

Catalysis by 12-Heteropolymolybdic Acid. II. Friedel-Crafts-type Reaction of Aromatic Compounds

Kenji NOMIYA, Yoshio SUGAYA, Sadayoshi SASA, and Makoto MIWA*

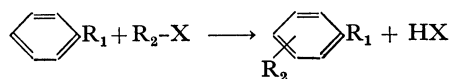
Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino-shi, Tokyo 180

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Synopsis. 12-Heteropolymolybdic acid, a heteropolyacid of Keggin-structure, behaves as an effective catalyst of the Friedel-Crafts-type reactions for aromatic compounds, such as alkylation by benzyl chloride and *t*-butyl chloride, acylation by acetyl chloride, and sulfonylation by tosyl chloride. The catalyst mainly gives para-substituted products for phenol and anisole. The reactions proceed *via* carbocation-generation mechanism brought about by the strong Brønsted acid.

Except for the catalytic alkylation of benzene with 1-dodecene by silicotungstic acid supported on silica gel,¹⁾ no typical reaction catalyzed by heteropolyacid, recognized as a solid-acid, has been demonstrated in spite of advanced studies on its structure.^{2–10)}

Nomiya *et al.* have shown the catalytic polycondensation of benzyl alcohol and its derivatives by heteropolyacids of Keggin-structure such as $H_4SiM_{12}O_{40}$ and $H_3PM_{12}O_{40}$ ($M=Mo$ and W).¹¹⁾ These acids also give the same polybenzyl from benzyl chloride by dehydrohalogenation as that obtained from benzyl alcohol in comparably high yields. We wish to report that these heteropolymolybdic acids are active catalysts in substitution reactions such as alkylation, acylation, and sulfonylation of aromatic systems as well as polymerization reactions. The reaction scheme is as follows.



The reactions were performed by refluxing a mixture of reactants A and B in the presence of the heteropolyacid. The results of typical experiments are given in Table 1. The heteropolyacid homogeneously catalyzes all reactions. The reaction products were identified by IR and ^1H -NMR spectra. No poly-branched product was detected. The substituent groups are oriented mainly to the para-position of six-membered aromatic rings of phenol and anisole, and the 2-position of five-membered ring of thiophene. In the former case, only a slight ortho-substitution was detected in the products; no meta-substituted product was observed, indicating that the reaction proceeds by an ionic mechanism. On the benzyl chloride–benzene system the alkylation takes place sparingly, albeit catalytically, whereas on the benzyl alcohol–benzene system, instead of such a reaction, condensation-etherization and polymerization of benzyl alcohol take place. In the acylation of toluene by acetyl chloride, only a trace of the product was obtained.

In all polymerization and alkylation reactions, the catalyst undergoes color change corresponding to the reduced stages of molybdenum ions from original yellow to green and finally to blue.¹²⁾ However, the reduction of catalyst would not be essential in the coupling reaction since the initial activity of catalyst and the

selectivity and yields of products were not influenced by the recharge of excess amount of reactants to the blue acid obtained. The blue acid appears to be an active catalyst.

In the acylation and sulfonylation reactions the catalyst partly decomposes, producing an unidentified black solid. This might be caused by a specific reaction between the acetyl chloride or the tosyl chloride and the catalyst. No typical color change of yellow–green–blue was observed.

In the reaction of six-membered aromatic substrates, the ease of coupling decreases in the order, alkylation > acylation > sulfonylation. However, in the five-membered substrate such as thiophene, alkylation scarcely takes place by *t*-butyl chloride. Thus, in the case of five-membered substrate, acylation by acetyl chloride takes place more easily than alkylation under the same conditions.

Since the tetrabutylammonium salts of both the unreduced yellow and the reduced blue heteropolyanions show no catalytic activity, the remarkable strong acidity of catalyst would be important.

The catalytic activity of the acid appears to be comparable to that of $\text{Mo}(\text{CO})_6$ and Arene– $\text{Mo}(\text{CO})_3$ previously reported as “Friedel-Crafts” like catalysts, with respect to the coupling reaction concerned.^{13,14)} Although typical Friedel-Crafts catalysts, whether homogeneous or heterogeneous, are all Lewis acids and are capable of promoting carbonium ion formation from certain organic molecules, the heteropolyacid and the “Friedel-Crafts” like catalysts would show no Lewis acid property; particularly the former behaves as Brønsted acid. $\text{Mo}(\text{CO})_6$ is coordinatively saturated molecules. However, the complex added in the aromatic solvent is easily converted into Arene– $\text{Mo}(\text{CO})_3$ prior to the coupling reaction.¹⁵⁾ In the present work, no evidence has been obtained for the direct coordination of arene rings of reactants to the molybdenum ions in the blue heteropolyacid during the course of reaction. The type of reactions studied here appears to be a carbonium-ion generation mechanism brought about by the strong Brønsted acid.

The essential feature of the heteropolymolybdic acid is the stability of catalyst, appearing in particular in the polymerization and alkylation, and the yielding of products with high selectivity in the case of phenol and anisole.

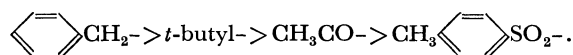
Although the heteropolyacid contains twelve molybdenums, all of them would not play a direct role as active site as in the case of solid-surface catalyst. Thus the turn-over numbers of catalyst have been simply calculated as the molar ratio of catalyst to product. The turn-over number per unit hour (Table 1) shows that (1) all reactions proceed catalytically, not stoichiometrically, and (2) the ease of carbocation forma-

TABLE 1. EXAMPLES OF REACTIONS CATALYZED BY $H_4SiMo_{12}O_{40}$

| Reactant | | Amount of catalyst (mol) | Reflux time (h) | Remarks | Turn-over number per hour | | |
|------------------|---------------------------------|--------------------------|-----------------|-------------------------------|---------------------------|--|---------------------------------------|
| A (mol) | B (mol) | | | | This work | Mo(CO) ₆ ^{b)} catalyst | Friedel-Crafts ^{c)} catalyst |
| — | Benzyl chloride (0.1) | 4.81×10^{-5} | 0.1 | 100% polybenzyl ^{a)} | | | |
| — | Benzyl alcohol (0.1) | 4.81×10^{-5} | 0.1 | 100% polybenzyl ^{a)} | | | |
| Benzene (0.1) | Benzyl chloride (0.1) | 4.00×10^{-5} | 3 | 5% alkylation | 42 | | 2.5×10^{-3} |
| Toluene (1.0) | Benzyl chloride (0.05) | 9.90×10^{-5} | 8 | 74% alkylation | 47 | 66 | |
| Toluene (0.3) | Benzyl alcohol (0.1) | 7.68×10^{-5} | 16 | 74% alkylation | 60 | | |
| Toluene (0.05) | <i>t</i> -Butyl chloride (0.1) | 2.63×10^{-4} | 5 | 87% alkylation | 33 | 32 | |
| Phenol (0.05) | <i>t</i> -Butyl chloride (0.05) | 8.01×10^{-5} | 8.5 | 40% alkylation | 29 | | $2.4 \times 10^{-}$ |
| Anisole (0.3) | <i>t</i> -Butyl chloride (0.1) | 8.23×10^{-5} | 23 | 49% alkylation | 26 | 21 | |
| Toluene (0.24) | Tosyl chloride (0.01) | 2.75×10^{-5} | 20 | 23% sulfonylation | 4 | 3 | |
| Anisole (0.23) | Tosyl chloride (0.026) | 5.49×10^{-5} | 23 | 14% sulfonylation | 3 | 2 | |
| Anisole (0.23) | Acetyl chloride (0.1) | 5.49×10^{-5} | 20 | 19% acylation | 17 | 25 | |
| Thiophene (0.06) | Acetyl chloride (0.1) | 5.49×10^{-5} | 30 | 44% acylation | 16 | | |

a) Ref. 11. b) Ref. 13. c) Ref. 15.

tion may be related to the electronic structure of the halides, decreasing in the order



This tendency corresponds to that in the reactions catalyzed by AlCl_3 , Mo(CO)_6 .

The parameters on the corresponding reactions by Mo(CO)_6 catalyst and Friedel-Crafts catalyst have been conveniently calculated by the data of Farona and White,¹³⁾ and reported data,¹⁵⁾ respectively. The parameters reflect the catalytic efficiency of catalysts, indicating that the former reactions, including the case of the 12-heteropolyacid, are catalytic, and the latter reaction stoichiometric.

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