and Liebhafsky, that the fourth order rate determining reaction is reversible, so that the maximum rate of reaction can be obtained only when a primary reaction product is removed with sufficient rapidity to prevent a reversal of the reaction. Allyl alcohol has been found to be about as efficient as hydrogen peroxide in removing a primary reaction product of the bromate–bromide reaction.

PHILADELPHIA, PA. RECEIVED JANUARY 15, 1936

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Vapor Pressures of the Xylenes and Mesitylene[1]

BY LOUIS S. KASSEL[2]

The vapor pressure data given in the "International Critical Tables" for the xylenes, mesitylene, cumene, pseudocumene, *n*-propylbenzene, cymene and isobutylbenzene are based on measurements of Woringer.[3] These results give very strongly curved plots of log p against $1/T$, indicative of serious error, and indeed a few measurements made by Linder[4] near 0° for several of these compounds showed that Woringer's values at the lower temperatures were much too high. Since it became necessary to calculate entropies of vaporization for the xylenes and mesitylene, the vapor pressures of these substances were remeasured.

Eastman chemicals were used in all cases without further purification other than degassing. The liquid being used was contained in a side tube attached to one arm of a mercury manometer. Both arms were evacuated by a high-speed, mercury diffusion pump until 30–50% of the liquid had evaporated and were then sealed off. The entire manometer system was then immersed in an unsilvered, unevacuated Dewar vessel filled with hot water. Pressures were read with a cathetometer and temperatures with two thermometers calibrated by the Bureau of Standards. With this arrangement it was possible to obtain the vapor pressure curve from 90 to 30° in a few hours. Lower temperatures were obtained by starting with cold water. The accuracy thus attainable is naturally limited, but it is probably as good as the purity of the materials justified. The cathetometer readings were reduced to mm. of a mercury column at 0°.

Consideration of all the measurements and data for benzene and toluene led to choice of the equation

$$\log_{10}P = -A/T - 5\log_{10}T + B$$

The experimental values were fitted by least squares to equations of this type with the following results

$$\begin{array}{lrcl}
o\text{-xylene} & \log_{10}P & = & -2830.0/T - 5\log_{10}T + 22.7480 \\
m\text{-xylene} & \log_{10}P & = & -2876.3/T - 5\log_{10}T + 22.9425 \\
p\text{-xylene} & \log_{10}P & = & -2930.0/T - 5\log_{10}T + 23.1000 \\
\text{mesitylene} & \log_{10}P & = & -3104.5/T - 5\log_{10}T + 23.1929
\end{array}$$

In these equations 0°C. = 273.2°K. The mean deviation of individual experimental values from the equations is approximately 1% in pressure or 0.2° in temperature for pressures above 10 mm. Table I contains pressures calculated from the equations.

TABLE I

VAPOR PRESSURES, MM.

Temp., °C.	*o*-Xylene	*m*-Xylene	*p*-Xylene	Mesitylene
0	1.61	1.71	1.56	0.44
10	3.13	3.35	3.11	.93
20	5.75	6.25	5.90	1.86
30	10.1	11.1	10.7	3.51
40	17.1	19.0	18.4	6.33
50	27.6	31.3	30.7	11.0
60	43.7	49.7	49.3	18.3
70	66.7	76.6	76.7	29.5
80	98.9	114.6	115.9	46.0
90	..	..	..	69.9
100	..	..	..	103.4

Woringer gave 4.0, 1.75, 8.29 and 15.6 mm., respectively, at 0°. These values illustrate the large errors possible in a static method without sufficient degassing. Linder found 1.06, 1.68, 0.95 and 0.375 mm. at 0°. It is difficult to reconcile his low values for *o*- and *p*-xylenes with the present measurements.

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(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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(3) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

(4) Linder, *J. Phys. Chem.*, **35**, 351 (1931).

The calculated entropies of vaporization to the hypothetical perfect gas at 25° and atmospheric pressure are 24.35 e. u. for *o*-xylene, 25.24 e. u. for *m*-xylene, 25.96 e. u. for *p*-xylene and 26.39 e. u. for mesitylene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Isomeric Monoalkyl Ethers of 2-Methyl-1,2-propanediol from 1,2-Epoxy-2-methylpropane[1]

BY C. E. SPARKS AND R. E. NELSON

Introduction

The monoalkyl ethers of 2-methyl-1,2-propanediol, the alkyl group of which is methyl, ethyl or propyl and containing a tertiary alcohol group, have been prepared[2] from the methyl ester of the alkoxyethanoic acid by use of methylmagnesium iodide.

The monoalkyl ethers of 2-methyl-1,2-propanediol, the alkyl group of which is methyl or ethyl and containing a primary alcohol group, have been prepared by Edlund.[3] This method consisted in refluxing 1,2-epoxy-2-methylpropane with the alcohol in the presence of 10% sulfuric acid. Edlund did not report the formation under these conditions of ethers containing the tertiary alcohol groups. This work was confirmed by the authors.

The purpose of this investigation is to show that both of the isomeric monoalkyl ethers of 2-methyl-1,2-propanediol are formed when 1,2-epoxy-2-methylpropane and absolute alcohols are permitted to react under pressure.

Discussion

When 1,2-epoxy-2-methylpropane is heated at 230–270° in an autoclave with absolute methanol, ethanol or 1-propanol, both of the isomeric monoalkyl ethers of 2-methyl-1,2-propanediol are formed. The pressure developed depends on the alcohol used. As the reaction takes place there is a drop in pressure. A mole ratio of three of alcohol to one of 1,2-epoxy-2-methylpropane was used. The excess alcohol was used to decrease the probability of the reaction of the monoalkyl ethers with 1,2-epoxy-2-methylpropane. The fractional distillation of the reaction mixtures indicated that one or more products in addition to the desired ethers were formed.

An examination of Table I reveals that the percentage conversion of 1,2-epoxy-2-methylpropane to the monoalkyl ethers of 2-methyl-1,2-propanediol decreases in the order methyl > ethyl > propyl. The rate of the reaction decreases in the same order as indicated by the fact that the time required was the least with methanol and less with ethanol than with 1-propanol. It is evident that this phenomenon is dependent upon the property of the alcohol used, since identical mole ratios of the reactants were taken.

Experimental

The reactions were carried out in a stainless steel autoclave. The heating was continued until there was a drop in pressure of approximately 300–400 lb. per sq. in. The reaction mixtures were fractionally distilled. The column used was packed with Penn-State spirals[4] and is described in the literature.[5] The unreacted 1,2-epoxy-2-methylpropane and the alcohol were removed at atmospheric pressure. The remaining mixture was fractionally distilled at a suitable pressure. A constant pressure was maintained during the vacuum fractional distillations by means of a regulator similar in principle to that described by Munch.[6] The products were purified by fractional distillation with the above column or by means of a Podbielniak column.

The value of $n^{20}\text{D}$ for the compounds was determined by means of a Pulfrich refractometer. The liquid was cooled to 20° with water from an electrically controlled thermostat.

The reaction of 1,2-epoxy-2-methylpropane with absolute 1-propanol is described below. The reaction of 1,2-epoxy-2-methylpropane with absolute methanol and with absolute ethanol was carried out in a similar manner.

Reaction of 1,2-Epoxy-2-methylpropane with Absolute 1-Propanol.—Five runs were made using 144 g. of 1,2-epoxy-2-methylpropane and 360 g. of absolute 1-propanol. The temperature varied from 235 to 260°, the average temperature being about 255°. Approximately twenty

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[1] Based upon a portion of a thesis submitted by C. E. Sparks to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] Palomaa, *C. A.*, **13**, 2863 (1919).

[3] U. S. Patent No. 1,968,032, July 31, 1934.

[4] Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1932).

[5] Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1195 (1935).

[6] Munch, *J. Chem. Ed.*, **9**, 1275 (1932).