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A Study of the Reaction between Diazotized 2-Amino-1,4-Benzenedisulphonic Acid and 8-Amino-1-Naphthol-3,6-Disulphonic Acid. Part I: Use of a Simulated Program in the Reaction Kinetics of the Formation of the Dyes

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ABSTRACT

The simulation program PPSSS performs rapid and practical experimental work with chosen values. These values can be changed until experimental verification is achieved. Such model figures objectively vary the time dependence of all components of the reaction, and enable estimation of the final situation.

1 INTRODUCTION

The object of the study was to verify our hypothesis of the overall reaction scheme. We solved the suggested mathematical model, which was derived using a system of differential kinetic equations. The results obtained were compared with the experimental results of the pertinent reactions (Part II).[1]

2 RESULTS AND DISCUSSION

The products of the azo coupling reaction between diazotized 2-amino-1,4-benzenedisulphonic acid (**D**) and 8-amino-1-naphthol-3,6-disulphonic

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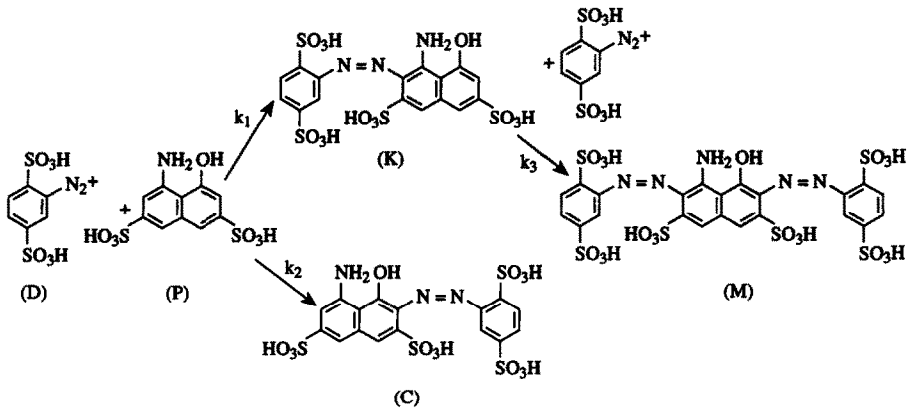
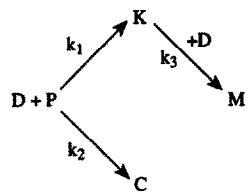
acid (**P**) in acidic media can afford three compounds, viz. **K**, **C** and **M**:



The mono-azo compound (**K**) is the basic source material for the production of Ostazin Blue S-2G; compounds **C** and **M** do not take part in further reactions, but reduce the overall yield of the required dye.

The general processes involved can be represented as shown in Scheme 1.



Scheme 1

The mathematical model (Model 1) of this scheme can be represented by the differential kinetic equations:

$$\frac{d[\mathbf{M}]}{dt} = k_3 \,.\, [\mathbf{K}] \,.\, [\mathbf{D}]$$

$$\frac{d[\mathbf{K}]}{dt} = k_1 \,.\, [\mathbf{D}] \,.\, [\mathbf{P}] - k_3 \,.\, [\mathbf{K}] \,.\, [\mathbf{D}]$$

$$\frac{d[\mathbf{C}]}{dt} = k_2 \,.\, [\mathbf{D}] \,.\, [\mathbf{P}]$$

$$\frac{d[\mathbf{D}]}{dt} = -k_2[\mathbf{D}] \,.\, [\mathbf{P}] - k_1[\mathbf{P}] \,.\, [\mathbf{D}] - k_3[\mathbf{K}] \,.\, [\mathbf{D}]$$

$$\frac{d[\mathbf{P}]}{dt} = -k_1[\mathbf{D}] \,.\, [\mathbf{P}] - k_2[\mathbf{D}] \,.\, [\mathbf{P}]$$

Model 1

TABLE 1

Dimension	*($dm^3\ mol^{-1}\ s^{-1}$)*	*($dm^3\ mol^{-1}\ min^{-1}$)*
k_1	55·54	3332·4
k_2	11·22	673·2
k_3	1·58	94·8

This system of differential equations was solved for 12 alternatives of initial conditions (concentrations) in time $t = 0$. In the initial studies we measured the time intervals in seconds; however, satisfactory results were obtained after 3 h, so we therefore measured the time of the text experiments in minutes. The experimentally determined values of the rate constants k_1, k_2 and k_3 are shown in Table 1.

It was necessary to change the steps of printing and of integration of the numerical solving, as well as the start and the end of the simulation for solving the differential equations. In this respect, there was adapted the simulation program PPSSS, developed at the Department of Computers, FEL VUT, Brno.[2] This program was tested on PCAT and PCXT computers and provided facile access to Model 1, with the aforementioned modifications.

The simulation language is simple and consists of blocks; the Model 1, in this language (time in seconds) is given in Table 2, The initial conditions were: $[\mathbf{P}]_{t=0} = [\mathbf{D}]_{t=0} = 0{\cdot}0001$; $[\mathbf{M}]_{t=0} = [\mathbf{K}]_{t=0} = [\mathbf{C}]_{t=0} = 0$. Its name is 'DLASK'. Further data with respect to this program are available

TABLE 2
Model of simulation ***DLASK***

```
1. block:  INTEGRATOR#1
               Input: 1·5*INT#2*INT#4
           Initial value: 0
2. block:  INTEGRATOR#2
               Input: 55*INT#4*INT#5–1·5*INT#2*INT#4
           Initial value: 0
3. block:  INTEGRATOR#3
               Input: 12*INT#4*INT#5
           Initial value: 0
4. block:  INTEGRATOR#4
               Input: −12*INT#4*INT#5−55*INT#5*INT#4−1·5INT#2
                   *INT#4
           Initial value: 0·00001
5. block:  INTEGRATOR#5
               Input: −55*INT#4*INT#5−12*INT#4*INT#5
           Initial value: 0·00001
```

TABLE 3
Simulation of Model ***DLASK***

Start of simulation: 0·000
End of simulation: 10·000
Step of simulation: 0·010
Step of printing: 0·100
Simulation by the method Runge-Kutta of 4th power:

T	INT#1 [M]	INT#2 [K]	INT#3 [C]	INT#4 [D]	INT#5 [P]
0·000	0·00E+00	0·00E+00	0·00E+00	1·00E−05	1·00E−05
0·100	4·12E−16	5·50E−10	1·20E−10	1·00E−05	1·00E−05
0·200	1·65E−15	1·10E−09	2·40E−10	1·00E−05	1·00E−05
0·300	3·71E−15	1·65E−09	3·60E−10	1·00E−05	1·00E−05
0·400	6·60E−15	2·20E−09	4·80E−10	1·00E−05	1·00E−05
0·500	1·03E−14	2·75E−09	6·00E−10	1·00E−05	1·00E−05
0·600	1·48E−14	3·30E−09	7·20E−10	1·00E−05	1·00E−05
0·700	2·02E−14	3·85E−09	8·40E−10	1·00E−05	1·00E−05
0·800	2·64E−14	4·40E−09	9·59E−10	9·99E−06	9·99E−06
0·900	3·34E−14	4·95E−09	1·08E−09	9·99E−06	9·99E−06
1·000	4·12E−14	5·50E−09	1·20E−09	9·99E−06	9·99E−06

TABLE 4
Model of Simulation ***DLASK 1***

1. block: INTEGRATOR#1
   Input: UNI#3*INT#2*INT#4
   Initial value: 0
2. block: INTEGRATOR#2
   Input: UNI#1*INT#4*INT#5−UNI#3*INT#2*INT#4
   Initial value: 0
3. block: INTEGRATOR#3
   Input: UNI#2*INT#4*INT#5
   Initial value: 0
4. block: INTEGRATOR#4
   Input: −UNI#2*INT#4*INT#5−UNI#1*INT#5*INT#4−
   UNI#3*INT#2*INT#4
   Initial value: 0·0000258
5. block: INTEGRATOR#5
   Input: −(UNI#1*INT#2)*INT#4*INT#5
   Initial value: 0·0000258
6. block: UNIVERSAL#1
   Input: 3332·4
7. block: UNIVERSAL#2
   Input: 673·2
8. block: UNIVERSAL#3
   Input: 94·8

TABLE 5
Simulation of Model ***DLASK 1***

Start of simulation: 0·000
End of simulation: 500·000
Step of simulation: 0·010
Step of printing: 50·000
Simulation by the method Runge-Kutta of 2nd power:*

T	INT#1 [M]	INT#2 [K]	INT#3 [C]	INT#4 [D]	INT#5 [P]
0·000	0·00E+00	0·00E+00	0·00E+00	2·58E−05	2·58E−05
50·000	4·75E−07	1·74E−05	3·61E−06	3·87E−06	4·34E−06
100·000	7·03E−07	1·86E−05	3·91E−06	1·85E−06	2·55E−06
150·000	8·30E−07	1·90E−05	4·01E−06	1·09E−06	1·92E−06
200·000	9·09E−07	1·92E−05	4·07E−06	7·01E−07	1·61E−06
250·000	9·62E−07	1·93E−05	4·10E−06	4·72E−07	1·43E−06
300·000	9·98E−07	1·94E−05	4·11E−06	3·27E−07	1·33E−06
350·000	1·02E−06	1·94E−05	4·13E−06	2·31E−07	1·25E−06
400·000	1·04E−06	1·94E−05	4·13E−06	1·64E−07	1·21E−06
450·000	1·05E−06	1·94E−05	4·14E−06	1·18E−07	1·17E−06
500·000	1·06E−06	1·94E−05	4·14E−06	8·54E−08	1·15E−06

* When the more precise 4th order Runge–Kutta (R–K) method was used, the difference between the 2nd order R–K was below 1%, with the same stepwise parameters. 2nd order parameters are, therefore, shown in the Tables, since the calculation process for them is faster.

from the authors (Dr V. Dlask) on request. In this simulation model the notation is as follows:

[M] . . . . . INT#1
[K] . . . . . INT#2
[C] . . . . . INT#3
[D] . . . . . INT#4
[P] . . . . . INT#5

It took approximately 10–15 min for the calculation and printout of the results using this program.

The results are tabulated in Table 3. It is apparent that the concentrations changed slowly.

Another simulation run, viz. 'DLASK 1' is shown in Table 4. Different initial concentrations were used and the time was in minutes. The rate constants have the dimension $dm^3\ mol^{-1}\ min^{-1}$ and they were filed in special blocks:

k_1 = UNIVERSAL#1
k_2 = UNIVERSAL#2
k_3 = UNIVERSAL#3

TABLE 6
Percentage Content of **K**, **C** and **M**

$[D]_0$ (mol . dm^{-3})	K%	C%	M%
$7{\cdot}05 \cdot 10^{-4}$	4·22	75·48	16·03
$6{\cdot}34 \cdot 10^{-4}$	4·20	75·39	16·08
$5{\cdot}13 \cdot 10^{-4}$	4·19	75·43	16·10
$4{\cdot}64 \cdot 10^{-4}$	4·17	75·43	16·09
$3{\cdot}90 \cdot 10^{-4}$	4·04	75·38	16·10
$2{\cdot}63 \cdot 10^{-4}$	4·04	75·28	16·08
$2{\cdot}58 \cdot 10^{-5}$	4·22	75·58	16·08
$2{\cdot}08 \cdot 10^{-5}$	4·23	75·48	16·10
$1{\cdot}83 \cdot 10^{-5}$	4·22	75·40	16·06
$1{\cdot}57 \cdot 10^{-5}$	4·23	75·15	16·05
$1{\cdot}32 \cdot 10^{-5}$	4·22	75·37	16·06
$1{\cdot}06 \cdot 10^{-5}$	4·22	75·28	16·03

$$\mathbf{K}\% = \frac{[\mathbf{K}]_{t=\infty}}{[\mathbf{P}]_{t=0}} \cdot 100;\quad \mathbf{C}\% = \frac{[\mathbf{C}]_{t=\infty}}{[\mathbf{P}]_{t=0}} \cdot 100;\quad \mathbf{M}\% = \frac{[\mathbf{M}]_{t=\infty}}{[\mathbf{P}]_{t=0}} \cdot 100.$$

This filing procedure allowed us to change the constant without intervention in the equations.

Table 5 shows part of the results. The numerical values of the constants k_1, k_2 and k_3 were chosen to be the same as those estimated experimentally. The values of [**K**], [**M**] and [**C**] are very important when the reactions are completed ($t \rightarrow \infty$). The ratios $[\mathbf{K}]_{t=\infty}/[\mathbf{P}]_{t=0}$; $[\mathbf{M}]_{t=\infty}/[\mathbf{P}]_{t=0}$; $[\mathbf{C}]_{t=0}/[\mathbf{P}]_{t=0}$ (the yield of reactions) are shown in Table 6. They correspond very well to the experimental results, details of which will be reported separately.

The main menu of the simulation system provides easy monitoring of the results in the form of graphs and tables. The graphs are not presented here and we consider that the tabulation and printout are sufficient.

REFERENCES

1. Dlask, V. & Plocek, J., *Dyes and Pigments* (in press).
2. FEL Faculty VUT Brno, Dept. of Computers: PPSSS program.