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Catalysis by Heteropolyacid. III. Acylation and Sulfonylation of Aromatic Compounds Catalyzed by Keggin-structure Heteropolyacids

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Synopsis. Catalytic acylation and sulfonylation reactions of aromatic compounds by Keggin-structure heteropolyacids, $H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$, have been studied. Tungsten is more effective than molybdenum for the reactions.

Brønsted acidity of Keggin-structure heteropolyacid is a key factor in the catalysis for polycondensation of benzyl alcohols[1)] and Friedel-Crafts-type reaction.[2)] These reactions proceed *via* a carbonium ion mechanism. The constitutional metal of the Keggin-unit is another important factor, molybdenum, rather than tungsten, being effective for the alkylation reaction.[3)] We have examined the role of the metal and the hetero atom in the catalytic acylation and sulfonylation for aromatic compounds.

The heteropolyacids, $H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$, were prepared according to the usual method. The mononuclear complex, H_2MO_4 (M=Mo, W), was prepared by heating a hydrochloric aqueous solution of MO_3 at 40—60 °C and cooling. All organic reagents were purified by the usual methods. Acylation was carried out with acetyl chloride and sulfonylation with *p*-tolylsulfonyl chloride (tosyl chloride). Dried toluene, anisole, thiophene and furan were used as aromatic substrates. The reaction mixture was refluxed in the presence of heteropolyacid or mononuclear complex. After refluxing, the cata-

Table 1. Acylation and sulfonylation reactions catalyzed by heteropolyacids

Heteropolyacid	Reactant		Amount of catalyst (10^{-5} mol)	Reflux time (h)	Products	Turn-over number per hour
	A (mol)	B (mol)				
$H_4[SiMo_{12}O_{40}]$	Toluene	Tosyl chloride				
	(0.24)	(0.01)	2.75	20	23% DTS	4
	(0.91)	(0.026)	5.49	19	13% DTS	3
	Anisole	Tosyl chloride				
	(0.23)	(0.026)	5.49	23	14% MMXDPS	3
	(0.23)	(0.026)	5.49	22	11% MMXDPS	2
	Anisole	Acetyl chloride				
	(0.23)	(0.1)	5.49	20	19% MXAP	17
	(0.23)	(0.1)	5.49	24	17% MXAP	13
	Thiophene	Acetyl chloride				
	(0.06)	(0.1)	5.49	30	44% AT	16
	(0.06)	(0.1)	5.49	17	36% AT	23
$H_3[PMo_{12}O_{40}]$	Toluene	Tosyl chloride				
	(0.094)	(0.01)	2.74	18	27% DTS	5
	(0.141)	(0.01)	2.74	19	37% DTS	7
	Anisole	Tosyl chloride				
	(0.14)	(0.01)	2.74	18	29% MMXDPS	6
	(0.14)	(0.01)	2.74	18	21% MMXDPS	4
	Anisole	Acetyl chloride				
	(0.093)	(0.056)	2.74	20	15% MXAP	15
	(0.14)	(0.056)	2.74	20	19% MXAP	19
	Thiophene	Acetyl chloride				
	(0.038)	(0.07)	2.74	17.5	22% AT	17
	(0.05)	(0.056)	2.74	5	6% AT	22
$H_4[SiW_{12}O_{40}]$	Toluene	Tosyl chloride				
	(0.094)	(0.01)	1.74	20.5	38% DTS	11
	(0.141)	(0.01)	1.74	19	48% DTS	15
	Anisole	Tosyl chloride				
	(0.14)	(0.01)	1.74	21	36% MMXDPS	10
	(0.14)	(0.01)	1.74	21	26% MMXDPS	8
	Anisole	Acetyl chloride				
	(0.23)	(0.1)	3.47	18	16% MXAP	26
	(0.14)	(0.056)	1.91	17	18% MXAP	31
	Thiophene	Acetyl chloride				
	(0.063)	(0.1)	3.47	3	6% AT	36
	(0.05)	(0.056)	1.74	5	5% AT	32

Abbreviation; DTS: 4,4′-di-*p*-tolyl sulfone, MMXDPS: 4-methyl-4′-methoxydiphenyl sulfone, MXAP: 4-methoxyacetophenone, AT: 2-acetylthiophene.

lyst was removed by filtration and acylated products were isolated by distillation under reduced pressure and sulfonylated products by recrystallization from ethanol.[4] They were identified by IR, ^{1}H-NMR and their melting points.

Three heteropolyacids showed effective activity, but the mononuclear complexes showed hardly any. The acylated compounds were obtained from anisole and thiophene, not from toluene and furan, and the sulfonylated compounds from toluene and anisole, not from thiophene and furan. Products were para-substituted for six-membered ring and oriented to 2-position for five-membered ring.

Reaction conditions, yields and turn-over numbers per hour are given in Table 1. The turn-over number per hour, conveniently estimated by a molar ratio of the amount of catalyst used and that of the product obtained per hour, is interpreted not only as a diagnostic parameter of whether the reaction proceeds catalytically or stoichiometrically, but also as a criterion for efficiency of the catalyst. The results are summarized as follows. (1) All the reactions are catalyzed by each heteropolyacid. (2) Acylation proceeds more easily than sulfonylation. (3) The reactions are largely influenced by the kind of metal constituting the Keggin unit, rather than the kind of hetero atom. (4) Of constitutional metals, tungsten, rather than molybdenum, is effective in the reactions; this aspect is contrary to the case of alkylation of toluene with benzyl chloride.[3]

Since the Keggin formula is designated by twelve sexivalent metals, forty bivalent oxygens and one hetero atom, the number of protons as counter ion is determined by the charge of hetero atom, *e.g.*, four for Si, three for P and As. Thus the difference in the number of protons between $H_4[SiMo_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ is not important in the catalysis.

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