shift the equilibrium to the Y and Z or even to the X forms before the dehydrating effect of the sulfuric acid, *per se*, comes into play.

Consequently, the effect on the relative concentrations of the various colored components will differ from that induced by the hydrogen ion alone. It is in this way that the extremely high concentrations of the X component, observed in Fig. 5, can be explained.

To recapitulate our argument in general terms, we may say that a substance not giving too high a hydrogen ion concentration when it, itself, is in relatively low concentrations, but possessing a tendency to dehydrate the system when it is taken in higher concentrations, will be effective in favoring high concentrations of X components. Such is the case of sulfuric acid, and such is the case for the hydrobromic acid systems.

In advancing an hydration mechanism it is important to emphasize that this need not necessarily be the sole process involved. Often, in equilibria of this sort autocomplex formation occurs. Usually such complex formation is indicated at least in this region of the periodic table by anomalous colors. Thus anhydrous cupric chloride is brownish-yellow, whereas in the hydrated state it has the characteristic blue-green color. Cobalt chloride shows an analogous color change.[7]

From the studies of quinquevalent molybdenum so far considered, it has not been possible to establish whether autocomplex formation analogous to the above is responsible for the phenomena observed. Additional studies involving measurements of ionic mobilities should help to solve this problem.

Acknowledgments.—The authors would like to express their appreciation to the Work Projects Administration for financial support for all of this work; to the Brittingham Foundation for the use of some of the spectrophotometric equipment and particularly to Mr. Max Wolf for his assistance in the experiments. Professors Norris F. Hall and Casimir Fajans were particularly helpful in their discussions of the problem.

Summary

A study of the transition of quinquevalent molybdenum from the colorless to the amber forms was made. The relative effect of a group of alkali chlorides in inducing the transition from the colorless to the amber form, was determined. The effect of hydrobromic acid and of magnesium bromide on the reaction was also measured. In addition the effect of sulfuric acid in various hydrochloric solutions was studied.

The data obtained were interpreted in terms of two factors which would have a dehydrating effect on the system under discussion. These factors were the hydrogen ion concentration and the tendency of an added solvent to unite with the water of the system by means of dipole–dipole interactions.

MADISON, WISCONSIN RECEIVED DECEMBER 16, 1940

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[7] Howell, *et al.*, *Phil. Mag.*, **48**, 833 (1924); *J. Chem. Soc.*, 162 (1929); *Proc. Roy. Soc.* (London), **A142**, 587 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY AND FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

The Catalytic Preparation and Interconversion of Simple and Mixed Ethers

BY V. N. IPATIEFF AND ROBERT L. BURWELL, JR.

It has been shown[1] that at high temperatures and pressures alumina serves as catalyst for the dehydration of methyl alcohol to form dimethyl ether. The behavior of alcohols and ethers in the presence of a "solid phosphoric acid" catalyst[2] was the subject of the present investigation.

The preparation of dimethyl ether represents a special case in the dehydration of alcohols in that an olefin cannot be formed. Continuous flow experiments at 350° and under 55 atmospheres pressure showed that solid phosphoric acid is an excellent catalyst for the production of dimethyl ether. It is durable and permits the use of very high space velocities.

At temperatures between 400 and 450° decomposition of dimethyl ether occurred.

The passage of an equimolar mixture of methanol and ethanol over the solid phosphoric acid catalyst at 336° under a pressure of 60 atm. pro-

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[1] Ipatieff, *Ber.*, **37**, 2961 (1904).

[2] Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, N. Y., 1936, p. 623.

vides a new method for the production of ethyl methyl ether. Dimethyl ether and diethyl ether are produced simultaneously though the latter compound is extensively decomposed to ethylene and water.

With the same catalyst, the exchange of radicals between diethyl and dimethyl ethers to form ethyl methyl ether was found to occur at 150° in experiments carried out in an autoclave.

The reaction between benzyl and methyl alcohols also was studied. Benzyl methyl ether and dibenzyl ether were isolated.

Experimental

Most of the experiments were performed in a continuous flow system. The liquid charge was kept under nitrogen pressure in a steel charger from the bottom of which it passed to the top of a chromium–molybdenum steel catalyst tube encased in a thermostatically controlled electric furnace. A constant rate of flow of the liquid was maintained with the aid of a pressure flowmeter. The valve at the bottom of the catalyst tube released the products to atmospheric pressure, the collecting system consisting of a copper coil cooled with tap water, a receiver, a calcium chloride tube, a receiver cooled with dry ice and a wet test meter.

Formation of Dimethyl Ether.—Seventy cubic centimeters (63.6 g.) of "solid phosphoric acid" in the form of pellets (5 × 7 mm.) served as the catalyst.

Upon the initial passage of methanol over the fresh catalyst a small amount of a *greenish liquid* which contained methyl phosphate was obtained. However, the succeeding portions of the liquid product which collected in the first receiver contained no phosphoric acid or phosphates. This initial extraction of phosphoric acid *stabilizes* the catalyst and it can be used for a long time without decreased activity. In the run which followed the stabilization of the catalyst, the temperature of the catalyst bed was 350°, the pressure, 55 atm. Table I summarizes the results obtained using various space velocities.

TABLE I

FORMATION OF DIMETHYL ETHER FROM METHANOL

Run	Flow rate cc./hr.	Space velocity cc./hr./cc. catalyst	Conversion, %
1	110	1.6	87.0
2	200	2.9	86.5
3	253	3.6	86.0
4	361	5.0	86.0

In these experiments no evidence of decomposition of dimethyl ether was observed; only at 450° does decomposition occur.

Dimethyl ether was passed over the catalyst at 450° under a pressure of 50 atm. with a rather slow rate (Gas Analysis: CH_4, 95.5%; CO, 2.8%; CO_2, 1.6%). After reaction the catalyst was found to be considerably carbonized in contrast to catalysts used at 350° which exhibited no such carbonization.

Formation of Ethyl Methyl Ether from Mixed Alcohols.—The charge was an equimolar mixture of methanol and ethanol; stabilized solid phosphoric acid was used as catalyst. In 1.33 hours at 336° under 60 atm. pressure, the products listed in Table II were obtained. The residue boiled at about 75° and consisted of methanol and ethanol. The effluent gas consisted of ethylene.

TABLE II

FORMATION OF ETHYL METHYL ETHER FROM MIXED ALCOHOLS

Dimethyl ether	18.4 g.
Ethyl methyl ether	22.4 g., b. p. 6°
Diethyl ether	5.6 g.
Residue	1.6 g.
Non-condensable gas	11.8 liters (22°, 750 mm.)

Preparation of Benzyl Methyl Ether.—An equimolar mixture of benzyl and methyl alcohols was passed over 75 cc. of fresh catalyst at 350° and 50 atm. pressure; 69.3 g. of the organic layer (collected during forty-five minutes) gave 31 cc. of oil upon steam distillation. After drying with calcium chloride, this was distilled in a 5–6 plate column to yield 25 cc. of benzyl methyl ether which was then distilled in a 25 plate column. The boiling point was found to be 170.4° at 749.3 mm. (cor. 171.1°); $n^{20}\text{D}$ –1.5031; $d^{25}{}_4$ 0.9745.

Exchange of Simple Ethers to Form Mixed Ethers.—About 120 cc. of an equimolar mixture of diethyl and dimethyl ethers was released from a charger into a 425-cc. Ipatieff rotating autoclave[3] in which 10 g. of catalyst had been placed; 14 atm. of hydrogen was admitted to hinder diffusion to and condensation in the head and pressure gage. The autoclave was heated six hours at 150°. While still warm the contents were released through a dry-ice trap and a wet test meter. The contents of the dry-ice trap were subjected to a distillation analysis in a small bore column (24–26 theoretical plates) with a double internal spiral. The effluent gas, without considering the hydrogen, consisted almost entirely of ethylene. The results are given in Table III.

TABLE III

REACTION OF DIMETHYL AND DIETHYL ETHERS

	Grams	Moles
Ethylene	1.8	0.06
Dimethyl ether	18.7	.41
Ethyl methyl ether	15.0	.25
Diethyl ether	27.5	.37

In these experiments, the ethyl methyl ether distilled at 6° at a pressure of 749–750 mm., $n^{4}\text{D}$ 1.3420.

In view of the fact that the "International Critical Tables" and other references give the b. p. of ethyl methyl ether as 7.5 or 10.8°, it was synthesized by the Williamson reaction. Distillation in the 25 plate column yielded a liquid of b. p. 6.6° (cor. to 760 mm.).

Summary

1. "Solid phosphoric acid" is an excellent catalyst for the production of dimethyl ether from methanol.

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[3] Ref. 2, p. 31.

2. "Solid phosphoric acid" will catalyze the following reactions: between ethanol and methanol to form ethyl methyl ether; between diethyl and dimethyl ethers to form ethyl methyl ether; between benzyl and methyl alcohols to form benzyl methyl ether.

EVANSTON, ILLINOIS,
AND RIVERSIDE, ILLINOIS RECEIVED NOVEMBER 7, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIAMI UNIVERSITY]

Reactions of Monoalkylanilines with β,β'-Dichlorodiethyl Ether: 4-Phenylmorpholine

BY H. C. BRILL, C. N. WEBB AND H. S. HALBEDEL[1]

A study of the reaction of β,β'-dichlorodiethyl ether with methyl, ethyl, *n*-butyl and isoamylanilines was undertaken in the expectation of preparing phenylalkylaminoethyl-β-chloroethyl ether and using it in further reactions in the preparation of other compounds that might possess local anesthetic properties.

In their investigation of the preparation of divinyl ether by treatment of β,β'-dichloro and of β,β'-diiodo-diethyl ether with various bases, Ruigh and Major[2] found the dichloro to be unreactive with dimethylaniline but that the diiodo yielded the diiodide of *bis*-β,β'-phenyldimethylaminoethyl. The dichloro ether produced no identifiable products when heated with quinoline. Apparently tertiary bases of this nature do not split out hydrogen chloride or hydrogen iodide.

No such trouble was anticipated with the secondary amines which we contemplated using. Nevertheless, in actuality a reaction of quite another type took place.

Dichlorodiethyl ether was refluxed with the above-mentioned monoalkyl anilines. Two-tenths of a mole each of the ethyl- and methylanilines and 0.06 and 0.1 mole of the *n*-butyl and isoamylanilines were taken, respectively. Equal molar quantities of the amines were taken in each case and the time of heating varied between two and four hours. The boiling points of all the mixtures rose to approximately 225°, although with the two higher alkyl anilines a temporary drop in temperature occurred prior to the distillation of the volatile liquid. Hydrogen chloride was evolved in all cases. With methyl- and ethylaniline gases (3 liters) were given off insoluble in water, heavier than air, with a sweetish odor, and burning with a green flame yielding hydrogen chloride. The gas obtained from the ethylaniline, tested by the method of Demer and Dysinger,[3] gave no indication of ethylene. With *n*-butyl- and isoamylanilines, low-boiling liquids were produced in amounts of 1.1 and 4 g. These were distilled off in the middle of the refluxing period and after purification by redistillation boiled at 77–77.5 and 98–102° and had refractive indices (n^{20}_{D}) of 1.4027 and (n^{18}_{D}) 1.4110, respectively. *n*-Butyl chloride and isoamyl chloride have boiling points of 78 and 99.7°, and refractive indices (n^{20}_{D}) of 1.4015 and (n^{18}_{D}) 1.4112, respectively. It is evident that the gases are methyl and ethyl chlorides, and the volatile liquids *n*-butyl and isoamyl chlorides, respectively.

The original reaction mixtures on cooling gave a mixture of oil (unchanged reactants) and crystals. The oil was removed by a porous plate and the crystals purified by recrystallization from 50% alcohol using boneblack. A yield of about 15 g. was obtained from the methyl and ethyl anilines and 3 g. and 1 g., respectively, from the *n*-butyl and isoamylanilines.

A molecular weight determination was made on the product of the ethylaniline, with the following results.

Mol. wt., subs. 0.2725 g., benzene 19.06 g. Δt 0.420°. Found: mol. wt., 162; mol. wt., 4, phenylmorpholine, 163.

Mixed melting point determinations on the four solid products with known 4-phenylmorpholine prepared by the method of Cretcher, Koch and Pittenger[4] showed that they all were 4-phenylmorpholine.

Attempts to run this reaction with ethylaniline in the presence of 10% aqueous sodium hydroxide or in toluene solution were unsuccessful.

While no intermediate products have been

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(1) Abstract of a thesis submitted in partial fulfillment of the requirements for a degree of Master of Arts.

(2) Ruigh and Major, THIS JOURNAL, 53, 2662 (1931).

(3) Demer and Dysinger, *ibid.*, 61, 750 (1939).

(4) Cretcher, Koch and Pittenger, *ibid.*, 47, 1174 (1925).