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Coupling of Phenol with Ketones in the Presence of Heteropoly Acids with Different Structures and Compositions

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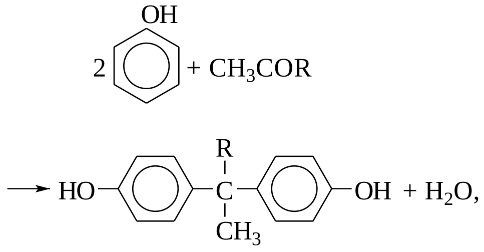
Abstract—The reactions of phenol coupling with ketones MeCOR (R = CH_3, C_2H_5, C_3H_7, and C_4H_9) are studied in the presence of heteropoly acids with different structures and compositions in toluene solutions ([PhOH]/[MeCOR] = (2–8)/1 mol/mol; 50–70°C) with thioglycolic acid added as a promoter. The reaction rate depends on ketone and heteropoly acid, and the yield of bisphenols is as high as 24–72%. The reaction orders are 0.68, 0.77, and 0.97 with respect to $H_6P_2W_{21}O_{71}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, respectively, and the activation energies are 25.1, 21.0, and 20.6 kcal/mol, respectively. Heteropoly acids of the Dawson structure exhibited the highest activity.

INTRODUCTION

The following reaction of phenol coupling with ketones is of considerable interest as a method for preparing various bisphenols, which are widely used in the synthesis of high-molecular-weight compounds, epoxy resins, and antioxidants [1]:



(I)

R = CH_3, C_2H_5, C_3H_7, and *tert*-C_4H_9.

Reaction (I) occurs in the presence of homogeneous or heterogeneous acid catalysts such as H_2SO_4 [1, 2], HCl [3], BF_3, SbF_5, and $AlCl_3$ in combination with hydrogen chloride [1], sulfo cation exchangers [4], and zeolites (HZSM-5, HY, and H-mordenite) [5]. It was found [6–8] that the heteropoly acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ also successfully catalyze the coupling of phenol with acetone. It was proposed to use $H_3PW_{12}O_{40}$ supported on clay [7] or $(NH_4)_2HPW_{12}O_{40}$ immobilized on polysiloxane [9] as a catalyst of this reaction. In all cases, the yield of bisphenol in the presence of heteropoly acids was as high as 65–75%. The catalysts were promoted with sulfur-containing compounds to inhibit side processes and to accelerate the reaction. It was proposed to use thio-substituted aliphatic carboxylic acids, mercaptoamines, mercaptans, sodium or potassium thiosulfate, hydrogen sulfide, boric acid, etc., as promoters [1–5]. The best results were obtained with thioglycolic acid [1]. In this work, we studied the kinetics and mechanism of reaction (I) in the presence of heteropoly acids with different structures and compositions of thioglycolic acid as a promoter.

EXPERIMENTAL

Chemicals. The chemically pure heteropoly acids $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ used in this study were additionally purified by recrystallization from water. $H_8CeMo_{12}O_{42}$ was prepared according to the procedure in [10]; and $H_6P_2W_{21}O_{71}$, $H_6P_2W_{18}O_{62}$, $H_5PW_{11}ZrO_{40}$, $H_5PW_{11}TiO_{40}$, $H_6P_2Mo_{18}O_{62}$, $H_{10}(PW_{11}O_{39})_2Ce$, and $H_3PW_6Mo_6O_{40}$ were synthesized electrochemically [11–13]. The heteropoly acids were taken as crystal hydrates and heated in a nitrogen flow at 100°C for 4 h before use. Phenol of reagent grade and toluene and thioglycolic acid of analytical grade were used without additional purification. The following freshly distilled ketones were taken: acetone of analytical grade, methyl ethyl ketone of analytical grade, methyl propyl ketone of reagent grade, and methyl *tert*-butyl ketone of reagent grade.

Coupling. The reaction was performed in a constant-temperature glass reactor equipped with a magnetic stirrer and a reflux condenser in a toluene solution at 60–100°C. Phenol (9.8 g; 0.104 mol), toluene (20 ml; 0.19 mol), thioglycolic acid (TGA) (0.2 ml; 0.0028 mol, which corresponds to [TGA] = 0.054 mol/l) and a heteropoly acid (1.5–4.5 wt % based on phenol) were placed in the reactor. The mixture was heated to 60–90°C; a ketone was added in the molar ratio [PhOH]/[MeCOR] = (2–8)/1; and the mixture was stirred at 300 rpm at this temperature for 7–15 h. Samples for GLC analysis were taken at regular intervals. A Tsvet-500 chromatograph with a glass column (1 m × 3 mm) packed with 3% OV-17 on Chromaton W and a flame-ionization detector was used for the analysis under conditions of programmed temperature increase from 90 to 270°C (20 K/min). Octadecane was used as an internal standard.

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Table 1. Mass spectra of bisphenols containing various substituents*

CH_3		C_2H_5		C_3H_7		C_4H_9	
m/*e*	%	*m*/*e*	%	*m*/*e*	%	*m*/*e*	%
27	4.7	39	13.7	41	19.0	29	23.2
65	5.1	65	12.9	91	42.6	41	13.2
91	9.0	91	34.0	108	18.7	91	34.5
99	8.5	119	40.8	119	37.4	108	16.0
119	18.9	212	54.9	211	66.1	119	33.2
214	100	214	100	213	36.8	212	24.0
215	10.0	215	16.9	214	100	214	100
$\underline{228}$	26.7	$\underline{242}$	18.4	$\underline{256}$	25.5	$\underline{270}$	18.0

* Molecular ions are underscored; *m*/*e* = 214 was taken as 100%.

The GC–MS identification of products was performed on an LKB-2091 instrument (Sweden) with a glass capillary column (40 m; Carbowax 20M–Lukopren G1000 (1 : 3) as a stationary phase with an ionization energy of 70 eV). Table 1 summarizes mass spectroscopic data for major products.

Calculation of rate constants. According to [3], under the conditions of substantial excess of phenol ([PhOH]/[MeCOR] = 8 : 1 mol/mol) in the presence of acid catalysts, reaction (I) follows the second-order rate equation

$$w = k[\mathrm{MeCOR}][\mathrm{PhOH}]. \qquad (1)$$

On this basis, the rate constants of second-order reactions were calculated (at the linear portion of a plot of the bisphenol yield as a function of time) by the equation

$$k = \frac{2.303}{([\mathrm{P}]_0 - 2[\mathrm{K}]_0)t}\log\frac{([\mathrm{P}]_0 - 2[\mathrm{BP}]_t)[\mathrm{K}]_0}{([\mathrm{K}]_0 - 2[\mathrm{BP}]_t)[\mathrm{P}]_0}, \qquad (2)$$

where $[\mathrm{K}]_0$ and $[\mathrm{P}]_0$ are the initial ketone and phenol concentrations, respectively, and $[\mathrm{BP}]_t$ is the bisphenol concentration at the point *t* in time.

Table 2. Bisphenol yield in the coupling of phenol with acetone in the presence of various heteropoly acids (HPAs) (65°C; [HPA] = 4.15 wt %)

Catalyst	[PhOH]/[MeCOMe], mol/mol	Time, min	Bisphenol yield, % (relative to theory)
$H_3PW_{12}O_{40}$	3 : 1	720	8
		840	12
$H_3PW_{12}O_{40}$	8 : 1	610	21
		720	27
$H_3PMo_{12}O_{40}$	8 : 1	720	12
$H_6P_2W_{21}O_{71}$	8 : 1	610	46
		720	60
		820	66
$H_6P_2W_{18}O_{62}$	8 : 1	360	55
		450	66
		500	73
$H_5PW_{11}ZrO_{40}$	8 : 1	720	28
$H_{10}(PW_{11}O_{39})_2Ce$	8 : 1	720	13

RESULTS AND DISCUSSION

Tables 2 and 3 summarize the results obtained with the use of heteropoly acids as catalysts of reaction (I). We found that under these conditions bisphenols can be prepared in 60–70% yields. The [PhOH]/[MeCOR] ratio and temperature considerably affected the yields of bisphenols. The reaction time decreased and the product yield increased with an increase in the phenol-to-ketone ratio or temperature.

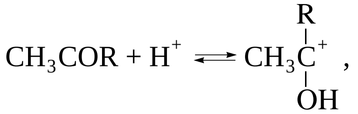
Along with the main reaction, side processes resulting in a number of products occurred in the synthesis of bisphenols. Many of these products reacted with each other or with one of the reactants to give additional products. The major by-product was an ortho–para isomer, the amount of which reached 20% under some reaction conditions. An ortho–ortho isomer was formed in a much smaller amount (1–2%).

The reaction was much slower in the absence of a promoter (thioglycolic acid). Thus, in the reaction of phenol coupling with acetone ([PhOH] : [MeCOMe] = 8 : 1 mol/mol; $[H_6P_2W_{21}O_{71}]$ = 4.15 wt %) in the absence of thioglycolic acid, the bisphenol yield was 10.4% in 350 min, whereas it was 26.5% in the presence of thioglycolic acid.

Note that ~0.04 wt % of heteropoly acids (on the basis of the reaction mixture) dissolve in the reactants; however, this heteropoly acid amount is insufficient for the reaction to occur at a reasonable rate.

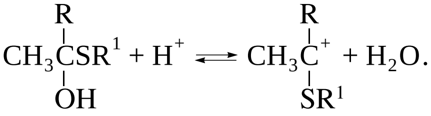
We found that the reaction orders of phenol coupling with acetone with respect to heteropoly acids are close to unity or lower (Fig. 1), namely: 0.68, 0.77, and 0.97 for $H_6P_2W_{21}O_{71}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, respectively. The corresponding activation energies are equal to 25.1, 21.0, and 20.6 kcal/mol, respectively.

We found that the rate constant is a linear function of the promoter (thioglycolic acid) concentration (Fig. 2). These data are consistent with a traditional understanding of the mechanism of reaction (I), according to which the following two carbocations occur in the system:



$$CH_3COR + H^+ \rightleftharpoons CH_3\overset{R}{\underset{OH}{C^+}}, \quad (II)$$

A



$$CH_3\overset{R}{\underset{OH}{C}}SR^1 + H^+ \rightleftharpoons CH_3\overset{R}{\underset{SR^1}{C^+}} + H_2O. \quad (III)$$

B

The reactivity of carbocation **B** is higher than that of carbocation **A**. Both of reactions (II) and (III) of carbocation formation are equilibrium reactions; the concentrations of carbocations depend on the degree of positive-charge compensation by π-electrons of oxygen and sulfur atoms. In the case of thioglycolic acid, this compensation is more pronounced because of the lower electronegativity of the sulfur atom; consequently, the energy barrier for its formation is lower. In turn, this leads to a higher concentration of carbocations **B** than of **A**. This fact is consistent with the direct proportionality of the rate of a rate-limiting step of the coupling of phenol with acetone to the concentration of the sulfur-containing promoter thioglycolic acid (Fig. 2).

We experimentally found a particular relationship between the structure and reactivity of ketones. The reaction rate dramatically decreased together with the bisphenol yield as the length of an alkyl radical increased from CH_3 to C_4H_9 (Table 3); in this case, the activation energy increased. Thus, the activation energy was equal to 25.1, 26.3, or 28.4 kcal/mol for R = CH_3, C_2H_5, or C_3H_7, respectively. The experimental data are consistent with the theory of ketone reactivity of [2, 14]. The activity of a carbonyl group strongly depends on the nature of adjacent substituents. The electrophilicity and hence the reactivity of ketones decreases with the chain length of alkyl radicals. It is likely that a decrease in the reactivity in methyl *tert*-butyl ketone is due to stronger steric hindrances as a result of higher branching at the α-carbon atom of an alkyl group of the ketone.

Table 4 summarizes the results of kinetic measurements for the coupling of phenol with acetone in the presence of various heteropoly acids. It can be seen that the activity of heteropoly acids essentially depends on the composition and structure of the anion. For tungsten heteropoly acids, the activity depending on the structure decreases in the order

$$\text{Dawson} > 2:21 > \text{Keggin} > (1:11)_2:1.$$

$$H_5PW_{11}ZrO_{40} > H_5PW_{11}TiO_{40},$$

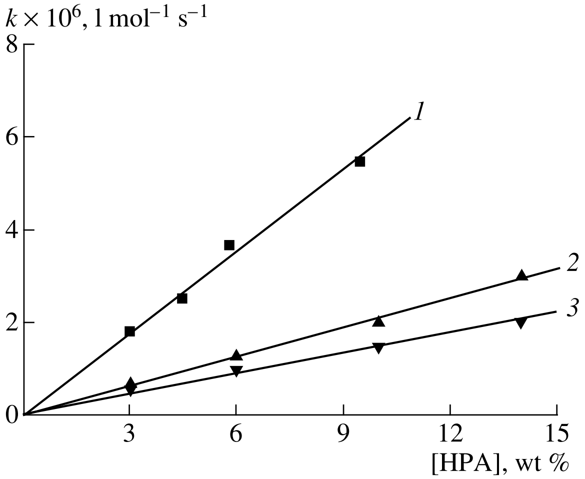


Fig. 1. Reaction rate constant *k* of phenol coupling with acetone as a function of heteropoly acid (HPA) concentration at 65°C; [PhOH] : [MeCOMe] = 8 : 1 mol/mol: (*1*) $H_6P_2W_{21}O_{71}$, (*2*) $H_4SiW_{12}O_{40}$, and (*3*) $H_3PW_{12}O_{40}$.

For similar heteropolyacids (Keggin structures), the following activity series is observed:

$$H_4SiW_{12}O_{40} > H_3PW_{12}O_{40}.$$

For heteropoly acids of the same type (Keggin structures), $H_3PW_{12}O_{40}$ is considered to be the strongest acid [15]. However, it exhibited the lowest activity in the given reaction. This can be explained by different

Table 3. Coupling of phenol with ketones in the presence of 2.5 wt % $H_6P_2W_{21}O_{71}$

R	[PhOH]/[RCOMe]	*T*, °C	Time, min	Bisphenol yield, % (relative to theory)
CH_3	8 : 1	60	360	26
			720	60
			820	64
C_2H_5	8 : 1	60	360	Traces
	8 : 1	70	360	15
	8 : 1	80	380	60
	4 : 1	70	360	7
			720	14
	2 : 1	70	360	4
			720	9
C_3H_7	8 : 1	70	360	1
			720	6
	8 : 1	80	360	15
			720	35
		90	380	58
C_4H_9	8 : 1	90	380	14
			720	18
			920	25

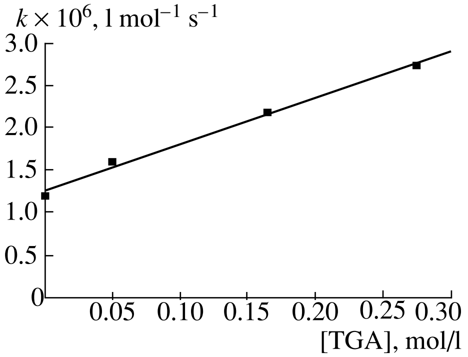


Fig. 2. Reaction rate constant k of phenol coupling with acetone as a function of thioglycolic acid concentration at 65.4°C; [$H_6P_2W_{21}O_{71}$] = 4.15 wt %; [PhOH] : [MeCOMe] = 8 : 1 mol/mol.

behaviors of heteropoly acids in a quasi-liquid state due to which a heteropoly acid can heterogeneously catalyze various reactions [15]. Another explanation is the presence of an additional ion (Zr^{4+} or Ti^{4+}) in the complex heteropoly anions. In principle, this additional ion can activate substrate molecules or stabilize organic molecules in a transition state by a coordination position oriented toward the outer coordination sphere of the heteropoly anion [16].

Molybdenum heteropoly acids, which have a higher oxidation potential, are easily reduced under reaction conditions and become inactive. However, they can also be arranged in the following order of activity depending on the structure:

Dawson > Dexter–Silverton > Keggin.

The dependence of the catalytic activity on the structure and composition of heteropoly acids was also observed in other reactions [17–19]. Note that these relationships are different for various reactions. Because data on the acidity of structurally different heteropoly acids are yet very incomplete [20], we cannot conclude about the degree to which the acidity is responsible for the catalytic activity of a heteropoly acid in a particular reaction. The results of this study and data published before [17–19] allow us to conclude that, in addition to the acidity, the structure and composition of heteropoly anions play an important role in heteropoly acid catalysis.

Table 4. Reaction rate constants of phenol coupling with acetone. [PhOH]/[MeCOMe] = 8 : 1; [Cat] = 3.0 wt %; 60°C

Catalyst	Heteropoly acid type [20]	$k \times 10^7$, mol l^{-1} s^{-1}
$H_6P_2W_{21}O_{71}$	2 : 21*	18
$H_6P_2W_{18}O_{62}$	Dawson	19
$H_3PW_{12}O_{40}$	Keggin	6.1
$H_5PW_{11}TiO_{40}$	Keggin	6.9
$H_5PW_{11}ZrO_{40}$	Keggin	9.7
$H_{10}(PW_{11}O_{39})Ce$	$(1 : 11)_2 : 1$**	4.9
$H_4SiW_{12}O_{40}$	Keggin	6.9
$H_8CeMo_{12}O_{42}$	Dexter–Silverton	8.6
$H_6P_2Mo_{18}O_{62}$	Dawson	11
$H_3PMo_{12}O_{40}$	Keggin	1.8
$H_3PMo_6W_6O_{40}$	Keggin	4.5

* The P : W ratio in the formula.

** The ratio between P, W, and Ce.

REFERENCES

1. Verkhovskaya, Z.N., *Difenilolpropan* (Diphenylpropane), Moscow: Khimiya, 1971.
2. Kazakova, G.S., Machtina, K.A., Vorenkov, V.V., and Moskvin, A.F., *Zh. Prikl. Khim.*, 1973, vol. 46, no. 7, p. 1880.
3. Grosh, P.K., Guha, T., and Saha, A.N., *Pure Appl. Chem.*, 1967, vol. 17, no. 7, p. 241.
4. Maksudova, Kh.Ya., Rustamov, Kh.R., and Usmanov, R.U., *Uzb. Khim. Zh.*, 1969, vol. 1, p. 27.
5. Singh, A., *Catal. Lett.*, 1992, vol. 27, p. 431.
6. Zhang, J., Ge, X., and Wu, G., *Shiyou Huagong*, 1993, vol. 22, no. 2, p. 77.
7. Yadav, G.D. and Kirthivasan, N., *Appl. Catal.*, 1997, vol. 154, p. 29.
8. JPN Patent 02-454339, 1990; *Chem. Abstr.*, 1991, vol. 113, abstract no. 24665.
9. EUR Patent 693470, 1995; *Chem. Abstr.*, 1996, vol. 124, abstract no. 203320.
10. Baidla, P., Torchenkova, E.A., and Spitsin, V.I., *Dokl. Akad. Nauk SSSR*, 1971, vol. 196, no. 6, p. 1341.
11. Kulikov, S.M., Maksimovskaya, R.I., Kulikova, O.M., and Kozhevnikov, I.V., *Izv. Akad. Nauk, Ser. Khim.*, 1992, no. 3, p. 494.
12. Maksimov, G.M., Maksimovskaya, R.I., and Kozhevnikov, I.V., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 4, p. 623.
13. Maksimov, G.M., Maksimovskaya, R.I., and Kozhevnikov, I.V., *Zh. Neorg. Khim.*, 1992, vol. 37, no. 10, p. 2279.
14. Backer, H., *Einführung in die Elektronen-theoril Organoschemisher Reaktionen*, Berlin, 1964.
15. Misono, M., Mizuno, N., and Okuhara, T., *Adv. Catal.*, 1996, vol. 41, p. 113.
16. Hill, C.L. and Prosser-McCartha, C.M., *Coord. Chem. Rev.*, 1995, vol. 143, p. 407.
17. Maksimov, G.M. and Kozhevnikov, I.V., *React. Kinet. Catal. Lett.*, 1989, vol. 39, no. 2, p. 317.
18. Hu, C., Hashimoto, M., Okuhara, T., and Mimsono, M., *J. Catal.*, 1993, vol. 143, no. 2, p. 437.
19. Maksimov, G.M. and Timofeeva, M.N., *React. Kinet. Catal. Lett.*, 1995, vol. 56, no. 1, p. 191.
20. Maksimov, G.M., *Usp. Khim.*, 1995, vol. 64, no. 5, p. 480.