

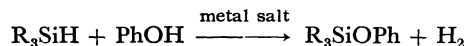
The Synthesis of the Polymer Containing the Si-O-phenylene Bond, using Transition Metal Salts as Catalysts¹⁾

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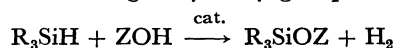
(Received November 20, 1970)

Various transition metals were found to be effective as catalysts in the dehydrocondensation of phenols and silanes.



The effective species were PdCl_2 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, PtCl_2 , RhCl_3 , NiCl_2 , silane-treated NiCl_2 , PtI_2 , PtS , Raney Ni, Pd-black, Pt-black, Au-black, FeCl_3 , ZnCl_2 , CuSO_4 , CuCl , Cu-Cr, $\text{Cu}(\text{CH}_3\text{CO}_2) \cdot \text{CuO}$, the methyl ethyl ketoxime complex of Pd, $\text{Pt}(\text{OX})_3$, and $\text{Pd}(\text{OX})_2$. The ineffective species were metal mirrors of Pd, Au, Ag, Pt, and Cu, and the acetylacetonato complex of Ni, Co(II), Co(III), and Cu. The reaction was then extended to the preparation of polymers containing a Si-O-phenylene linkage in the main chain. Dihydricphenols, *e.g.*, bisphenol A, hydroquinone, 4,4'-dihydroxydiphenyl gave high-molecular-weight polymers with an equimolar amount of a dihydrosilane, *e.g.*, diphenylsilane, *p*-toluylmethylsilane and *p*-bisdimethylsilylphenylene, in bulk or in a solvent at temperatures above 150°C. The polymer obtained began to flow above 100°C.

It has been known that Group VIII metals and metal halides catalyze the reaction of an organosilane with compounds containing a hydroxy group:²⁻⁷⁾



Z = H, alkyl, aryl, acyl, *etc.*

Dolgov *et al.*⁷⁾ reported that the dehydrocondensation of trialkylsilanes with alcohols and mono- or polyhydric phenols proceeded smoothly at the temperature of 100°C and that gave alkoxy- and phenoxysilanes in almost quantitative yields in the presence of a catalytic amount of colloidal nickel prepared from NiCl_2 .

We now wish to report in the catalytic activity of various transition metals, especially the salts of Ni, Pd, and Pt, in the reactions of organosilanes and phenols. Among these catalysts, several metal salts, such as PdCl_2 and the Pd complex of methyl ethyl ketoxime, initiated the reaction, even at room temperature. Such a reaction was used in the preparation of polymers containing siloxane linkage in the main chain from difunctional phenols and difunctional silanes.

Polyaryloxysilanes have been reported to be obtained from difunctional phenols and dianilino- or diphenoxysilanes through a melt-polycondensation reaction procedure at temperatures above 200°C and under reduced

pressure.^{8,9)} Here, a similar polymer was prepared under much milder conditions.

Experimental

Materials. 4,4'-Dihydroxydiphenyl was prepared by the hydrolysis of a diazonium compound derived from commercial 4,4'-benzidine according to the usual method. Recrystallization from dioxane gave pure 4,4'-dihydroxydiphenyl; mp 277—278°C. All the other phenols were commercially available, and they were recrystallized before use. The phenyldimethylsilane, *p*-toluylmethylsilane,¹⁰⁾ diphenylsilane,¹¹⁾ and *p*-bis(dimethylsilyl)-benzene¹²⁾ were prepared by methods previously reported. The purity of the silanes was ascertained by gas chromatography, using dioctyl phthalate (D.O.P.) or thermol-3 as the liquid phase.

The Reaction of Silane with Phenol. To a mixture of 3.0 g of phenyldimethylsilane and 2.35 g of phenol, were added 0.02 g of metal salt. In the case of a very active catalyst, PdCl_2 , for example, a vigorous exothermic reaction occurred, hydrogen gas evolved immediately after the addition of the catalyst at room temperature, and the solution turned dark. In the case of a catalyst with a mild activity, such as NiCl_2 , an exothermic reaction occurred when the bath temperature was 110°C. After the reaction, the catalyst was removed by filtration and the product was distilled under reduced pressure to give phenoxysilane. The identity of the product was confirmed by infrared spectroscopy and gas chromatographs. The evolved gas was analysed by gas chromatography using a Molecular Sieve 13X column.

Polycondensation. The polymerization was carried out by heating a mixture of 5.00 g of bisphenol A and 4.03 g of diphenylsilane with 0.02 g of PdCl_2 at 150—160°C for 10 hr. The resulting polymer was purified by reprecipitation from THF-*n*-hexane and dried. The powdery polymer thus obtained was submitted to elemental analysis and other analyses. The other polymers were prepared by a similar method. The viscosity was determined by the use of an Ubbelohde viscometer at 30°C in a tetrahydrofuran solution and in a concentration of 0.5 g/dl.

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13) Pt complex of 8-hydroxyquinoline.

Results and Discussion

Activity of Catalyst in the Reaction of Silane and Phenol.

The reaction of phenyldimethylsilane with phenol and bisphenol-A was carried out in the presence of a metal salt as a catalyst. The reaction products were confirmed to be siloxanes by elemental analysis, as is shown in

TABLE 1. REACTION BETWEEN SILANE AND PHENOL WITH PdCl_2 AS CATALYST

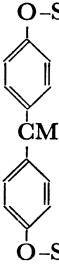
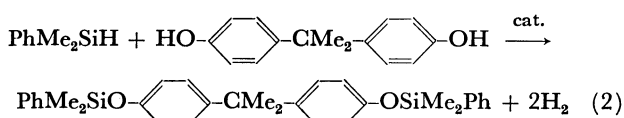
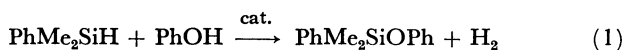
Product	Bp °C/mmHg	Yield %	Elemental analysis Found (Calcd)		
			C%	H%	Si%
$\text{PhMe}_2\text{SiOPh}$	94—95/0.3	93	74.19 (74.68)	7.26 (7.02)	12.9 (12.3)
$\text{O-SiMe}_2\text{Ph}$ 	220—223/0.2	92	74.63 (74.95)	7.32 (7.30)	11.1 (11.3)

Table 1. The yield of the products was almost quantitative, and the gas evolved was found to be composed of hydrogen and a trace of methane. From these results, therefore, the reaction was considered to proceed as is shown in Eqs. (1) and (2):

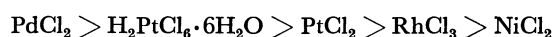


The infrared spectra of phenyldimethylphenoxysilane, phenyldimethylsilane, and phenol are summarized in Fig. 1. In this figure, the absorptions around 3300,

2100, 920, and 880 cm^{-1} were identified as the absorptions of OH(3300), SiH(2100, 880), and Si-O- (920) respectively. When the reaction proceeded, the absorptions of OH and SiH diminished and the appearance of a new absorption of Si-O- was observed.

The rates of the reactions using various kinds of metal derivatives as catalysis were estimated by the volumetry of the hydrogen gas evolved and by infrared spectroscopy. The order of the rates thus obtained may be attributed to the order of the activity of the catalysis used, because all the reactions were carried out under the same conditions. The orders of the activity of catalysts used were as follows:

1) For metal halide:



2) For metal black:



3) For other metal salts:

PtI_2 , PtS , Pt(OX)_3 ,¹³⁾ Pd(OX)_2 , methyl ethyl ketoxime of Pd, CuSO_4 , CuCl , Cu-Cr , $\text{Cu(CH}_3\text{CO}_2)_2$, CuO , FeCl_3 , ZnCl_2

The metal mirrors of Pd, Au, Ag, Pt, and Cu showed little activity. We tried to use acetylacetonato complexes of Ni, Cu, Co(II), and Co(III) as homogeneous catalysts, but they provoked no reaction. As is shown in Table 2, all the metals which are active as catalysts in the reactions of phenols and silanes were found to be transition metals.

TABLE 2. THE CATALYTIC METALS IN PERIODIC TABLE OF THE REACTION BETWEEN PHENOLS AND SILANES

VIa	VIIIb			Ib	IIb
Cr	Fe	Co	Ni	Cu	Zn
Mo	Ru	Rh	Pd	Ag	
W			Pt	Au	Hg

: highly active; : active; : slightly active.

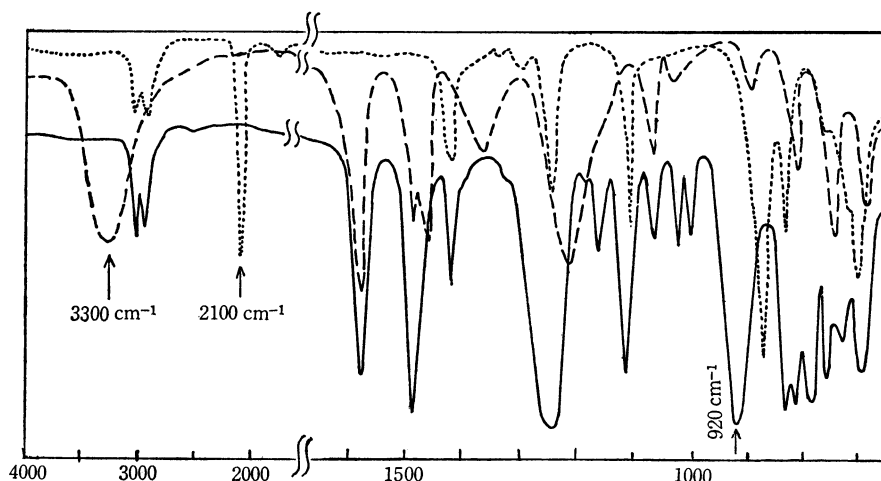


Fig. 1. Infrared spectra of phenyldimethylsilane, phenol, and phenyldimethylphenoxysilane.

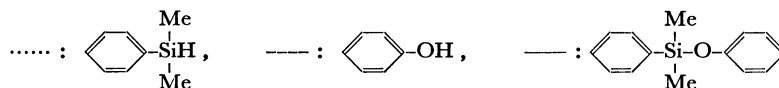


TABLE 3. BULK OR SOLUTION POLYMERIZATION OF DIHYDRIC AND DIHYDROSILANES

Dihydric phenol	Dihydro silane	Polymerization condition (in N ₂) cat. PdCl ₂			η_{inh} in THF at 30 °C	Elemental analysis		
		temp (°C)	time (hr)	solvent		C % Found (Calcd)	H % Found (Calcd)	Si % Found (Calcd)
B.P.A.	TMS	110	20	none	(0.100) ^{b)}	75.84 (76.62)	6.84 (6.71)	7.77 (7.79)
B.P.A.	DPS	150	10	diglyme	0.122	78.41 (79.37)	6.22 (5.92)	6.47 (6.88)
HQ.	DPS	150	10	diglyme	0.079	71.55 (74.45)	4.66 (4.86)	9.35 (9.67)
DHDP.	DPS	210	1.5	none	0.079	74.77 (78.65)	5.46 (4.95)	7.10 (7.65)
DHDP.	BDMSP	210	1.5	none	0.103	68.39 (68.02)	6.22 (6.80)	15.1 (15.0)
DHDP.	BDMSP	160 ^{a)}	12	THF	(0.090) ^{b)}	67.96 (68.02)	6.44 (6.80)	15.4 (15.0)

B.P.A. bisphenol A T.M.S. *p*-toluylmethylsilane

HQ. hydroquinone D.P.S. diphenylsilane

DHDP. 4,4'-dihydroxydiphenyl BDMSP. *p*-bis-dimethylsilylphenylenea) cat: Pt(OX)₃ b) in toluene

In these reactions, the reaction mixtures turned dark when heated, and the formation of colloidal metal was observed in the reactions, using almost all of the metal salts. The metal salts seemed to be reduced by silane; the colloidal metal black thus formed had a high catalytic activity in the reaction of silane and phenol. The results will be presented in detail in the following paper.

Polycondensation. The polycondensation reactions

of various phenols and dihydrosilanes were carried out in bulk (or in solution); the results are shown in Table 3. These polymers tend to flow above 100°C as a consequence of the chain mobility of the silicon-oxygen bond.

The authors are grateful to the Shinetsu Chem. Ind. Co. for the supply of the chlorosilanes used in this experiment.