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

THE UNIVERSITY OF HAWAII
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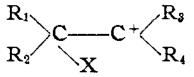
[1] Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

[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.