Alkali Catalyzed Phenol Formaldehyde Reaction – Part II

Formation of Dimethylol Phenols

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SUMMARY:

The kinetic study has been made of the sodium hydroxide-catalyzed interaction of o- and p-methylol phenols with formaldehyde to give dimethylol phenols. At 0.006 M NaOH and within less than 10% of the reaction, first order kinetic behaviour was obtained. The rate constant, at 80°C., for the formation of 2,4-dimethylol phenol from p-methylol phenol and formaldehyde, was found to be $1.17 \cdot 10^{-5} \text{ sec}^{-1}$ and the activation energy, 23.92 kcal/mole, whereas for formation of 2,6- and 2,4-dimethylol phenols from o-methylol phenol, the rate constants were respectively 0.55 and $1.11 \cdot 10^{-5} \text{ sec}^{-1}$, the corresponding activation energies being, 25.10 and 23.37 kcal/mole. In terms of these data and those present in Part I, the relative reactivities of the free ortho and para positions in phenol and substituted phenols are evaluated, and shown to be, unlike those reported by FREEMAN et al.⁶), consistent among themselves and with theoretical requirements.

ZUSAMMENFASSUNG:

Es wurde die Bildung von Dimethylolphenolen bei der Einwirkung von Formaldehyd auf o- und p-Methylolphenole in Gegenwart von Natriumhydroxyd als Katalysator kinetisch untersucht. In Gegenwart von 0,006 M NaOH und bei weniger als 10 % iger Reaktion zeigt sich das Verhalten einer Reaktion 1. Ordnung. Für die Bildung von 2,4-Dimethylolphenol aus p-Methylolphenol und Formaldehyd bei 80 °C beträgt die Geschwindigkeitskonstante $1.17 \cdot 10^{-5}$ sec⁻¹, die Aktivierungsenergie 23,92 kcal/Mol., für die Bildung der 2,6- und 2,4-Dimethylolphenole aus o-Methylolphenol dagegen sind die Geschwindigkeitskonstanten 0,55 bzw. $1,11 \cdot 10^{-5}$ sec⁻¹ und die Aktivierungsenergien 25,10 und 23,37 kcal/Mol. Aus diesen Daten und denen von Teil I werden die relativen Reaktivitäten der freien ortho- und para-Stellungen bei Phenol und bei substituierten Phenolen bestimmt, die, ungleich denen von FREEMAN und Mitarbeitern⁵), sowohl unter sich als auch mit den theoretischen Erfordernissen übereinstimmen.

Introduction

The kinetic study of the formation of o- and p-methylol phenols from phenol and formaldehyde in the presence of sodium hydroxide catalyst was presented in Part I. This paper deals with the further interaction of the two mono-methylol phenols with formaldehyde in the presence of sodium hydroxide catalyst to give 0,0'- and 0,p'-dimethylol phenols according to the equations:



Chromatographic Analysis

The reaction between the mono-methylol phenols and formaldehyde may lead to, besides the dimethylol phenols, condensation products such as dihydroxy dibenzyl ether and methylol dihydroxy diphenyl methanes. Since these latter compounds could not be separated by butanol-ammonia solvent used for mono-methylol phenols (cf. Part I), the single-phase three component solvent system developed by YEDDANA-PALLI et al.¹), consisting of benzene, water and acetic acid, was employed which by one dimensional development could satisfactorily separate the mono- and di-nuclear products. In this solvent, the R_f values of 2.4- and 2.6-dimethylol phenols were found to be quite close to those of 2.4.6-trimethylol phenol and p-methylol phenol respectively. Hence these latter compounds were used as standards in the quantitative estimation, by spot-weight method, of the former compounds, trial experiments confirming the validity of this procedure. The chromatographic technique was identical with that indicated in Part I.

Experimental

Materials

2,4,6-Trimethylol phenol was prepared according to the method of FREEMAN²) 2,4'and 4,4'-dihydroxy diphenyl methanes according to the procedure given by FINN and MUSTX³), and 2,2'-dihydroxy dibenzyl ether as suggested by ZIEGLER and LERCHER⁴).

¹) L. M. YEDDANAPALLI, A. K. KURIAKOSE, and V. V. GOPALAKRISHNA, Proceedings of the 45th Indian Science Congress, Part III (Abstracts) 1958, p. 162.

²) J. H. FREEMAN, J. Amer. chem. Soc. 74 (1952) 6257.

³) S. R. FINN and J. W. G. MUSTY, J. Soc. chem. Ind. [London] 69 (1950) 549.

⁴⁾ E. ZIEGLER and L. LERCHER, Ber. dtsch. chem. Ges. 74B (1941) 841.

p-Methylol Phenol and Formaldehyde

Equimolar concentrations of p-methylol phenol and formaldehyde, about 0.2 M, and 0.006 M NaOH, were chosen for the experiment in order to prevent the selfcondensation of the phenol alcohol to give dibenzyl ethers. Furthermore, the reaction was allowed to proceed to less than 10% formaldehyde consumption, so that the concentration of the reactive phenolic species, resulting from the methylol phenol and sodium hydroxide, 0.006 M, could be considered fairly constant during the limited extent of the reaction, and the reaction rate would be proportional only to the formaldehyde concentration. The analytical data obtained at 70 °C. are presented in Table 1 from which it is seen that there

Time [min.]	2,4-Dimethylol phenol [mole/l. · 10 ³]	% CH₂O bound in dialcohol	% CH2O consumed	k·10⁵ [sec ^{−1}] Dialcohol	k · 10 ⁵ [sec ⁻¹] CH ₂ O
50	2.56	1.29	1.30	0.42	0.42
100	5.01	2.50	2.50	0.42	0.42
150	7.63	3.81	3.79	0.43	0.43
200	10.32	5.15	5.19	0.44	0.45
250	12.80	6.39	6.54	0.44	0.45
300	15.40	7.69	7.84	0.44	0.45
			A	V = 0.43	

Table I. Kinetic data for p-methylol phenol and formaldehyde reaction

Concentration: p-Methylol phenol = 0.2000 mole/l.; Formaldehyde: 0.2004 mole/l.; Catalyst: 0.006 M NaOH; Temp.: 70°C.

is satisfactory agreement between the formaldehyde estimated volumetrically and that bound in the 2,4-dimethylol phenol, and also between the first order rate constants based on formaldehyde consumption and on the formation of the dimethylol phenol, the average values of the constants in the two cases being respectively, $0.44 \cdot 10^{-5}$ and $0.43 \cdot 10^{-5}$ sec⁻¹.

The first order rate constants under identical conditions at 80° C. were $1.19 \cdot 10^{-5}$ for formaldehyde and $1.17 \cdot 10^{-5}$ sec⁻¹ for the dimethylol phenol. The calculated apparent energy of activation was found to be 24.12 kcal/mole for the disappearance of formaldehyde and 23.92 kcal/mole for the formation of 2,4-dimethylol phenol.

o-Methylol Phenol and Formaldehyde

Here also, the concentrations of the two reactants were about 0.2 M, that of the catalyst 0.006 M NaOH and the extent of the reaction, limited to about 10% formaldehyde reacted, so as to maintain the conditions necessary for first order kinetics and avoid the formation of tri-methylol phenol. The experimental results are presented in Table II. The difference between the formaldehyde estimated directly and that calculated from the two dimethylol phenols does not exceed 5%, inspite of the small amounts involved of these dialcohols. The ratio between the molar amounts of 2,6- and 2,4-dimethylol phenols at different times of the reaction, given in column 4 of the Table, is fairly constant, the average value being 0.51, which suggests that the two compounds are being formed from o-methylol phenol and formaldehyde by two parallel reactions, Since under the experimental conditions, the concentration of the phenolic ion from o-methylol phenol and formaldehyde is practically constant, the two parallel reactions may each be regarded as of first order in formaldehyde.

Table II. Kinetic data for the reaction between o-methylol phenol and formaldehyde o-Methylol phenol: 0.2000 mole/l.; Formaldehyde: 0.2044 mole/l.; Catalyst: 0.006 M NaOH; Temp.: 70 °C.

Time [min.]	2,4-Dialcohol [mole/l.·10 ³]	2,6-Dialcohol [mole/l.·10 ³]	2,6-Dialcohol 2,4-Dialcohol	% CH ₂ O bound in products	% CH2O consumed	$f k \cdot 10^5 \ [sec^{-1}] \ CH_2O$
60	3.2	1.59	0.50	2.34	2.25	0.62
120	6.14	3.12	0.51	· 4.52	4.35	0.62
180	8.94	4.61	0.52	6.63	6.46	0.62
240	12.26	6.05	0.49	8.96	8.42	0.61
300	14.64	7.42	0.51	10.80	10.28	0.60
					A.V. =	= 0.61

A.V. = 0.61

By a procedure similar to that adopted in Part I for parallel reactions, the following expressions can be derived:

$$F = F_0 e^{-kt}; \quad M_1 = (kF_0/k)(1 - e^{-kt});$$
$$M_2 = (k_0F_0/k)(1 - e^{-kt})$$

where F_0 and F stand for initial concentration and concentration at time t of formaldehyde, and M_1 and M_2 for concentrations of 2,6- and 2,4-dimethylol phenols respectively. Since k is known from the last column of Tabel II, the plot of $(1 - e^{-kt})$ versus M_1 and M_2 is given in Fig. 1. From the slopes of the straight lines k_1 and k_2 are found to be $0.19 \cdot 10^{-5}$ and $0.42 \cdot 10^{-5} \sec^{-1}$. The sum of the two constants, viz., $0.61 \cdot 10^{-5}$ is in agreement with $0.61 \cdot 10^{-5} \sec^{-1}$ for k based on formaldehyde.



Fig. 1. Plot for parallel first-order reactions Saligenin, 0.2000 M; Formaldehyde, 0.2044 M; NaOH, 0.006 M; Temp. 70 °C. (A) 2,4-Dimethylol phenol; (B) 2,6-Dimethylol phenol

The same reaction conducted at 80 °C. gave the following rate constants: $k_1 = 0.55 \cdot 10^{-5}$, $k_2 = 1.11 \cdot 10^{-5}$, and $k = 1.82 \cdot 10^{-5} \text{ sec}^{-1}$. The apparent energies of activation calculated on the basis of the above rate constants at 70 and 80 °C. are 25.1 for 2,6-dimethylol phenol, 23.37 for 2,4-dimethylol phenol and 26.1 kcal/mole for the overall reaction in terms of formaldehyde reacted.

It is to be noted that the E for formation of 2,4-dimethylol phenol obtained here, viz., 23.37 kcal/mole, compares well with the value of 23.92 kcal/mole for the same compound derived from p-methylol phenol.

Discussion

In order to obtain a quantitative idea of the relative reactivities of the free positions in phenol and in mono-methylol phenols, it is of interest to compare the rate constants, at identical concentrations of reactants, about 0.2 M each of phenol or monomethylol phenol and formaldehyde, and catalyst, 0.006 M NaOH at 80 °C., for the formation of monomethylol phenols from phenol, and dimethylol phenols from mono-methylol phenols. They are listed in Table III in which column 3 gives the number of reactive positions of the phenolic compound in question, column 5, the apparent energy of activation for the particular reactive position, and the last column, the second order rate constants deduced by FREE-MAN⁵) from his analysis of the reaction products from phenol and formaldehyde at 30 °C. Since there are in phenol and in p-methylol phenol two reactive ortho positions, the rate constants for the production of o-methylol phenol and of 2,4-dimethylol phenol have been divided by 2 to get the reactivity of each ortho position.

Compound	Position	No. of positions available	Positional rate constant · 10 ⁵	Activation Energy kcals/mole	
Phenol	ortho	2	0.97	19.77	
Phenol	para	1	1.94	19.77	
Saligenin	ortho	1	0.55	25.10	
Saligenin	para	1.	1.11	23.37	
p-Methyl phenol .	ortho	2	0.59	23.95	

Table III. Relative reactivities of the free positions in phenol and mono-methylol phenols, and the corresponding activation energies.

From column, 4, it is evident that the para position in phenol is twice as reactive as the ortho position, and the same relative reactivity holds good for the para and ortho positions in o-methylol phenol. The reactivity of the ortho position on p-methylol phenol, though of the same order of magnitude as in o-methylol phenol, is slightly greater, 0.59

⁵) J. H. FREEMAN and C. W. LEWIS, J. Amer. chem. Soc. 76 (1954) 2080.

compared to 0.55, which difference is paralleled by a corresponding change in activation energy, namely, 23.95 and 25.10 kcal/mole respectively. This difference in the reactivities and in activation energies of the two ortho positions may very well be due to the steric hindrance caused by the presence of the methylol group in the case of o-methylol phenol and its absence in p-methylol phenol.

The above regularities are not observed in FREEMAN and LEWIS's⁵) data according to which the para position in phenol is only a little more reactive than the ortho position, 6.20 compared to 5.25, whereas the reverse seems to hold good for the same positions in o-methylol phenol, the least reactive being the ortho position in p-methylol phenol. It is also surprising that the presence of a methylol group in phenol, as in saligenin, activates both the remaining ortho and para positions, rendering them more reactive than in phenol, and the same methylol group in p-methylol phenol deactivates the two free ortho positions.

According to the data obtained in this investigation, the methylol group either in ortho or para position in phenol deactivates the remaining positions, ortho as well as para, as can be seen from the values in column 4 of Table III. This seems quite reasonable, since the methylol group is essentially electron-attracting, so that the electron density on the phenolic oxygen atom capable of mesomeric shift is thereby reduced, and the negative charge density both in ortho and para positions of the monomethylol phenols becomes less than in the case of phenol, with a consequent decrease in the reactivities of these positions. If this is so, then an electron repelling group such as a methyl group would be expected to increase the reactivity of the ortho and para positions in phenol compared to those of phenol itself. Actually this has been found to be true in the case of o- and p-cresols, the work on which is still in progress and will be reported later on.

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