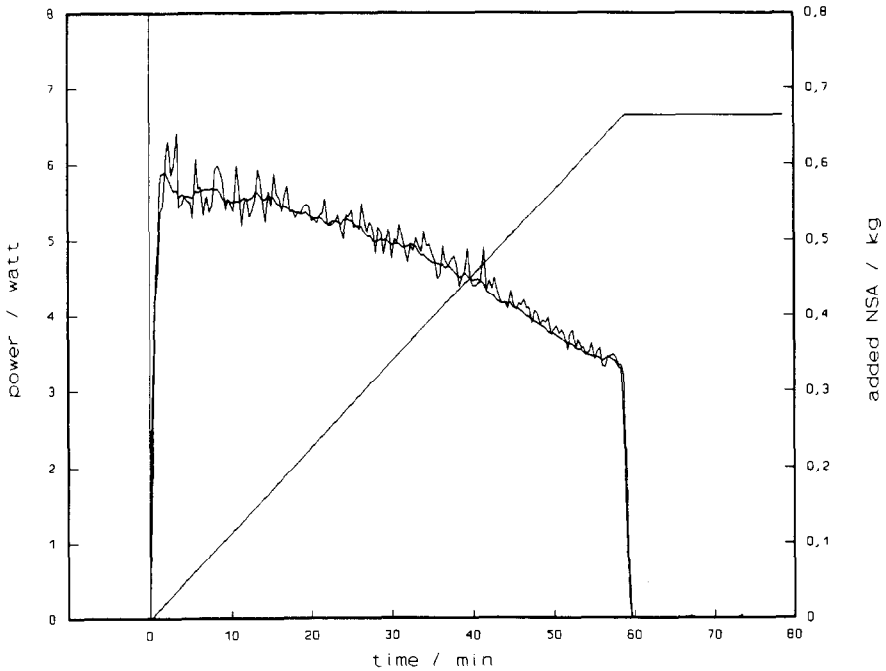

Fig. 1. Addition of nitrosylsulphuric acid (NDA) to sulphuric acid: calculation of mixing heat.

energy released by the mixing of the acids amounts to $\Delta H_{mix} = -9$ kJ mol NSA added (Fig. 1).

The magnitude of the fraction of enthalpy attributed to the mixing heat, relative to the total amount, influences the determination of the kinetic quantities in the experiment, especially for slow reactions and in the case of large mixing heats. If this contribution is not taken into account and is treated as part of the reaction enthalpy, the reaction rate will be overestimated and the accumulation of reactants underestimated. The water formed in the reaction is proportional to the reaction power. Water formation has no effect on the determination of the actual concentrations at the stoichiometric point.

3.2. *Determination of the reaction rates*

The diazotisation of 6-bromo-2,4-dinitroaniline (BDNA) was investigated in the acidity range of about $H_0 = -10$, at temperatures of 15 and 25°C with dry BDNA and with BDNA containing 10.7% water. Technical grade sulphuric acid was used as the solvent for dry BDNA and 100% sulphuric acid was used for moist BDNA.

The reaction rate constant can be determined by various methods. An evaluation in the post-reaction stage is possible where the reaction power is

expressed in terms of the concentration of the reactants. The initial concentration is determined by comparing the heat released up to the stoichiometric point with the total reaction enthalpy. Here the mixing or dilution heat has an effect on the initial concentrations and, hence, on the result.

Another method, which was also used here, is to simulate the reaction power and compare it with the experimentally measured curve. For this purpose, a dimensionless formulation [6] for the semi-batch process was used which permits the reaction power to be calculated over the entire time period with

$$\theta = t/\tau_D \quad \text{and} \quad \varepsilon = V_D/V_S,$$

where t is the reaction time, τ_D the dosing time, V_D the dosing volume and V_S the start volume. The conversion X of the reaction can be calculated from

$$dX/d\theta = D_a\Phi(X, \theta)$$

where D_a is the Damköhler number and

$$\Phi(X, \theta) = (\theta - X)(1 - X)/(1 + \varepsilon\theta)$$

is the second-order dimensionless kinetics. D_a is the fit parameter given by

$$D_a = k_2 n_S \tau_D/(V_D + V_S)$$

and it is used to calculate the reaction power

$$Q_{r,c} = D_a\Phi(X, \theta)\,\Delta H_r n_D/\tau_D$$

In these equations n_S, and n_D are the mole numbers of educt and added moles, respectively, and ΔH_r is the reaction enthalpy.

When highly concentrated sulphuric acid is used as the solvent, the reaction kinetics behaves in accordance with the second-order mechanism proposed in ref. 1. The rate constant is applicable to the slowest reaction step, i.e. the donation of the H^+ ion to the solvent. For the evaluation we chose a formulation for a bimolecular reaction which fits the data well.

Figure 2 shows the results based on the measurements with dry BDNA at a temperature of 25°C. In this experiment the adjustment of the Damköhler number yields a value of $D_a = 120$, which in turn yields a rate constant of $k_2 = 1.2 \pm 0.2\,\mathrm{l\,mol^{-1}\,min^{-1}}$. Experimental results with dry BDNA are compiled in Table 1.

The evaluation of the post-reaction stage based on the same measurements yields a rate constant in good agreement with the first evaluation: $k_2 = 1.4 \pm 0.2\,\mathrm{l\,mol^{-1}\,min^{-1}}$ (Fig. 3).

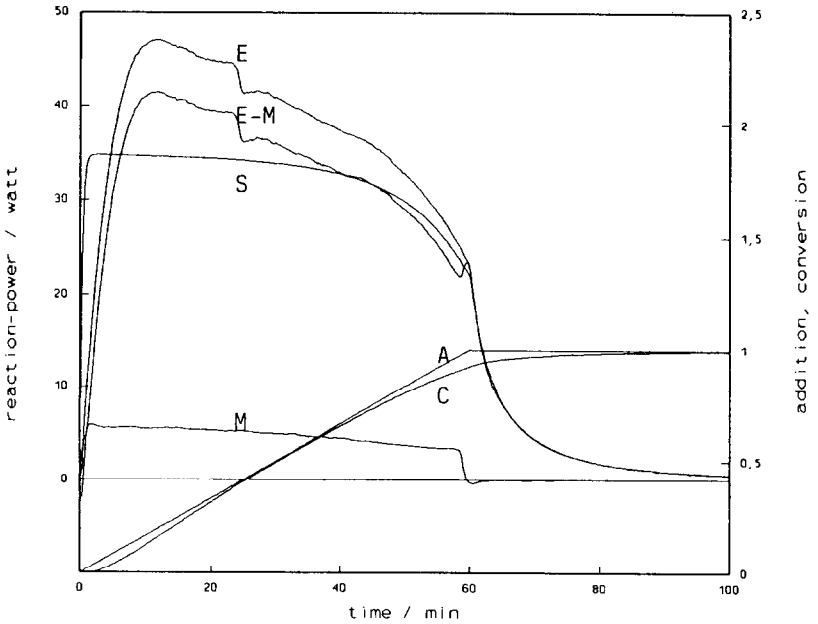

Fig. 2. Diazotisation of dry BDNA. $T = 25°C$. E, M, E–M, experimental and S, simulated reaction powers plotted against time; A, addition and C, conversion. Damköhler number for the fitted curve $D_a = 120$; $k_2 = 1.21\ \mathrm{l\ mol^{-1}\ min^{-1}}$

It has been found that the influence of the mixing heat on the results is relatively small. If the mixing heat is considered as part of the reaction enthalpy, the amount reacted up to the stoichiometric point is 93.5%; if not, it is 92%.

TABLE 1

Experimental parameters and results for dry BDNA

	$T_R = 25°C$	$T_R = 15°C$
NSA added/mol	2.1	2.1
BDNA starting material/mol	2	2
Mixing heat/W	$\phi 6$	$\phi 6$
Addition time/min	60	60
Total released energy/kJ	143	137
Reaction enthalpy/kJ per mol BDNA	71.5	68.5
Damköhler number	120	30
Rate constant k_2/l mol^{-1} min^{-1}	1.2	0.5
Thermochemical conversion at the end of addition/%	93.5	87.2
k_2 from post-reaction/l mol^{-1} min^{-1}	1.4	0.7

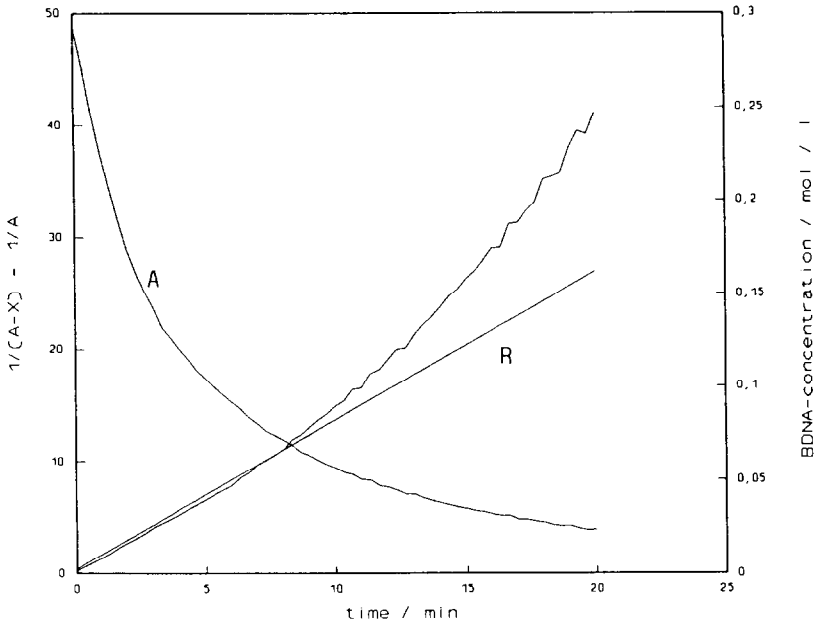

Fig. 3. Diazotisation of dry BDNA at $T = 25°C$; evaluation of the rate constants from the post-reaction. In the formula, A stands for the BDNA concentration and X is the conversion. The slope of the regression line yields $k_2 = 1.4\,l\,mol^{-1}\,min^{-1}$. Regression range, 0–10 min.

3.3. *Comparison of the reaction rates in media containing a higher amount of water*

For the experiment with moist BDNA, the calculated curve with Damköhler number $D_a = 300$ only fits the data satisfactorily at the beginning of the reaction. At the end, the reaction is faster than predicted by the simulation. This is shown in Fig. 4, where D_a was chosen to be 550. Thus the reaction rate increases in the course of the experiment. With $k_2 > 5.6\,l\,mol^{-1}\,min^{-1}$, the value is increased by a factor of five compared to the measurement with the dry product.

The reaction proceeds rapidly, so there is no accumulation of the educt. The conversion and the amount added yield the same straight line. A similar result is obtained for the curves fitted at 15°C. Here the accumulation is more distinct. The reaction rate is six times faster than in the experiment with dry BDNA. Table 2 lists the results with moist BDNA.

The final water content for dry BDNA due to water formation and the addition of reactant was 3.8% of the reaction mass. With moist BDNA, the

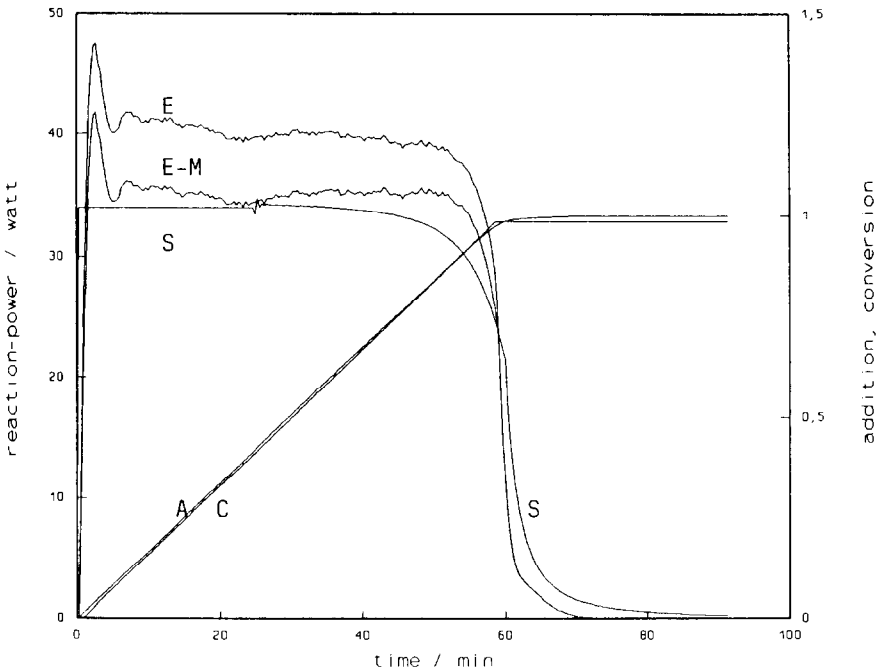

Fig. 4. Diazotisation of moist BDNA at $T = 25°C$. E, E–M, experimental and S, simulated reaction power, plotted against time; A, addition and C, conversion. Damköhler number $D_a = 550$, $k_2 = 5.6\,l\,mol^{-1}\,min^{-1}$.

final water content was 5.8%. The small increase in water causes the higher reaction rate.

3.4. *Comparison to measurements with 6-chloro-2,4-dinitroaniline (CDNA)*

Other substituents on the aniline can influence the reaction rate because of different electronegativity or steric effects. This influence is observed in

TABLE 2

Experimental parameters and results for moist BDNA (10.7%)

	$T_R = 25°C$	$T_R = 15°C$
NSA added/mol	2.1	2.1
BDNA starting material/mol	2	2
Mixing heat/W	$\phi 6$	$\phi 6$
Addition time/min	60	60
Total released energy/kJ	141.1	141
Reaction enthalpy/kJ per mol BDNA	70.5	70.5
Damköhler number	>550	300
Rate constant k_2/l mol^{-1} min^{-1}	>5.6	3

TABLE 3

Experimental parameters and results for dry CDNA evaluated with and without consideration of mixing heat

Parameters	25°C	25°C	15°C	15°C
NSA added/mol	1.6	1.6	1.6	1.6
BDNA starting material/mol	1.7	1.7	1.7	1.7
Mixing heat/W	0	$\phi 7$	0	$\phi 7$
Addition time/min	60	60	40	40
Total released energy/kJ	112	112	100	100
Reaction enthalpy/kJ per mol NSA	70	70	62	62
Thermochemical conversion at the end of addition/%	77	70	61	52.5
Rate constant k_2 from post-reaction/l mol^{-1} min^{-1}	0.5	0.4	0.2	0.15

certain acidity ranges. At high acidity, different substitutents should not show an effect on the reaction rate [1, 3]. However, it was found that the reaction proceeds more slowly than the analogous BDNA diazotisation. But this difference in rate is small compared to the rate changes caused by variation in the acidity. The mixing heat exerts a greater influence on the evaluation of the CDNA data. The result obtained for the reaction rate is about 20% smaller if the mixing heat is taken into account. The results are given in Table 3.

4. THERMAL STABILITY OF THE REACTION MASS

From the safety point-of-view, diazotisations are dangerous and difficult reactions. The decomposition of the reaction mass can take place at temperatures relatively close to the normal reaction temperature.

DSC investigations of the diazonium solution in closed sample containers show high exothermal decomposition energies, which can theoretically heat the sample up to about 400°C. But in practice, open vessels are used and evaporation processes prevent such high temperatures. The DSC diagrams show several stages of decomposition, starting at about 90°C with the separation of nitrogen, followed by the nitrogen dioxide groups.

For further investigation of the exothermic reactions, especially decomposition reactions at higher temperatures, the adiabatic Dewar-test method was used [7]. In addition, the Dewar flask containing the sample was placed in an oven to ensure a controlled adiabatic shield. An increase in storage temperature of the sample causes a decrease in induction time, which is the time until decomposition occurs. The plot of induction time against the inverse absolute temperature yields a straight line. The results are listed in Table 4 and are shown graphically in Fig. 5, where the storage temperature is given in °C.

TABLE 4

Adiabatic induction time of final products with moist and dry BDNA

Temperature/°C	Moist BDNA		Dry BDNA	
	Induction time	T_{max}/°C	Induction time	T_{max}/°C
60	>180 h	–	3860 min	266
80	658 min	265	399 min	262
90	206 min	268	150 min	272
100	65 min	283	77 min	269

Deflagration tests of the substances, performed in a Dewar vessel, showed positive results as low as room temperature. The maximum temperature reached was 300°C, where deflagration proceeds with a velocity of about 1 cm min^{-1}. Formation of white smoke was seen, which was not inflammable.

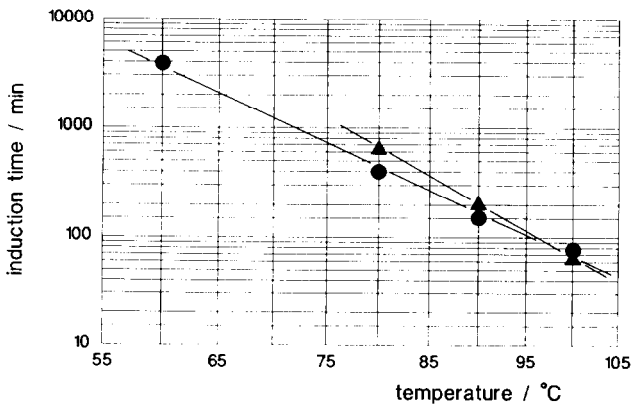

Fig. 5. Adiabatic induction times of the diazonium solutions as a function of storage temperature: ▲, moist BDNA; ●, dry BDNA.

5. DISCUSSION

The water content of the reaction mass increases during the course of the reaction and leads to an acceleration of the reaction. According to a rough estimate, the reaction rate must be about a quarter as fast as at the start. The rate constant of diazotisation is three times faster with bromine than with chlorine substituent on the aniline.

The reaction enthalpies are very similar in all the diazotisations investigated. The average obtained in five experiments with BDNA was $\Delta H_r = -70\,kJ\,mol^{-1}$, and in two experiments with CDNA, $\Delta H_r = -66\,kJ\,mol^{-1}$.

The adiabatic temperature increase is also comparable, $\Delta T_{ad} = 50$ K. This temperature increase appears only subsequent to a major error in adding reactant (batch conditions right from the start) and in conjunction with failure of the vessel cooling. The simultanous occurrence of both events is rather improbable.

Due to an adiabatic temperature rise, the reaction mass can reach a maximum temperature of 75°C. The induction times found for this temperature are about 21 h (BDNA moist) and 12.5 h (BDNA dry). In the case of a runaway of the primary reaction, this period of time is big enough to take additional steps to prevent major damage.

To ensure safe conditions during a diazotisation process, the use of a solvent for the aniline is important and the concentration of the nitrosylsulphuric acid (NSA) must be limited. Earlier investigations [8], which were carried out after a serious accident with a similar diazotisation process, included a comparison of different process instructions. It was found that the concentration of the NSA should not be more than 12% (w/w) of the reaction mass.

REFERENCES

1 J.D. Ridd, The dependence of diazotisation rates on acidity, J. Soc. Dyers Colour, (1965) 355.
2 E.S. Gould, Mechanismus und Struktur in der organischen Chemie, Verlag Chemie, Weinheim, 1964.
3 J. Konecny and H. Wenger, Zur Diazotierung aromatischer Amine in Schwefelsäure, Helv. Chim. Acta, 55(1) (1972) 16.
4 B. Challis and J.H. Ridd, The mechanism of diazotation of aniline at high acidities, Proc. Chem. Soc., (1960) 245.
5 K.H. Saunders and R.L.M. Allen, Aromatic Diazo Compounds, Edward Arnold, 3rd edn., 1985.
6 J. Steinbach, Dissertation, Techn. Universität Berlin, 1985.
7 T. Grewer, Adiabatic methods for the investigation of exothermic reactions, Thermochim. Acta, 119 (1987) 1–15.
8 T. Grewer and W. Steckleberg, Forschungsbericht Hoechst AG, 1970.