looked this publication[1] and the statement in our publication, "Posternak did not report, however, the preparation of allomucic acid," does a grave injustice to Dr. Posternak. After having read his paper no one can doubt Dr. Posternak's claim of priority of the preparation of allomucic acid.

[1] Posternak, *Helv. Chim. Acta*, **18**, 1283 (1935).

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Hydrogen-Deuterium Exchange in Acetate Solution

BY SYLVESTER LIOTTA AND VICTOR K. LA MER

In the course of a study of acetate-ion catalyzed reactions in heavy water, it became necessary to determine the extent of the exchange between the hydrogens of the methyl group and the deuterium of the solvent. From the results of early investigations[1,2,3] little or no exchange was to be expected, while from later work[4,5] varying degrees of exchange could be expected, depending upon temperature and time of contact.

Heavy water (d^{25}_{25} 1.1000, approximately 93% D) was purified by distillation *in vacuo* to remove possible catalysts. Anhydrous sodium acetate was added to produce a 10% solution. After standing for two weeks in a Pyrex vessel at 25–30°, the solvent was recovered by distillation *in vacuo*. The density was redetermined by filling the same pycnometer. Sodium acetate and acetic anhydride were then added to make a final concentration of 10% and 1%, respectively. After two weeks at 25–30°, the solution was neutralized with caustic soda and the same procedure repeated.

Solvent before addn. of sodium acetate, g.	10.5417
Solvent after first distn., g.	10.5413
Solvent after second distn., g.	10.5420

If any exchange occurs either in slightly acid or slightly alkaline solution at room temperature it is exceedingly slow.

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[1] Bonhoeffer, *et al.*, *Z. physik. Chem.*, **B23**, 171 (1933).

[2] Lewis and Schutz, THIS JOURNAL, **56**, 493 (1934).

[3] Klar, *Z. physik. Chem.*, **B26**, 335 (1934).

[4] Hall, Bowden and Jones, THIS JOURNAL, **56**, 750 (1934).

[5] Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935). Results of Turkevich. Table 3, 200 hrs. at 80° yields 85% exchange.

An Improved Method for Synthesizing Isobutyl Ethyl Ether

BY E. M. MARKS, DAVID LIPKIN AND BERNARD BETTMAN

According to Cerchez[1] aliphatic ethers can be synthesized from alkyl sulfates and magnesium alcoholates. In several instances he obtained yields of 60–70%. In preparing isobutyl ethyl ether by this method from diethyl sulfate and magnesium isobutylate, we obtained the product in only about 30% yield.

By substituting sodium for magnesium in the Cerchez method we have succeeded in raising the yield of isobutyl ethyl ether to 70%. Experimental conditions for optimum results are as follows: 93 g. (1.25 mole) of anhydrous isobutyl alcohol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and 12.5 g. (0.54 mole) of sodium added. The mixture is allowed to react until refluxing has ceased, after which it is heated in an oil-bath at 120–130° for two and three-quarters hours. At the end of this time a portion of the sodium remains undissolved. The mixture is then cooled to 105–115° and 77.1 g. (0.5 mole) of pure diethyl sulfate added gradually during a two-hour period. Reaction is vigorous and steady refluxing takes place during addition of the sulfate. After all has been added, refluxing is continued for two hours. The reaction mixture is then permitted to cool to room temperature (overnight) after which an equal weight of crushed ice is added, followed by a slight excess of dilute sulfuric acid. The ether is then steam-distilled out of the flask, separated from the aqueous portion of the distillate, given three equal-volume washes of 30% sulfuric acid, to remove most of the unreacted isobutyl alcohol, washed twice with water and dried over anhydrous potassium carbonate. The dried product is then refluxed over sodium ribbon for three hours to remove all traces of alcohol and finally is distilled through a precision fractionating column of the type recommended by Podbielniak.[2] The yield of isobutyl ethyl ether was 70%, based on diethyl sulfate. The boiling point, density and refractive index of our ether agreed with the recorded values[3] within the experimental error.

Several variables in this synthesis have been studied. (1) If the isobutyl alcohol is not dried rigorously, the yield of ether is reduced to

[1] Cerchez, *Bull. soc. chim.*, **43**, 762 (1928).

[2] Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 135 (1933).

[3] Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932).

67%. (2) Increasing the quantity of alcohol to 1.5 mole, in an attempt to dissolve more of the sodium, has no appreciable effect on the yield. (3) Prolonged heating of alcohol with sodium (eight hours) results in a darker colored crude product and also a reduction in yield to 65%. It is unnecessary that all of the sodium be dissolved before the diethyl sulfate is added. Apparently as the sodium isobutylate is used up in the reaction, more sodium goes into solution until all is dissolved. (4) A temperature range of 105–140° is permissible during reaction with the diethyl sulfate. If the temperature is kept lower (95°), the yield of ether is reduced (58%). (5) If only the theoretical amount of sodium (0.5 mole) is used, the yield of ether amounts to 65%. (6) Isobutyl alcohol, diethyl sulfate and solid potassium hydroxide react to form isobutyl ethyl ether in 22.5% yield. If the solid alkali is replaced by a 50% aqueous solution, no ether is formed.

It is possible also to synthesize *s*-butyl ethyl ether by this method, using sodium *s*-butylate and diethyl sulfate. Our data at this time are rather incomplete, but indications point to a maximum yield about 48%.

THE ATLANTIC REFINING CO.
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The Solubility of Lithium and Sodium Fluorides

BY JOHN H. PAYNE

In view of the discordancy in the data for the solubility of lithium and sodium fluorides in water,[1] we have conducted careful determinations of these data at 0, 25 and 35°.

Lithium sulfate made from Kahlbaum pure lithium carbonate was recrystallized until the reaction was neutral, and the fluoride precipitated by means of Merck "Zur Analyse" ammonium fluoride. Sodium fluoride was prepared from Kahlbaum pure sodium carbonate and hydrofluoric acid by the method of McAdams and Smith.[2] Both preparations were conducted entirely in platinum. Analysis by conversion to the sulfate gave an average of 99.94% purity. The purity of the fluorides was also checked by a spectroscopic examination. The solubility vessels, coated internally with several layers of a specially purified high-melting paraffin wax, were immersed completely in a thermostat with delivery tubes, also paraffined, to permit the removal of samples without removing the vessels from the thermostat. The samples were rotated for from forty-four to seventy-two hours until equilibrium was reached, then filtered into a 50-cc. pycnometer, also immersed in the thermostat. After weighing, the entire contents of the pycnometer were washed into a platinum vessel, evaporated to dryness, and weighed. All determinations were made in triplicate and equilibrium was approached from both directions in each case. The average deviation of the triplicates was 0.13% and the maximum deviation 0.38%. The thermostat was regulated to within 0.02°.

TABLE I

SOLUBILITY OF LITHIUM AND SODIUM FLUORIDES

	Lithium fluoride		Sodium fluoride	
Temp., °C.	Soly. mole/ 1000 g. water	d^t_4 satd. soln.	Soly. mole/ 1000 g. water	d^t_4 satd. soln.
0	0.0464	....	0.871	....
25	.0513	0.9984	.983	1.0384
35	.0522	.9958	.989	1.0354

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HONOLULU, HAWAII RECEIVED FEBRUARY 9, 1937

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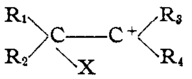
[1] Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

[2] McAdams and Smith, THIS JOURNAL, **34**, 593 (1912).

The Halogenation of Ethylenes

BY IRVING ROBERTS AND GEORGE E. KIMBALL

Recent work by Bartlett and Tarbell[1,2] has shown that the first step in the reaction of halogen molecules with the ethylene linkage leads to the formation of a negative halide ion and a positively charged organic ion. This ion has been postulated by Robinson[3] to have the structure


(1)

Some doubt has been cast on this mechanism[4] because of the presumption that there should be free rotation about the C–C single bond, which would lead to a mixture of equal amounts of the *cis* and *trans* halogenation products. In those cases in which the halogenation is homogeneous and not photochemical it is observed that either the *cis* or *trans* halogenation reaction predominates, forming at least 80% of the product.[5] It

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[1] Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

[2] Tarbell and Bartlett, *ibid.*, **59**, 407 (1937).

[3] Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932; Ingold, *Chem. Rev.*, **15**, 225 (1934).

[4] See, *e. g.*, Ogg, THIS JOURNAL, **57**, 2727 (1935).

[5] *Cf.* Freudenberg, "Stereochemie," Verlag Franz Deuticke Vienna, 1933, p. 520. Some of the reactions listed here are photochemical or complicated by side reactions.