

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 <i>M</i> : 0.00659	} quotient 2.73
	k_{25}° with KI <i>M</i> : 0.00241	
Mesodibromosuccinic acid:	k_{25}° with KI 0.5 <i>M</i> : 0.00103	} quotient 1.88
	k_{25}° with KI <i>M</i> : 0.000548	

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.

THE VAN'T HOFF LABORATORY
UTRECHT, HOLLAND

C. F. VAN DUIN

RECEIVED MARCH 20, 1924
PUBLISHED FEBRUARY 5, 1925

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.

⁷ Unpublished results of the author.

TABLE I

Compound	Concn. of org. halide	Concn. of KI	Temp. °C.	k (Calcd. from equation for bimolecular reaction)
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$	0.20	0.04	50	0.0540
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$.0667	.0134	50	.0529
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^*$.20	.04	25	.774
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.0667	.0134	25	.769
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Cl}^*$.20	.04	25	6.37
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Cl}$.0667	.0134	25	6.32

TABLE II

Benzyl chloride and potassium iodide at 25°

Concn. of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} = 0.0667 M$
Concn. of KI = 0.0134 M

t (hrs.)	% reacted	k
1.50	15.83	0.759
3.00	29.56	.783
6.00	48.91	.769
8.00	58.50	.765

Av. .769

Amyl chloride and potassium iodide at 50°

Concn. of $\text{C}_5\text{H}_{11}\text{Cl} = 0.2 M$
Concn. of KI = 0.04 M

t (hrs.)	% reacted	k
4.00	9.40	0.0541
6.00	13.70	.0540
18.00	35.03	.0540
20.00	38.30	.0541

Av. .0540

Amyl chloride and potassium iodide at 50°

Concn. of $\text{C}_5\text{H}_{11}\text{Cl} = 0.0667 M$
Concn. of KI = 0.0134 M

t (hrs.)	% reacted	k
18.00	13.50	0.0530
30.00	20.94	.0520
48.00	31.40	.0527
64.00	39.94	.0539

Av. .0529

Ethyl chloro-acetate and potassium iodide at 25°

Concn. of halide = 0.0667 M
Concn. of KI = 0.0134 M

t (hrs.)	% reacted	k
0.25	22.10	6.59
.50	38.59	6.60
.75	50.55	6.48
1.50	69.29	5.60

Av. 6.32

It is evident from Table I that the variations in k (calculated from the usual bimolecular equation) are no greater than our experimental error.

The reaction in question thus appears to be bimolecular and free from complications under the conditions we have employed and *the relative reactivities are independent of the concentration*. The validity of calculating our reaction constants with the aid of a bimolecular reaction seems established. We regret that Dr. van Duin has been misled by the experiments with benzyl chloride previously reported in which the deviation from a bimolecular reaction was much greater than our present experimental error; we did not consider this deviation significant from the point of view of comparing the relative reactivities of a series of organic halides and, therefore, did not carry out further experiments such as those now recorded in Tables I and II. The deviations in the values of k for a given compound did not show a decided drift as Dr. van Duin states; an examination of Table III of our paper will convince anyone that in the great majority of cases the value of k is constant (within our limits of error)

over an unusually wide range (10% to 70% complete in many cases); this could hardly have occurred if Dr. van Duin's interpretation of our reaction had been correct.

It seems to us that Dr. van Duin has erred in applying his interpretation of his much more complicated reaction to our relatively simple reaction. Dr. van Duin finds that his values for k , calculated on the basis that his reaction is trimolecular, change with the dilution; this may be due to changes in ionization as he suggests, but it is hardly fair to assume that the differences he observes between 1 N aqueous potassium iodide and 0.5 N solution will find their parallel in our 0.04 M absolute acetone solution. Similarly, he finds a change in the value of k on adding potassium ions corresponding to a molar solution; it is hardly safe to assume from this that the removal of potassium (as potassium chloride) from our 0.04 M acetone solution will cause a similar result, whether or not one designates the influence of 2 M potassium chloride in his experiments by the term catalysis.

CHEMICAL LABORATORY OF
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

JAMES B. CONANT
W. R. KIRNER
R. E. HUSSEY

RECEIVED APRIL 18, 1924
PUBLISHED FEBRUARY 5, 1925

Detection of Diethylphthalate in Ethyl Alcohol.—The following is the official test for the detection of diethylphthalate in ethyl alcohol, given in the Appendix, United States Government Regulations No. 61, to be used in connection with 39-B specially denatured alcohol.

"Take five drops of diethylphthalate or ten cc. of the 2.5% solution (39-B), place in a small casserole and add 5 cc. of a 10% solution of sodium hydroxide. Evaporate practically to dryness on a steam-bath and then to complete dryness over a low Bunsen flame. Continue heating until the mass is in gentle fusion. Discontinue heating and add at once approximately 0.5 g. of resorcinol. The mass effervesces and turns dark brown. Place a small portion of this mass in a test-tube and add water. The characteristic color of fluorescein develops at once."

This test has been found by the writers to be unreliable, as a distinct fluorescence will develop with grain alcohol known to be free from diethylphthalate.

A blank test was run as follows. Five cc. of a 10% solution of sodium hydroxide was evaporated to complete dryness and immediately 0.5 g. of c.p. resorcinol was added. The mass effervesced and turned a dark brown. A small portion was placed in a test-tube with water, when a distinct fluorescence developed. This proves conclusively that diethylphthalate is not necessary to bring about a fluorescence.

While it is true that the color of the fluorescence is slightly different when diethylphthalate is present, the degree of dilution may cause erroneous conclusions to be drawn.