JOURNAL OF CATALYSIS 63, 433–437 (1980)

Reactions of Phenols and Alcohols over Thoria

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Received October 2, 1979

Alkylphenols when dehydrated over thoria at 500°C gave diaryl ethers as main products. In addition to diaryl ethers, minor products were also formed, which were identified as xanthene and substituted xanthenes. Xanthenes were also formed in the reactions of phenol with alcohols over thoria. A mechanism is proposed for the formation of xanthenes.

INTRODUCTION

Thoria has the ability to catalyze the dehydration of phenols to diaryl ethers (*1*, *2*), a reaction which does not take place over the more familiar dehydration catalyst, alumina (*3*). Dehydration of alcohols to dialkyl ethers, on the other hand, does not take place over thoria (*1*). Mixed ethers from alcohols and phenols are formed on both catalysts. During the reactions of alkylphenols over thoria, xanthenes are formed as by-products. These peculiarities of thoria prompted us to investigate the reactions of phenols and alcohols over thoria. The present study deals with an investigation of the nature and mode of formation of xanthenes from cresols over thoria.

EXPERIMENTAL

Catalysts

The thoria catalyst was prepared by the precipitation method from thorium nitrate as reported by Brey *et al.* (*4*). The precipitation was carried out by the addition of 25% ammonia to a 0.3 *M* solution of thorium nitrate. The precipitated hydroxide was filtered, washed, and dried for approximately 24 hr. The results reported in Table 1 were obtained on this catalyst. Thoria catalysts were also prepared by the thermal decomposition of thorium nitrate and thorium oxalate in air at 600°C for 6–8 hr. Results of reactions on these catalysts were comparable qualitatively with those reported here.

Procedure and Analyses

The reactions were carried out in a flow-type reactor. The reactants were introduced into the reactor at the required flow rate using a syringe pump. The products were analyzed by gas chromatography using an SE-30 column. In almost all the reactions, the xanthenes were isolated by preparative gas chromatography. In the case of *p*-cresol and *m*-cresol, the dimethylxanthenes were separated from other products by fractional crystallisation. These xanthenes were identified by their melting

TABLE 1

Reaction of Cresols over Thoria[a]

Reactant	Percentage conversion[b]	Product distribution		
		Ditolyl ether	Xanthene	Unaccounted[c,d]
p-Cresol	34	25	2[e]	7
m-Cresol	23	18	1[f]	4
o-Cresol	20	12	traces[g]	8

[a] Temp. 500°C; flow rate, 18 ml/hr; catalyst, thoria from the hydroxide, 5 g; no carrier gas.

[b] Based on recovered cresol.

[c] Mainly due to coke formation.

[d] Phenol and 2,4-dimethylphenol in the reaction of *p*-cresol, phenol in the reaction of *m*-cresol and phenol, and 2,6-dimethylphenol and phenyl *o*-tolyl ether in the reaction of *o*-cresol were formed in trace quantities.

[e] 2,7-Dimethylxanthene.

[f] 3,6-Dimethylxanthene.

[g] Mixture of xanthene, 4-methylxanthene, and 4,5-dimethylxanthene.

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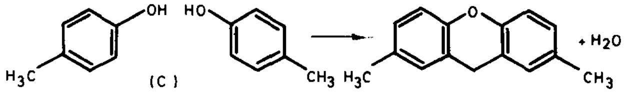
0021-9517/80/060433-05$02.00/0

points as well as by elemental analysis, ir, NMR, and mass spectral analysis. All xanthenes gave a characteristic green fluorescence in sulfuric acid.

RESULTS AND DISCUSSION

Results of the reaction of the three cresols over thoria prepared by precipitation method are given in Table 1. Diaryl ethers are the major products. The reactions are accompanied by considerable coke formation. In all three cases several by-products were detected. As early as 1910, Sabatier and Mailhe (*5*) had reported the formation of diphenylene oxides in trace quantities, along with diaryl ethers during the catalytic decomposition of phenols and cresols over thoria. However, in a study reported in 1933, Sengoku (*6*) obtained xanthene and methylxanthenes during the distillation of cresols with thoria and had claimed that the by-products reported by Sabatier and Mailhe had been wrongly identified as diphenylene oxides. In 1966, Knözinger and Kudla (*7*), in their study of the mechanism of ether formation, detected the by-products in the reaction of cresols over thoria and assigned them the diphenylene oxide structure, after Sabatier. In view of these conflicting reports, in the present study a rigorous attempt was made to identify the by-products. The reaction product was separated into phenolic and neutral fractions by alkali extraction. The phenolic fraction was analyzed by gas chromatography and the components were identified by comparison with authentic samples. In all cases, in addition to the unreacted starting material, the only phenolic products identified were those corresponding to transmethylation, namely, phenol and xylenol in trace quantities. The major component in the neutral fraction was the expected diaryl ether. This was subjected directly to gas chromatographic separation. The components, in the case of *o*-cresol reaction, were isolated by preparative gas chromatography and identified by spectral analysis as xanthene, 4-methylxanthene, and 4,5-dimethylxanthene. In the case of *m*- and *p*-cresol, the xanthenes were separated from diaryl ethers by fractional crystallization. NMR and mass spectral analysis showed that these were 3,6-dimethylxanthene and 2,7-dimethylxanthene, respectively. When the mother liquor was subjected to gas chromatogrpahy, no peaks other than those corresponding to diaryl ethers were noticed. It is of interest to note that there are reports in the literature referring to the formation of such dimethylxanthenes during the thermal decomposition of aluminum cresylates (*8*, *9*). The various xanthenes obtained in the present study along with their NMR characteristics are listed in Table 2.

In order to get 2,7-dimethylxanthene (**I**) from *p*-cresol, an extra carbon is required (Eq. (1)).

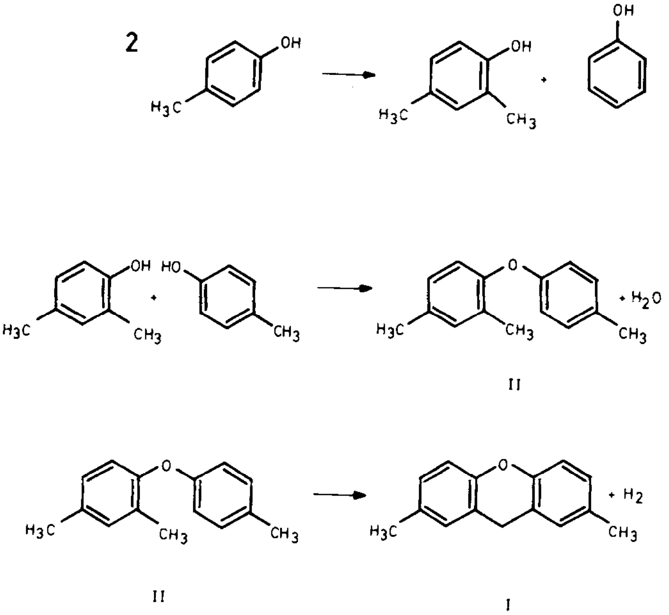


I

(1)

This has to come from a third molecule of *p*-cresol, the following sequence of reactions being envisaged for the purpose (Scheme 1).

Phenol and 2,4-xylenol were detected in the reaction products. However, 2,4,4′-trimethyldiphenyl ether (**II**) was not detected. When phenyl *o*-tolyl ether was passed over



SCHEME 1

TABLE 2

By-products in the Reactions of Phenols and Alcohols over Thoria

Reactant(s)	Xanthene formed	mp (°C)	NMR (δ)		Mass spectrum (m/z)
o-Cresol	xanthene	100	$Ar-CH_2-Ar$	4.04 (s) 2H	182 (74.8%) (M^+)
		(100.5)[a]	H–Ar	7.06 (m) 8H	181 (100%)
	4-methylxanthene	108–110	CH_3-Ar	2.2 (s) 3H	
			$Ar-CH_2-Ar$	3.98 (s) 2H	
			H–Ar	6.9–7.2 (m) 7H	
	4,5-dimethylxanthene	124–125	CH_3-Ar	2.14 (s) 6H	210 (60.4%) (M^+)
			$Ar-CH_2-Ar$	3.96 (s) 2H	209 (100%)
			H–Ar	6.8–7.1 (m) 6H	
m-Cresol	3,6-dimethylxanthene	200	CH_3-Ar	2.36 (s) 6H	210 (58.3%) (M^+)
		(201)[b]	$Ar-CH_2-Ar$	3.96 (s) 2H	209 (100%)
			H–Ar	6.8–7.0 (m) 6H	
p-Cresol	2,7-dimethylxanthene (I)	166	CH_3-Ar	2.28 (s) 6H	210 (76%) (M^+)
		(165.5–167)[c]	$Ar-CH_2-Ar$	3.96 (s) 2H	209 (100%)
			H–Ar	6.88 (s) 6H	
Phenol + ethanol	9-methylxanthene (III)	d	$-CH_3$	1.45 (d) 3H	
			$-CH<$	4.05 (q) 1H	
			H–Ar	7.05 (m) 8H	
Phenol + 1-propanol	9-ethylxanthene (IV)	d	$-CH_3$	0.76 (t) 3H	
			$-CH_2-$	1.76 (m) 2H	
			$-CH<$	3.94 (t) 1H	
			H–Ar	7.08 (m) 8H	
Phenol + 2-propanol	9,9-dimethylxanthene (V)	d	$-CH_3$	1.4 (s) 6H	
			H–Ar	7.12 (m) 8H	

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[a] CRC Handbook of Chemistry and Physics (R. C. Weast, Ed.), 47th ed., p. C598, Chem. Rubber Co., Cleveland.

[b] Rodd, E. H., "Chemistry of Carbon Compounds," Vol. 4, p. 968. Elsevier, Amsterdam, 1954.

[c] Carpenter, A. T., and Hunter, R. F., *J. Chem. Soc.*, 2731 (1954).

[d] Liquid sample, collected by preparative gas chromatography.

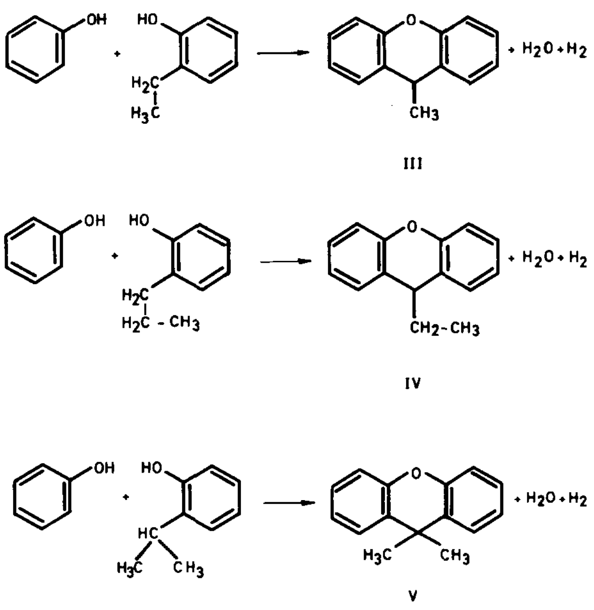
thoria under the reaction conditions, xanthene was formed. It is reasonable to assume that an *o*-methyldiphenyl ether is the key intermediate for the formation of xanthenes via a dehydrocyclization step.

An alternative route for the formation of this intermediate is the transmethylation of the diaryl ether by a cresol molecule. However, the reaction of diphenyl ether and *p*-cresol over thoria gave only small quantities of phenol, phenyl *p*-tolyl ether, but no *o*-methyldiphenyl ether corresponding to transmethylation. Hence, alkylation of diaryl ether appears unlikely.

From the foregoing considerations, it was expected that the reaction of alcohols with phenol over thoria should lead to xanthenes. A solution of phenol in methanol, when passed over thoria at 500°C, gave xanthene in small quantities in addition to diphenyl ether, anisole, and *o*-cresol. Use of ethanol, 1-propanol, and 2-propanol in place of methanol gave 9-methylxanthene (III), 9-ethylxanthene (IV), and 9,9-dimethylxanthene (V). These substituted xanthenes evidently result from the interaction between the initially formed *o*-alkylphenol with another molecule of phenol (Scheme 2).

The formation of *o*-alkylphenols, in the alkylation of phenol by alcohols as well as in the transmethylation of cresols, can be visualized as due to the chemisorption of two molecules on adjacent active sites of the catalyst, the *ortho* positions being closer to the catalyst surface than the *meta* and *para* positions. Transalkylation is a property of acidic catalysts. Though thoria is generally described as a basic catalyst it has measurable acidity (unpublished studies in our laboratory) and transmethylation catalyzed by thoria is not unexpected. The dehydrocyclization following dehydration at 500°C is quite likely considering the fact that thoria is a dehydrogenating catalyst (*4*).

The formation of xanthenes does not seem to have any direct bearing on the ether formation mechanism. It arises from a combination of the ability of thoria to catalyze *ortho*-alkylation of phenol (either by direct alkylation by alcohols or by transalkylation) and the ability to cause dehydrocyclization.



SCHEME 2

ACKNOWLEDGMENT

Grateful acknowledgement is made to the University Grants Commission, New Delhi for the award of a Teacher Fellowship to one of us (S.K.).

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