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Mechanism of the *meta*-Alkylation of Phenol on Condensed Phosphoric Acid-Kieselguhr

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The alkylation of phenol to *meta* position takes place on condensed phosphoric acid-kieselguhr catalysts with C_2—C_4 olefins or C_1—C_4 alcohols as alkylating reagents.

In our experiments, the yield of the *meta* isomer was 40%. From the distribution of the isomers of the compound, we deduced that this alkylation reaction takes place *via* phenylether and *ortho* alkylphenol consecutively. The mechanism of the reaction was investigated in detail, using radiogaschromatography; the ratio of the intramolecular rearrangement of alkyl group to the intermolecular one was evaluated. Intra- and intermolecular rearrangements of phenylether to *ortho* alkylphenols occured in the same extent. On the other hand, for the isomerization of *ortho* alkylphenol to *meta* and *para* position, the intermolecular reaction was estimated to be only 20%.

When the number of carbons of the alkyl group increased, the ratio increased. The mechanism of the alkylation is then discussed on the basis of the infrared spectra of phenol and methanol adsorbed on the catalyst at 450°.

Introduction

Alkylphenols are used in drugs, insecticides, plastics and so forth. In particular, *meta* alkylphenols have more interesting properties than the *ortho* and *para* isomers.

To synthesize *meta* alkylphenols, multiple steps have so far been adopted.[2] The present authors found that phenol is alkylated to *meta* position on a condensed phosphoric acid-kieselguhr through one step using C_2—C_4 olefins or C_1—C_4 alcohols as alkylating reagents at temperatures ranging from 250° to 450°.[3] For example, the yield on *m*-cresol was 40% of the isomers formed when methanol was used as an alkylating reagent.

An important information concerning the reaction process has been obtained from the dynamical behavior of alkyl groups during the rearrangement. For instance, Ryan and O'Connor[4] reported the thermal rearrangement of phenyl allylether as an intramolecular reaction using 3-phenoxy-1-propene-1-^{14}C as a tracer. Furuyama[5] proved the Henkel reaction to be intermolecular one, using benzoic acid-1-^{14}C and benzoic acid-7-^{14}C. But the process of the alkylation of phenol to the *meta* position was not clear.

In this report, the rearrangement of phenylethers and the isomerization of *ortho* alkylphenols were traced with phenol-^{14}C using the radiogaschromatographic technique. The adsorbed state of phenol and methanol on the catalyst was investigated by infrared (IR) spectra. The mechanism of alkylation is suggested on such grounds.

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1) Location: *3190, Gofuku, Toyama.*

2) M.S. Kharasch, A. Fono and W. Nadenberg, *J. Org. Chem.*, **15**, 748 (1950); J. Kenner and F.S. Statham, *J. Chem. Soc.*, **1935**, 299; Dow. Chem. Co., *U.S. Patent*, 2, 193, 760 (1937); J.F. Olin, *U.S. Patent*, 3, 014, 079 (1961).

3) T. Nakagawa and S. Enomoto, *Shokubai* (*Catalyst*), **8**, No. 3, 230 (1966); M. Inoue and S. Enomoto, *ibid.*, **10**, 106 (1968); M. Inoue, T. Nakagawa and S. Enomoto, *Yuki Gosei Kagaku Kyokai Shi*, **28**, No. 11, 1127 (1970).

4) J.P. Ryan and P.R. O'Connor, *J. Am. Chem. Soc.*, **74**, 5866 (1952).

5) S. Furuyama, *Shokubai* (*Catalyst*), **9**, No. 4, 238 (1967).

Experimental

Catalyst——Fivefold the weight of 85% phosphoric acid was mixed to kieselguhr (Johns Manville Co., Ltd.) and calcined at 450° for five hours. The specific surface area of this catalyst was 34 m^2/g measured with the BET method using argon as an adsorbate. The strongest acid strength, H_0, was -3.0. The acidity of $H_0 \leqq +4.8$ reached to 4.2 mmole/g measured with the Benesi's *n*-butylamine titration method.

Phenol-14C (U)——We used a product supplied by The Radiochemical Centre, Amersham.

Apparatus and Procedure——An usual type of flow reactor was used to perform catalytic alkylations in vapor phase. Two ml of the mixture of phenylethers or *ortho* alkylphenols and phenol-^{14}C (4 μCi/ml), were injected from the microfeeder into the preheater kept at 250° for half an hour. Then the reactant vapor was introduced into the catalyst bed (17 mm in diameter and 120 mm in length), with nitrogen as carrier gas. The outlet vapor was condensed in a trap cooled with an ice bath, and the product was radiogaschromatographed. In each test, phenol and alkylphenol were recovered in 85—90% of the initial materials.

Radiogaschromatography——Ten μl of the sample were injected into a gaschromatograph, Yanaco G-800T: liquid phase, tricresyl phosphate (25%)+H_3PO_4 (3%); column, 3 mm × 2 m; helium flow rate, 18 ml/min; temperature, 120°; detector, TCD. The separated phenol and alkylphenols were recorded on one side of the two-pen recorder, and introduced into the oxidation furnace packed with CuO through a leading tube kept at 380°. The oxidation was carried out at 700° and gave carbon dioxide and water. After having dehydrated the mixture with magnesium perchlorate, carbon dioxide was mixed with propane as an quenching gas and introduced continuously into the 10 ml proportional counter and counted with a ratemeter (Aloka RD-4). The radioactivity was recorded with another side of the two-pen recorder with respect to phenol and alkylphenols.

IR Spectra of adsorbed Phenol and Methanol——Reversed T shaped cell, equipped with NaCl windows (7 mm × 20 mm), and protected with water jackets on both sides, was constructed and used for IR absorption measurements. A thin NaCl crystal plate (0.5 mm in thickness, 5 mm in width and 20 mm in length) put in the centre of the cell was coated with the catalyst dispersed with a supersonic wave of 400 kc for a few minutes in hexane. After drying the plate, the cell was connected to a vacuum apparatus followed by heating to 450° under a reduced pressure (~10^{-2} mmHg). Then the phenol or methanol vapor was brought into contact with the catalyst. IR spectra of the adsorbed species were recorded by a Jasco IR-E from room temperature to 450°.

Result and Discussion

The Rearrangement of Phenylether in the Presence of Phenol-^{14}C

In a previous report,[6] the process of the alkylation of phenol to *meta* position has been examined from the differences of the distribution of isomers and the reacting conditions as a consecutive one (Chart 1). But we still do not know whether steps, (1), (2), (3), (4), and (5), involve intra- or intermolecular reactions.

On condensed phosphoric acid-kieselguhr, phenylethers are rearranged giving *ortho*, *meta* and *para* alkylphenols, and partly dealkylated giving phenol. The rearrangement of anisole takes place rapidly at 450°, giving rise to a *meta* isomer. The formation of *meta* isomers is also quickly occuring for phenetole at 400°, and for propylphenylether at 350°. If the alkyl cation is produced as an intermediate on the surface of the catalyst during the reaction of phenol and methanol, the rearrangement of phenylethers is expected to occur *via* an intermolecular reaction.

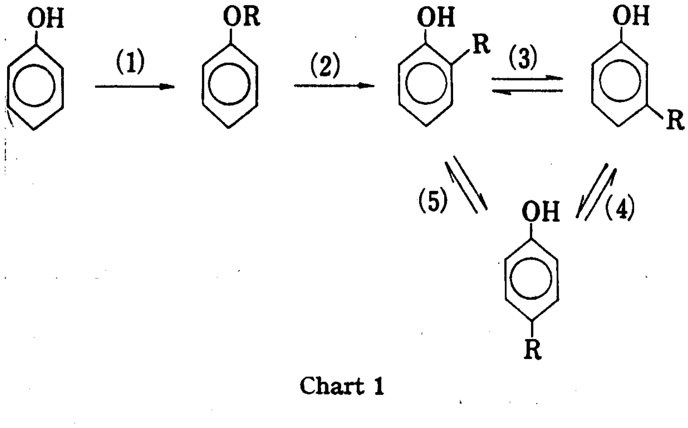

Chart 1

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[6] M. Inoue and S. Enomoto, *Shokubai* (*Catalyst*), **11**, 27 (1969).

To corroborate this, the rearrangement of phenylethers in the presence of phenol-^{14}C has been carried out, and the reaction products were analyzed by radiogaschromatography. If no radioactivity is detected in the alkylphenols produced, we can put forward that the rearrangement of alkyl group takes place *via* an intramolecular rearrangement (case I). On the other hand, if the alkylphenols produced are radioactive, either the rearrangement of phenylether or the isomerization of *ortho*, *meta* and *para* alkylphenols may be regarded as intermolecular reactions (case II). Of course, it is possible that intra- and intermolecular reactions do take place simultaneously (case III).

Table I. Rearrangement of Phenylethers in the Presence of Labeled Phenol on Condensed Phosphoric Acid-Kieselguhr

Phenylethers[a]	Temp. (°C)	Reaction products					
		Phenol (%)	Mono-alkylphenols			Phenyl-ethers (%)	Di-alkyl-phenols (%)
			ortho (%)	*meta* (%)	*para* (%)		
Methyl	450	77.6	19.1			1.5	1.8
			38.9	42.8	18.3		
(A/B%)[b]		(52)	(50)	(45)	(52)	(0)	—[c]
Ethyl	400	82.2	16.8			1.0	0
			33.0	48.6	18.3		
(A/B%)		(55)	(50)	(45)	(45)	(0)	(0)
iso-Propyl	350	80.5	19.5			0	0
			28.8	46.0	25.2		
(A/B %)		(57)	(57)	(55)	(52)	(0)	(0)

a) mixed with an equal weight of phenol-^{14}C
b) A: specific radioactivity of the products
B: specific radioactivity of the initial phenol-^{14}C (4 μci/ml)
c) Counts were too small to be calculated.

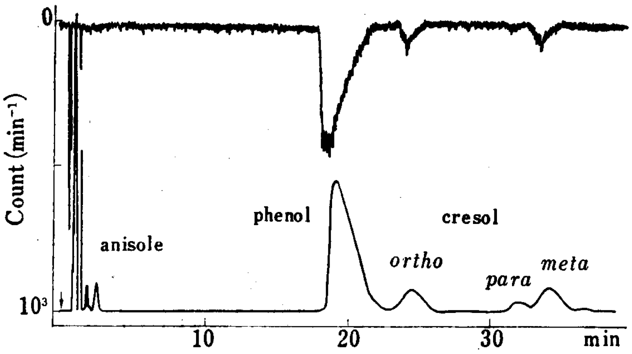

Fig. 1. Radiogaschromatogram of the Rearrangement of Anisole in the Presence of Labeled Phenol on Condensed Phosphoric Acid–Kieselguhr at 450°

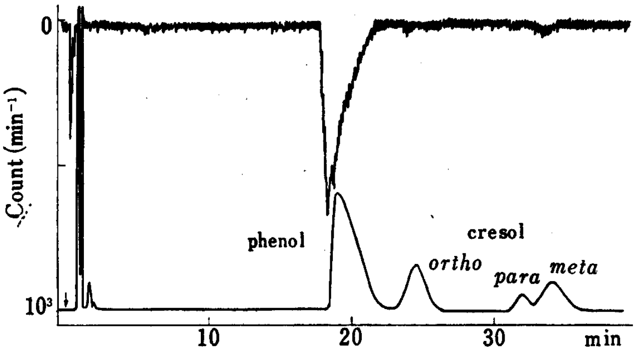

Fig. 2. Radiogaschromatogram of the Isomerization of *ortho* Cresol in the Presence of Labeled Phenol on Condensed Phosphoric Acid–Kieselguhr at 450°

Figure 1 shows a typical example of the radiogaschromatogram obtained by the rearrangement of anisole giving cresol. In Fig. 1 and 2, the lower curve shows the ordinary gaschromatogram, while the upper one shows the radiogaschromatogram. Only 1.5% anisole secured to remain, indicating that the rearrangement took place rapidly. As shown in Fig. 1, produced cresols were radioactive; the rearrangement reaction can be considered to occur in case II or case III.

Table I shows also the results of the rearrangement of C_1—C_3 phenylethers; the specific radioactivity of phenol and alkylphenol after the rearrangement was given in per cent with reference to that of the initial phenol-^{14}C.

All data were in accord with case II as expected. The specific radioactivity of phenol and alkylphenol was found to decrease to a half of the phenol-^{14}C added.

From these results, we can say that in either one or in both steps (the rearrangement of phenylether to *ortho* alkylphenol, and *ortho* to *meta* or *para* isomer) an intermolecular reaction took place, suggesting that an alkyl cation was formed as an intermediate on the surface of the catalyst.

The Isomerization of *ortho* Alkylphenol in the Presence of Phenol-^{14}C

On the surface of condensed phosphoric acid-kieselguhr catalyst, the alkyl group of phenylether migrates to form *ortho* alkylphenol, followed by the migration to *meta* and *para* position. From the previous experiments, it became obvious that alkyl groups are adsorbed dissociatively on the catalyst as alkyl cations. But it is not yet obvious which of the steps (2), (3), (4) and (5) in Chart 1, involve this sort of dissociation. An attempt was made, therefore, to investigate the isomerization of *ortho* alkylphenols to *meta* and *para* isomers in the presence of phenol-^{14}C.

Figure 2 shows the result of the isomerization of *o*-cresol. Kochloefl, Kraus and Bažant[7] reported that the equilibrium constant, $K_{m/p}$, between *m*- and *p*-cresol at 450° is 1.52. On condensed phosphoric acid-kieselguhr, the ratio of *o*-:*m*-:*p*- is found to be 2:2:1. The composition of the isomers is nearly equilibrated. So we think that the isomerization is rapid enough on our catalyst.

The radioactivity of *m*- and *p*-cresol was very weak, and was estimated to be about 20% of the phenol-^{14}C added. So, most cresols are believed to isomerize through an intramolecular reaction. Consequently, the possibility of the intermolecular rearrangement of (3) as well as (4) and (5) (in Chart 1) should be excluded. The transformation of phenylether to *ortho* alkylphenol is the only possible intermolecular reaction. As for the isomerization

Table II. Isomerization of *ortho* Alkylphenols in the Presence of Labeled Phenol on Condensed Phosphoric Acid–Kieselguhr

		Reaction products			
ortho Alkylphenols[a]	Temp. (°C)		Mono-alkylphenols (wt%)		
		Phenol (wt%)	*ortho* (%)	*meta* (%)	*para* (%)
Methyl	450	65.1	34.9		
			50.5	36.2	13.3
(A/B%)[b]		(75)	(8)	(21)	(19)
Ethyl	400	69.5	30.5		
			31.4	56.0	12.6
(A/B%)		(64)	(26)	(29)	(26)
iso-Propyl	350	85.7	14.3		
			27.4	48.4	24.2
(A/B%)		(64)	(45)	(55)	(56)

a) mixed with an equal weight of phenol-^{14}C
b) A: specific radioactivity of the products
B: specific radioactivity of the initial phenol-^{14}C (4 μci/ml)

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7) K. Kochloefl, M. Kraus and V. Bažant, *Chem. Listy*, **51**, 2295 (1957).

of *ortho* alkylphenols, when the number of carbons of the alkyl group increased to ethyl and propyl, the specific radioactivity also increased to 30% and 50%, respectively, as shown in Table II. These results suggest that the alky groups of C_2 and C_3 exist as stable alkyl cations on the catalyst in the course of the migration to *meta* and *para* position. Then, it rebounds to phenol. It is suggested therefore that the propyl cation is produced from propyl alcohol or propylene and attacks phenol without passing through the propylphenylether.

IR Spectra of adsorbed Phenol and Methanol

The alkylation of phenol by methanol may start, in the present work, with both or either one of the reactants adsorbed on the catalyst. To investigate this point, IR spectra of phenol and methanol adsorbed on the catalyst were measured at the temperature of the reaction.

As shown in Fig. 3, the adsorbability of phenol on condensed phosphoric acid–kieselguhr, as monitored by 3300 cm^{-1} of phenolic OH band, was very weak at 350° and disappeared at 450°. On the other hand, methanol showed weak absorptions at 1050, 1250, 2900 cm^{-1}, respectively. The P–O bond of 1130—1300 cm^{-1} 8) showed also a broad and strong absorption, but the spectrum was broadened and dispersed with the fall of the transparency.

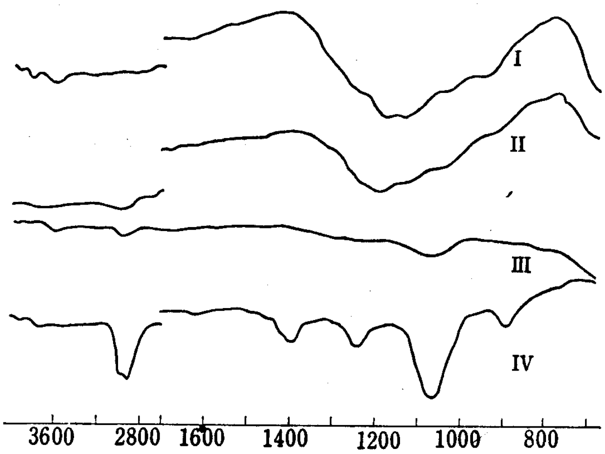

Fig. 3. Infrared Spectra of Phenol and Methanol adsorbed on Condensed Phosphoric Acid–Kieselguhr

I: condensed phosphoric acid–kieselguhr at 450°
II: phenol, at 450°.
III: methanol, at 450°
IV: methanol, at room temperature

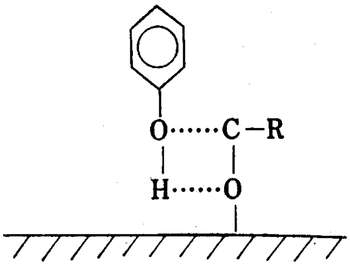

Fig. 4

Anyway, the spectra indicated that the adsorbability of methanol is much stronger than phenol, suggesting that adsorbed methanol reacts with phenol vapor. In fact, this spectral information is in accordance with the fact that the carbon deposited on the catalyst during the reaction is mostly originated from methanol. Then we can consider that the alkylation process of phenol on condensed phosphoric acid–kieselguhr begins with alcohols tightly held on to the acid sites of the catalyst. Phenol approaches the adsorbed alcohols and probably reacts to form phenylethers (Fig. 4). The alkyl groups are immediately rearranged to the *ortho* position of the phenol, and then to the *meta* and the *para* positions. With increasing the number of carbons of the alkyl groups, stable alkyl cations may be formed on the catalyst, so that direct alkylations may occur without passing through phenylethers.

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8) L.W. Daasch and D.C. Smith, *Anal. Chem.*, 23, No. 6, 853 (1951).