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.
PHILADELPHIA, PA. RECEIVED FEBRUARY 11, 1937

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

Temp., °C.	Lithium fluoride Soly. mole/1000 g. water	Lithium fluoride d^{t}_{4} satd. soln.	Sodium fluoride Soly. mole/1000 g. water	Sodium fluoride 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
HONOLULU, HAWAII RECEIVED FEBRUARY 9, 1937

---

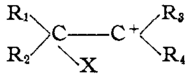
[1] Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

[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

---

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

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

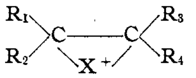
[3] Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932; Ingold, *Chem. Rev.*, **15**, 225 (1934).

[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.

has, therefore, been postulated that the second step of the reaction (the addition of halide ion to the positive organic ion) takes place so rapidly that there is not sufficient time for rotation about the single bond to take place.

We would like to point out that free rotation about the C–C bond is *not* to be expected. If this structure is assumed, one of the orbitals of the C^+ must be completely empty. The X atom on the other hand has three orbitals occupied by pairs of electrons. This arrangement is such that a coordinate link will almost certainly be formed by the sharing of one of the pairs of electrons of the halogen with the unoccupied orbital of the carbon. Another possible structure of the ion is one in which the positive charge is on the halogen. The X^+, being isoelectronic with a member of the oxygen family, should show a valence of two, *i. e.*, it should form a structure of the ethylene oxide type


(2)

From an electronic viewpoint structures (1) and (2) are identical. The difference between the ionization potential of carbon (11.22 volts) and that of a halogen (*e. g.*, 11.80 volts for bromine) is so small that the actual structure of the ion is undoubtedly intermediate between (1) and (2). Since the two carbons in either structure are joined by a single bond and by a halogen bridge, free rotation is not to be expected.

If, however, R_1 and R_3 (or R_2 and R_4) are similarly charged groups (*e. g.*, COO^-) there may be sufficient repulsion between them to overcome the restraining force of the double linkage, and rotation to the opposite configuration may take place before the second step of the reaction occurs.

This second step, which may be the addition of either a halogen ion X^- or some other atom or molecule, is probably a simple "three-atom" reaction of the type proposed by London,[6] and developed by Polanyi[7] and Olson.[8] In this case the new atom will approach one of the carbon atoms from the side opposite to the X atom already present. A bond to this carbon will be formed while the bond from the original X to the carbon is broken, with simultaneous neutralization of the charge of the ion. This process will always lead to *trans* addition, except in the previously mentioned case in which there are two like charged groups initially in the *cis* position.

With this modification the mechanism suggested by Robinson and by Bartlett and Tarbell explains all the existing data on the reactions of the halogens with ethylene linkages. The additions of bromine and chlorine to maleic and fumaric acids are very largely *trans*,[9] as the theory predicts. The additions of bromine and chlorine to fumarate ion are again predominantly *trans*, but the addition of bromine or chlorine to maleate ion, with its two negatively charged *cis*-carboxylate ions, is almost entirely *cis*.[10]

The difficulty of explaining the maintenance of configuration in the bromination of stilbene and isostilbene, which yield different methoxybromides and different dibromides[1] no longer exists if this structure of the intermediate ion is postulated. This is also true of the formation of the halo-beta-lactones from dimethylmaleic and dimethylfumaric acids.[2]

The authors wish to thank Prof. L. P. Hammett for his helpful discussions of this problem.

---

(6) London, *Z. Elektrochem.*, **35**, 552 (1929).

(7) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Bergmann, Polanyi, and Szabo, *ibid.*, **B20**, 161 (1933).

(8) Olson, *J. Chem. Phys.*, **1**, 418 (1933); Olson and Voge, THIS JOURNAL, **56**, 1690 (1934).

(9) McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912).

(10) Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925); Kuhn and Wagner-Jauregg, *Ber.*, **61**, 519 (1928).

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

RECEIVED MARCH 4, 1937

A Fermentation Test for Vitamin B_1

BY ALFRED SCHULTZ, LAWRENCE ATKIN AND CHARLES N. FREY

Vitamin B_1 (Merck's natural-crystalline) exerts a powerful action on the rate of alcoholic fermentation. In the presence of a suitable sugar–salt buffer mixture as little as one gamma (0.000001 g.) of the vitamin may be detected.

Table I gives the results of a typical test.

TABLE I

Total volume in each case, 100 cc. (distilled water). Yeast for each, 1 g. commercial bakers' yeast (Fleischmann). Sugar, 3 grams Merck C. P. Dextrose, plus synthetic salt mixture and buffer. Temperature, 30°. Oscillations, 100 per minute.

Natural crystalline vit. B_1 mg.	Cc. of gas in 3 hours
None	185
0.001	215
.005	305
.010	350
.040	395
.100	405