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NITROSATION KINETICS OF 5-METHYLRESORCINOL

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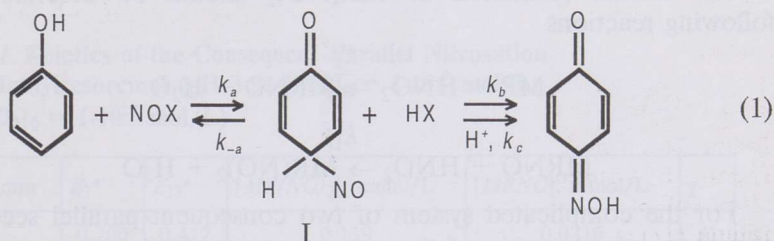
The kinetics of the acidic nitrosation of 5-methylresorcinol (MR), the main component of oil shale originated phenols, has been studied. Formation of 2,4-dinitroso-5-methylresorcinol was followed by an increase in optical density and temperature of the reaction mixtures over the initial concentrations of the reagents $1 \cdot 10^{-4}$ -0.05 mol/L and over the acidities pH 4.38-1.5 mol/L of H_2SO_4 . The kinetic model for the two-step consequent-parallel nitrosation was approximated to the second-order rate equation. The apparent rate constant was revealed as the result of three rate constants for the contributing nitrosation reactions of MR with HNO_2 , $H_2NO_2^+$ and of the proton-catalysed reaction with $H_2NO_2^+$. The constants K_1 and K_2 for the two-step protonisation of NO_2^- were determined.

Introduction

5-Methylresorcinol (MR) is the major component of phenolic compounds formed upon the retorting of kukersite oil shales [1]. Crystalline MR is isolated from the mixture of water-soluble phenols by combination of distillation, extraction and crystallisation procedures in *Kiviter* Ltd. In our previous work [2], the synthesis of a new family of reagents from oil shale phenols by nitrosation of resorcinol alkyl derivatives was studied in relation to the reagents ratio and temperature. It was found that the reaction of MR with nitrous acid generated *in situ* by neutralisation of sodium or potassium nitrite with sulfuric acid yields exclusively 2,4-dinitroso-5-methylresorcinol (MR(NO)₂).

No information about nitrosation rate and mechanism of MR neither of any reagent yielding a dinitroso compound was found. Under the high acidic conditions NO^+ is reported as the effective reagent. When the concentration of acid is below 5 M, the formula of the nitrosating agent is regarded to be unidentified. Reliable information on the efficacy of various protonated species of nitrite is absent.

In the works of B. C. Challis *et al.* [3-5], the nitrosation kinetics of phenolic compounds was examined by the concentration of unchanged nitrous acid. The reaction rate showed the first-order dependence on both phenol and nitrite concentration. On the basis of the trivial kinetic acidity dependence below 1 mol/L of HClO_4 , and deuterium isotope effect, $k^H/k^D = 3.3$, the unusual rate-limiting step for $\text{S}_{\text{E}}2$ substitutions was suggested. Namely, proton-loss from the Whealand intermediate (I) by the spontaneous or acid-catalysed pathway



was regarded as the rate-limiting for nitrosation of aromatic compounds. Attempts to isolate (I) or to detect it spectrometrically have been unsuccessful. So, this structure is supposed to be formed in a rapid reversible step with rate constants $k_{-a} \gg k_a > k_c > k_b$.

In our opinion, evaluation of the second step for the consequent reaction (1) by the concentration of a reagent participating only in the first step can give artefacts.

In this paper, kinetics of the acidic nitrosation of MR was studied under the wide range of concentrations and acidity. A kinetic model for the reaction resulting $\text{MR}(\text{NO})_2$ was created. The nitrosation rate constants and acidic dissociation constants for various nitrosating species were determined.

Experimental

All the chemicals applied were of analytical grade and used as received. Fresh solutions of MR were prepared on the day of use from crystalline $\text{C}_7\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$ purchased from MERCK. The reaction temperature was $22 \pm 2^\circ\text{C}$.

Kinetics of the nitrosation was examined by monitoring

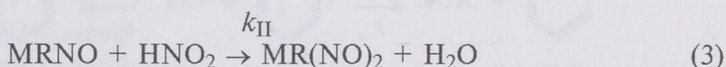
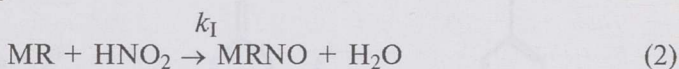
- The increase in optical density of the reaction mixtures under low concentrations of MR, characteristic to the new colorimetric test method of alkylresorcinols elaborated in our previous work [6].

- The increase in temperature of reaction mixtures under relatively high concentrations of MR, characteristic to the synthesis of $\text{MR}(\text{NO})_2$ in our previous work [2].

The optical density of the samples was estimated by a spectrophotometer SPECOL 10 at 420 nm in cells with optical path length 5 cm. The initial concentration of MR and NaNO_2 was varied in the range 0.1-1 mmol/L. The acidity range studied was from pH 4.28 to 1.5 mol/L of H_2SO_4 . It was unrealisable to investigate the nitrosation kinetics under more acidic conditions by the test-sets described because in such solutions the rate was diffusion controlled. That means the process was practically completed during the reagents were mixed.

The conversion of MR in time was tested by the optical density, E , of the coloured anionic form of the nitrosation products in the periodically drawn and immediately alkalisied samples.

The overall formation of $\text{MR}(\text{NO})_2$ should be described by the following reactions



For the complicated system of two consequent-parallel second-order reactions only the ratio of the rate constants, $k_{\text{II}}/k_{\text{I}} = \chi$, can be found from the relationship brought in [7]

$$\frac{[\text{MRNO}]}{[\text{MR}]} = (\chi - 1)^{-1} \left[1 - \left(\frac{[\text{MR}]}{[\text{MR}]_0} \right)^{\chi-1} \right] \quad (4)$$

The anions of mono- and dinitroso compounds have different molar extinction coefficients, ε_1 and ε_2 , and acidic dissociation coefficients $pK_{a1}(\text{MRNO}) = 3.31$, $pK_{a1}(\text{MR}(\text{NO})_2) = 4.62$, and $pK_{a2}(\text{MR}(\text{NO})_2) = 9.48$ [8]. So, we can find the concentrations, $[\text{MRNO}]$ and $[\text{MR}(\text{NO})_2]$, spectrophotometrically from the optical densities, E_7 and E_{12} , (measured at pH 6-7 and 11-12) using the following relationships

$$E_{12} = (\varepsilon_1[\text{MRNO}] + \varepsilon_{2-12}[\text{MR}(\text{NO})_2])l \quad (5)$$

$$E_7 = (\varepsilon_1[\text{MRNO}] + \varepsilon_{2-7}[\text{MR}(\text{NO})_2])l \quad (6)$$

where l is the optical path length and

$$\varepsilon_1 = 22000, \varepsilon_{2-7} = 500 \text{ and } \varepsilon_{2-12} = 1575 \text{ L}/(\text{mol}\cdot\text{cm}) \text{ at } 420 \text{ nm [8].}$$

The high exothermic effect of the nitrosation reaction, $200(\pm 9)$ kJ/mol, established in [2] makes possible to follow the rate of the nitrosation process by the temperature rising. The calorimetric experiments were conducted in a thermostated stirred reactor of 200 mL capacity. As the maximum increase in temperature observed, 0.7-1.4 K, was attained during tens of seconds, a special experimental set-up was compiled. The temperature rising was measured by digital multimeter Fluke-8842A (6 1/2 digits) and recorded via IEEE-488 interface by

computer with sampling rate 1 s. The method of recording of small temperature differences is most noiseless. The thermocouple converting equation was added to the data logging software. In the test-sets, 37.5 or 75 mL of the thermostated 0.1 mol/L of MR and a required volume of 0.5 mol/L of H_2SO_4 or pH-buffer were diluted to 140 mL. A test was started when 10 mL of 0.75 or 0.375 mol/L of $NaNO_2$ in an ampoule was broken. The equimolar concentrations of MR and $NaNO_2$ were applied to avoid destruction of the nitrosated products by an excess of nitrite observed in [2].

Results and Discussion

Results of the colorimetric tests represented in Table 1 reveal that the ratio of the second- and first-step rate constants, k_{II}/k_I , in Equation (4) is $19(\pm 5)$.

Table 1. Kinetics of the Consequent-Parallel Nitrosation of 5-Methylresorcinol (pH 3.9; $[MR]_0 = 1 \cdot 10^{-3}$ mol/L; $[NaNO_2]_0 = 1 \cdot 10^{-3}$ mol/L)

Time, min	E_7^*	E_{12}^*	$[MR(NO)_2]$, mmol/L	$[MRNO]$, mmol/L	χ
50	0.200	0.412	0.119	0.0216	31
60	0.219	0.465	0.138	0.0284	29
80	0.255	0.565	0.174	0.0301	26
100	0.290	0.660	0.207	0.0320	24
120	0.320	0.730	0.230	0.0351	21
140	0.339	0.775	0.244	0.0370	19
160	0.360	0.813	0.254	0.0406	17
180	0.380	0.850	0.263	0.0438	16
200	0.390	0.880	0.274	0.0440	15
220	0.405	0.935	0.294	0.0430	15
240	0.410	0.970	0.313	0.0406	16
260	0.420	0.992	0.320	0.0418	15
280	0.430	1.020	0.330	0.0422	16
300	0.435	1.030	0.333	0.0429	15
320	0.440	1.040	0.336	0.0437	14
340	0.448	1.051	0.340	0.0423	15
360	0.450	1.071	0.348	0.0437	14

* Optical density of 1 : 2 diluted samples at 420 nm, $l = 5$ cm.

Therefore, the complicated kinetic model for the dinitrosation can be simplified assuming that the formation of MRNO is the rate limiting. Whereas the optical density measured is resulted mainly by the fast formation of $MR(NO)_2$, the apparent rate constant, k_H , was calculated as follows

$$k_H = t^{-1} \int_0^{[MR(NO)_2]} \frac{d[MR(NO)_2]}{([MR]_0 - [MR(NO)_2]) ([NaNO_2]_0 - 2[MR(NO)_2])} \quad (7)$$

where

the approximated concentration $[MR(NO)_2] = 0.5[NaNO_2]_0 E/E(\max)$.

The harmony of k_H found in colorimetric tests under the acidity 0.05 mol/L of H_2SO_4 for various initial concentrations of the reagents (Table 2) prove the validity of Equation (7).

Table 2. The Second-Order Apparent Rate Constants from Colorimetric Tests
($[H_2SO_4]_0 = 0.05$ mol/L)

t , min	$10^4 [MR(NO)_2]$, mol/L	$k_{0.05}$, L/(mol s)
$[MR]_0 = [NaNO_2]_0 = 1 \cdot 10^{-4}$ mol/L		
10	0.0825	1.60
15	0.114	1.53
20	0.138	1.45
25	0.164	1.43
30	0.186	1.43
$[MR]_0 = [NaNO_2]_0 = 2.5 \cdot 10^{-4}$ mol/L		
10	0.490	1.52
15	0.620	1.57
20	0.713	1.53
25	0.782	1.47
30	0.843	1.45
$[MR]_0 = [NaNO_2]_0 = 5 \cdot 10^{-4}$ mol/L		
10	1.65	1.48
15	1.88	1.55
20	2.01	1.47
25	2.10	1.38
30	2.22	1.45
$[MR]_0 = [NaNO_2]_0 = 1 \cdot 10^{-3}$ mol/L		
10	3.83	1.62
15	4.36	1.67
20	4.66	1.75
25	4.80	1.73
30	4.88	1.72
Mean $k_{0.05}$		1.56(± 0.13)

Table 3. The Apparent Second-Order Rate Constants from Colorimetric Tests

Test number	$[MR]_0 = [NaNO_2]_0$, mol/L	$[H_2SO_4]_0$, mol/L	$t_{0.5}$, s	$k_H(II)$, L/(mol·s)
1	0.025	0.50	2.3	7.0
2	0.050	0.50	1.0	8.1
3	0.025	0.265	4.1	4.0
4	0.025	0.255	4.2	3.9
5	0.025	pH 2*	18.4	0.88
6	0.050	pH 2*	9.7	0.84

* Glycine buffer.

The results of calorimetric experiments (Fig. 1; Table 3) obtained under 25-50 times higher concentrations of MR and $NaNO_2$ agree with the colorimetric results above. In these experiments the characteristic plots of temperature versus time at two initial concentrations and at three acidity conditions were obtained. For estimation of the rate constants,

the half-life period, $t_{0.5}$, was determined as the time for obtaining a half of the maximum increase in temperature.

The second-order apparent rate constants were calculated by Equation (7) assuming that $[MR(NO)_2] = 0.25[NaNO_2]_0$. The values of k_H found suggest that the nitrosation rate is very sensitive to the acidity of the reaction mixtures.

Table 4 lists the values of k_H obtained in the colorimetric and calorimetric tests under the wide range of acidity and initial concentrations of the reagents.

The results demonstrate the significant influence of acidity on the nitrosation rate.

$\Delta T, K$

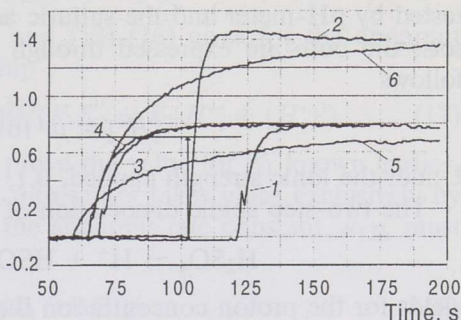


Fig. 1. Plot of temperature in reaction mixtures versus nitrosation time. The graph numbers refer to the test numbers in Table 3

Table 4. Effect of Acidity on the Apparent Rate Constant

pH or $[H_2SO_4]$, mol/L	$[H^+]_0$, mol/L	$10^3 [MR]_0$ (mol/L) = $= 10^3 [NaNO_2]_0$ (mol/L)	H_0^{*1}	k_H , L/(mol·s)
pH buffers, $\mu = 0.1$				
4.28	$6.38 \cdot 10^{-5}$	1.0	-	0.062
3.97	$1.29 \cdot 10^{-4}$	1.0	-	0.10
3.61	$2.96 \cdot 10^{-4}$	1.0	-	0.20
3.35	$5.38 \cdot 10^{-4}$	1.0	-	0.28
2.99	$1.23 \cdot 10^{-3}$	1.0	-	0.40
2.38	$5.02 \cdot 10^{-3}$	1.0	-	0.62
1.80	0.0191	1.0	-	0.92
Sulfuric acid solutions				
0.050	0.060	0.1-1.0	0.468	1.55^{*2}
0.150	0.161	0.5	0.393	3.17
0.250	0.261	0.5	0.318	3.83
0.255	0.265	25	0.314	3.9^{*3}
0.265	0.276	25	0.306	4.0^{*3}
0.375	0.386	0.1	0.224	6.5
0.500	0.512	25	0.130	7.1^{*3}
0.500	0.512	50	0.130	8.1^{*3}
0.500	0.512	0.1	0.130	8.7
0.625	0.636	0.2	0.035	10.5
0.750	0.762	0.2	-0.059	12.3
0.875	0.887	0.2	-0.152	16.0
1.00	1.01	0.1	-0.247	20.7
1.25	1.26	0.1	-0.435	33.2
1.50	1.51	0.1	-0.624	53.5

*1 H_0 is the Hammett's acidity function.

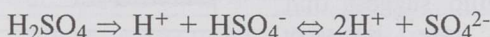
*2 Mean value from Table 2.

*3 From Table 3.

To fit together the proton activity, a_H , in the pH-buffered solutions tested by pH-meter and the sulfuric acid concentrations in the most test-sets, the both are expressed through the proton concentration, $[H^+]$, as follows

$$[H^+] = \mu^{-1} 10 \exp(-a_H) \quad (8)$$

Under the ionic strength applied, 0.1, the activity coefficient $\mu = 0.83$ [9]. The two-step acidic dissociation of sulfuric acid

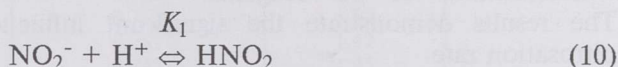


yields for the proton concentration the following relationship

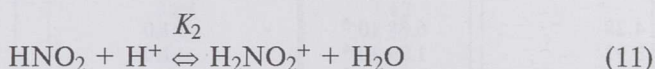
$$[H^+] = [H_2SO_4]_0 (2K_a + [H^+]) / (K_a + [H^+]) \quad (9)$$

At 25 °C the second dissociation constant for H_2SO_4 , $K_a = 0.012$ [9].

The results in Table 4 testify that the apparent rate constant increases with an increase in acidity not only in the pH region due to the transition



defined by the acidic dissociation constant $pK_1 = 3.29$ at 25 °C [9], but all the more when the concentration of sulfuric acid is increased at the acidity conditions where the reaction (10) should be completed. Such a behaviour might be explained by the reaction with more active species, hypothetically, with the nitrous acidium cations, $H_2NO_2^+$, originated from the second protonisation



Reliable information on the occurrence and reaction rate of various nitrosating agents is not available. The species of NO^+ are reported in [3] to predominate when $[H^+] > 5$ mol/L. Due to the relatively low value of K_2 , found below in this study, $0.38(\pm 0.11)$ mol/L, NO^+ is excluded in this step. Any value for K_2 has not been published earlier.

The kinetic equation that depicts formation of the dinitroso compound $MR(NO)_2$ by two contributing reactions of MR with HNO_2 and $H_2NO_2^+$, having kinetic constants k_1 and k_2 , can be written as follows

$$d[MR(NO)_2]/dt = k_1[MR][HNO_2] + k_2[MR][H_2NO_2^+] \quad (12)$$

Equation (12) can be modified writing the current concentrations of the reagents through the current concentration of $MR(NO)_2$ tested. For this aim, the following mass balances and acidic dissociation equilibriums are taken into account

$$[NaNO_2]_0 = [NO_2^-] + [HNO_2] + [H_2NO_2^+] + 2[MR(NO)_2] \quad (13)$$

$$[MR]_0 = [MR] + [MR(NO)_2] \quad (14)$$

$$K_1 = [H^+][NO_2^-]/[HNO_2] \quad (15)$$

$$K_2 = [H^+] [HNO_2]/[H_2NO_2^+] \quad (16)$$

A combination of Equations (7) and (13)-(16) gives for the apparent rate constant the following relationship

$$k_H = (k_1 K_2 [H^+] + k_2 [H^+]^2) / (K_1 K_2 + K_2 [H^+] + [H^+]^2) \quad (17)$$

To establish the value for k_1 and prove the value for K_1 known earlier, the pH region was studied where the nitrosation takes place exclusively by the species of HNO_2 . In this region the apparent rate constant, k_{1H} , must depend on $[H^+]$ as follows

$$k_{1H} = k_1 K_1 / (K_1 + [H^+]) \quad (18)$$

Equation (18) can be written as a linear regression of the experimentally established apparent rate constant, k_{1H} , versus a variable $k_{1H}/[H^+]$

$$k_{1H} = k_1 - K_1 (k_{1H}/[H^+]) \quad (19)$$

where the values for constants k_1 and K_1 are equal to the formula constant term and regression coefficient, respectively.

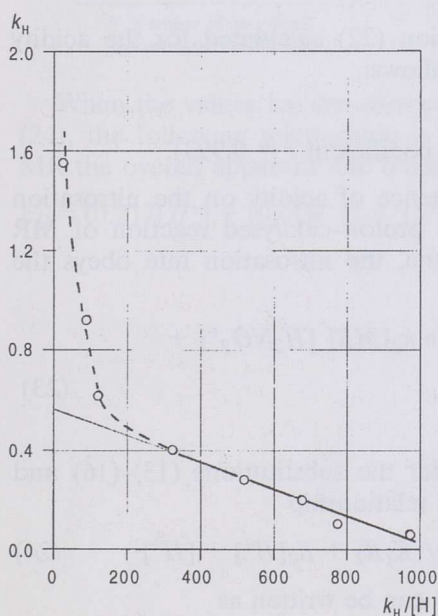


Fig. 2. Plot of k_H versus $k_H/[H^+]$

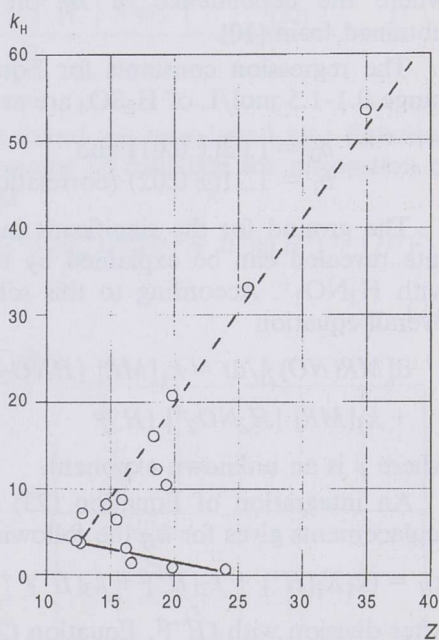


Fig. 3. Plot of k_H versus Z

Figure 2 testifies that the plot of k_H versus $k_{1H}/[H^+]$ is a straight line only when $\text{pH} \geq 2.99$. For this pH-region, the data in Table 3 give by Equation (19) the values $k_1 = 0.57 \text{ L}/(\text{mol}\cdot\text{s})$ and $K_1 = 5.48 \cdot 10^{-4} \text{ mol}/\text{L}$ ($\text{p}K_1 = 3.26$). The value for k_1 is reported the first time. The value for $\text{p}K_1$ found in this study at 22°C , agrees with $\text{p}K_1 = 3.37$ at 12.5°C published in [9].

When k_1 and K_1 are established, k_2 and K_2 can be found from Equation (17) replaced as a linear regression of k_H versus the function Z

$$k_H = k_2 - K_2 Z \quad (20)$$

where

$$Z = k_H K_1 / [H^+]^2 + (k_H - k_1) / [H^+] \quad (21)$$

Figure 3 demonstrates that actually the plot of k_H versus Z has two branches. The negative slope predicted by Equation (20) takes place only when $[H^+]$ is less than 0.3 mol/L. The corresponding data in Table 3 give for k_2 and K_2 the values 7.77 L/(mol·s) and 0.32 mol/L. When $[H^+]$ is over 0.3 mol/L, the real k_H is significantly higher than the value predicted by Equation (20). So, in the higher acidity region, the third nitrosation pathway is evident.

All the values for the apparent rate constant found in sulfuric acid solutions can be successfully related to the linear regression of $\log k_H$ on the Hammet acidity function, H_0

$$\log k_H = b_0 + b_1 H_0 \quad (22)$$

where the dependence of H_0 on the sulfuric acid concentration is obtained from [10].

The regression constants for Equation (22) calculated for the acidity range 0.1-1.5 mol/L of H_2SO_4 are as follows:

$$b_0 = 1.02(\pm 0.01) \text{ and} \\ b_1 = 1.21(\pm 0.02) \text{ (correlation coefficient } r = 0.993).$$

The ground for the significant influence of acidity on the nitrosation rate revealed can be explained by the proton-catalysed reaction of MR with $H_2NO_2^+$. According to this scheme, the nitrosation rate obeys the overall equation

$$d[MR(NO)_2]/dt = k_1[MR] [HNO_2] + k_2[MR] [H_2NO_2^+] + \\ + k_3[MR] [H_2NO_2^+] [H^+]^p \quad (23)$$

where p is an unknown exponent.

An integration of Equation (23) after the substitutions (13)-(16) and replacements gives for k_H the following relationship

$$k_H = (k_1 K_2 [H^+] + k_2 [H^+]^2 + k_3 [H^+]^{p+2}) / (K_1 K_2 + K_2 [H^+] + [H^+]^2) \quad (24)$$

After division with $[H^+]^2$, Equation (24) can be written as

$$k_H = k_2 + k_3 [H^+]^p - K_2 \{ (k_H K_1 / [H^+]^2 + (k_H - k_1) / [H^+] \} \quad (25)$$

which represents the two-parameter linear regression

$$k_H = a_0 + a_1 x_1 + a_2 x_2 \quad (26)$$

where $x_1 = k_H K_1 / [H^+]^2 + (k_H - k_1) / [H^+]$;

$$x_2 = [H^+]^p;$$

$$a_0 = k_2;$$

$$a_1 = -K_2;$$

$$a_2 = k_3.$$

The constants a_0 , a_1 and a_2 in Equation (26) were computed on the basis of the results in Table 4, assuming that p is 1, 2, 3 and 4. The regression obtains the lowest standard deviations of the constants and the highest correlation coefficient when $p = 3$.

All the constants for the three pathways of nitrosation estimated at $22(\pm 2)$ °C are listed in Table 5.

Table 5. Characteristic Constants for Nitrosation Kinetics of 5-Methylresorcinol

Symbol	Value	N^{*1}	R^{*2}	Equation number
k_1 , L/(mol s)	$0.57(\pm 0.04)$	5	0.982	(19)
k_2 , L/(mol s)	$10.0(\pm 1.8)$	17	0.994	(25)
	$7.77(\pm 0.92)$	7	0.934	(20)
k_3 , L ⁴ /(mol ⁻⁴ s)	$16.7(\pm 0.7)$	17	0.994	(25)
K_1 , mol/L	$5.48(\pm 0.61) \cdot 10^{-4}$	5	0.982	(19)
K_2 , mol/L	$0.38(\pm 0.11)$	17	0.994	(25)
	$0.32(\pm 0.06)$	7	0.934	(20)
b_0	$1.02(\pm 0.01)$	15	0.993	(22)
b_1	$1.21(\pm 0.04)$	15	0.993	(22)

*1 Number of data items.

*2 Correlation coefficient.

When the values for the constants found are introduced into Equation (24), the following relationship is revealed to calculate for nitrosation of MR the overall apparent rate constant

$$k_H = (0.217[H^+] + 10.0[H^+]^2 + 16.7[H^+]^5) / (2.08 \cdot 10^{-4} + 0.38[H^+] + [H^+]^2)$$

(27)

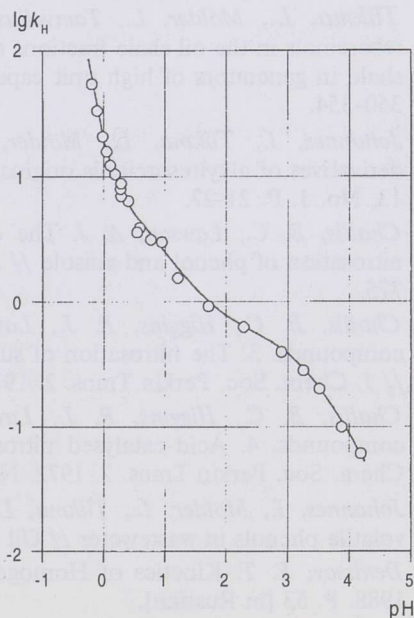


Fig. 4. Plot of $\log k_H$ versus pH.
Curve - calculated,
points - experimental

The validity of the model deduced is proved in Fig. 4 by a satisfactory harmony of the theoretical graph depicting the values of $\log k_H$, calculated by Equation (27) versus pH and the points of $\log k_H$ obtained on the basis of the increase in temperature and optical density tested.

The rate-acidity profile obtained suggests that the nitrosation mechanism of MR differs from that reported in [3] for phenol. The kinetics of the acidic dinitrosation of MR can be approximated rather to the kinetics of the first attack by nitrosating species as the rate-limiting reaction.

Conclusions

1. A kinetic model for acidic nitrosation of 5-methylresorcinol is created. The rate of the two consequent second-order reactions yielding 2,4-di-nitroso-5-methylresorcinol is approximated to the first-order dependence on the current concentration of the both 5-methyl-resorcinol and nitrite.
2. The overall apparent rate constant relies on the partial contributions of the parallel reactions of 5-methylresorcinol with species of HNO_2 , H_2NO_2^+ and the proton-catalysed reaction with H_2NO_2^+ species. The values for the corresponding rate constants, k_1 , k_2 and k_3 , and for the nitrite two-step acidic dissociation constants, K_1 and K_2 , at 22 °C are estimated.

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