the enzyme content. It is impossible to determine without actual experimentation which drying temperature should be employed.

The data show that it is impossible to dry certain tissues without changing their sugar content. In order to analyze such tissues, the alcohol method of preservation recommended by Davis, Daish and Sawyer must be adopted.[22] This method was tried by the writer[3] with beet leaves and corn ears and was found to be effective. It is interesting to note that Appleman and Arthur[15] used the alcohol method in preserving their corn samples for analysis.

Summary

1. Drying at temperatures below 65° changed the sugar content of beet, corn and barberry leaves and corn ears.
2. Drying at 65° and 80° proved successful with beet and corn leaves, which are tissues that dry rapidly.
3. Killing and drying for 24 hours at 98° lowered the sugar content by caramelization and leaching in beet and corn leaves and corn ears and caused hydrolysis of the sucrose in barberry leaves.
4. The Spoehr method of heating the tissue in a closed vessel for 30 minutes at 98° raises the temperature to the killing point more quickly than direct heating at the same temperature in an open system. It is suggested that subsequent drying should be at a reduced temperature in a well-ventilated oven, thereby minimizing losses by leaching and caramelization.
5. It has been shown that the method of preservation by heat is inapplicable with certain tissues. In such cases the method of preservation with alcohol is the only alternative.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE RELATION BETWEEN THE STRUCTURE OF ORGANIC HALIDES AND THE SPEEDS OF THEIR REACTION WITH INORGANIC IODIDES. II. A STUDY OF THE ALKYL CHLORIDES

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The first paper of this series[1] outlined a method of comparing the reactivities of the halogen atoms in organic compounds by measuring the rates at which the organic halides reacted with potassium iodide in acetone. This general reaction ($RX + KI \longrightarrow RI + KX$) is free from side reactions such as hydrolysis and formation of unsaturated or cyclic compounds and, therefore, significant measurements can be obtained with

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[22] Davis, Daish and Sawyer, *J. Agr. Sci.*, **7**, 255 (1916).

[1] THIS JOURNAL, **46**, 232 (1924).

a wide variety of organic halides. In order to measure conveniently the rate of the reaction with substances differing a millionfold in reactivity, measurements were made at different temperatures and the results calculated to some standard temperature with the aid of the temperature coefficient of the reaction velocity. From our first results it seemed as though this temperature coefficient might be somewhat different for each series of compounds but a more complete study of a larger number of substances has now convinced us that the temperature coefficient is the same for all the great variety of compounds studied. As a consequence certain corrections must be made in the data given in the first paper but the changes are not large enough to affect our conclusions or, indeed, to be perceptible on the diagrammatic representation[2] of the relative reactivities of the various series of compounds. The corrected data are presented in the next paper in connection with the general problem of the effect of activating groups; the present communication deals with the reactivity of alkyl chlorides and a comparison of the rate of reaction of potassium, lithium and sodium iodides with five different organic halides.

TABLE I

SUMMARY OF RESULTS

Compound	k_{50}	k_{60}	A	Relative reactivity at 50° R_{50}	Relative reactivity at 60° R_{60}
[CH_3CH_2Cl	0.101	0.196	3100	2.52	1.94]
n-C_3H_7Cl	.0434	.104	4100	1.08	1.03
n-C_4H_9Cl	.0402	.101	4300	1.00	1.00
n-$C_5H_{11}Cl$	.0540	.128[a]	4000	1.35	1.26
n-$C_6H_{13}Cl$	.0521	.125	4100	1.30	1.22
n-$C_7H_{15}Cl$	.0500	.122	4100	1.25	1.20
n-$C_8H_{17}Cl$	.0540	.134	4200	1.35	1.32
n-$C_{12}H_{25}Cl$	.047	.102	3600	1.17	1.00
n-$C_{14}H_{29}Cl$	.0400	.098	4200	1.00	0.97
n-$C_{16}H_{33}Cl$	.0369	.0905	4200	0.92	.90
n-$C_{30}H_{61}Cl$	.0370	.0890	4100	.92	.88
iso-$C_5H_{11}Cl$	....	.0678	..	..	.65
$(CH_3)_2CHCl$	....	.0015	..	..	.015
$C_2H_5CHClCH_3$	....	.0022	..	..	.022
$CH_3CH_2CH_2CHClCH_3$	....	.0048	..	..	.048
n-$C_4H_9CHClCH_3$	....	.0075	..	..	.075
n-$C_6H_{13}CHClCH_3$	....	.0026	..	..	.026
$(CH_3)_2CClCH_2CH_2CH_3$	....	.0029	..	..	.029
$(CH_3)_3CCl$	....	.0018	..	..	.018
$C_6H_{11}Cl$(cyclohexyl chloride)	....	$<.0001$	..	..	$<.0001$

[a] From first paper of this series.

Table I is a summary of the data obtained with the alkyl chlorides; the experimental details are given in the second part of this paper. The

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[2] Ref. 1, p. 237.

value of k was calculated from the usual equation for a bimolecular reaction, the time being expressed in hours; the concentration of the reactants in every case was potassium iodide, 0.04 M; organic chloride, 0.2 M. A comparison of the average values for k_{50} and k_{60} for butyl chloride with the corresponding values given in the first paper indicates the extent to which these velocity constants are reproducible with different samples of materials. Our previous values were 0.0415 and 0.119 as compared with 0.0402 and 0.101 given in Table I; probably the error is somewhat greater in this instance than with most other compounds, as the individual values for k_{60} in the earlier work were among the first measurements and were not very concordant. This is borne out by a comparison of k_{25} for benzyl chloride given in Table II (0.786) and our previous figure (0.774); the difference is here only 1.5%. In general we believe that our results are significant within 5 or 10% and are not influenced by small amounts of impurities which would vary with the source of the compound used. The experimental difficulties due to the volatility of ethyl chloride made the determinations with this substance somewhat uncertain and the values are bracketed in Table I.

The value of A was calculated for each of the primary chlorides from the average values for k_{50} and k_{60} according to the equation $\log k_{50}/k_{60} = A\ (1/333 - 1/323)$. It is evident from an inspection of Table I that A is constant within the limits of the experimental error, with an average value of 4090. It might be mentioned at this point that the validity of this equation over a range of 25° is demonstrated by an experiment with benzyl chloride. From the values k_{25} and k_{30} given in Table II and the value of A(4000), k_{50} was calculated as 8.59 and found experimentally as 7.89, a difference of 8%.

In the last column of the table are given the relative reactivities at 50° and 60° compared with that of butyl chloride which is taken as unity; essentially the same figures are obtained whichever temperature is chosen for the comparison. The striking contrast between the primary chlorides on the one hand and the secondary and tertiary compounds on the other is at once apparent. With the primary straight-chain compounds containing three or more carbon atoms, there is but little change from propyl to myricyl ($C_{30}H_{61}Cl$), the slight decrease in reactivity of cetyl ($C_{16}H_{33}Cl$) and myricyl chlorides as compared with lauryl ($C_{12}H_{25}Cl$) and myristyl ($C_{14}H_{29}Cl$) being hardly greater than the experimental errors. The 20% increase in reactivity of amyl, hexyl, heptyl and octyl as compared with propyl, butyl and lauryl is undoubtably real, but is a second-order effect when compared with other changes in reactivity caused by changes in structure. Ethyl chloride is about twice as reactive as *n*-propyl or *n*-butyl chloride and the forking of the chain in *n*-*iso*-amyl chloride decreases the reactivity by half. It is evident that the molecular weight is of little or no significance in determining the reactivity of these substances.

The secondary chlorides are all much less reactive than the corresponding primary compounds. The two tertiary chlorides examined do not differ greatly from the secondary compounds; apparently the linkage of a second group to the terminal carbon atom has a great effect on the reactivity but the introduction of a third group is of relatively little significance. The variations in the reactivity of the secondary chlorides examined are considerable and much greater than the changes noted in the series of primary chlorides. Without attempting any explanation of these changes it is perhaps worthy of note that the facts in regard to both series may be summarized as follows. In the series $CH_3(CH_2)_nCl$, the reactivity decreases from $n = 1$ to $n = 2$ or 3 and then increases very slightly when $n = 4, 5, 6, 7$ and slightly decreases again for the higher compounds ($n = 12, 14, 16, 31$) whose reactivity is about that of the substances in which $n = 2$ or 3; in the series $CH_3(CH_2)_nCHClCH_3$, the reactivity increases from $n = 0$ to $n = 3$, and decreases when $n = 5$. The lack of information with the secondary compounds in regard to the higher members and the $n = 4$ compound as well as the gaps in the primary series ($n = 0, 8, 9, 13, 15, 17$) make these generalizations incomplete, but it is interesting that in both series there seem to be two changes as n increases and that these changes are to a certain extent in the opposite direction in the two series.

The behavior of cyclohexyl chloride is most peculiar, as it proved to be so unreactive that the reactivity could not be measured by our present methods. We estimate that its reactivity is less than one-fifteenth that of the least reactive substance measured (*iso*propyl chloride). The identity of the compound was carefully established and the absence of any "negative catalyst" was shown by adding some cyclohexychloride to ethyl chloroacetate and determining the rate, which was not in the least affected by the presence of the cyclic chloride. Until measurements are made with diethyl- and dipropyl-chloromethane one cannot be certain whether this marked decrease in reactivity is due to the accumulation of CH_2 groups on both sides of the CHCl group or whether the cyclic structure has profoundly influenced the reactivity of the chlorine atom. However, in view of the fact that methyl-*n*-propyl-chloromethane is more reactive than *iso*propyl chloride it would seem as if the CH_2 groups exercised a favorable influence and that the cyclohexane ring were responsible for the abnormal behavior of cyclohexyl chloride.

Comparison with Results of Previous Investigators

A number of investigators have studied the rates of reaction of a series of alkyl halides (for the most part iodides) with different reagents. One of the latest investigators in this field[3] has given an excellent critical survey

[3] Haywood, *J. Chem. Soc.*, **121**, 1904 (1922).

of most of the earlier work and has tabulated the results of the different experimenters. Since this recent résumé is readily available we shall not attempt an exhaustive survey of the literature. With the exception of Burke and Donnan's[4] results with silver nitrate in alcoholic solution, all investigators place the halides (irrespective of the nature of the halogen atom) in the following order: $CH_3— > CH_3CH_2— > n\text{-}C_3H_7—$. There is considerable numerical divergence, however, the values for methyl being given as 4 to 18 times as great as for ethyl, which in turn is rated as 2 to 7 times as reactive as the *n*-propyl compound. The few investigators who have examined an extended list of alkyl halides agree that there is no great change in reactivity in the primary compounds as one increases the number of carbon atoms above 4. Thus, Hecht, Conrad and Brückner[5] using sodium methylate, found about a 30% decrease in the reactivity of heptyl and octyl iodides as compared with *n*-propyl iodide, while the corresponding differences found by Segaller[6] with sodium phenolate, Haywood[3] with sodium benzylate and Menschutkin[7] with tertiary amines were even less. Both Segaller and Haywood give values for *n*-heptyl, *n*-octyl and cetyl ($C_{16}H_{33}X$) which are within 8% of one another. The agreement in regard to the relation between secondary and primary compounds is less unanimous; one investigator (Segaller) finds that the values for *iso*propyl and *n*-propyl iodides are within a few per cent. of each other, while Menschutkin gives figures showing that the *iso* is only one-tenth as reactive as the normal halide in addition reactions with amines; the values of four other workers fall between these extremes. Segaller and Haywood both find the reactivity of secondary hexyl and secondary octyl iodides to be essentially that of a primary compound such as butyl iodide. No reliable data are available for tertiary compounds although it is certain that the rate of their reaction with amines is very low.

For purposes of expressing numerically the factors governing the behavior of organic substances as we deal with them in the laboratory, differences in reactivity of 25 or even 50% are of relatively little importance. Variations of threefold, a hundred-fold and a millionfold are the cause of the vagaries which make our present structural formulas so often unreliable in predicting reactions. From this point of view the results of all the previous studies of *primary* halides and the data here presented may be said to be in general agreement. *In a great variety of reactions a methyl halide is 5 to 20 times more reactive than the ethyl compound which in turn is only about twice as reactive as the other primary straight chain compounds that do not differ materially from one another, at least as high in the series as*

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[4] Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

[5] Hecht, Conrad and Brückner, *Z. physik. Chem.*, **4**, 273 (1889).

[6] Segaller, *J. Chem. Soc.*, **103**, 1154 (1913).

[7] Menschutkin, *Z. physik. Chem.*, **5**, 589 (1890).

$C_{30}H_{61}Cl$. The forking of the chain diminishes the reactivity of primary compounds, which diminution in the case of amyl is about 100% (our results are in agreement with those of two other investigators on this point).

The discrepancies in regard to the comparison of primary and secondary halides are serious; they may be real differences, specific for each of the reagents employed or they may be due to the fact that in certain instances some unsuspected reaction may be taking place with the secondary compounds which is absent from the primary series. For example, any comparison of the action of alcoholates on primary and tertiary halides is meaningless because in the one case ethers are formed and in the second olefines.[8] We have chosen the reaction with an inorganic iodide in absolute acetone because of the impossibility of many side reactions which may complicate the results with other reagents used in aqueous or alcoholic solution and because the reaction has been widely used for preparative purposes and is known to give excellent yields.[9] We are, therefore, inclined to believe that our results showing that secondary and tertiary halides are only 0.05 to 0.01 as reactive as primary compounds represent a correct formulation of the behavior of these substances, at least in simple metathetical reactions. There is already some evidence that seems to indicate that the rate of hydrolysis (and perhaps alcoholysis) in neutral solution does not parallel the rate of our metathetical reaction. Thus, in the previous paper[1] ω-chloro-acetophenone was found to be by far the most reactive substance, and yet it can be recrystallized without appreciable loss from mixtures of water and alcohol; a similar drastic treatment of benzoyl chloride or ethyl chlorocarbonate would insure very considerable hydrolysis and yet their relative reactivity on our scale is about one one-hundredth that of chloroacetophenone. Possibly some similar direct action between the secondary halides and the alcohol used as a solvent may be the cause of the relatively high reactivity found by some workers for these compounds.

Measurements with Sodium and Lithium Iodides

In order to investigate the effect of varying the metallic iodide, experiments were made with five representative organic chlorides having widely different velocity coefficients; the substances chosen were butyl chloride, benzyl chloride, *o*-chlorobenzyl chloride, ethyl chloro-acetate and chloroacetophenone which on our scale have reactivities of about 1, 200, 700, 1700 and 105,000, respectively. The results obtained with sodium and lithium iodides in absolute acetone are summarized in Table II, together with the values for the reaction with potassium iodide.

It is apparent that for each substance the velocity coefficient is the same for all three iodides and the temperature coefficients are identical within

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[8] Brussoff, *Z. physik. Chem.*, **34**, 129 (1900); see also Segaller, *J. Chem. Soc.*, **103**, 1421 (1913).

[9] Finkelstein, *Ber.*, **43**, 1528 (1910).

Table II

Comparison of Lithium, Sodium and Potassium Iodides

Inorganic iodide, 0.04 mole per liter; organic chloride, 0.20 mole per liter

	KI		NaI		LiI	
	k	A	k	A	k	A
n-Butyl chloride 50°	0.0402		0.0409		0.0396	
60°	.101		.100		.099	
		4300		4200		4300
Benzyl chloride 25°	0.786		0.766		0.771	
30°	1.31		1.34		1.31	
		4000		4300		4100
o-Chlorobenzyl chloride 25°	2.68		2.71		2.73	
30°	4.38		4.42		4.45	
		3800		3900		3800
Ethyl chloro-acetate 25°	6.37[a]		6.51		6.43	
30°	10.5		10.7		10.6	
		3900		3900		3800
Chloro-acetophenone −10°	5.91		5.80		5.72	
0°	22.4[a]		20.9		21.5	
		4200		4000		4100

[a] From results in the first paper.

the limits of experimental error. The results with lithium iodide are interesting as no solid separates during this reaction since lithium chloride is soluble in acetone, in contrast to sodium and potassium chlorides. That the separation of the solid inorganic chloride does not introduce any uncertainty in the method is shown by the agreement of the values of k for all three iodides.[9a]

The most probable interpretation of this similar action of the three inorganic iodides is that only the iodide ion in each case reacts with the organic chloride. It is interesting to note that if this is the case this reaction is of the zero type listed by Brönsted[10] in his treatment of reaction kinetics and assuming similar *changes* in activity coefficients with dilution in acetone and in water, would be influenced but very slightly by changes in total salt concentration (about 3% from 0.1 to 0.02 M). Reactions of this type conform much more nearly to the simple kinetic formulation of a bimolecular reaction than do reactions between ions and it would be expected, from this point of view, that the velocity coefficient of the reaction in dilute solution when calculated by the simple bimolecular formula would be nearly independent of the dilution or the presence or absence of salts.[11]

[9a] This fact affords additional evidence that the objections of Van Duin to our method are not valid (This Journal, **47**, 585 (1925)).

[10] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922). Bjerrum, *ibid.*, **108**, 82 (1924).

[11] Brönsted has applied his theory to a number of reactions involving organic halogen compounds and has successfully formulated some of the cases involving α-halogen acids and their salts. The reaction between neutral organic halides and alcoholates in alcohol solution has not yet been considered from this point of view. Such reactions should apparently belong to the zero type, but the reaction velocity coefficient is greatly

We have found this to be the case, as the results given in Table III show. The concentrations were diminished a third in a number of experiments with potassium iodide and three different organic chlorides, while in one set of experiments with benzyl chloride and sodium iodide the ratio of organic chloride was changed from the usual 5:1 to 5:2. The average values of k calculated from the equation, $k = \frac{1}{t} \cdot \frac{1}{a-b} \log \frac{b(a-x)}{a(b-x)}$ are identical within our experimental error (10%).

TABLE III

THE EFFECT OF CHANGING THE CONCENTRATION

	KI		NaI	
Concd. org. chloride (moles per liter)	0.20	0.067	0.20	0.20
Concd. inorg. iodide (moles per liter)	.04	.0134	.04	.08
n-Amyl chloride at 50°	.0540	.0529	...	...
Benzyl chloride at 25°	.786	.769	.766	.791
Ethyl chloro-acetate at 25°	6.37[a]	6.32	...	...

[a] Results in the first paper.

We wish to acknowledge our indebtedness to the Elizabeth Thompson Science Fund for a grant which has largely defrayed the expense of this investigation.

Experimental Part

Materials Employed.—The reagents used in this work, acetone, potassium iodide and potassium iodate, were carefully purified as described in the first paper of this series. The sodium iodide was recrystallized twice from distilled water and dried in a vacuum for a week before using; the lithium iodide was also twice recrystallized and then fused in a porcelain boat in a stream of carbon dioxide. The alkyl chlorides were for the most part prepared, in good yields, from the corresponding alcohols by Norris' method[12] or by heating in a sealed tube with fuming hydrochloric acid; their purity was established by a Carius method for total halogen as well as by the usual physical criteria of purity. In a few cases (ethyl, *iso*propyl, *n*-butyl and cyclohexyl chlorides) it was possible to purchase alkyl halides of high purity and these were redistilled before use. The preparation or purification of chloro-acetophenone, benzyl chloride and ethyl chloro-acetate have been previously described. The identity of the cyclohexyl chloride, whose anomalous behavior has been discussed above, was established by conversion into the Grignard reagent and the preparation of cyclohexylcarboxylic acid by means of carbon dioxide. We are indebted to Mr. L. F. Small for this work. The corrected boiling points or melting points of the compounds employed are given in the tabulation of results.

Procedure.—The experimental details of the procedure have been fully described before and need not be repeated. The solutions of sodium and lithium iodides in acetone were prepared and employed in exactly the same manner as the solution of potassium iodide. In all the experiments

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influenced by the initial concentration. [Segaller, Ref. 6 and Shroder and Acree, *J. Chem. Soc.*, **105,** 2582 (1914).]

[12] Norris, THIS JOURNAL, **46,** 753 (1924); **38,** 1071 (1911); **42,** 2093 (1920).

except those specially designated in Table VI, each tube contained 0.001 mole of organic chloride and 5 cc. of acetone containing 0.0002 mole of the inorganic iodide; the concentration of the reactants was thus inorganic iodide 0.04 *M*, organic halide 0.2 *M*. The value of k was calculated from the usual equation for a bimolecular reaction which in this case takes the form $k = \frac{1}{t4b} \log \frac{5 - z}{5(1 - z)}$ where t is the time in hours, z the fraction of the inorganic iodide which has reacted and b the concentration in moles per liter of the inorganic iodide (0.04).

The titration of the inorganic iodide with potassium iodate must be carried out under the conditions which have been previously described in detail. In every experiment the exact initial concentration of the inorganic iodide was determined by a "blank" determination carried out at the time that the tubes were filled; errors due to evaporation of acetone from the stock solution were thus avoided. In those cases in which iodine was liberated when the reaction tube was broken in the cold hydrochloric acid, the iodine was determined by extraction with chloroform and titration

TABLE IV

RESULTS

REACTION BETWEEN ETHYL CHLORIDE AND POTASSIUM IODIDE

At 60°			At 50°		
Time Hours	Per cent. reacted (100 z)	k	Time Hours	Per cent. reacted (100 z)	k
1.5	10.25	0.185	5.0	17.36	0.098
2.0	15.10	.214	5.5	18.73	.099
3.0	18.52	.211	7.0	22.40	.110
4.0	22.79	.172	8.0	25.29	.097
	Av.	.196		Av.	.101
n-PROPYL CHLORIDE (B. P., 46–47°) AND POTASSIUM IODIDE					
17.0	52.63	0.101	4.0	7.36	0.042
18.0	55.40	.104	7.0	13.35	.045
20.5	59.28	.102	18.5	31.34	.044
22.0	63.16	.106	24.0	36.29	.042
	Av.	.104		Av.	.0434
n-BUTYL CHLORIDE (B. P., 78–79°) AND POTASSIUM IODIDE					
2.0	8.56	0.098	5.0	8.86	0.0423
3.0	12.77	.100	6.0	9.60	.0385
5.0	19.57	.096	6.0	11.02	.0426
8.25	32.34	.106	18.0	25.62	.0370
16.0	52.17	.106	24.0	39.36	.0421
18.0	54.80	.102	40.0	49.31	.0391
24.0	64.13	.100			
24.0	64.20	.100		Av.	.0402
	Av.	.101			

TABLE V

Chloride	Boiling point °C.	Temp. of experiments °C.	No. of experiments	Range of measurements in terms of percentage reacted	Average deviation of constants from mean %	Greatest deviation of constants from mean %	Mean value of k
A. With Potassium Iodide							
n-Butyl	78–79	60	8	9–64	3	5	0.101
n-Amyl	107–108	50	4	9–38	<2	<2	.0540
n-Hexyl	132.7–133.3	50	4	20–43	1	1	.0521
n-Hexyl	132.7–133.3	60	4	22–66	2	4	.125
n-Heptyl	117–117.5 (163 mm.)	50	5	20–42	1	1	.050
n-Heptyl	117–117.5 (163 mm.)	60	4	15–63	3	5	.122
n-Octyl	183–183.5	50	4	9–42	6	10	.054
n-Octyl	183–183.5	60	4	12–72	3	4	.134
Lauryl ($C_{12}H_{25}Cl$)	243–244	50	4	8–37	3	6	.047
Lauryl ($C_{12}H_{25}Cl$)	243–244	60	4	16–65	1	2	.102
Myristyl ($C_{14}H_{29}Cl$)	154–155 (15 mm.)	50	4	7–34	4	6	.040
Myristyl ($C_{14}H_{29}Cl$)	154–155 (15 mm.)	60	4	8–65	8	11	.098
Cetyl ($C_{16}H_{33}Cl$)	m. p., 13	50	4	9–38	6	12	.0369
Cetyl ($C_{16}H_{33}Cl$)	m. p., 13	60	4	8–61	1	1	.0905
Myricyl ($C_{30}H_{61}Cl$)	m. p., 46–46.5	50	4	8–29	7	9	.037
Myricyl ($C_{30}H_{61}Cl$)	m. p., 46–46.5	60	4	8–57	6	12	.089
*iso*Propyl	36–37	60	3	6–15	13	13	.0015
sec.-Butyl	69–70	60	3	9–20	2	5	.0022
Methyl-*n*-propyl-chloromethane	96–97	60	3	13–30	1	2	.0048
Prim.-*iso*-amyl	100–101	60	5	14–57	1	2	.0678
Methyl *n*-hexyl-chloromethane	169–171	60	3	12–21	10	12	.0026
Methyl-*n*-butyl-chloromethane	123–126	60	2	28–41	4	4	.0075
Dimethyl-*n*-propyl-chloromethane	36–37 (15 mm.)	60	3	11–26	5	6	.0029
tert.-Butyl	50–51.2	60	2	13–16	<5	<5	.0018
Chlorocyclohexane	23–24 (10 mm.)	60	3	Diff. between titrations and blank too small to measure			<.0001
Benzyl	61–62 (11 mm.)	25	4	28–51	2	4	.786
Benzyl	61–62 (11 mm.)	30	4	26–56	3	6	1.311

TABLE V (*Concluded*)

Chloride	Boiling point °C.	Temp. of experiments °C.	No. of experiments	Range of measurements in terms of percentage reacted	Average deviation of constants from mean %	Greatest deviation of constants from mean %	Mean value of *k*
Benzyl	61–62 (11 mm.)	50	2	23–47	8	8	7.889
o-Chlorobenzyl	94–95 (10 mm.)	25	4	4	5	5	2.68
o-Chlorobenzyl	94–95 (10 mm.)	30	4	4	2	2	4.38
ω-Chloro-acetophenone	m. p., 57	−10	5	37–60	8	14	5.91[a]
B. WITH LITHIUM IODIDE							
Benzyl	61–62 (11 mm.)	25	4	16–57	1	2	0.771
Benzyl	61–62 (11 mm.)	30	4	25–69	4	6	1.31
n-Butyl	78–79	50	4	10–51	3	6	0.0396
n-Butyl	78–79	60	4	12–64	1	3	.099
o-Chlorobenzyl	94–95 (10 mm.)	25	4	25–69	3	4	2.73
o-Chlorobenzyl	94–95 (10 mm.)	30	4	28–61	1	3	4.45
Ethyl chloro-acetate	142.2–142.8	25	4	21–76	1	2	6.43
Ethyl chloro-acetate	142.2–142.8	30	4	35–65	6	11	10.6
ω-Chloro-acetophenone	m. p., 57	−10	4	22–56	2	4	5.72[a]
ω-Chloro-acetophenone	m. p., 57	0	4	52–71	10	20	21.5[a]
C. WITH SODIUM IODIDE							
Benzyl	61–62 (11 mm.)	25	4	16–55	3	3	0.766
Benzyl	61–62 (11 mm.)	30	4	25–69	4	8	1.34
n-Butyl	78–79	50	4	11–50	2	2	0.0409
n-Butyl	78–79	60	7	8–64	3	6	.100
o-Chlorobenzyl	94–95 (10 mm.)	25	4	24–69	2	4	2.71
o-Chlorobenzyl	94–95 (10 mm.)	30	4	28–61	<1	1	4.42
Ethyl chloro-acetate	142.2–142.8	25	4	21–76	1	2	6.51
Ethyl chloro-acetate	142.2–142.8	30	4	32–69	4	4	10.7
ω-Chloro-acetophenone	m. p., 57	−10	4	23–57	2	5	5.80[a]
ω-Chloro-acetophenone	m. p., 57	0	4	52–71	10	25	20.9[a]

[a] Iodine was liberated when the tubes were broken in the hydrochloric acid due to the reduction of the iodo-acetophenone; this iodine was extracted with chloroform, titrated with $Na_2S_2O_3$ and a correction applied as explained above.

with thiosulfate and a correction was applied as explained in our first paper. The same procedure and correction were employed in the case of *tert.*-butyl chloride and dimethylpropyl-chloromethane which liberated a little iodine directly in the reaction mixture. To save space, the time, percentage reacted (100 z) and the values of k are reported in full only in the case of a few compounds in Table IV. Table V is a condensed summary of the other data, those for *n*-butyl chloride being given in both Tables IV and V to illustrate the method of tabulation. On account of the great volatility of ethyl chloride this substance was dissolved in absolute acetone and the solution made up so that 0.5 g. would contain exactly 0.001 mole of the chloride. Because of this volatility the experimental error was greater than in the measurements of the other chlorides.

TABLE VI

REACTION WITH VARIOUS CONCENTRATIONS OF REACTANTS

(A) In the following three experiments the concentration of the organic chloride was 0.0667 mole per liter and of the inorganic iodide, 0.0134 mole per liter. Each tube contained 0.001 mole of the organic halide and 0.0002 mole of the inorganic iodide dissolved in 15 cc. of acetone. The value of k was calculated from the usual bimolecular equation which has the same form as that used for calculating k in Table IV, except that the value of b is now 0.0134.

BENZYL CHLORIDE AND POTASSIUM IODIDE AT 25°			ETHYL CHLORO-ACETATE AND POTASSIUM IODIDE			AMYL CHLORIDE AND POTASSIUM IODIDE AT 50°		
Time Hours	Percentage reacted	k	Time Hours	Percentage reacted	k	Time Hours	Percentage reacted	k
1.50	15.83	0.759	0.25	22.10	6.63	18.0	13.50	0.0530
3.0	29.56	.783	.50	38.59	6.60	30.0	20.94	.0520
6.0	48.91	.769	.75	50.55	6.48	48.0	31.40	.0527
8.0	58.50	.765	1.50	69.29	5.60	64.0	39.94	.0539
	Av.	.769		Av.	6.32		Av.,	.0529

(B) In the following experiment each tube contained 0.001 mole of benzyl chloride and 0.0004 mole of sodium iodide dissolved in 5 cc. of acetone. The concentrations were therefore benzyl chloride, 0.020 mole per liter, sodium iodide, 0.08 mole per liter. The value for k was calculated from the bimolecular equation which now takes the form, $k = \frac{1}{3/2\ bt} \log \frac{5/2 - z}{5/2\ (1 - z)}$, and in which $b = 0.08$.

REACTION BETWEEN BENZYL CHLORIDE AND SODIUM IODIDE AT 25°

Time, hours	0.5	1.0	2.0	3.0	
Percentage reacted	16.23	29.50	47.99	60.33	
k	0.783	0.809	0.787	0.774	Av., 0.791

Summary

1. The rate of the reaction of 20 alkyl chlorides with potassium iodide in acetone solution has been determined. With the exception of ethyl chloride, all the primary straight-chain compounds have the same reactivity within 20%; ethyl chloride is about twice as reactive as the other compounds; methyl chloride was not measured. The secondary and tertiary halides are much less reactive than the primary. Cyclohexyl chloride is surprisingly unreactive.

2. The results obtained with potassium iodide have been compared with those obtained by other investigators with other reagents and found to be in general agreement in regard to the primary compounds. The secondary halides appear to be less reactive in the reaction in question than in the majority of cases hitherto examined.

3. The rates of the reaction of five widely different halides with potassium, lithium and sodium iodides have been measured. The rate of the reaction of a given halide is the same with all three inorganic iodides. This points to the reaction being between the iodide ion and the organic chloride.

4. Additional evidence is presented that the velocity coefficient may be calculated from the usual bimolecular equation and is independent of the concentration of the reactants in the range of concentrations employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE RELATION BETWEEN THE STRUCTURE OF ORGANIC HALIDES AND THE SPEEDS OF THEIR REACTION WITH INORGANIC IODIDES. III. THE INFLUENCE OF UNSATURATED GROUPS

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It is a well-known fact that a halogen atom in the alpha position to many unsaturated groups is extraordinarily reactive. The so-called negative groups such as the carbonyl, carbethoxy and phenyl manifest the property of activating halogen atoms and it is the purpose of this paper to attempt to evaluate this influence. Our method of comparing the reactivity of halogen atoms in organic compounds consists in measuring the rate of the reaction, $RX + MeI \longrightarrow RI + MeX$, absolute acetone being employed as the solvent and potassium iodide as the inorganic iodide; sodium or lithium iodides might be employed equally well, as the rate of a given reaction is essentially *the same with all three substances,*[1] the reaction probably being between the organic halide and the iodide ion. The reaction velocity corresponds to that of a simple bimolecular reaction and a comparison of the reaction velocity coefficients calculated on this basis is an index of the relative reactivities of the substances examined.

The average values of the reaction velocity coefficients are given in Table I for substances of the type ACH_2Cl where A is an unsaturated group; the experimental details are given in the latter part of this paper. With the aid of the equation, $\log k_{50}/\log k_{+t} = A\left(\frac{1}{273+t} - \frac{1}{323}\right)$ we have

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[1] (a) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925). (b) Conant and Kirner, *ibid.*, **46**, 232 (1924).