SYNTHESIS OF NITROSO DERIVATIVES OF ALKYLRESORCINOLS ORIGINATED FROM OIL SHALE

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The effect of the reaction temperature and reactant concentration on the yield of the nitrosation of 5-methylresorcinol and 2,5-dimethylresorcinol were studied. The thermal effect of the reactions and the solubility of synthesized 2,4-dinitroso-5-methylresorcinol and 4-nitroso-2,5-dimethylresorcinol were determined.

Introduction

By retorting of Estonian "kukersite" oil shale and the subsequent dephenolization of the retort water, 3-4 kg of so-called water-soluble phenols per tonne have been obtained (the potential yield is 7 kg per tonne). As a specific feature, these phenols consist of 90-95 % of 1,3-dihydroxybenzene (resorcinol) series alkyl derivatives (AR), among which 5-methylresorcinol (MR) and 2,5-dimethylresorcinol (DMR) prevail. Methods for the obtaining of crystalline MR and DMR have been worked out and their commercial production has been realized partially [1-4]. Nevertheless, the synthesis of alkylresorcinols is known as a multistep expensive process, the oil-shale-originated AR have not found sufficient qualified application. Up to the present, distillate fractions of AR have been used for the production of epoxy and resorcinol-formaldehyde resins, glues, tanning agents, corrosion inhibitors, rubber modifiers, etc.

The electron-donating coinfluence of two OH-groups at the positions 1 and 3 activates the aromatic ring of AR toward an electrophilic attack at the positions 2, 4, and 6. The high reactivity of AR have been used for the substitution of aromatic hydrogen atoms by SO_3H- and NO_2-groups [5, 6].

The aim of this paper is to report the first results obtained in the study of substitution of aromatic hydrogen atoms in MR and DMR by NO-groups. Particularly, the effect of the reagents mole ratio and the

medium temperature on the yield of nitrosoalkylresorcinols will be described, and the thermal effect of the reaction and some characteristics of the nitroso products will be presented.

Nitrosophenols are known as effective modifiers for rubber and polymers [7-9], nitrosonaphtols – as selective reagents for cobalt cations [10]. Information about the synthesis of nitrosoalkylresorcinols is negligible. Any information about their application as modifiers is not available, probably due to the short supply of alkylresorcinols. The ability of nitroso derivatives of AR to form cobalt complexes has been used in analytical chemistry for the selective determination of AR as cobalt nitrosoalkylresorcinolates [11].

The high reactivity of MR and DMR allows their nitroso derivatives to be obtained according to the simplest and cheapest route, analogous to that used for the synthesis of 4-nitrosophenol and 1-nitroso-2-naphtol [12, 13]. The preferred route involves a dropwise addition of H_2SO_4 to an alkaline water solution of MR or DMR and $NaNO_2$ at 10 °C or less.

Experimental

In our experiments a varied quantity (0.5-2 mole per mole AR) of $NaNO_2$ was dissolved in a 0.5-molar solution of MR or DMR. Then the solution was cooled to ca 0 °C, and H_2SO_4 (0.14-10 mole per mole AR) was added at controlled 0-10 °C. After acidification, the reaction mixture was stirred for 1 h. The yield of the nitroso derivatives was estimated colorimetrically. For that purpose the precipitated nitroso derivative was dissolved by the addition of NaOH to the sample.

In the case of the nitroso derivative of DMR, the reaction mixture was diluted up to the 0.0004 M, regarding the initial concentration of DMR. The absorbance of the solution was measured directly, using cell length as 1 cm and wavelength as 420 nm.

In the case of the nitroso derivative of MR, colour varies from yellow to brown. The yield of the reaction was estimated by forming a coloured cobalt complex. The latter was synthesized adding 1 cm³ of a 0.0004 M (regarding the initial concentration of MR) alkaline solution of the nitrosation product to 20 cm³ of a 0.001 M solution of $CoSO_4$.

During the optimization of the concentration of $NaNO_2$ the addition of H_2SO_4 was completed when the mole ratio H_2SO_4 / MR was 1.9 or that of H_2SO_4 / DMR - 1.45. During the optimization of the concentration of H_2SO_4, the mole ratio of $NaNO_2$ / MR was 2.2 and the mole ratio of $NaNO_2$ / DMR - 1.1.

When the influence of temperature was studied an ultrathermostat was used, and the mole ratios MR / $NaNO_2$ / H_2SO_4 and DMR / $NaNO_2$ / H_2SO_4 were 1/2.2/4 and 1/1.1/4, respectively.

The thermal effect of the nitrosation process was determined following a known procedure [14] in an air calorimeter, equipped with a Beckman thermometer. The energy equivalent (effective heat capacity) of the calorimeter was found by the heat of dilution of H_2SO_4 at any temperature under study (9-60 °C). For the determination of the heat of nitrosation an

ampoule, containing 10 cm^3 of a 1.69 M solution of H_2SO_4, was broken in a calorimetric vessel, containing 150 cm^3 of a 0.075 M solution of MR or DMR and 12 cm^3 of a 2 M (in the case of DMR – 1 M) solution of $NaNO_2$.

The solubility of the products was determined colorimetrically, after stirring the suspension of MR or DMR in 0.1 M HCl for 2 h and filtering through a layer of the respective AR at the temperature required.

The absorbance of the solutions was measured on a SPEKOL 11 spectrophotometer.
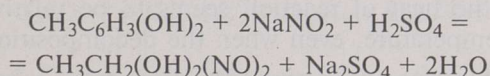
Results and Discussion

Synthesis

The yield of the nitrosation reactions is plotted against the mole ratios $NaNO_2$ / MR (or DMR), H_2SO_4 / MR (or DMR) and the temperature of the mixture in Figure.
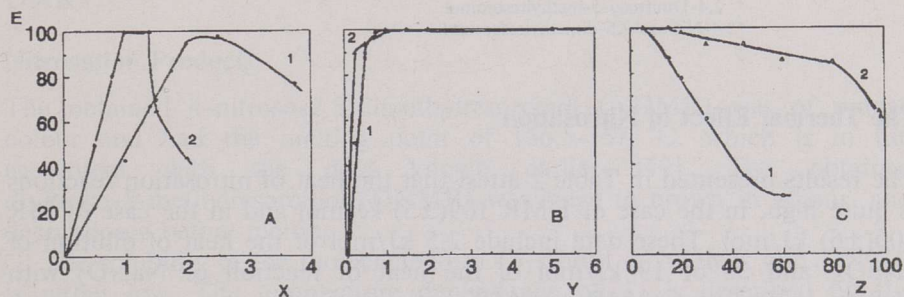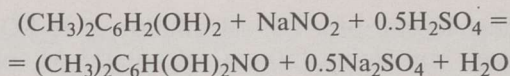

The yield of the nitrosation reaction (E, %) of MR (*1*) and DMR (*2*) versus: *A* - mole ratio $NaNO_2$ / resorcinol derivative (X), *B* - mole ratio H_2SO_4 / resorcinol derivative (Y), *C* - reaction temperature (Z, °C)

It can be seen that the nitrosation is almost completed (the yield is over 90 %) at the mole ratios $NaNO_2$ / DMR = 1, H_2SO_4 / DMR = 0.5 and $NaNO_2$ / MR = 2, H_2SO_4 / MR = 1. An increase in the $NaNO_2$ content over the equivalent (Figure,*A*) leads to the decomposition of the nitroso derivative, especially in the case of DMR. An excess of H_2SO_4 (Figure,*B*) does not decrease the yield of either nitroso derivative. The need for the cooling of the reaction mixture below 10 °C, especially in the case of nitrosation of MR, becomes obvious from Figure,*C*.

The results reported above as well as the results of the elemental analysis of the products dried at room temperature (Table 1) suggest the following summary reactions:

$$CH_3C_6H_3(OH)_2 + 2NaNO_2 + H_2SO_4 =$$
$$= CH_3CH_2(OH)_2(NO)_2 + Na_2SO_4 + 2H_2O$$

$$(CH_3)_2C_6H_2(OH)_2 + NaNO_2 + 0.5H_2SO_4 =$$
$$= (CH_3)_2C_6H(OH)_2NO + 0.5Na_2SO_4 + H_2O$$

Consequently, a dinitroso- or mononitrosoalkylresorcinol can be easily synthesized, depending on the number of alkyl groups in the initial resorcinol series phenol.

Table 1. **Elemental Composition of Nitroso Derivatives Synthesized, %**

Element	DNMR*·H$_2$O		NDMR**	
	Found	Calculated	Found	Calculated
C	42.7	42.0	57.8	57.5
H	3.9	4.0	5.3	5.4
N	13.4	14.0	8.4	8.4
O	40.1	40.0	28.7	28.7

* 2,4-Dinitroso-5-methylresorcinol.
** 4-Nitroso-2,5-dimethylresorcinol.

The Thermal Effect of Nitrosation

The results presented in Table 2 attest that the heat of nitrosation reactions is quite high, in the case of DMR 109($\pm$5) kJ/mol and in the case of MR 200($\pm$6) kJ/mol. These data include 2.5 kJ/mol of the heat of dilution of H_2SO_4, and 38 or 19 kJ/mol of the heat of reaction of $NaNO_2$ with H_2SO_4, in the cases of MR or DMR, respectively.

Table 2. **Heat of Nitrosation Reactions**

Initial temperature, °C	MR		DMR	
	t, K	Q, kJ/mol	t, K	Q, kJ/mol
9	3.28	195	1.75	104
20	3.35	200	1.73	103
25	3.41	206	1.89	114
30	3.44	209	1.86	113
40	3.15	195	1.75	108
50	-	-	1.81	114
60	-	-	1.64	106
Mean		200($\pm$9)		109($\pm$5)

Furthermore, the heat of reaction seems to be relatively independent on the reaction temperature, even when the decomposition of the product is remarkable.

Kinetics

The dependence of the temperature increase on time ΔT, found at the determination of the heat of reaction, is in good agreement ($r \geq 0.99$) with the kinetic equation of a first-order reaction. Consequently, the process studied should be limited not by the reaction of NO^+ with AR, but by a monomolecular transformation reaction of an intermediate product. The mechanism and the kinetics of the nitrosation reactions need further and more detailed examination.

Some data of rate constants (k_1) were found from the Equation (1):

$$k_1 = \frac{1}{t} \ln \frac{\Delta T_{max}}{\Delta T_{max} - \Delta T} \qquad (1)$$

Under the conditions studied (7-9 °C; a 0.0654-molar solution of MR or DMR; a 0.14-molar solution of $NaNO_2$ in the case of MR, and a 0.07-molar one in the case of DMR; a 0.1-molar solution of H_2SO_4), the result was $k_1 = 7.30(\pm 0.10) \cdot 10^{-3}$ s^{-1} for MR and $k_1 = 1.68(\pm 0.11) \cdot 10^{-2}$ s^{-1} for DMR.

Nitrosation Products

The obtained 4-nitroso-2,5-dimethylresorcinol (NDMR) was of orange colour and had the melting point of 156.5-157 °C, which is in full agreement with the data known earlier [12]. The obtained dinitroso-5-methylresorcinol (DNMR) was beige to brown in colour, and decomposed before melting.

The solubility of the molecular form (S_T) both of NDMR and DNMR is rather low. The temperature dependence of S_T is described by the Equation (2):

$$\ln S_T = \ln S_{298} + 1000 \, b(1 - 298.15 \, / \, T), \qquad (2)$$

where S_{298} is the solubility at 298.15 K;
      b is a factor;
      T is the temperature, K.

The acidic dissociation of nitrosoalkylresorcinols containing OH- and NO-substituents at *ortho*-position increases the total solubility (ΣS_T) of NDMR according to the Equation (3):

$$\Sigma S_T = S_T (1 + K_a / [H^+]), \qquad (3)$$

and of DNMR according to the Equation (4):

$$\Sigma S_T = S_T (1 + K_a / [H^+] + K_{a1} \cdot K_{a2} / [H^+]^2), \qquad (4)$$

where K_a, K_{a1} and K_{a2} are the coefficients of the acidic dissociation.

The following values have been found [15] for the factors in the Equations (2)-(4):

NDMR - $S_{298} = 1.86(\pm0.04) \times 10^{-3}$ mol/dm^3, $b = 18.4(\pm0.2)$,

$\qquad K_a = 3.35(\pm0.2) \times 10^{-4}$ mol/dm^3;

DNMR - $S_{298} = 9.1(\pm0.2) \times 10^{-4}$ mol/dm^3, $b = 18.4(\pm0.2)$,

$\qquad K_{a1} = 2.4(\pm0.1) \times 10^{-5}$ mol/dm^3,

$\qquad K_{a2} = 3.3(\pm0.3) \times 10^{-10}$ mol/dm^3.

Conclusions

1. Resorcinol series phenols, the main components of oil shale phenols, can be easily nitrosed. In an aqueous solution the interaction of H_2SO_4 and $NaNO_2$ with 2.5-dimethylresorcinol results in the precipitation of 4-nitroso-2.5-dimethylresorcinol, and with 5-methylresorcinol – of 2,4-dinitroso-5-methylresorcinol.

2. The yield of nitrosation reactions exceeds 90 % even at the equivalent quantity of the reagents. An excess of $NaNO_2$ decreases the yield of the reaction, particularly in the case of 2.5-dimethylresorcinol. An excess of H_2SO_4 does not affect the yield of the reaction noticeably.

3. Any elevation of the temperature over 10 °C should be avoided during the nitrosation to prevent the decomposition of the products, in particular in the case of 5-methylresorcinol.

4. The high thermal effect of the nitrosation reactions, 200(±9) kJ/mol for 5-methylresorcinol and 109(±5) kJ/mol for 2.5-dimethylresorcinol, make obvious the need for the cooling of the reaction mixture.

Acknowledgments

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