

Reactions of Phenols and Alcohols over Thoria: Mechanism of Ether Formation

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The dehydration of phenols and alkylation of phenols by alcohols over thoria were studied at 400–500°C and atmospheric pressure. Phenol and cresols, when dehydrated gave diaryl ethers as main products. With *para*-substituted phenols such as *p*-methoxy, *p*-*t*-butyl, *p*-chloro, and *p*-nitrophenol no ether formation was noticed. All the reactions were accompanied by considerable amount of coke formation. Alkylation of phenols by alcohols gave a mixture of O- and C-alkylated products under the same reaction conditions. O-alkylation and C-alkylation are parallel reactions. The mechanistic aspects of the reactions are discussed.

INTRODUCTION

Thoria is known to catalyze the dehydration of alcohols to form olefins and phenols to ethers (1, 2). In recent years, it has been shown to be a selective catalyst for the conversion of 2-alkanols to 1-alkenes (3, 4). Thoria does not catalyze the formation of dialkyl ethers even from simple alcohols (1). However, thoria-catalyzed formation of aralkyl ethers by alkylation of phenol with alcohols such as methanol (5) and ethanol (6) is known. Recently we reported the formation of xanthenes (dibenzo-1, 4-pyrans) (7) in trace quantities in the alkylation of phenol by alcohols over thoria. Considerable work has been done to elucidate the mechanism of olefin formation over thoria (8, 9). But the mechanism of ether formation was not studied in detail. The present paper reports a study of the thoria-catalyzed dehydration of phenols and alkylation of phenol by alcohols from a mechanistic point of view.

EXPERIMENTAL

Catalysts

Thoria samples were prepared by three different methods, namely, (i) thermal de-

composition of thorium nitrate in air at 600°C for 6 hr, (ii) calcination of thorium hydroxide (10), and (iii) thermal decomposition of thorium oxalate. The results on all the three catalyst samples were qualitatively similar. The results reported here were obtained using the catalyst prepared by the third method. To an aqueous solution of thorium nitrate (0.3 M), a saturated solution of oxalic acid was added in excess and the precipitated thorium oxalate was filtered, washed, dried, and calcined in a muffle furnace at 600°C for 6–8 hr.

Reagents

Alcohols and phenols used were of analytical grade. *o*-Ethylphenol and xylenols used for comparison in identifying products in the gas chromatographic analyses were from a phenol kit supplied by Polyscience Corporation (Evanston, Ill.). Aralkyl ethers (11) and diaryl ethers (12) used for comparison were prepared according to known procedures.

Apparatus and Procedure

The catalytic flow-reactor and the general procedures have been described previously (13). All the runs were at atmospheric pressure without added carrier gas. Products were analyzed by gas chromatography using a SE-30 column (20% on 60–80

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mesh chromosorb-W, acid-washed). Identifications were made by comparison of retention times with those of authentic samples.

Stereochemical Study

Optically active D(-) 2-butanol was prepared by the hydroboration of optically active D(+) α -pinene as reported by Brown and Zweifel (14). A 3:7 molar mixture of phenol and D(-) 2-butanol ($[\alpha]_D^{30} = -6.9^\circ$, pure liquid) was passed over the catalyst at 450°C , at a flow rate of 18 ml/hr, and, after recycling, the product mixture was subjected to preparative gas chromatography. 2-Butyl phenyl ether and unreacted 2-butanol were collected and their optical activities were found to be $+4^\circ$ and -4.8° , respectively.

RESULTS AND DISCUSSION

Results of reaction between mixtures of methanol and phenol of different compositions over thoria at 500°C are shown in Fig. 1. The main products were anisole (by O-alkylation), *o*-cresol (by C-alkylation selectively at *ortho* position) and diphenyl ether (by dehydration of phenol). Contrary to previous reports, dimethyl ether was formed in small quantities when methanol alone was passed over thoria. Yield of dimethyl ether was sharply suppressed by

the addition of phenol and at 0.1 mole fraction of phenol, no dimethyl ether could be detected. It can be seen from Fig. 1 that anisole formation is maximum at a 3:7 molar ratio of phenol and methanol. Similarly the formation of *o*-cresol shows a maximum that corresponds to a composition of 5:5 molar mixture.

To determine whether these reactions occurred by the interaction of adsorbed phenol molecules with the adsorbed alcohol molecules, the effect of an inert diluent, namely, benzene on the rate of reaction of a 3:7 molar mixture of phenol and methanol was studied since this composition corresponded to the maximum formation of anisole on the surface. The results are given in Fig. 2. It can be seen that at low benzene content, the rate of formation of anisole reaches a maximum and remains independent of benzene concentration. This region must correspond to partial pressures of phenol and methanol at which they together saturate all the adsorption sites. For a series of reactions during the duration of which the activity of the catalyst remains constant, the shape of the curve in Fig. 2 is reproducible. This condition, namely, constant activity of catalyst during a series of reactions, was verified by repeating the runs representing the different points in the curve at random. The activity of a particu-

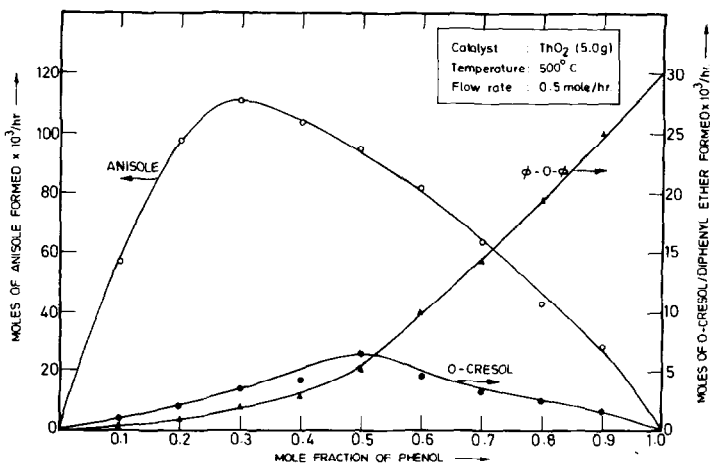


FIG. 1. Reaction of phenol with methanol at different mole fractions.

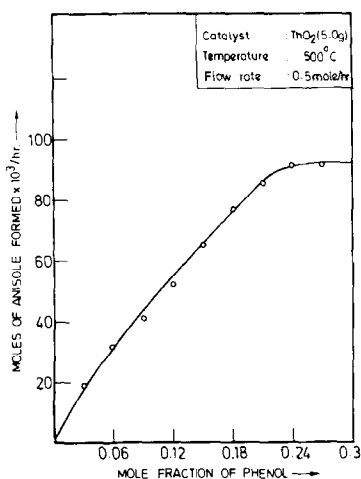


FIG. 2. Reaction of 3 : 7 molar mixture of phenol and methanol with benzene as diluent.

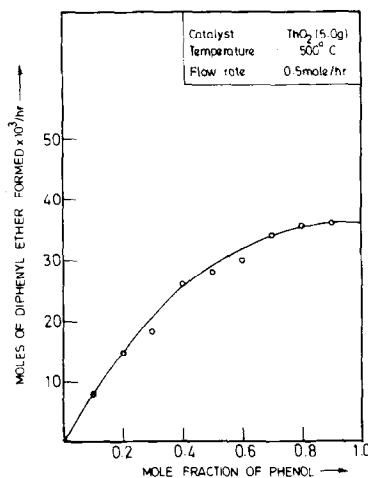


FIG. 3. Dehydration of phenol with benzene as diluent.

lar sample of catalyst did change on prolonged use and regeneration. The horizontal portion of the curve could not have been obtained if either one of the reactants was reacting from the gas phase. A similar trend was observed for the dehydration of phenol alone on the surface (Fig. 3) indicating that the dehydration of phenol as well as the alkylation of it follows a Langmuir-Hinshelwood mechanism.

The results of the reaction between phenol and alcohols are listed in Table 1. Alkylation takes place both at oxygen (O-alkylation) and selectively at *ortho* carbon in preference to *para* (C-alkylation). Alkylation decreases in the series methanol, ethanol, isopropyl alcohol, and *t*-butyl alcohol. Alkyl phenyl ethers were found to undergo thermal as well as catalytic decomposition at the reaction temperature (Table 2). In the

TABLE 1

Alkylation of Phenol by Alcohols^a

Sl number	Alcohol ^b	Percentage conversion ^c	Production distribution ^d			Percentage Olefin ^e
			Alkylphenyl ether	<i>o</i> -Alkylphenol	Diphenyl ether	
1.	Methanol	53	86	10	4	—
2.	Ethanol	37	78	14	8	—
3.	1-Propanol	36	72	16	12	32
4.	2-Propanol	20	45	40	15	61
5.	1-Butanol	16	56	19	25	31
6.	Isobutyl alcohol	13	70	15	15	37
7.	2-Butanol	15	40	40	20	49
8.	<i>t</i> -Butyl alcohol	5	—	60	40	66

^a Temperature, 500°C; flow rate, 18 ml/hr; thoria from oxalate, 5 g; no carrier gas.

^b Phenol : alcohol molar ratio 3 : 7.

^c Percentage conversion based on phenol.

^d In addition to the above products, xanthene and substituted xanthenes were identified in the reactions of methanol, ethanol, 1-propanol, and 2-propanol. In almost all the reactions dialkylphenols were noticed in traces.

^e Percentage conversion based on alcohol.

TABLE 2
Decomposition of Butyl Phenyl Ethers^a

Sl number	Reactant	Catalytic				Thermal			
		Percentage conversion	Phenol	Butene	Unaccounted	Percentage conversion	Phenol	Butene	Unaccounted
1.	<i>n</i> -Butyl phenyl ether	30	15	11	4	20	9	7	4
2.	2-Butyl phenyl ether	55	30	20	5	36	20	13	3
3.	<i>t</i> -Butyl phenyl ether	84	46	32	6	58	34	22	2

^a Temperature, 500°C; flow rate, 18 ml/hr; thoria from oxalate, 5 g; no carrier gas.

series 1-butyl, 2-butyl, and *t*-butyl phenyl ether, the proneness to decomposition increased in that order. The data in Table 1 also seem to reflect this tendency of alkyl phenyl ethers to decompose under the reaction conditions. Steric factors may also contribute to the decrease in reactivity in the series primary alcohol > secondary alcohol > tertiary alcohol.

Phenol and cresols (*o*-, *m*-, and *p*-), when dehydrated alone over thoria at 500°C, gave symmetrical diaryl ethers while other substituted phenols such as *p-t*-butyl, *p*-methoxy, *p*-chloro, and *p*-nitrophenol underwent much coking and no symmetrical diaryl ether was noticed. Cresols, in addition to ditolyl ethers which were the main products, gave xanthene (dibenzo-1,4-pyran) and substituted xanthenes as minor products (7). Reactions of phenol with cresols gave phenyl tolyl ethers in addition to diphenyl and ditolyl ethers. The results of the reactions are given in Table 3. The nonformation of ditolyl ether in the reaction of phenol and *o*-cresol must be due to steric factors. The formation of phenyl tolyl ether is also less when compared to that of diphenyl ether in the reaction of phenol and *o*-cresol. On the other hand, in the case of *p*-cresol and *m*-cresol more phenyl tolyl ether is formed than diphenyl ether. In the mixed dehydration of phenol with the above mentioned *p*-substituted phenols, only *p-t*-butylphenol and *p*-methoxyphenol gave ethers (4-*t*-butyldiphenyl ether and 4-methoxydiphenyl ether, respectively) in addition to diphenyl ether, while with *p*-chlorophenol and *p*-nitrophenol no mixed ether was found.

O-Alkylation and *C*-Alkylation

C-Alkylation can take place either by a direct route or by the isomerization of the *O*-alkylation product. To decide between these two routes, anisole and phenetole were passed over the catalyst at 500°C separately. No isomerized products (cresols or ethylphenols) were noticed. It can be concluded that *C*-alkylation is a direct

TABLE 3
Dehydration of Substituted Phenols in Presence of Phenol^a

Sl number	Substituted phenol	Reactants (g)		Product distribution (g)					Unac-counted ^b
		Phenol	Substituted phenol	Phenol (unreacted)	Substituted phenol (unreacted)	Diphenyl ether	Monosubstituted diphenyl ether	Disubstituted diphenyl ether	
1.	<i>o</i> -Cresol	1.88	2.12	1.59	1.91	0.10	0.07	—	0.33
2.	<i>m</i> -Cresol	1.88	2.12	1.40	1.56	0.16	0.25	0.08	0.55
3.	<i>p</i> -Cresol	1.88	2.12	1.29	1.40	0.20	0.32	0.12	0.67
4.	<i>p</i> -Methoxyphenol	1.88	2.48	1.37	2.00	0.20	0.20	—	0.59 ^c
5.	<i>p</i> - <i>t</i> -Butylphenol	1.88	3.00	1.24 ^d	2.34	0.24	0.28	—	0.78 ^e
6.	<i>p</i> -Chlorophenol	1.88	2.56	1.31	2.04	0.30	—	—	0.79
7.	<i>p</i> -Nitrophenol	1.88	2.78	1.41 ^d	2.25	0.24	—	—	0.76

^a Temperature, 500°C; flow rate, 18 ml/hr; thoria from oxalate, 5 g; no carrier gas.

^b Mainly due to coke formation.

^c Includes traces of hydroquinone.

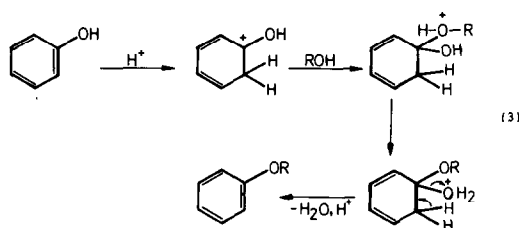
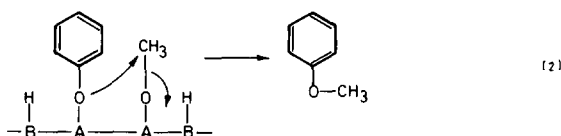
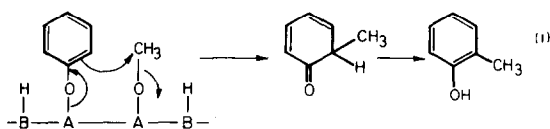
^d Includes phenol formed as one of the products.

^e Includes 0.14 g of butene gas collected.

process and that O-alkylation and C-alkylation are parallel reactions. It may be recalled that this is in contrast to the behavior of alumina, on which alkyl phenyl ethers undergo isomerization to alkylphenols (13, 15).

The selectivity of C-alkylation at the *ortho* position may be best explained by assuming a dissociative adsorption of phenol in the form of phenoxide at the catalyst surface and the proximity of the adsorbed

alcohol fragment to the *ortho* position of the surface phenoxide. Surface alkoxides in the adsorption of alcohols on thoria have been demonstrated (9). The *ortho* positions are closer to the catalyst surface than the *meta* and *para* positions and this argument has been used to explain the *ortho* directing effect of alumina (13, 16). Equations (1) and (2) represent C-alkylation and O-alkylation respectively. A and B represent acidic and basic sites on the catalyst surface.



O-Alkylation can be considered as a nucleophilic displacement by the phenoxide at the positively polarized α -carbon atom of the alcohol, analogous to the mechanism proposed for ether formation from alcohols over alumina (17).

Isomerization of the alkyl group was observed in the case of C-alkylation alone over alumina (13) whereas no such isomerization was noticed either in O-alkylation or C-alkylation over thoria. For example, isobutyl alcohol gave isobutyl ether and *o*-isobutylphenol; no *t*-butyl derivatives were observed. The absence of skeletal isomerization suggests the absence of

cationic intermediates in the reaction and points to a concerted nucleophilic displacement for both O-alkylation and C-alkylation.

For the acid-catalyzed alkylation of phenol by alcohols, a mechanism involving initial protonation of the phenol nucleus (Eq. (3)) had been proposed (18). Protonation of the naphthol nucleus had been shown for the reaction between 2-naphthol and methanol (19) and 2-naphthol and thiols (20).

Our results, discussed below on the alkylation of phenol by the chiral alcohol, namely, (-) 2-butanol show that this route,

if it operates for the reaction on thoria, is of minor significance and the major mechanism for aralkyl ether formation involves nucleophilic displacement by phenoxide on the alcohol (Eq. (2)).

The recovered (–) 2-butanol, in the reaction of phenol with (–) 2-butanol over thoria was found to have an optical activity of $[\alpha]_D^{30} = -4.8^\circ$ (5% in ethanol) as compared to -6.9° (pure liquid) for the sample of alcohol used. This showed that the alcohol was partially racemized under the experimental conditions. The 2-butyl phenyl ether formed was found to be dextro-rotatory $[\alpha]_D^{30} = +4^\circ$, 5% in ethanol). Since (+) 2-butanol and (+) 2-butyl phenyl ether are known to have same configurations (21), the positive sign of rotation of 2-butyl phenyl ether formed in the reaction shows that the reaction has proceeded with at least a partial inversion of configuration and thus points to a nucleophilic attack by the phenoxide on 2-butanol. Partial racemization of 2-butanol itself under the reaction conditions makes it impossible to say whether the reaction takes place solely through this pathway. A contribution by the alternative pathway represented by Eq. (3) cannot be ruled out. Studies made by us with sulfur compounds (unpublished results) have shown that reaction of phenol with *n*-butyl mercaptan gave butyl phenyl sulfide and that of thiophenol with methanol gave anisole in small yields. The formation of these products must involve an aryl-oxygen-sulfur cleavage process. A mechanism similar to Eq. (3) (cf. Eq. (5a) and (5b)) may be operating in these reactions.

Mechanism of the Formation of Diaryl Ether

The dehydration of phenols, if similar to the formation of ethers over alumina (17), should involve a nucleophilic displacement by a phenoxide ion on an aromatic nucleus. The role of thoria in activating the phenol nucleus for nucleophilic attack has not been satisfactorily explained.

Keeping in view the basic nature of thoria, an attractive possibility was that phenol could decompose on the catalyst to yield benzyne and water and the former can interact with another molecule of phenol to give diphenyl ether. However, our studies with cresols did not substantiate this mechanism. For example, in the dehydration of *p*-cresol, only di-*p*-tolyl ether was obtained while no *m*-tolyl *p*-tolyl ether was noticed.

The salient features of the formation of diaryl ethers are the following:

(i) Diaryl ethers are not formed if strongly or moderately electron-releasing (e.g., *p*-OCH₃, *p*-, *t*-butyl) or electron-withdrawing (e.g., *p*-NO₂, *p*-Cl) groups are present.

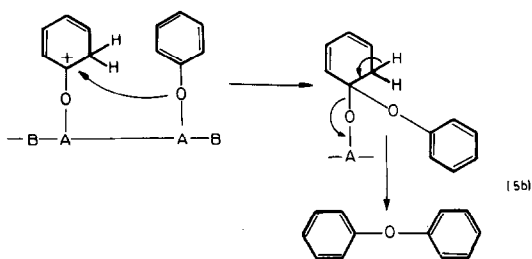
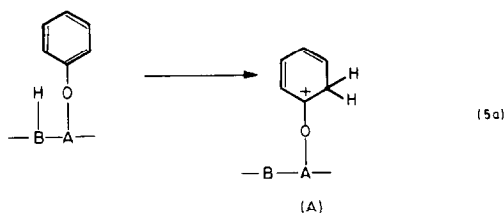
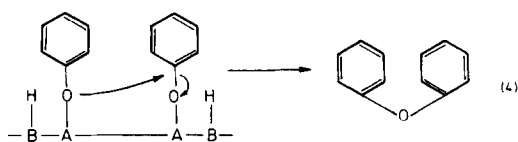
(ii) Cresols form diaryl ethers, i.e., weakly electron-releasing methyl group does not prevent the formation of diaryl ether.

(iii) Mixed ether between phenol and substituted phenol was formed only when the substituent was electron-releasing (*p*-OCH₃, *p*-, *t*-butyl, *o*-, *m*-, and *p*-CH₃).

Two mechanisms can be considered for the formation of diaryl ether. The first involves a direct nucleophilic displacement by a phenoxide species on another adsorbed phenol molecule as represented in Eq. (4).

The second involves a protonation of the dissociatively adsorbed phenol to give a positively charged adsorbed intermediate (A) followed by a nucleophilic attack by a phenoxide on this as in Eqs. (5a) and (5b).

This mechanism (Eq. (5)) is analogous to the protonation mechanism for aralkyl ether formation (Eq. (3)). The possibility of the formation of an intermediate of the type (A) is maximum when the ring bears electron-releasing groups. When the substituent is strongly electron-releasing all the adsorbed phenol molecules may have structure (A) so that the species necessary for the nucleophilic attack in step (Eq. (5b)) will not be available, accounting for the absence of symmetrical ethers from such phenols. The adsorbed species from cresols



and unsubstituted phenol may consist of both (A) and the parent phenoxide species. This may account for the formation of symmetrical ether from phenol and cresols and mixed ether from phenol and substituted phenols containing electron-releasing substituents. In the latter situation phenol supplies the nucleophile, phenoxide, and the substituted phenol supplies the positive species (A). With phenols containing electron-withdrawing substituents, species (A) is impossible and hence no ether is formed. Since the phenoxide derived from such a phenol will be highly unreactive, mixed ether by the nucleophilic attack of such a phenoxide on the positive species from another phenol molecule is also unlikely accounting for the fact that mixtures of *p*-chlorophenol or *p*-nitrophenol with phenol did not yield the mixed ether.

If direct interaction between two adsorbed phenoxides as in Eq. (4) were involved, mixed ether formation should have been quite facile between phenol and sub-

stituted phenols containing electron-withdrawing substituents since the latter are expected to be prone to nucleophilic displacement.

Thus our observations suggest that surface phenoxide arising from dissociative adsorption of phenol on thoria undergoes protonation to yield a positively charged species which is susceptible to nucleophilic attack by another phenoxide species. Thoria has only weak protonic acidity. Hence, if a protonation of the type visualized were to take place, it cannot be due to the acidity of the catalyst. It could be that the dissociatively adsorbed species undergoes a rearrangement to the protonated species as represented in Eq. (5a). The adsorbed phenoxide ion will be highly prone to such a protonation since the reaction involved is an electrophilic addition to an activated benzene ring. Why such a process should take place on thoria, but not on alumina, is a question for which this study has not provided any answer.

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