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Preparation of Vinyl Ethers by Transesterification in the Presence of Molecular Sieves

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The interchange reaction: $\text{CH}_3\text{OCH}=\text{CH}_2 + \text{ROH} \rightleftharpoons \text{ROCH}=\text{CH}_2 + \text{CH}_3\text{OH}$, which is catalyzed by $\text{Hg}(\text{OAc})_2$, has been studied. It was found that the equilibrium could be smoothly shifted toward the product by the selective absorption of the produced methanol on molecular sieves of the type 4A (MS-4A) and that the yield of the desired vinyl ether could be increased. According to this method, we prepared various vinyl ethers, including ethyl, isopropyl, isobutyl, *t*-butyl vinyl ether, and benzyl vinyl ethers. The yields of the alkyl vinyl ethers decrease as their alkyl groups become more electron-donating. The effects of the reaction conditions and the pretreatment of the molecular sieves have been investigated.

The vinyl transesterification catalyzed by mercuric salt is known to have a wide utility in the preparation of various vinyl ethers.¹⁾ As the reaction is reversible, it is necessary to drive the reaction to



completion by appropriate methods. One is the fractionation of a desired vinyl ether out of the reaction mixture in order to shift the reaction continuously toward the product. Another is the equilibration of a mixture of vinyl ether in excess alcohol and a catalyst, and the subsequent freezing of the equilibrium by the flash-stripping of the volatile components or by inactivating the catalyst. The former method, however, has restrictions related as to the boiling points of the components, while the latter gives a lower yield.

In this work we studied this transesterification reaction, using methyl vinyl ether (MVE) as a starting vinyl ether and mercuric acetate ($\text{Hg}(\text{OAc})_2$) as the catalyst, and found that the reaction could be smoothly shifted toward the product by the absorption of the methanol produced selectively on molecular sieves of the type 4A (MS-4A). Molecular sieves have been used by several investigators²⁻⁴⁾ for shifting the chemical equilibria by the selective absorption of one of the products. We prepared vinyl ethers, including ethyl, isopropyl isobutyl, *t*-butyl, vinyl ether and benzyl vinyl ethers, and studied the effects of the reaction conditions as

2) Y. Ito, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 195 (1962).

3) P. Lowenberg, *J. Appl. Chem. (London)*, **9**, 417, (1959).

4) D. P. Roelofsen, J. A. Hagendoorn and H. Bekkum *Chem. & Ind.*, **1966**, 1622.

1) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

well as those of the pretreatment of the molecular sieves.

Experimental

Materials. Gaseous methyl vinyl ether was purified by passing it successively through a saturated aqueous solution of potassium hydroxide and a column packed with potassium hydroxide pellets, it was collected over calcium hydride in a cold trap cooled at -78°C . Then it was distilled under reduced pressure and stored over lithium aluminum hydride. The ether thus purified was redistilled under a vacuum just before use.

All the alcohols used were purified by refluxing them over calcium oxide and by subsequent distillation, they were stored under nitrogen pressure.

The triethylamine was purified by the usual method. The mercuric acetate used as the catalyst was commercially obtained and was used without further purification. The molecular sieves were products of the Union Carbide Corporation and were predried at the desired temperature under a high vacuum for 2 hr just before use.

Preparation of Vinyl Ether. A typical example of the method of preparing isobutyl vinyl ether will now be described. A 100 ml two-necked flask, equipped with a special reflux condenser for low-boiling liquid⁵ and a thermometer, was flushed with dry nitrogen and charged with 20.0 g of MS-4A (1/16 inch pellets) which had been heated at 200°C for 2 hr under a high vacuum. Then 5.8 g (0.1 mol) of methyl vinyl ether, 7.4 g (0.1 mol) of isobutyl alcohol, and 0.5 g (0.0016 mol) of mercuric acetate were introduced into the flask under a nitrogen atmosphere. The reaction was carried out at 0°C for 1 hr with occasional shaking and was then stopped by adding one gram of anhydrous potassium carbonate. The reaction mixture was flash-distilled under a high vacuum. The distillate was shown by a gas chromatographic analysis to contain 6.0 g of isobutyl vinyl ether, 1.8 g of methyl vinyl ether, 2.3 g of isobutyl alcohol, and a trace of methanol. The fractional dis-

tillation of this distillate gave 5.2 g of isobutyl vinyl ether; bp $82.5-83.0^{\circ}\text{C}$, $n_D^{20}=1.3962$. The non-volatile residue of the reaction contained a small amount of the polymeric product. This was shown by NMR spectroscopy to be predominantly poly(isobutyl vinyl ether); it seems to have resulted from the cationic polymerization of the isobutyl vinyl ether by the catalytic action of the molecular sieves. The amount of this polymeric product was estimated roughly by means of the difference between the amount of the residue and the total amount of molecular sieves, mercuric acetate, potassium carbonate used and the methanol adsorbed on the sieves.

Analytical Procedures. The distillate from the reaction mixture was inspected on a Shimadzu Seisakusho gas-liquid chromatograph equipped with a column (2 m long, 4 mm i.d.) containing 30% dioctyl phthalate on Shimalite B and operated at 80°C with a helium-carrier gas stream of 68 ml/min. The calibration curves were used for determining the product compositions, employing toluene as the intensity standard.

The properties of the molecular sieves preheated at various temperatures were investigated in the following manner. One gram of the predried sieves was suspended in 25 ml of conductivity water and stirred for 24 hr under dry nitrogen pressure at 20°C . The pH value of the supernatant liquid was then measured with a pH meter (Yanagimoto Mfg. Co.) at 20°C under dry nitrogen.

Results

Reaction of MVE and Isobutyl Alcohol (*i*-BuOH) Catalyzed by $\text{Hg}(\text{OAc})_2$ in the Presence of MS-4A. The reaction between MVE and *i*-BuOH was carried out in the presence of MS-4A (1/16 inch pellets), using $\text{Hg}(\text{OAc})_2$ as the catalyst. The results are summarized in Table 1. In the reactions without the sieves, the yields of isobutyl vinyl ether (*i*-BVE) were lower. The use of the molecular sieves gave a higher yield of the vinyl

TABLE 1. SYNTHESIS OF *i*-BVE FROM MVE AND *i*-BuOH BY TRANSESTERIFICATION WITH MS-4A PREHEATED AT 200°C FOR 2 hr
Reaction conditions: MVE 0.1 mol, *i*-BuOH 0.1 mol, $\text{Hg}(\text{OAc})_2$ 0.0016 mol.

No.	Solvent	Reaction		MS-4A (g)	Conversion (%)	<i>i</i> -BVE (%)	Polymeric product (%)
		Temp. ($^{\circ}\text{C}$)	Time (hr)				
16	none	0	1	0	24	24	0
20	none	0	1	20	67	60	7
39	none	0	3	20	81	76	5
22	none	30	1	0	38	38	0
19	none	30	1	20	77	73	4
81	none	30	2	20	83	72	11
44	none	0	1	10	50	44	6
18 ^a)	none	0	1	20	0	0	0
28	Benzene 18 ml	0	1	20	48	37	11
105	$(\text{C}_2\text{H}_5)_2\text{O}$ 18 ml	0	1	20	29	29	0
116	$(\text{C}_2\text{H}_5)_2\text{O}$ 18 ml	0	5	20	66	60	6

^a) The reaction was carried out without $\text{Hg}(\text{OAc})_2$ catalyst.

5) R. P. Linstead, J. A. Elvidge and M. Whalley, "A Course in Modern Techniques of Organic Chemistry," Butterworths Scientific Publications (1955), p. 82.

ether as a result of the selective adsorption of methanol. A longer reaction time increased the yield of *i*-BVE at both 0 and 30°C, although it also increased the polymeric product at 30°C. The yield of *i*-BVE was lower when the amount of the sieves was decreased. The reaction without $\text{Hg}(\text{OAc})_2$ gave no *i*-BVE even in the presence of molecular sieves. The use of benzene or diethyl ether as a solvent caused a decrease in the rate of the reaction.

The addition of a small amount of triethylamine to the reaction mixture strongly decreased the yield of the vinyl ether. The results are shown in Table 2.

TABLE 2. EFFECT OF TRIETHYLAMINE ON THE TRANS-ETHERIFICATION OF MVE AND *i*-BuOH IN THE PRESENCE OF MS-4A PREHEATED AT 200°C FOR 2 hr

Reaction conditions: MVE 0.1 mol, *i*-BuOH 0.1 mol, $\text{Hg}(\text{OAc})_2$ 0.0016 mol, reaction time 1 hr, reaction temp. 0°C, MS-4A 20 g.

No.	Et_3N (mmol)	Conversion (%)	<i>i</i> -BVE (%)	Polymeric product (%)
20	0	67	60	7
37	0.07	33	27	6
26	0.7	7	7	0
21	6.9	0	0	0

Effect of the Character of Molecular Sieves on the Transesterification of MVE and *i*-BuOH. The reactions of MVE and *i*-BuOH were carried out at 0°C for 1 hr with MS-4A preheated at various temperatures for 2 hr under a high vacuum. The results are shown in Fig. 1. The maximum yield of *i*-BVE was obtained when sieves preheated at 200°C were used. The amounts of the polymeric products decreased with an increase in the preheating temperature of the sieves, nearly reaching zero when the temperature was 300°C.

When the powdered MS-4A was used, a lower yield of *i*-BVE and a higher yield of polymer were obtained than in the case of the pellet type (Table 3). The molecular sieves 3A and the beads of the MS-4A also gave a lower yield of *i*-BVE.

TABLE 3. EFFECT OF THE TYPES OF MS-4A ON THE TRANS-ETHERIFICATION OF MVE AND *i*-BuOH
Reaction conditions: MVE 0.1 mol, *i*-BuOH 0.1 mol, $\text{Hg}(\text{OAc})_2$ 0.0016 mol, reaction time 1 hr, reaction temp. 0°C, The sieves were preheated at 200°C for 2 hr under high vacuum.

No.	MS-4A		Conversion (%)	<i>i</i> -BVE (%)	Polymeric product (%)
	Type	(g)			
20	pellets	20	67	60	7
42	beads	20	55	49	6
61	powder	20	31	9	22
82	pellets ^{a)}	20	46	38	8

^{a)} Type 3A molecular sieves were used.

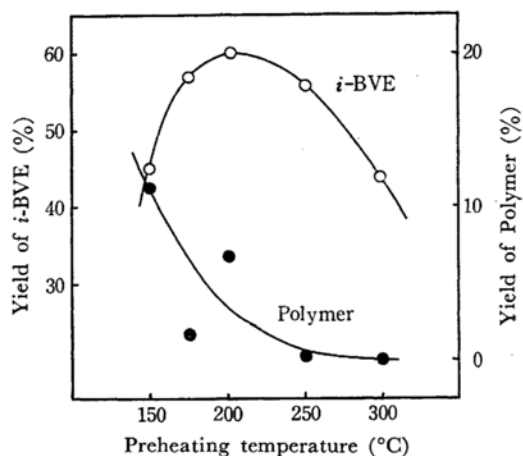


Fig. 1. Effect of the preheating temperature of MS-4A on the transesterification reaction of MVE and *i*-BuOH.

Reaction conditions: MVE 0.1 mol, *i*-BuOH 0.1 mol, $\text{Hg}(\text{OAc})_2$ 0.0016 mol, Temp. 0°C, Time 1 hr, MS-4A was preheated for 2 hr under high vacuum.

Preparation of Other Vinyl Ethers. Transesterification reactions of MVE and various alcohols were carried out at 30°C for 1 hr with and without MS-4A. The results are shown in Table 4. The reactions proceeded smoothly in the presence of the sieves, and this technique for transesterification was proved successful for various combinations including various other aliphatic and aromatic alcohols with MVE. The yields of the desired alkyl vinyl ethers decreased, and the fractions of the polymeric product against the reacted MVE increased, as their alkyl groups were more electron-donating.

The reaction of MVE and *t*-butyl alcohol gave no *t*-butyl vinyl ether in the absence of molecular sieves, but a fairly good yield of *t*-butyl vinyl ether was obtained in the reaction with the sieves. The use of diethyl ether as a solvent reduced the fraction of the polymeric product, although the yield of the vinyl ether was also decreased. A prolonged reaction time resulted in a remarkable increase in the fraction of the polymer.

TABLE 4. PREPARATION OF VARIOUS VINYL ETHERS FROM MVE AND THE ALCOHOL BY TRANSESTERIFICATION AT 30°C FOR 1 hr WITH MS-4A PREHEATED AT 200°C FOR 2 hr

Reaction conditions: MVE 0.1 mol, alcohol 0.1 mol, Hg(OAc)₂ 0.0016 mol.

No.	Alcohol	MS-4A (g)	Conversion (%)	Vinyl ether (%)	Polymeric product (%)
47	Ethyl alcohol	0	26	26	0
46	Ethyl alcohol	20	78	70	8
51	Isopropyl alcohol	0	8	8	0
50	Isopropyl alcohol	20	71	46	25
52	<i>t</i> -Butyl alcohol	0	0	0	0
8	<i>t</i> -Butyl alcohol	20	29	18	11
113 ^{a)}	<i>t</i> -Butyl alcohol	20	10	8	2
110 ^{a,c)}	<i>t</i> -Butyl alcohol	20	6	6	0
121 ^{a,b,c)}	<i>t</i> -Butyl alcohol	20	31	16	15
145	Benzyl alcohol	0	14	14	0
86 ^{d)}	Benzyl alcohol	20	55	42	13
129 ^{e)}	<i>p</i> -Chlorobenzyl alcohol	20	95	57	38
130 ^{e)}	<i>p</i> -Methylbenzyl alcohol	20	87	43	44

^{a)} As a solvent 18 ml of diethyl ether were used.^{b)} Reaction time 5 hr.^{c)} Reaction temp. 0°C.^{d)} Alcohol 0.3 mol, reaction time 3 hr.^{e)} Alcohol 0.6 mol, reaction time 3 hr, as a solvent 18 ml of benzene were used.

Properties of Molecular Sieves Preheated at Various Temperatures. The pH value of a water suspension of MS-4A is shown in Fig. 2. With an increase in the temperature at which the sieves are preheated, the pH value increases; it passes through a maximum value of 9.96 at 200°C and then gradually falls off.

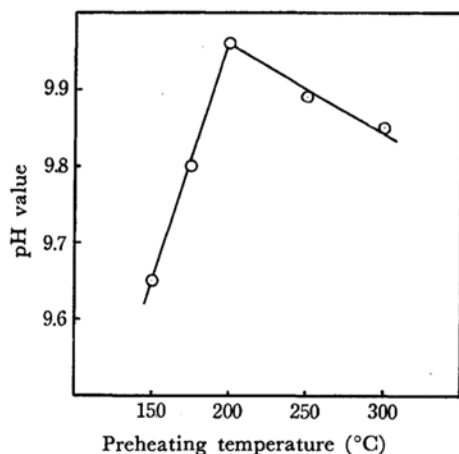
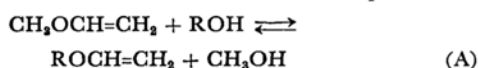


Fig. 2. pH Value of water suspension of MS-4A preheated at various temperatures.

Discussion

It has been ascertained that the equilibrium:



was rapidly established by the Hg(OAc)₂ catalyst.⁶⁾ In this work we found that the reaction goes *smoothly* toward the right-hand side by the absorption of methanol selectively on MS-4A. The molecular sieves of the type 4A permit the reaction of MVE with any alcohol. The sieves of the type 3A work similarly, although the yield of vinyl ether is lower than in the case of the type 4A. The sieves of the type 5A, 10X or 13X have no absorption selectivity for methanol and produce a large amount of the polymeric product because of their higher catalytic activities for cationic polymerization.

The equilibration of the interchange reaction of MVE and *i*-BuOH is rapidly attained at 30°C, and the equilibrium constant is 0.570.⁶⁾ On the other hand, the absorption capacity of 20 g of MS-4A for methanol is about 0.09 mol at 30°C. From these data it may be expected that the reaction between 0.1 mol of MVE and *i*-BuOH catalyzed by Hg(OAc)₂ will go nearly to completion in the presence of 20 g of MS-4A. However, the actual conversion in the reaction is 83% for 3 hr. This appears to result from the occlusion of the molecular sieves with a polymeric product of *i*-BVE.

The only disadvantage of this ether-interchange technique is the decrease in the yield of the desired ether because of the polymer formation on the surface of the molecular sieves, as has been mentioned above. The attempt to prevent the polymerization of the resulting ether by the addition of a

6) H. Yuki, K. Hatada and K. Nagata, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **73**, No. 4 (1970), in press.

small amount of triethylamine was not successful because of the decrease in the yield of the ether. The added amine may inactivate the mercuric acetate catalyst.

In the interchange reaction of MVE and alcohol with molecular sieves, lower yields of vinyl ethers were obtained when the alkyl groups of the resulting ethers were more electron-donating. This result may arise from the fact that the reactivity of the resulting vinyl ether for the cationic polymerization is higher,⁷⁾ as the alkyl group, R, in the reaction (A) is more electron-donating. The use of MVE as a starting vinyl ether is favorable for this technique because of its low polymerizability

and the ease of its separation from the product by fractional distillation.

As is shown in Fig. 2, a water suspension of MS-4A preheated at temperatures from 150°C to 300°C had a pH value between 9.65 and 9.96, the maximum pH being obtained when the sieves were preheated at 200°C. This correlation resembles that between the yield of vinyl ether in the transesterification with molecular sieves and the preheating temperature of the sieves given in Fig. 1. However, the true significance of this interrelation is not certain at the present time.

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7) H. Yuki, K. Hatada and M. Takeshita, *J. Polymer Sci., A-1*, **7**, 667 (1969).