[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Mechanism of Substitution Reactions: the Reaction of Benzyl Chloride with Mercuric Salts[1]

BY IRVING ROBERTS AND LOUIS P. HAMMETT

By far the most illuminating picture of the typical substitution reaction of organic chemistry is that suggested by London[2] and developed and applied by Polanyi[3] and by Olson.[4] In this there is a simultaneous addition and dissociation of reactants, a simultaneous formation and breaking of linkages. Thus in the reaction of an alkyl chloride with iodide ion[5]

$$I^- + R_3CCl \longrightarrow ICR_3 + Cl^- \qquad (1)$$

the carbon–iodine linkage is thought of as being formed at the same time that the carbon–chlorine linkage is dissociating. While the stereochemical corollaries of this mechanism are important and have been considerably investigated[3b,4b] the energetics of the process lead to even more interesting conclusions. It is in fact an essential part of this theory that the energy of formation of a new linkage may contribute largely toward doing the very considerable amount of work necessary to break an old one. In the above example it is possible to break the carbon–chlorine linkage only because the simultaneous formation of the carbon–iodine linkage involves a considerable decrease in potential energy. In terms of this energy interchange or compensation we can immediately understand the principle which every organic chemist uses that silver salts are the proper reagents to react with chlorine compounds and that strong acids like sulfuric are the proper reagents to use in condensation reactions of hydroxyl compounds. The reason is that the large energy of formation of silver halide or of water furnishes the necessary driving force. Reactions of the type of equation (1) have been much investigated as have also the undoubtedly similar reactions of the type[6]

$$H_3N + R_3CCl \longrightarrow H_3NCR_3^+ + Cl^- \qquad (2)$$

There is, however, an entirely different class of reactions of alkyl halides in which the driving force is clearly derived from the energy of formation of a linkage of halide ion to metallic ion. For instance, the rate of hydrolysis of an alkyl halide may be increased by several orders of magnitude by the addition of silver or mercuric salts. This important type of reaction has been subjected to detailed kinetic study in only one case, the reaction of silver nitrate with alkyl halides. Unfortunately, this particular reaction is badly complicated by a pronounced catalysis by the solid silver halide formed in the reaction.[7]

We have therefore studied the corresponding mercuric nitrate reaction with benzyl chloride for which this complication does not exist. As in the silver nitrate reaction, benzyl nitrate is formed in addition to the benzyl alcohol which results from the hydrolysis. The stoichiometric equations are

$$2C_6H_5CH_2Cl + Hg(NO_3)_2 \longrightarrow 2C_6H_5CH_2NO_3 + HgCl_2 \qquad (3)$$

$$2C_6H_5CH_2Cl + Hg(NO_3)_2 + 2H_2O \longrightarrow 2C_6H_5CH_2OH + 2HNO_3 + HgCl_2 \qquad (4)$$

The total rate of reaction of mercuric nitrate and benzyl chloride could therefore be followed by titration of the mercuric nitrate with chloride ion using diphenylcarbazide indicator,[8] while the relative amounts of the two products benzyl nitrate and benzyl alcohol could be determined by an acidimetric titration. As media we have used dioxane–water mixtures containing 60, 75 and 95% dioxane by volume. These were used because the resulting reaction mixtures are homogeneous, and because the solvent does not react with mercuric compounds, as do alcoholic and ketonic solvents.

The Kinetic Order of the Reaction

The reaction is essentially a second order one of mercuric nitrate and benzyl chloride, uncomplicated by reversibility, or by hydrolysis of benzyl nitrate. There are, however, appreciable de-

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(1) Dissertation submitted by Irving Roberts in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The material was presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

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

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

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

(5) Conant and Kirner, *ibid.*, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476 (1925).

(6) Menschutkin, *Z. physik. Chem.*, **17**, 193 (1895); Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933).

(7) Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904); Burke and Donnan, *Z. physik. Chem.*, **69**, 148 (1909); Donnan and Potts, *J. Chem. Soc.*, **97**, 1882 (1910); Senter, *ibid.*, **97**, 357 (1910); Baker, *ibid.*, 990 (1934).

(8) Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

viations from second order kinetics which are very important for the understanding of the nature of the reaction. A systematic study of the initial rate of reaction showed that it is rigidly first order with respect to benzyl chloride and unaffected by the addition of benzyl nitrate or of benzyl alcohol under all conditions studied. In 75% dioxane, but not in the other media, the reaction is essentially first order with respect to mercuric nitrate, and the rate is unaffected by the addition of mercuric chloride and only slightly affected by the addition of inorganic nitrates. Nevertheless, the second order constant obtained in this medium showed a steady downward drift during the course of the reaction.

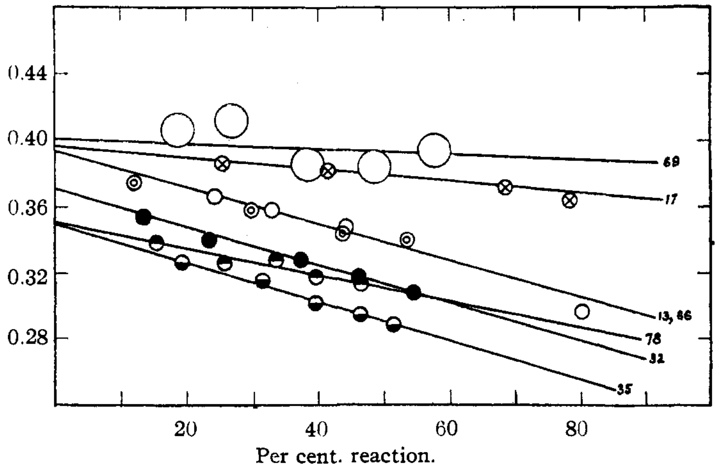

Fig. 1.—The retarding effect in 75% dioxane: ◉ no. 66, $(Hg(NO_3)_2) = 0.025$ *N*, $(BCl) = 0.050$ *N*; ○ no. 13, $(Hg(NO_3)_2) = 0.025$ *N*, $(BCl) = 0.025$ *N*; ⊗ no. 17, $(Hg(NO_3)_2) = 0.050$ *N*, $(BCl) = 0.025$ *N*; ○ no. 69, $(Hg(NO_3)_2) = 0.105$ *N*, $(BCl) = 0.025$ *N*; ● no. 32, a reaction in which $(Hg(NO_3)_2) = (BCl) = 0.025$ *N* is allowed to go to completion, new reactants (0.025 *N*) were then added and the kinetics followed; ◒ no. 35, a reaction in which $(Hg(NO_3)_2) = (BCl) = 0.050$ *N* is allowed to go to completion, new reactants (0.025 *N*) were then added and the kinetics followed; ◓ no. 78, 0.025 *N* $HgCl_2$, $Hg(NO_3)_2$, and BOH allowed to stand for seven hours, BCl was then added and the kinetics followed.

The Retarding Secondary Reaction.—In Fig. 1 we have plotted the second order rate constant *k* against the per cent. of reaction for a number of initial conditions, the solvent being in every case 75% dioxane. The radius of each circle represents the probable error. This is especially large in expt. 69 because of the exceptionally high rate. The resulting series of points, for a given experiment, is linear within experimental error and can be extrapolated satisfactorily to give the initial constant. The identity of the values of this initial constant for expts. 13, 66, 17 and 69, which involve different concentrations of mercuric nitrate and benzyl chloride, demonstrates the true second order nature of the initial reaction. The decrease in slope observed as the concentration of mercuric nitrate is increased suggests that a retarding factor operates by preventing some of the mercuric nitrate from participating in the reaction. Although none of the previously known products of the reaction retard it, something produced in the reaction does retard, as the data plotted in lines 32 and 35 of Fig. 1 demonstrate. Here new mercuric nitrate and benzyl chloride were added to spent reaction mixtures and the extrapolated initial reaction rates were found to be considerably decreased. The magnitude of this decrease was 6.5% when the initial mixture contained 0.025 *N* concentrations of mercuric nitrate and benzyl chloride (expt. 32); it was 11.5% when these concentrations were 0.05 *N* (expt. 35).

To isolate this retarding substance, a large amount of reaction mixture of high concentration (1.0 *N*) was prepared, and the reaction product was subjected to various operations of separation. The efficacy of each such operation was tested by observing the effect of the fractions upon the rate of the mercuric nitrate–benzyl chloride reaction. In this way a new substance which possesses a marked retarding effect upon the reaction was isolated. This substance has the composition of a chloromercuri-benzyl alcohol, and the properties of a weak acid. Its structure has not yet been determined. Subsequently it was found that this substance can be prepared by the action of mercuric nitrate upon benzyl alcohol followed by the addition of chloride ion, and it is apparently produced during the mercuric nitrate–benzyl chloride reaction in this way, the benzyl alcohol being produced in the primary reaction.

That this compound is at least partly responsible for the deviation from the second order course of the primary reaction is shown by the data of line 78 of Fig. 1. Here the new compound was allowed to form by the reaction of mercuric nitrate, mercuric chloride and benzyl alcohol. When benzyl chloride was added the initial reaction rate was as low as in expt. 35. It should be noted that separate experiments showed that the mere presence without previous reaction of benzyl alcohol and mercuric chloride in a reaction mixture has a negligible effect upon the rate.

That there are still further complications due to side reactions is demonstrated by the fact that the slope of 32, 35 and 78 is no greater than that of lines 13 and 66, whereas the initial presence of benzyl alcohol in these runs would be expected to produce a more rapid formation of the retardant and greater drift in the second order constants. It seems evident, however, that no matter how involved the mechanism of the drift, its cause is a subsequent reaction of a product of the primary reaction. Consequently, we can assume that the initial extrapolated second order constant is the correct one for the mercuric nitrate–benzyl chloride reaction. That this secondary reaction also takes place in 60% dioxane even though the constant increases during the course of the reaction, is evidenced by the fact that the same retardant compound can be isolated from this medium in about the same yield as from 75% dioxane.

The Effects of Nitrates and of Perchlorates.—Nitrates accelerate the reaction in all the media studied, but the effect is largest in 60% dioxane, in which there also appears a deviation from proportionality between rate and mercuric nitrate concentration. The effect of added nitrates in the 60% mixture is shown in Table I and plotted in Fig. 2. The three nitrates used have practically the same effect at equivalent concentrations. Some measurements with calcium nitrate deviate considerably but have been omitted because the solutions were turbid, showing that some complication enters in this case. As Table II shows, a decrease in mercuric nitrate concentration with a constant concentration of nitric acid produces an increase in the second order constant.

TABLE I

EFFECT OF NITRATES AND PERCHLORATES ON k IN 60% DIOXANE. (BCl)[a] = 0.025 N

Expt.	Reactant	Other electrolytes	k
45	0.025 N $Hg(NO_3)_2$	0.013 N HNO_3	0.956
53	.025 N $Hg(NO_3)_2$	.030 N HNO_3	1.002
54	.025 N $Hg(NO_3)_2$	.085 N HNO_3	1.070
61	.025 N $Hg(NO_3)_2$	.140 N HNO_3	1.080
59	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .06 N KNO_3	1.042
60	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .15 N KNO_3	1.060
62	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .135 N $Mg(NO_3)_2$	1.078
51	.025 N $Hg(ClO_4)_2$	.016 N $HClO_4$	1.320
52	.025 N $Hg(ClO_4)_2$	.037 N $HClO_4$	1.406
63	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .045 N $KClO_4$	1.122

[a] B = benzyl, $C_6H_5CH_2$.

TABLE II

EFFECT OF ($Hg(NO_3)_2$) ON k IN 60% DIOXANE (BCl) = 0.025 N

Expt.	$Hg(NO_3)_2$, N	HNO_3, N	k
65	0.050	0.029	0.956
53	.025	.030	1.002
74	.012	.030	1.038

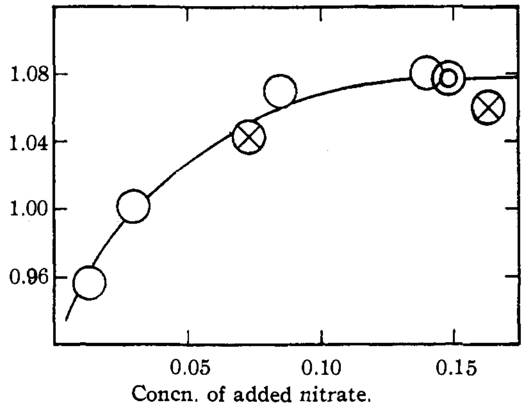

Fig. 2.—Effect of added nitrate on k in 60% dioxane: ○, HNO_3; ⊗, KNO_3; ●, $Mg(NO_3)_2$.

These phenomena are no doubt due in part to salt effects, and it is therefore impossible to decide from them alone whether the actual reactant is mercuric ion, non-ionized mercuric nitrate, or the intermediate ion $HgNO_3^+$. Conclusive evidence that mercuric ion is not the sole reactant is, however, offered by our experiments with mercuric perchlorate. This reacts much more rapidly with benzyl chloride than does the nitrate, as experiments 51 and 52 in Table I demonstrate. Furthermore, the addition of alkali perchlorate to mercuric nitrate results in a considerably increased rate (expt. 63). Consequently some new more reactive substance is formed when perchlorate is added to the nitrate solution and this can only be $Hg(ClO_4)_2$ or $HgClO_4^+$. But there may be expected to be even more non-ionized nitrate in the mercuric nitrate solution than there is non-ionized perchlorate in the mercuric perchlorate solution, because of the considerably greater tendency toward the formation of non-ionogen compounds exhibited by nitrate ion. The idea that these mercuric salts should not be completely ionized is entirely reasonable in view of the known tendency of mercuric salts toward complex formation and the favorable effect of the low dielectric constant of the medium.

The Effect of Mercuric Chloride.—As has been stated previously, addition of mercuric chloride to the reaction mixture in 75% dioxane has no effect upon the rate. In 95% dioxane, however, 0.05 *N* mercuric chloride lowers the rate constant from 0.116 to 0.072. Since mercuric chloride is produced as the reaction goes on, this negative catalysis explains the larger downward drift found in this medium, a drift so large as to make accurate extrapolation difficult. On the other hand, in 60% dioxane where mercuric chloride speeds up the reaction, the small upward drifts or constant values of the specific rate observed may be attributed to the opposing effects of the retarding secondary reaction and the accelerating products, mercuric chloride and nitric acid.

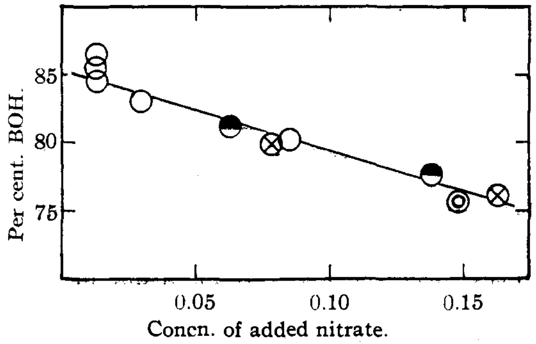

Fig. 3.—Effect of added nitrate on % BOH in 60% dioxane: ○, HNO_3; ⊗, KNO_3; ◉, $Mg(NO_3)_2$; ◓, $Ca(NO_3)_2$.

Table III shows the effect of mercuric chloride on the velocity in 60% dioxane. Concentrations higher than 0.04 *N* could not be used because of the low solubility of mercuric chloride in this medium. It can be seen, however, that the catalysis is a large one with no sign of levelling off in this concentration range.

TABLE III

EFFECT OF MERCURIC CHLORIDE ON *k* IN 60% DIOXANE (BCl) = 0.025 *N*

Expt.	Reactant	Acid	$HgCl_2$, *N*	*k*
45	0.025 *N* $Hg(NO_3)_2$	0.013 *N* HNO_3	0.000	0.956
49	.025 *N* $Hg(NO_3)_2$	.013 *N* HNO_3	.026	1.130
50	.025 *N* $Hg(NO_3)_2$	.013 *N* HNO_3	.039	1.184
64	.025 *N* $Hg(ClO_4)_2$	016 *N* $HClO_4$	.040	1.924

Morse[9] has demonstrated the existence in water of the ion $HgCl^+$ as the result of the first dissociation of mercuric chloride. The equilibrium constant for the equilibrium $HgCl_2 + Hg^{++} \rightleftarrows 2HgCl^+$, is the quotient of the first and second dissociation constants of mercuric chloride and has a value of about 8 in water. The above data on the effect of mercuric chloride on the reaction are completely explained if we assume that $HgCl^+$ (or $HgClNO_3$ in this solvent) also reacts with benzyl chloride. The differing effects of mercuric chloride in the various media may be attributed to a shift in the above equilibrium and in the relative velocities of the $Hg(NO_3)_2$ and the $HgClNO_3$ reactions.

The Distribution of Products

The most striking property of the reaction of silver nitrate with alkyl halides is the complete lack of dependence of the proportion of alkyl nitrate in the reaction product upon the concentration of ionic nitrate in the reacting mixture. By contrast, the mercuric nitrate reaction shows a distribution of product between benzyl alcohol and benzyl nitrate which varies with varying concentration of nitric acid or alkali nitrate in the solution. The results in 60% dioxane are shown in Table IV and plotted in Fig. 3. The distribution is, however, effectively independent of the concentration of mercuric nitrate as Table V indicates. This result supports our previous conclusion that much of the mercuric nitrate is in the non-ionized condition.

TABLE IV

EFFECT OF ADDED NO_3^- ON % BOH IN 60% DIOXANE ($Hg(NO_3)_2$) = (BCl) = 0.025 *N*

	Added NO_3^-	%BOH
HNO_3	0.013 *N*	86.5, 84.5, 85.5
HNO_3	.030	83.0
$Ca(NO_3)_2$	.063	81.1
KNO_3	.073	79.9
HNO_3	.085	80.2
$Ca(NO_3)_2$	.138	77.7
$Mg(NO_3)_2$	.148	75.7
KNO_3	.163	76.1

TABLE V

EFFECT OF ($Hg(NO_3)_2$) on % BOH IN 60% DIOXANE (BCl) = 0.025 *N*

$Hg(NO_3)_2$, *N*	HNO_3, *N*	%BOH
0.050	0.029	81.3
.025	.030	83.0
.012	.030	82.2

Table VI shows that mercuric chloride has no effect on the distribution of products, although it has a large effect on the velocity of the reaction (Table III).

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[9] Morse, *Z. physik. Chem.*, **41**, 709 (1902).

TABLE VI

EFFECT OF ($HgCl_2$) ON % BOH IN 60% DIOXANE

($Hg(NO_3)_2$) = (BCl) = 0.025 *N*; (HNO_3) = 0.013 *N*

$HgCl_2$, *N*	% BOH
0.000	85.5 (mean of 3)
.026	86.5
.039	85.4

The effect of nitrates and the lack of effect of mercuric chloride on the distribution applies in the same way to 75% dioxane. The percentage of benzyl alcohol decreases as the amount of dioxane in the medium is increased: in 75% dioxane, 68% of the product is benzyl alcohol, and in 95% dioxane, 35% of the product is benzyl alcohol.

In the perchlorate experiments in 60% dioxane the product is 100% benzyl alcohol during the whole course of the reaction, even in the presence of excess perchlorate. In the mixed nitrate–perchlorate run (expt. 63, Table I) the product was found to be 88.6% benzyl alcohol, an intermediate value.

The Mechanism of the Reaction

The possibilities may be classified into three general types.

(1) **Double Decomposition,** AB + CD ⟶ AC + BD.—Let us consider a pair of concurrent reactions, one of mercuric nitrate or of $HgNO_3^+$ to form benzyl nitrate, and one of mercuric ion, which is of course hydrated, to form benzyl alcohol. If we use the most probable formulas with a coördination number of four for the mercuric ion, the equations are

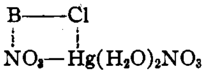
$$C_6H_5CH_2Cl + Hg(H_2O)_2(NO_3)_2 \longrightarrow C_6H_5CH_2NO_3 + Hg(H_2O)_2NO_3Cl \quad (5)$$

$$C_6H_5CH_2Cl + Hg(H_2O)_4^{++} \longrightarrow C_6H_5CH_2OH + Hg(H_2O)_3Cl^+ + H^+ \quad (6)$$

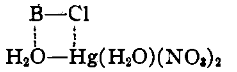
As we have indicated previously, however, one of the actual reactants, when perchlorates are present, must be mercuric perchlorate or the ion $HgClO_4^+$. On the basis of this mechanism these reactants could only form benzyl perchlorate. Actually no measurable amount of perchlorate ester is formed at any time, and it is most improbable that it is formed as an unstable intermediate, because the known alkyl perchlorates are far from instantaneously hydrolyzed.[10] Therefore, since benzyl alcohol may be formed by the reaction of mercuric perchlorate, there is every reason to expect that it should be formed by the reaction of mercuric nitrate. We must therefore add a third equation to the first two

$$C_6H_5CH_2Cl + Hg(H_2O)_2(NO_3)_2 \longrightarrow C_6H_5CH_2OH + Hg(H_2O)(NO_3)_2Cl^- + H^+ \quad (7)$$

This reaction scheme would suppose two possible modes of addition of the hydrated mercuric nitrate to benzyl chloride, one leading to benzyl nitrate, the other to benzyl alcohol



$$\begin{array}{ccc} B & \text{——} & Cl \\ \vdots & & \vdots \\ NO_3 & \text{—} & Hg(H_2O)_2NO_3 \end{array}$$



$$\begin{array}{ccc} B & \text{—} & Cl \\ \vdots & & \vdots \\ H_2O & \text{—} & Hg(H_2O)(NO_3)_2 \end{array}$$

On this basis the greater rate of benzyl alcohol formation from mercuric perchlorate than from mercuric nitrate may be attributed to a weaker binding of the water molecules in hydrated mercuric perchlorate than in the nitrate.

The objections to this mechanism are two-fold. In the first place, if this one-step picture is correct, there should be a parallelism between the effect of nitrates on the reaction velocity and on the proportion of benzyl nitrate produced. Actually the curve showing the former levels off at about 0.1 *N* added nitrate (Fig. 2), while the latter shows a linear relationship with concentration (Fig. 3).

In the second place, the failure of mercuric chloride to affect the distribution requires, if this mechanism is adopted, the assumption that the ratio of the rates of formation of benzyl nitrate and of benzyl alcohol from $HgClNO_3$ be the same as the corresponding ratio for the formation from $Hg(NO_3)_2$. There is no reason to expect so simple a relationship, and still less to expect that it should occur in both 60 and 75% dioxane.

(2) **The Termolecular Mechanism** A + BC + D ⟶ AC + BD.—This would be formulated as follows

$$C_6H_5CH_2Cl + Hg^{++} + NO_3^- \longrightarrow C_6H_5CH_2NO_3 + HgCl^+ \quad (8)$$

$$C_6H_5CH_2Cl + Hg^{++} + H_2O \longrightarrow C_6H_5CH_2OH + H^+ + HgCl^+ \quad (9)$$

The objections are of the same nature as for the first case, from which this mechanism is indeed kinetically indistinguishable.

(3) **The Ionic Intermediate Mechanism.**—These difficulties vanish if it is supposed that the reaction proceeds through an unstable intermediate which can react either with nitrate ion to form benzyl nitrate or with water to form benzyl alcohol. The effects of added nitrates upon the total rate of reaction are exerted only upon the rate of

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[10] Ethyl perchlorate may be distilled from water without hydrolysis [Roscoe, *Ann.*, **124**, 124 (1862)]. The compound Cl-$CH_2 \cdot CH(OH) \cdot CH_2 \cdot ClO_4$ in 0.5 molar concentration is half hydrolyzed at 17° after forty hours [Hoffman, Zedwitz and Wagner, *Ber.*, **42**, 4390 (1909)].

formation of this intermediate, whereas the effect of nitrate upon the distribution depends upon an increased rate of formation of benzyl nitrate from the intermediate and nitrate ion. The two effects are consequently independent. Since mercuric chloride does not affect the distribution, the intermediate formed when the reactant is $HgClNO_3$ must be the same as when the reactant is $Hg(NO_3)_2$, and the only substance which fits these requirements is a carbonium ion, benzyl ion, $C_6H_5CH_2^+$. The overwhelmingly probable mechanism for this reaction is therefore the rate determining step

$$\left\{\begin{array}{l} Hg(NO_3)_2(H_2O)_2 \\ HgClNO_3(H_2O)_2 \\ Hg(H_2O)_4^{++} \end{array}\right\} + C_6H_5CH_2Cl \longrightarrow \left\{\begin{array}{l} HgClNO_3(H_2O)_2 + NO_3^- \\ HgCl_2(H_2O)_2 + NO_3^- \\ HgCl(H_2O)_3^+ + H_2O \end{array}\right\} + C_6H_5CH_2^+ \qquad (10)$$

followed by the concurrent reactions

$$C_6H_5CH_2^+ + NO_3^- \longrightarrow C_6H_5CH_2NO_3 \qquad (11)$$

$$C_6H_5CH_2^+ + H_2O \longrightarrow C_6H_5CH_2OH + H^+ \qquad (12)$$

It is interesting to speculate on the possibility that the transient yellow color observed when the reaction is run in high concentration (see experimental part) is that of benzyl ion.

Since reaction (11) is subject to a large salt effect, and reaction (12) to a small one, the effect of added inorganic nitrates upon the distribution will not be a simple one. The fraction R of the product which is benzyl alcohol is easily shown to be given by the equation

$$R = 1/\left(1 + \frac{k_1}{k_2}\,[NO_3^-]f_1^2\right)$$

where k_2 and k_1 are rate constants for the reaction of benzyl ion with nitrate ion and with water, respectively, and f_1 is the activity coefficient of a singly charged ion. Addition of nitric acid or a nitrate increases (NO_3^-) but decreases f_1. In view of the incompletely ionized nature of mercuric nitrate and the low dielectric constant of the medium, it is hopeless to attempt to predict the value of f_1. Qualitatively, however, we do find that the rate of change of distribution with nitrate concentration is considerably smaller than that given by the assumption that f_1 is constant. It is rather surprising that the divalent nitrates fall on the same curve. The salt effect also accounts for the fact that the proportion of benzyl alcohol rises to 88.6% when perchlorate is added to the reaction mixture of mercuric nitrate and benzyl chloride.

We have assumed that a wide variety of mercuric compounds can react with alkyl halides by virtue of the tendency of mercuric ion to form stable compounds with chloride ion. Neglecting the dioxane-solvated compounds, the possibilities in this reaction are $Hg(H_2O)_4^{++}$, $Hg(H_2O)_3(NO_3)^+$, $Hg(H_2O)_2(NO_3)_2$, $Hg(H_2O)_3Cl^+$, $Hg(H_2O)_2ClNO_3$, $Hg(H_2O)_3(ClO_4)^+$, $Hg(H_2O)_2(ClO_4)_2$ and $Hg(H_2O)_2Cl(ClO_4)$. Further, Nicolet and Stevens[11] report that the alcoholysis of alkyl halides is accelerated by the corresponding mercuric halides, the mercuric halide being inactivated according to the equation $HgX_2 + 2X^- \rightleftarrows HgX_4^{=}$. These considerations result in a picture analogous to that of the generalized acid catalysis proposed by Brönsted.[12] If this is true, the velocity of reaction of each of these mercury compounds with alkyl halides should be a function of their tendency to combine with chloride ion as measured by equilibrium constants.

The hypothesis of a carbonium ion as an unstable intermediate has been used successfully to explain a variety of rearrangement reactions.[13] Such ions are certainly not set free in all reactions of substitution; they are very improbable intermediates for reactions of the type of equations (1) and (2). But it seems likely that they appear in many of the reactions of organic halogen compounds with mercuric and silver salts, and with other metallic salts which have a strong affinity for halogen ion.[14] A carbonium ion intermediate is also very probable in the many condensation and other reactions of hydroxyl compounds in which the very strong acid sulfuric is used as condensing agent. Here the driving force must be taken to be the energy of formation of water or of oxonium ion instead of the energy of linkage of metallic ion with chloride ion.

The process of formation of the carbonium ion in these cases may be considered to be a case of the London three-body substitution mechanism, just as much as is the reaction of iodide ion with an alkyl chloride, the type being

$$A + BC \longrightarrow AB + C \qquad (13)$$

$$I^- + RCl \longrightarrow IR + Cl^- \qquad (14)$$

$$Hg^{++} + ClR \longrightarrow HgCl^+ + R^+ \qquad (15)$$

The reaction of equation 14 may be called a sub-

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[11] Nicolet and Stevens, THIS JOURNAL, **50**, 135 (1928).

[12] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[13] (a) Lowry, *Chemistry and Industry*, **43**, 1128 (1924); (b) Meerwein, *Ann.*, **453**, 16 (1927); (c) Whitmore, THIS JOURNAL, **55**, 4153 (1933).

[14] (a) Meerwein and Van Emster, *Ber.*, **55B**, 2500 (1922); (b) Bodendorf and Boehme, *Ann.*, **516**, 1 (1935).

stitution on carbon, that of equation 15 a substitution on halogen.

Experimental

Materials and Solutions.—The preparation and purification of primary standard mercuric oxide have been described previously.[8] C. P. mercuric nitrate was used directly. All other metallic salts were purified by the usual methods. Reagent grade concentrated nitric acid and 20% perchloric acid were used. Benzyl chloride (Mallinckrodt Analytical Reagent) was fractionated *in vacuo*, the middle third (b. p. 56–58° at 4–5 mm.; $n^{25}\mathrm{D}$ 1.5363) being taken for kinetic experiments. Benzyl alcohol (Eastman Kodak Co.) was fractionated *in vacuo*, the middle third being taken; b. p. 77–78° at 4–5 mm. Benzyl nitrate was prepared by the method of Nef.[15] After two fractionations *in vacuo*, the material gave a negative test for chloride on long standing with alcoholic silver nitrate, b. p. 100–101° at 18 mm. Dioxane was purified by a modification of the method of Kraus and Vingee.[16] The sample was refluxed with solid sodium hydroxide until there was no further resin formation. After filtering, it was refluxed with metallic sodium for about six hours and distilled; b. p. 101.1–101.3° at 760 mm. On standing for several days this dioxane develops an impurity which slowly reacts with mercuric nitrate forming mercurous salt; this error was found to be negligible under the conditions of the kinetics.

Mercuric nitrate solutions were prepared both by dissolving mercuric nitrate in nitric acid and by dissolving mercuric oxide in nitric acid with consistent results. Mercuric perchlorate solutions were made up from primary standard mercuric oxide and perchloric acid. The preparation of all other standard solutions already has been described.[8]

Kinetic Experiments.—The details of the titration method for following the reactions have been discussed elsewhere.[8] Into a 300-cc. glass-stoppered bottle was pipetted the appropriate quantity of dioxane and water (or water solution of the other substance to be added). After weighing in the benzyl chloride from a weight buret, the bottle was set into the thermostat at 24.65 ± 0.01° for at least thirty minutes. The reaction was then started by pipetting in 5 cc. of standard mercuric nitrate prepared so as to give the desired concentration. At measured intervals, 10 cc. of the reaction mixture was delivered into 5 cc. of standard 0.1 N potassium chloride, thus effectively killing the reaction. The acidity was then titrated with 0.025 N sodium hydroxide to a brom phenol blue end-point. After the addition of 4 cc. of 0.2 N nitric acid to bring the solution to optimum acidity, and 5 drops of diphenylcarbazide indicator, the excess chloride present was titrated with 0.02 N mercuric nitrate. Thus, only one titration mixture was necessary to determine both the nitric acid produced and the mercuric nitrate used up in the reaction.

The initial mixing of the mercuric nitrate solution with the rest of the reaction mixture caused a momentary rise in temperature; the error was negligible except for the very fast runs, in which case the standard mercuric nitrate solutions were made up in 50% dioxane by volume, thus cutting down the heat of mixing.

Only calibrated weights and volumetric apparatus were used. In calculating velocity constants, the volume which in practically all runs was about 100 cc. was corrected for the shrinkage on mixing dioxane and water. Since one mole of mercuric nitrate reacts with two moles of benzyl chloride, the usual equation for a bimolecular reaction must be modified to

$$k = \frac{2}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

in which the quantities a and b are the concentrations in *equivalents* per liter of mercuric nitrate and benzyl chloride, respectively. The maximum error in any one constant is about 2%; the precision generally found was 1% or better.

Table VII shows the types of kinetics found under various conditions. In three runs presented the initial concentrations of mercuric nitrate and benzyl chloride were both 0.025 N. Experiment 66 performed in 75% dioxane by volume, shows the downward drift found in that medium. In 60% dioxane expt. 61 shows the second order constant found with a high concentration of nitrate ion, while with expt. 45, with only a small concentration of added nitrate, a small upward drift in the constants was found.

TABLE VII

TYPES OF KINETICS FOUND

t, min.	Expt. 66 $a - x$[a]	k
0	0.02474	...
10	.02358	0.398
30	.02173	.374
91.3	.01761	.358
180	.01400	.344
270	.01159	.340
	Expt. 61	
0	0.02525	...
10	.02222	1.080
30	.01792	1.080
60	.01381	1.094
105	.01046	1.066
150	.00831	1.080
	Mean	1.080
	Expt. 45	
0	0.02505	...
10	.02225	0.924
30	.01837	.968
60	.01442	.980
120	.01015	.976
150	.00869	1.002
180	.00760	1.018

[a] $a - x = (\mathrm{Hg(NO_3)_2}) = (\mathrm{BCl})$, in equivalents per liter, at the time t.

Representative data on the distribution of products are presented in Table VIII. It can be seen that the distribution of products is a constant throughout the reaction.

Products of the Reaction.—In order to obtain enough material to separate and identify the products, the reaction

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(15) Nef, *Ann.*, 309, 171 (1889).

(16) Kraus and Vingee, THIS JOURNAL, 56, 511 (1934).

TABLE VIII

DISTRIBUTION OF PRODUCTS IN 60% DIOXANE—EXPT. 49

Concn. NaOH solution/concn. $Hg(NO_3)_2$ solution = 1.075

t, min.	Acid titer, cc.	$Hg(NO_3)_2$ titer, cc.	100R (%BOH)
30	2.33	2.89	86.6
60	3.70	4.60	86.4
90	4.63	5.69	87.5
120	5.20	6.44	86.7
180	5.87	7.40	85.2
24 hrs.	7.73	9.69	86.5
		Mean	86.5

was run at 1.0 *N* concentrations in a volume of 500 cc. To a solution of 60 cc. (0.5 mole) of benzyl chloride in 300 cc. of dioxane was added a solution of 70 g. (0.65 equiv.) of mercuric oxide in 100 cc. of water and 55 cc. of concentrated nitric acid. After standing for a few minutes mercuric chloride crystallized out and the solution developed a yellow color which disappeared after about forty-five minutes. Twenty-four hours later the mercuric chloride was filtered off and solid potassium chloride was added to convert excess mercuric nitrate to mercuric chloride. Enough sodium bicarbonate was added to neutralize most of the nitric acid. The filtered solution was then extracted twice with ether and the combined ether layers distilled *in vacuo*. The first fraction containing ether, dioxane and a little nitric acid was discarded. The second fraction, b. p. 96–106° at 22 mm., was colorless and had the aromatic odor of benzyl nitrate; no higher boiling fraction was obtained.

That the second fraction was a mixture of benzyl alcohol and benzyl nitrate was proved in the following way.

A portion of the mixture gave a dinitrobenzoate, m. p. 112° after three recrystallizations. Known benzyl dinitrobenzoate melts at 112.5°; mixed melt, 112°. Pure benzyl nitrate alone will not react with dinitrobenzoyl chloride.

The fraction gave a strong nitrate test (diphenylamine) but the nitrate could not be extracted with water. A few cc. was boiled with strong sodium hydroxide for ten minutes, and the excess alkali neutralized with hydrochloric acid. After extracting several times with ether to remove organic material, the water layer gave a strong test for nitrate. The presence of a nitrate ester with the same boiling point as benzyl nitrate was thus proved.

No attempt was made to isolate the products of the mercuric perchlorate reaction because of the explosive nature of perchlorates in the presence of organic matter.

Isolation of the Retardant Compound.—After setting up a reaction mixture as described above, the various extracts, wherever practicable, were tested for their effect on the rate of the mercuric nitrate–benzyl chloride reaction in 75% dioxane. After pumping off the ether and dioxane, 5 cc. of the residue (I) (almost entirely benzyl alcohol, benzyl nitrate and mercuric chloride) was found to lower the velocity constant from 0.396 to 0.110. This residue was extracted with dilute sodium hydroxide; upon addition of hydrochloric acid to the sodium hydroxide layer, a white crystalline compound (II) precipitated. After completely extracting I with dilute sodium hydroxide, the organic layer (III) was washed twice with water, once with 0.2 *N* nitric acid, and once more with water. The washed residue (III) had no retarding effect, showing that the only retardant was the alkali soluble material.

A small portion of the white precipitate (II) was insoluble in hot water; its amount was too small for study. The yield of water-soluble material after four recrystallizations (once with norite) from water was 200 mg., m. p. 126–126.5°. Fifty mg. of the compound produced a retardation from 0.396 to 0.370.

Although the reaction is almost complete in a few hours, the fact that only small amounts of the compound are obtained if the reaction mixture is not allowed to stand overnight, indicates that it is formed by a secondary reaction. It was then found that the compound could also be prepared by allowing mercuric nitrate to stand with benzyl alcohol in dioxane–water, using the same method of extraction. Allowing the other products of the reaction to stand together or with mercuric nitrate gave no result. It thus appears that the retardant compound is formed solely by a slow reaction of mercuric nitrate and benzyl alcohol in these media.

The compound itself is a new one and answers to the empirical formula of a chloro-mercuri benzyl alcohol. This is surprising in view of its acidic nature, and its structure is now being investigated further. Calcd. for C_7H_7OHgCl: acid eq., 343; C, 24.49; H, 2.04. Found: acid eq., 345; C, 24.52, 24.47; H, 1.69, 1.99.[17]

Summary

The rate of the reaction of mercuric nitrate with benzyl chloride and the distribution between the two major products, benzyl nitrate and benzyl alcohol, have been studied in dioxane–water mixtures of various proportions. The effects of the addition of nitrates, of perchlorates and of mercuric chloride upon both rate and distribution have been investigated, and kinetic complications due to a slow secondary reaction have been unraveled. A two-step mechanism involving non-ionized mercuric nitrate as the principal reactant and benzyl ion as an intermediate has been shown to be extremely probable.

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[17] We are indebted to Dr. D. Price and Mr. S. Gottlieb for these analyses.