BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1817—1820 (1970)

On the Mechanism of the Vinyl Transetherification Reaction Catalyzed by Mercuric Acetate

Heimei YUKI, Koichi HATADA and Kazuhiko NAGATA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received November 26, 1969)

The vinyl interchange reaction of methyl vinyl ether and methanol, methanol-d_4, or ethanol catalyzed by mercuric acetate has been studied. Some organomercuric compounds have been isolated from the reaction mixture, and their catalytic activity for the interchange reaction has been examined. From these results, the mechanism proposed by Watanabe and Conlon (*J. Amer. Chem. Soc.*, **79**, 2828 (1957)) has been confirmed and further details of the reaction mechanism are discussed.

The vinyl transetherification catalyzed by mercuric salt is known to be of wide utility for the preparation of various vinyl ethers.

$$ROCH{=}CH_2 + R'OH \rightleftharpoons ROH + R'OCH{=}CH_2$$

In a previous work[1,2] we studied this transetherification reaction using methyl vinyl ether (MVE) as a starting vinyl ether and a mercuric acetate ($Hg(OAc)_2$) catalyst, and found that the reaction could be smoothly shifted toward the product by the selective absorption of the produced methanol on the molecular sieves. Although a probable mechanism of the reaction[3] has been proposed, sufficient evidence has not yet been obtained. In the present work we investigated the reaction of MVE and methanol, methanol-d_4, or ethanol in the presence of $Hg(OAc)_2$ to clarify the mechanism of the reaction.

Experimental

Materials. MVE was purified in a gas phase by being passed through a saturated aqueous solution of potassium hydroxide and a column packed with potassium hydroxide pellets successively; then it was collected over calcium hydride in a cold trap cooled at −78°C. It was subsequently distilled under reduced pressure and stored over lithium aluminum hydride. The MVE thus purified was redistilled under a vacuum just before use.

The methanol and ethanol were purified by refluxing them over calcium oxide and by subsequent distillation, and these were stored under a nitrogen atmosphere. The methanol-d_4 and mercuric acetate were commercially obtained and were used without further purification.

The 2-acetoxymercuri-1,1-dimethoxyethane was prepared from sodium methoxide, mercuric acetate, and methyl vinyl ether.[3] Mp 64.0—65.0°C.

Reaction of MVE and Alcohol in the Presence of $Hg(OAc)_2$. A two-necked flask, equipped with a special reflux condenser for low-boiling liquid[4] and a thermometer, was flushed with dry nitrogen and then charged with an equimolar mixture of MVE and the alcohol, and a mercuric acetate catalyst. The reaction was carried out at 30°C for 1 hr under a nitrogen atmosphere. The reaction mixture was then flash-distilled under a high vacuum, and the distillate was analyzed by gas-liquid chromatography or NMR spectroscopy. The remaining solid residue was recrystallized from ether and was identified by means of analyses.

In another experiment, the reaction mixture was treated with potassium carbonate before flash-distillation under a high vacuum.

Analytical Procedure. Gas-liquid chromatographic analysis was carried out using a Shimadzu Seisakusho gas-liquid chromatograph equipped with a column (2 m long, 4 mm I.D.) containing 30% dioctyl phthalate on Shimalite B (a kind of kieselguhr). The apparatus was operated at 80°C with a helium-carrier gas stream of 68 *ml*/min, while toluene was employed as the intensity standard for the determination of the product composition.

The NMR spectra were taken on a JNM-4H-100 spectrometer (JEOL) at 100 MHz in CCl_4 at 22.5°C. Tetramethylsilane was used as the internal reference.

The molecular weight was determined on a Mechrolab Vapor Pressure Osmometer (Model 310A) in carbon tetrachloride at 37.0°C.

Analysis for mercury was carried out by the decomposition of a sample with concentrated sulfuric acid and by subsequent titration with ammonium thiocyanate, according to the method of Hirai.[5]

---

[1] H. Yuki, K. Hatada and K. Nagata, This Bulletin, **42**, 3546 (1969).

[2] H. Yuki, K. Hatada and K. Nagata, *Kogyo Kagaku Zasshi*, **73**, 715 (1970).

[3] W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **79**, 2828 (1957).

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

[5] M. Hirai and R. Hayatsu, *Yakugaku Zasshi*, **70**, 670 (1950).

TABLE 1. REACTION OF METHYL VINYL ETHER AND METHANOL AT 30°C FOR 1 hr IN THE PRESENCE OF $Hg(OAc)_2$

Reaction Conditions: MVE 0.1 mole, MeOH 0.1 mole, $Hg(OAc)_2$ 0.0016 mole.

No.	K_2CO_3 (g)	Reaction product (g) I[b]	II[c]	Mp (°C)	Mol wt Found	Calcd	Elementary analysis[d] (%) C	H	Hg
123	0	0.6	0	64~5°C	352	348	20.76	3.29	57.4
117	1.0	0	0.5	liquid	367	378	25.89	4.88	51.7
118[a]	1.0	0	0.4	liquid	377	378	25.02	4.64	52.1

[a] Reaction temp. 0°C.

[b] 

$(CH_3O)_2CHCH_2HgOAc$

[c] 

$((CH_3O)_2CHCH_2-)_2Hg$

[d] Calcd for I ($C_6H_{12}O_4Hg$): C, 20.66; H, 3.47; Hg, 57.52%. Calcd for II ($C_8H_{18}O_4Hg$) C, 25.36; H, 4.79; Hg, 52.95%.

Results

Reaction of MVE and Methanol or Methanol-d_4 in the Presence of $Hg(OAc)_2$. An equimolar reaction of MVE and methanol in the presence of $Hg(OAc)_2$ was carried out at 30°C for 1 hr under a nitrogen atmosphere. The vacuum distillation of the reaction mixture gave a recovery of 93% of the equimolar mixture of MVE and methanol, leaving a solid residue. The recrystallization of this residue from ether gave 2-acetoxymercuri-1,1-dimethoxy-ethane (I), which was identified by an NMR spectral comparison with an authentic sample. This identification was also supported by the measurements of its melting point and molecular weight, and by the results of an elementary analysis (Table 1).

When the reaction mixture was treated with potassium carbonate before vacuum distillation and the residue was extracted with diethyl ether, a viscous liquid with a high boiling temperature was obtained after the removal of ether from the extract. This compound was found by NMR spectroscopy to be bis-2,2-dimethoxyethylmercury (II) (Fig. 1). This structure was also established by the measurements of the molecular weight and by the results of an elementary analysis (Table 1).

In order to examine the catalytic activity of these two compounds for transetherification, equimolar reactions of MVE and methanol-d_4 were performed in the presence of these compounds at 30°C for 1 hr, and the reaction mixtures were analyzed by NMR spectroscopy. The NMR spectrum of the reaction mixture of MVE, methanol-d_4 and

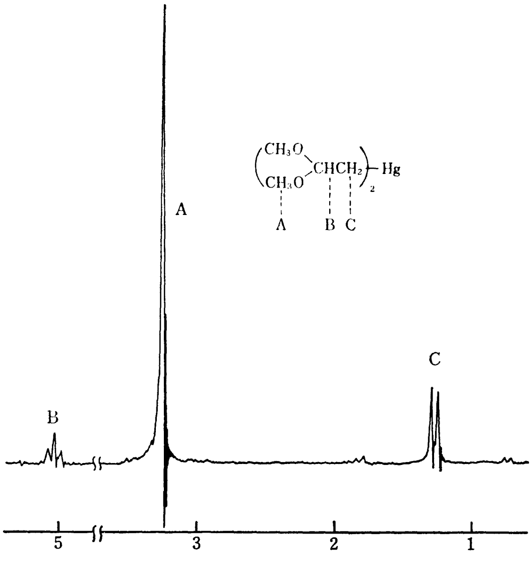


Fig. 1. NMR spectrum of bis-2,2-dimethoxyethylmercury. Intensity ratio of the signals: A : B : C=6.00 : 0.90 : 2.06.

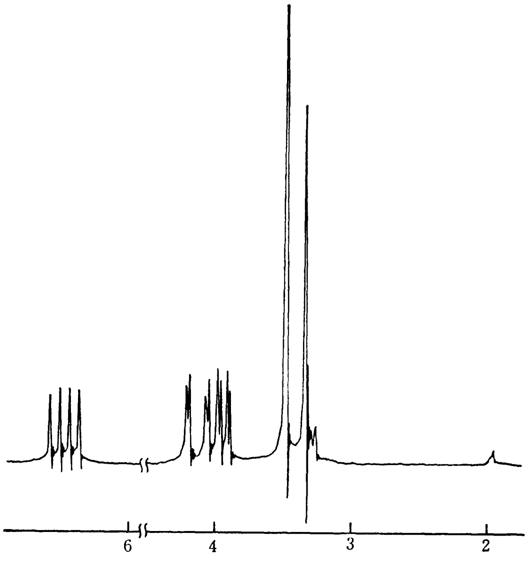


Fig. 2. NMR spectrum of the reaction mixture of MVE and methanol-d_4 in the presence of 2-acetoxymercuri-1,1-dimethoxyethane.

the compound I showed a sharp singlet

$$CH_3OCH{=}CH_2 + CD_3OD \rightleftharpoons CD_3OCH{=}CH_2 + CH_3OD$$

at 3.35 ppm due to the methyl protons of CH_3OD produced (Fig. 2). From the intensity ratio of this signal to the methoxy proton signal of MVE, the conversion of MVE to MVE-d_3 was calculated to be 44%. On the other hand, the compound II showed no catalytic activity in the interchange reaction. However, in the presence of a small amount of acetic acid, this compound catalyzed the reaction quite well and 50% of MVE-d_3 was produced.

Reaction of MVE and Ethanol in the Presence of $Hg(OAc)_2$. To prove that mercurial compounds such as I are formed in the interchange reaction of a combination of MVE and another alcohol, a mixture of 0.1 mol of MVE, 0.1 mol of ethanol, and 0.0016 mol of $Hg(OAc)_2$ was reacted at 30°C for 1 hr under a nitrogen atmosphere. From the reaction mixture the volatile component was then distilled off under a high vacuum. The residue was extracted with diethyl ether, the ether was then distilled off under a high vacuum. The NMR spectrum (Fig. 3) of the remaining liquid with a high boiling temperature (0.6 g) shows that the product is a mixture of 2-acetoxymercuri-1-methoxy-1-ethoxyethane (III) and 2-acetoxymercuri-1,1-diethoxyethane (IV). The ratio of the compounds III and IV was roughly estimated to be 1 : 1 by the intensity measurement of the NMR signals.

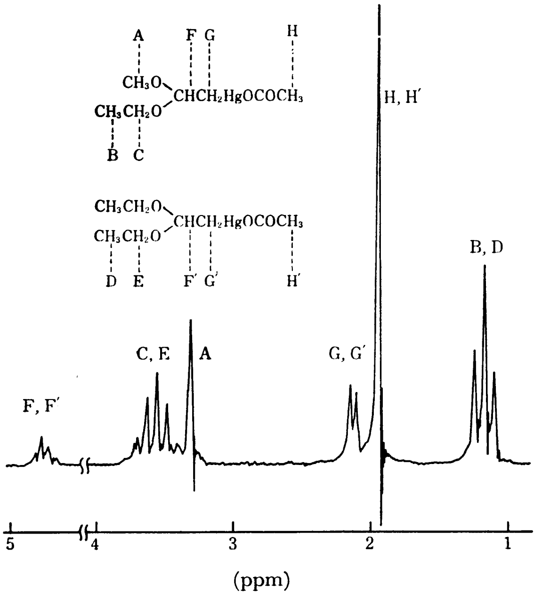


Fig. 3

When the reaction mixture was treated with potassium carbonate before vacuum distillation, 0.6 g of a liquid with a high boiling temperature was also obtained. The NMR spectrum (Fig. 4) shows that the product formed is probably a mixture of bis-2-methoxy-2-ethoxyethylmercury (V), bis-2,2-diethoxyethylmercury (VI), and a small quantity of acetoxymercuric compounds.

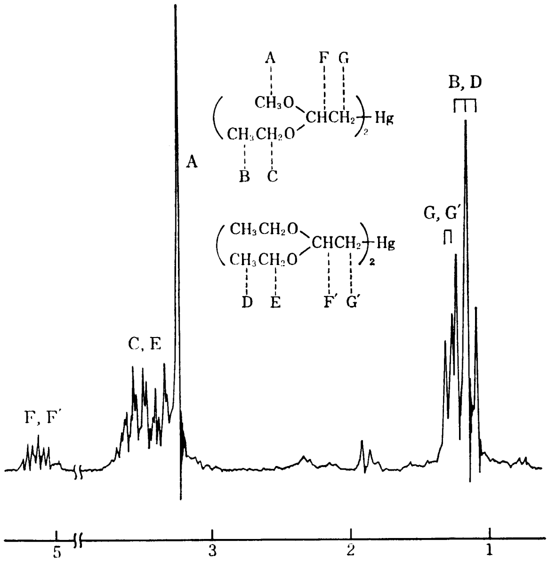
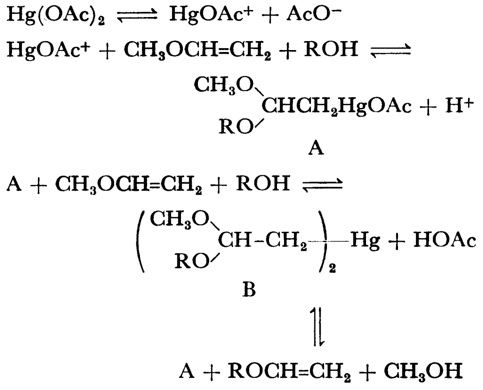


Fig. 4

Discussion

In 1957 Watanabe and Conlon[3] proposed a mechanism of the transetherification reaction on the basis of the fact that the 2-acetoxymercuri-1,1-diethoxyethane was decomposed readily by acetic acid to ethyl vinyl ether and ethyl alcohol. According to their proposal, the mechanism of the reaction starting with MVE can be illustrated as follows:



$$Hg(OAc)_2 \rightleftharpoons HgOAc^+ + AcO^-$$

$$HgOAc^+ + CH_3OCH{=}CH_2 + ROH \rightleftharpoons \underset{\text{A}}{\begin{matrix}CH_3O\diagdown\\ \quad CHCH_2HgOAc\\ RO\diagup\end{matrix}} + H^+$$

$$\text{A} + CH_3OCH{=}CH_2 + ROH \rightleftharpoons \underset{\text{B}}{\left(\begin{matrix}CH_3O\diagdown\\ \quad CH{-}CH_2\\ RO\diagup\end{matrix}\right)_2 Hg} + HOAc$$

$$\Updownarrow$$

$$\text{A} + ROCH{=}CH_2 + CH_3OH$$

In the present work we have been able to isolate the intermediate A(R$=CH_3$) directly from an equilibrium mixture of MVE, methanol, and mercuric acetate; and we found this intermediate to be catalytically active for the transetherification reaction of MVE and methanol-d_4. The intermediate B ($R=CH_3$), which was found to be catalytically inactive but become active in the presence of a small amount of acetic acid, was scarcely formed in the mixture. After the treatment of the equilibrium mixture with potassium carbonate, the intermediate A vanished and the intermediate B was formed. The formations of analogous intermediates were proved in the reaction of MVE and ethanol catalyzed by $Hg(OAc)_2$.

These results clearly confirm the mechanism proposed by Watanabe and Conlon. No direct evidence can be found for the existence of an intermediate of the type B in the reaction mixture. However, this must exist to a very small extent in equilibrium with other species. The addition of an excess of potassium carbonate to the reaction mixture causes the equilibrium to shift toward the intermediate B as a result of the salt formation with acetic acid; consequently, this inactivates the catalyst.

If a proton from the acetic acid attacks the oxygen atom of the CH_3O group in the intermediate B, the resulting oxonium ion decomposes to A and the desired vinyl ether, while the methanol is expelled. On the other hand, if the attack of a proton takes place on the oxygen atom of the RO group, the reaction proceeds to the left and the starting vinyl ether and alcohol are recovered. Therefore, it is expected that the larger the electron-repelling power of the R group, the greater the tendency for a proton attack to occur on the oxygen of the RO group and the less the tendency for the desired vinyl ether to be formed. The equilibrium constant of the transetherification reaction of MVE and alcohol (ROH) decreases in the order of; $R=C_2H_5>n\text{-}C_3H_7>i\text{-}C_3H_7>t\text{-}C_4H_9$.[2)]

$$CH_3OCH{=}CH_2 + ROH \overset{K}{\rightleftharpoons} ROCH{=}CH_2 + CH_3OH$$

This result exactly coincides with the above explanations and also supports the idea of the existence of the intermediate B.

The authors wish to express their thanks to Mr. K. Kajiyama for his help in the laboratory work and to Mrs. F. Yano for her clerical assistance in preparing the manuscript.