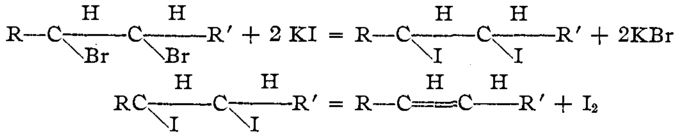
NOTES

The Problem of Alternating Polarity in Chain Compounds.—In a paper recently published in This Journal by Conant and Kirner[1] on the relation between the structure of organic halides and the speed of their reaction with inorganic iodides, these authors have studied the reaction between several organic chlorides with potassium iodide, in order to discover whether or not the "alternating polarity," predicted by various electronic theories of valence, would manifest itself by alternations in the reactivity of the halogen atom in various homologous series. They have chosen this reaction because it gives the same type of product with a large variety of halogen compounds and because they thought that it is as far as possible free from side reactions and other complicating possibilities, so that their results would be strictly comparable with one another. As a solvent they used pure anhydrous acetone, in which the potassium chloride which is formed during the reaction is practically insoluble so that it crystallizes from the reaction mixture. In all cases the molecular proportion of organic chloride to potassium iodide was 5:1, the concentration of the organic halide being 0.2 *M* and that of the potassium iodide 0.04 *M*. From the results of two experiments, carried out with benzyl chloride and potassium iodide in different concentrations they have drawn the conclusion that the reaction velocity was influenced by change of concentration of the factors in accord with a bimolecular equation; also they draw attention to the fact that potassium iodide is dissociated to a considerable extent in acetone and that the actual reaction may occur between the organic halide and the iodine ion.

Recently[2] the present author showed that the reaction between α,β-dibromo-compounds and inorganic iodides proceeds in accordance with the equations:



$$R\text{—}\underset{\diagdown Br}{\overset{H}{C}}\text{——}\underset{\diagdown Br}{\overset{H}{C}}\text{——}R' + 2\,KI = R\text{—}\underset{\diagdown I}{\overset{H}{C}}\text{——}\underset{\diagdown I}{\overset{H}{C}}\text{——}R' + 2KBr$$

$$R\underset{\diagdown I}{\overset{H}{C}}\text{——}\underset{\diagdown I}{\overset{H}{C}}\text{——}R' = R\text{—}\overset{H}{C}{=}{=}\overset{H}{C}\text{——}R' + I_2$$

and measured the velocity of the first reaction; this is essentially the same as the reaction investigated by Conant and Kirner. It has appeared, however, that this reaction is very complicated, the reactivity of the iodine ion being much greater than that of the undissociated iodide[3] and cations, except hydrogen ions, catalyzing the reaction considerably. The results obtained from the study of this reaction explain the irregulari-

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[1] Conant and Kirner, This Journal, **46**, 232 (1924).

[2] Van Duin, *Rec. trav. chim.*, **43**, 341 (1924).

[3] As a matter of fact it could not be decided whether or not the undissociated iodide shows any reactivity at all.

ties found by Conant and Kirner and show that their results are not comparable with one another, especially when different types of organic halides are used.

A calculation of the values of the reaction between benzyl chloride and potassium iodide in different concentrations[4] in accordance with the equation, $k = \frac{1}{4tb} \log \frac{5-z}{5(1-z)}$, used by Conant and Kirner, gives the following results.

TABLE I

INITIAL CONCN. OF THE BENZYL CHLORIDE, 0.2 *M;* OF POTASSIUM IODIDE, 0.04 *M;* T, 25°

Time hours	Percent. reacted (100 z)	k
0.5	15.41	0.739
1.0	27.52	.720
2.0	46.20	.710
3.0	57.50	.665

INITIAL CONCN. OF THE BENZYL CHLORIDE, 0.1 *M;* OF POTASSIUM IODIDE, 0.02 *M;* T, 25°

Time hours	Percent. reacted (100 z)	k
1.0	18.21	0.890
2.0	32.35	.879
4.0	52.55	.861
6.0	62.00	.756

The calculated reaction "constants" are not constant at all, but decrease continuously, and the same holds for many of the reaction constants, published in Table III;[5] also the velocity of the reaction increases, when the concentration decreases, whereas it should be independent of the initial concentration of the reactants when complications are absent. In accordance with the results obtained by the investigation of the course of the reaction between α,β-dibromo compounds and inorganic iodides, the increase of the reaction velocity in lower concentrations is easily explained by the difference in reactivity between the iodine ion and the undissociated iodide, whereas the continuous decrease of the reaction constants is due to the removal of the catalyzing potassium ions. Thus it appears *that any solvent, in which the potassium chloride, formed during the reaction, is insoluble, is unsuitable for these measurements and that it is necessary to use the potassium iodide in such an excess that the degree of dissociation is constant within the limits of error of these measurements.*

Because of the difference between the reactivity of the iodine ion and the undissociated iodide as well as the catalytic influence of cations it is necessary to investigate the reaction with at least two different concentrations of the iodide, in order to determine whether or not the sum of these influences[6] is the same with different types of organic halides. Probably the sum of these influences is about constant in an homologous series; with different types of α,β-dibromo compounds, however, relatively great

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[4] Ref. 1, p. 234, Table I.

[5] Ref. 1, p. 248.

[6] It is impossible to investigate the influence of the dissociation and of the cation catalysis separately; compare Ref. 2.

differences occur. Up to the present moment the most diverging results obtained in aqueous alcoholic solution are as follows:[7]

Mesityloxide dibromide:	$k_{25°}$ with KI 0.5 M : 0.00659 $k_{25°}$ with KI M : 0.00241	quotient 2.73
Mesodibromosuccinic acid:	$k_{25°}$ with KI 0.5 M : 0.00103 $k_{25°}$ with KI M : 0.000548	quotient 1.88

The initial concentration of the dibromo compounds are about 0.075 M and 0.025 M, respectively.

The values obtained with the isomeric racemic dibromosuccinic acid: $k_{25°}$ with KI 0.5 M : 0.0000840, $k_{25°}$ with KI M : 0.0000336, quotient, 2.50, however, show that even in an homologous series measurements with different concentrations of the iodide have to be carried out in order to be sure that the values obtained are really comparable with one another.

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The Problem of Alternating Polarity in Chain Compounds. A Reply to C. F. van Duin.—Dr. van Duin in the preceding note has questioned the significance of the relative reactivities of the organic chlorides reported in an earlier paper. As a result of his study of the reaction between certain α,β-dihalides and potassium iodide in aqueous solution, he concludes that the reaction we employed, namely, the reaction between an organic chloride and potassium iodide in absolute acetone, is not a simple bimolecular reaction but is complicated by changing dissociation of the inorganic iodide and subject to catalysis by potassium salts. He suggests that even with a closely related series of substances these complications may vitiate our comparison of the relative reactivities, since changes in the rate of the reaction with changes in concentration may differ from substance to substance. Though we were far from convinced of the soundness of Dr. van Duin's arguments, the simplest method of settling the point seemed to be to measure the rates of reaction of several widely different organic halides in some concentration other than that employed in our previous work. This we have now done, choosing such amounts of absolute acetone that the concentrations were one-third of those previously employed. We decided to use amyl chloride, benzyl chloride and ethyl chloro-acetate as examples of compounds with chlorine atoms of very different reactivity, as when compared at the same temperature the reactivities of these three substances are in the ratio 1: 200: 2800 (see previous paper). The results are summarized in Table I, the figures marked with an asterisk being those previously reported; the individual experiments are recorded in Table II.

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[7] Unpublished results of the author.