387. *The Effect of Mercuric Bromide on the Hydrolysis of Alkyl Bromides in Acetone.*

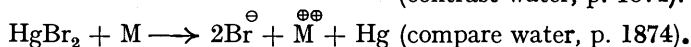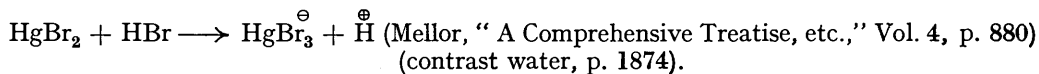By Dennis R. Read and William Taylor.

Mercuric bromide, an electrophilic reagent, has been found to exert an accelerating effect on the reaction AlkBr + H_2O ⟶ AlkOH + HBr (cf. Nicolet and Stevens, *J. Amer. Chem. Soc.*, 1928, **50**, 135). The effect is shown to increase rapidly along the series methyl, ethyl, *iso*propyl, and *tert.*-butyl bromides. Since nucleophilic reagents cause substitution at rapidly decreasing rates along the same series, the " trough " obtained in the rates when water reacts with the alkyl bromides is explained on the basis of water being both nucleo- and electro-philic. Relevant phenomena are discussed.

It is well known that, in the series of alkyl halides—methyl, ethyl, *iso*propyl, and *tert.*-butyl—attack at the α-carbon atom by a nucleophilic reagent (Ingold, J., 1933, 1121) such as the anion $CH_3 \cdot CO \cdot \overset{\ominus}{C}H \cdot CO_2Et$ (Wislicenus, *Annalen*, 1882, **212**, 239) proceeds at a decreasing rate along the series (reaction of type I; see figure). The reverse phenomenon, namely, that attack by an electrophilic reagent at the halogen atom proceeds at an increasing rate along this series, has not previously been shown in its entirety in solution (reaction of type II; see figure). Polanyi (" Atomic Reactions," 1932, pp. 56, 57) has, however, obtained such a sequence for the reaction AlkCl + Na ⟶ Alk + NaCl in the vapour phase at high temperatures and low pressures; and Burke and Donnan (J., 1904, **85**, 555) found partial evidence of this kind for the reaction AlkI + $AgNO_3$ ⟶ $Alk \cdot NO_3$ + AgI in alcoholic solution. The interpretation of the latter result is rendered difficult because of side reactions due to the alcohol and autocatalysis due to the silver iodide.

The primary object of our investigation was completely to observe this reverse phenomenon in solution, and for this purpose we had first to discover a reagent which was electrophilic towards all members of the series of alkyl bromides under discussion. Since, in every case where a " trough " appears, a reagent HX is responsible, and seeing that $\overset{\delta-}{X}$ undoubtedly effects the nucleophilic attack, it was at first intended to study the action of catalytic hydrogen on the bromides. (Attack by a proton, whilst theoretically desirable, was obviously impossible in solution owing to solvation and hence to complications; cf. J., 1937, 1962.) However, although catalytic hydrogenation of organic halogeno-compounds may be effected quantitatively in aqueous or alcoholic potassium hydroxide (Busch and Stöve, *Ber.*, 1916, **49**, 1063; Harington, *Biochem. J.*, 1926, **20**, 304), we have found it impossible to bring about any perceptible hydrogenation in dry dioxan, ether, and ethyl acetate (which are inert towards halogeno-compounds) containing platinum or palladium catalysts with excess of either calcium or zinc carbonate (see Table IX).

Because of Burke and Donnan's work (*loc. cit.*), and in view of Hughes, Ingold, and Masterman's interpretation of the reaction as being due to the $Ag^{\oplus}$ ion (J., 1937, 1239), we might have used this in the form of silver bromide as our electrophilic reagent, but this salt is too sparingly soluble, so we selected the much more soluble mercuric bromide instead. This reagent is clearly electrophilic, as is shown by the following :

$HgBr_2$ + HBr ⟶ $HgB\overset{\ominus}{r_3}$ + $\overset{\oplus}{H}$ (Mellor, " A Comprehensive Treatise, etc.," Vol. 4, p. 880) (contrast water, p. 1874).

$HgBr_2$ + M ⟶ $2\overset{\ominus}{Br}$ + $\overset{\oplus\oplus}{M}$ + Hg (compare water, p. 1874).

We had hoped, as in previous work (this vol., p. 478), to use dioxan as solvent, but were unable to do so since mercuric bromide was not sufficiently soluble therein and also because, when it was used, the end-points were not sharp. We therefore employed acetone, in which mercuric bromide is very soluble, and although this salt normally suffers slow hydrolysis in aqueous acetone this was entirely suppressed under our experimental conditions. End-points were therefore relatively sharp in spite of the brown colour which gradually developed in the reaction liquid. Hence, the investigation resolved itself into a

kinetics examination of the effect of dissolved mercuric bromide on the rates of hydrolysis of methyl, ethyl, *iso*propyl, and *tert.*-butyl bromides in acetone containing 5 g. and 10 g. of water per 100 ml. of solution at 50°. When required, a sealed tube containing 5 ml. of the reaction liquid was broken in 100 ml. of ethyl alcohol, and the solution was titrated with standard alkali, bromophenol-blue being used as indicator (Roberts and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1063). The results are summarised in Table I.

Because of the effect of mercuric bromide we took the opportunity to measure any possible effects of other dissolved bromides on the rate of hydrolysis of *tert.*-butyl bromide (see Table II).

TABLE I.

Second-order velocity coefficients (l. g.-mol.$^{-1}$ hr.$^{-1}$) for the hydrolysis of alkyl bromides in acetone in presence of mercuric bromide at 50°. The figures in parentheses are the ratios of the coefficients with and without mercuric bromide, other conditions being identical.

[AlkBr] $\sim$ 0·2 and [HBr] $\sim$ 0·05 throughout.

	tert.-Butyl bromide. [H$_2$O].				*iso*Propyl bromide. [H$_2$O].			
[HgBr$_2$].	2·7778.		5·5556.		2·7778.		5·5556.	
0·0000	0·0531*	(1·00)	0·144*	(1·00)	0·0000168*	(1·00)	0·0000391*	(1·00)
0·0500	0·546	(10·3)	0·708	(4·92)	0·000110	(6·55)	0·0000788	(2·02)
0·1000					0·00242	(144)	0·00150	(38·4)
0·2000					0·0123	(732)	0·0123	(315)
0·3000	immeasurably high initial rates				0·0195	(1160)	0·0150	(384)
0·4000					0·0289	(1720)	0·0220	(563)
0·5000					0·0384	(2290)	0·0289	(739)

	Ethyl bromide. [H$_2$O].				Methyl bromide. [H$_2$O].			
[HgBr$_2$].	2·7778.		5·5556.		2·7778.		5·5556.	
0·0000	0·0000239*	(1·00)	0·0000472*	(1·00)	0·0000715*	(1·00)	0·000126*	(1·00)
0·0500	0·0001980	(4·10)	0·0000536	(1·14)	0·000289	(4·00)	0·000127	(1·01)
0·1000	0·000483	(20·2)	0·000276	(5·85)	0·000604	(8·45)	0·000525	(4·17)
0·2000	0·00106	(44·4)	0·00110	(23·3)	0·00120	(16·8)	0·00117	(9·30)
0·3000	0·00155	(64·9)	0·00141	(29·9)	0·00162	(22·7)	0·00194	(15·4)
0·4000	0·00218	(91·2)	0·00189	(40·0)	0·00227	(31·7)	0·00224	(17·7)
0·5000	0·00279	(117)	0·00227	(48·4)	0·00293	(41·0)	0·00260	(20·6)

* These values correct those in J., 1938, 841.

TABLE II.

Second-order velocity coefficients (l. g.-mol.$^{-1}$ hr.$^{-1}$) for the hydrolysis of *tert.*-butyl bromide in presence of added dissolved bromides in acetone at 50°.

In (a), (b), and (c) : [Bu$^\gamma$Br] $\sim$ 0·2, [H$_2$O] = 2·7778.

(a) The effect of added HgBr$_2$ and HBr.

[HgBr$_2$].	[HBr].	*k*.	[HgBr$_2$].	[HBr].	*k*.
0·0100	0·05	0·0882	0·0250	0·05	0·155
0·0100	0·10	0·0930	0·0500	0·00	0·858
0·0100	0·15	0·101	0·0500	0·05	0·546
0·0250	0·00	rapidly falling, 0·531→0·165	0·0500	0·10	0·468
			0·0500	0·15	0·449

(b) The effect of added AgBr and HBr.

[AgBr].	[HBr].	*k*.	[AgBr].	[HBr].	*k*.
0·0100	0·05	0·0630	0·0150	0·20	0·0798
0·0100	0·10	0·0666	0·0000	0·05	0·0531
0·0150	0·10	0·0660	0·0000	0·15	0·0660

(c) The effect of added NaBr.

[NaBr].	[HBr].	*k*.
0·0250	0·00	0·0511

(d) The effect of excess Bu$^\gamma$Br (no HBr).

[Bu$^\gamma$Br].	[H$_2$O].	*k*.	[Bu$^\gamma$Br].	[H$_2$O].	*k*.
0·180	2·7778	0·0510	0·180	5·5556	0·132
1·170	2·7778	0·0547	0·770	5·5556	0·162
			1·163	5·5556	0·199

The results, where mercuric bromide was used, may be stated as follows :

(A) The reaction is solely one of substitution of the hydroxyl of water for bromine in the alkyl bromide, since good yields of *tert.*-butyl and *iso*propyl alcohols were obtained,

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and no evidence of olefin formation could be found. It is thus uncomplicated by side reactions and, on this account, the kinetic results are more easily interpreted than those from reactions employing alcoholic or aqueous-alcoholic solutions of silver nitrate (Burke and Donnan, *loc. cit.*; Hughes, Ingold, and Masterman, *loc. cit.*) or mercuric nitrate (Roberts and Hammett, *loc. cit.*).

(B) Mercuric bromide has a marked accelerating effect on the reaction, the effect increasing rapidly along the series Me, Et, Pr$^\beta$, Bu$^\gamma$ (see the figures in parentheses in Table I). However, it may be noted that ethyl bromide is still less reactive than methyl bromide.

(C) Water has a similar but smaller accelerating effect (see Table I).

(D) Mercuric bromide and water both retard the reverse process, *i.e.*, the esterification of an alcohol with hydrogen bromide (see Table VIII).

(E) The hydrogen bromide liberated during the forward reaction tends to deactivate the mercuric bromide, so that, where low concentrations of this are used, satisfactory rate constants cannot be obtained (see Table III; cf. also Nicolet and Stevens, *loc. cit.*). By the introduction of an initial concentration of 0·05M-hydrogen bromide good constants are obtained, for any one kinetic run, when calculated for a second-order reaction between water and the alkyl bromide (see Table IV). Obviously, owing to the high water concentrations employed, such a result cannot be used in support of the bimolecular or S_m mechanism.

(F) At the higher concentrations of mercuric bromide, *viz.*, 0·2—0·5M, when the deactivating effect of the added hydrogen bromide of 0·05M concentration is presumably small, the rates of hydrolysis are approximately a linear function of the concentration of mercuric bromide.

(G) The second-order velocity coefficients, with 0·2—0·5M-mercuric bromide present, are very approximately the same at both concentrations of water for any one alkyl bromide.

(H) Mercuric bromide causes negligible liberation of hydrogen bromide from *tert.*-butyl bromide in dioxan at 20° during 20 hours (see Table IX), although when water is also present the acid is rapidly formed.

For the other dissolved bromides the results are :

(I) Silver bromide, which is only slightly soluble in acetone and then only when hydrogen bromide is present, exerts a smaller accelerating effect than mercuric bromide on the hydrolysis of *tert.*-butyl bromide (see Table II).

(J) Hydrogen bromide apparently has a greater accelerating effect than water, but a smaller effect than silver bromide (see Table II).

(K) Sodium bromide has no effect (see Table II).

(L) *tert.*-Butyl bromide has a small accelerating effect on its own hydrolysis. This effect, unlike that due to mercuric bromide, is greater at the higher water concentration, as was the case for triphenylmethyl chloride (Read and Taylor, this vol., p. 478) (see Table II).

The " trough " (see figure) obtained for the reaction rates of water (Taylor, J., 1938, 840) or aqueous ethyl alcohol (Taylor, J., 1937, 992) on this series of alkyl bromides (reaction of type III, see figure), where the reagent, *viz.*, water or alcohol, is both nucleophilic and electrophilic, *e.g.*,

$$H_2O + HBr \longrightarrow H_3\overset{\oplus}{O} + \overset{\ominus}{Br}; \quad H_2O + M \longrightarrow \overset{\ominus}{OH} + \overset{\oplus}{M} + H$$
$$\text{(nucleophilic)} \qquad\qquad\qquad \text{(electrophilic)}$$

may now be interpreted on the basis of result (B). The reagent must function mainly

I. *Nucleophilic substitution.*
II. *Electrophilic substitution.*
III. *Simultaneous nucleophilic and electrophilic substitution.*

Velocity.

Me   Et   Pr$^\beta$ Bu$^\gamma$

as a nucleophilic reagent towards methyl bromide, but increasingly as an electrophilic reagent down the series until, with *tert.*-butyl bromide, this is the main effect. This interpretation, which follows the mechanism S_m previously put forward by Taylor (J., 1937, 1962), is in agreement with the postulated bimolecular mechanisms of reactions of Type I (*e.g.*, Haywood, J., 1922, **121**, 1904), of Type II (*e.g.*, Polanyi, *op. cit.*, p. 33), and of Type III, when low concentration of water and alkyl halides are employed (Taylor, J., 1937, 1853; Read and Taylor, *loc. cit.*). In our view this interpretation is to be preferred to that advanced by Gleave, Hughes, and Ingold (J., 1935, 238), since the latter rests ultimately on the as yet unproved ionisation of an alkyl halide in a completely anhydrous solvent (see, *e.g.*, Hughes, Ingold, and Scott, J., 1937, 1271). The same explanation will hold good for reactions of the type AlkY + HX $\rightleftharpoons$ AlkX + HY, in which a similar " trough " occurs, *e.g.*, where Alk = Me, Et, Pr^β, Bu^γ; Y = OPh, OAc, OH; X = Br (Taylor, *Rec. Trav. chim.*, 1937, **56**, 898).

From the foregoing, it follows that a molecular reagent such as water, alcohol, or hydrogen halide may behave mainly as a nucleophilic reagent towards certain members of a class of compounds, but mainly as an electrophilic reagent to other but structurally different members of the same class. This must be true, not only for the substitution of carbon, but also for that of nitrogen compounds, since Menschutkin (*Z. physikal. Chem.*, 1895, **17**, 2281) found that ethyl bromide reacted with ammonia, ethylamine, and diethyl-amine at rates which varied in the order $NH_3 < NH_2Et > NHEt_2$, whilst the strengths of the bases (*i.e.*, their powers as nucleophilic reagents) are given by $NH_3 < NH_2Et < NHEt_2$. From this evidence we infer that the reactivity of these " bases " (which contain hydrogen) must be partly electrophilic (contrast Ingold, *loc. cit.*; Roberts and Hammett, *loc. cit.*), and also the alkyl bromide must be capable of both electrophilic and nucleophilic activity.

In brief, such molecular reagents cannot be classified as being either nucleophilic or electrophilic without reference to the class *and structure* of the other reacting species. This observation removes the difficulty which Polanyi (*op. cit.*, p. 63) had in explaining the Walden inversion of optically active (*i.e.*, secondary) alcohols during esterification with hydrogen chloride. The mechanism here (see figure), on his nomenclature, is obviously mainly " negative," being a nucleophilic attack of α-carbon by hydrogen chloride, and is not " positive " as he supposed. Hence, the inversion would be expected. The inversion when α-phenylethyl chloride (a secondary chloride) is converted into the corresponding acetate by acetic acid (Steigman and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2536) may be interpreted similarly, and possibly also the results found by Hückel (*Oesterr. Chem.-Ztg.*, 1939, **42**, 105, 121) for the action of nitrous acid with various decalylamines and menthylamines. Retention of configuration during substitution can only be expected when Polanyi's positive mechanism is either mainly or exclusively in operation. For the substitution of bromine by hydroxyl, this is best illustrated by the hydrolysis of the α-bromopropionate ion (Cowdrey, Hughes, and Ingold, J., 1937, 1208), where the presence of a full ionic charge near the α-carbon renders it invulnerable to attack by water acting as a nucleophilic reagent, but the bromine, being strongly negative, is readily attacked by water acting as an electrophilic reagent. Hence, here the mechanism of substitution is " positive " and there is thus retention of configuration. Tertiary halides should also suffer substitution by water with retention of configuration for a similar reason.

EXPERIMENTAL.

The alkyl bromides were materials of constant b. p. " AnalaR " Acetone was purified according to Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 246). Mercuric bromide had m. p. 236° and gave a clear neutral solution in acetone. For the kinetic experiments on the reverse reaction, dioxan was purified by refluxing and distilling it over sodium and had b. p. 101·3—101·4°, and *iso*propyl alcohol dried over quick-lime and sodium had b. p. 82°. The kinetic experiments were performed at 50° as described previously (J., 1937, 1855) except that mercuric or other bromide was present in the solutions and that the indicator was bromophenol-blue (cf. Roberts and Hammett, *loc. cit.*). The second-order velocity coefficients of the forward reaction were calculated from the equation $k = [2·303/t(a - b)] \log_{10} b(a - x)/a(b - x)$, t being

the time in hours, and a and b the concentrations (in g.-mols./l.) of water and alkyl bromide respectively.

The Hydrolysis of the Alkyl Bromides.—In Table III are given details of representative experiments on the forward reaction : (1) showing the fall in the values of the second-order velocity coefficients when no hydrogen bromide is present initially and when low concentrations of mercuric bromide are employed; and (2) and (3) showing the initial values to be constant when higher concentrations of mercuric bromide are employed.

The Esterification of iso*Propyl Alcohol with Hydrogen Bromide.*—isoPropyl alcohol was first found to react too slowly with hydrogen bromide in acetone containing 2·7778M-water and, because acetone itself removes hydrogen bromide when the concentration of water is reduced to 1·1111M (J., 1937, 1856), at which concentration the reaction would be more rapid, dioxan containing this concentration of water was employed since hydrogen bromide is not removed by this solvent.

The velocity coefficients (Table VIII) were calculated from $k = [2·303/t] \log_{10} a/(a - x)$, where a is the concentration of both *iso*propyl alcohol and hydrogen bromide, and t the time in hours. The results show that mercuric bromide inhibits the reverse reaction.

TABLE III.

(1) [Bu$^\gamma$Br] = 0·1734, [HgBr$_2$] = 0·0250, [H$_2$O] = 2·7778.				(2) [MeBr] = 0·2000, [HgBr$_2$] = 0·1000, [H$_2$O] = 5·5556.			(3) [EtBr] = 0·2000, [HgBr$_2$] = 0·1000, [H$_2$O] = 5·5556.		
t.	[HBr].	x.	$k \times 10^3$.	t.	x.	$k \times 10^5$.	t.	x.	$k \times 10^6$.
0	0·0292*	—	—	16·41	0·0179	103	16·41	0·0121	684
0·0375	0·0369	0·0077	531	23·91	0·0225	97·9	23·91	0·0189	746
0·075	0·0405	0·0113	392	40·13	0·0405	102	40·13	0·0285	690
0·125	0·0441	0·0149	315	62·70	0·0517	86·2	62·70	0·400	642
0·225	0·0507	0·0215	259	93·70	0·0638	74·3	93·70	0·0512	570
0·475	0·0639	0·0347	230						
0·808	0·0782	0·0490	187						
1·642	0·1046	0·0754	165						
∞	0·1734	—	—						

* This concentration of acid was produced instantly during mixing at room temperature.

TABLE IV.

Showing the constant values of the second-order velocity coefficients in the forward reactions of methyl, ethyl, and *iso*propyl bromides when hydrogen bromide was added initially :

[HgBr$_2$] = 0·1000 and [H$_2$O] = 2·7778 throughout.

[MeBr] = 0·2000, [HBr] = 0·0561.				[EtBr] = 0·1932, [HBr] = 0·0606.				[Pr$^\beta$Br] = 0·1994, [HBr] = 0·0599.			
t.	[HBr].	x.	$k \times 10^6$.	t.	[HBr].	x.	$k \times 10^6$.	t.	[HBr].	x.	$k \times 10^5$.
28·12	0·0653	0·0092	601	68·9	0·0760	0·0154	483	5·85	0·0680	0·0081	255
49·5	0·0711	0·0150	566	115·3	0·0883	0·0277	485	22·52	0·0883	0·0284	247
98·8	0·0864	0·0303	601	167·4	0·0985	0·0379	483	46·95	0·1129	0·0530	239
107·2	0·0889	0·0328	605	236·0	0·1164	0·0558	481	56·7	0·1212	0·0613	236
141·6	0·0980	0·0419	615	275·1	0·1257	0·0651	484	70·9	0·1316	0·0717	230
172·0	0·1056	0·0495	601					78·2	0·1442	0·0843	257
189·8	0·1126	0·0565	636					94·7	0·1490	0·0891	230
								100·7	0·1569	0·0970	243

TABLE V.

Showing that mercuric bromide is slowly hydrolysed by water in acetone when no hydrogen bromide is present initially, but that this hydrolysis is entirely suppressed when [initial HBr] ～0·05.

[HgBr$_2$] = 0·2000, [H$_2$O] = 5·5556.				[HgBr$_2$] = 0·2000, [H$_2$O] = 5·5556, [HBr] = 0·0528.			
t.	[HBr].	t.	[HBr].	t.	[HBr].	t.	[HBr].
0	0·0000	166·6	0·0175	45·0	0·0528	168·5	0·0528
0·5	0·0000	238·6	0·0202	93·0	0·0529	213·4	0·0531
70·8	0·0104	314	0·0191				
95·0	0·0129						

TABLE VI.

Details of representative experiments on the forward reaction of *tert.*-butyl bromide showing the slightly different equilibrium positions (1) without and (2) with mercuric bromide. In these experiments 5 ml. of the reaction liquid were examined by placing it in 200 ml. of ethyl alcohol in order to diminish the deep colour of the former, and also more indicator was used.

(1) $[Bu^\gamma Br] = 0.1814$, $[HBr] = 0.0500$, $[H_2O] = 2.7778$.

(2) $[Bu^\gamma Br] = 0.1782$, $[HBr] = 0.0585$, $[H_2O] = 2.7778$, $[HgBr_2] = 0.0500$.

t.	[HBr].	x.	k.	t.	[HBr].	x.	k.
0.63	0.0658	0.0158	0.0517	0.175	0.0991	0.0406	0.535
1.13	0.0781	0.0281	0.0537	0.340	0.1300	0.0715	0.547
1.63	0.0903	0.0403	0.0558	0.508	0.1533	0.0948	0.548
2.47	0.1072	0.0572	0.0558	0.675	0.1720	0.1135	0.553
3.30	0.1213	0.0713	0.0552	119	0.2021	0.1436	—
4.97	0.1395	0.0895	0.0508	143	0.2116	0.1531	—
6.63	0.1522	0.1022	(0.0459)	198	0.2224	0.1639	—
∞	0.2110	0.1610	—	359	0.2223	0.1638	—

TABLE VII.

Showing the effect of dissolved (1) HBr, (2) NaBr, (3) AgBr, (4) excess $Bu^\gamma Br$, on the forward reaction of *tert.*-butyl bromide.

(1) $[Bu^\gamma Br] = 0.1787$, $[HBr] = 0.1473$, $[H_2O] = 2.7778$.

(2) $[Bu^\gamma Br] = 0.1767$, $[HBr] = 0.0000$, $[NaBr] = 0.8250$, $[H_2O] = 2.7778$.

(3) $[Bu^\gamma Br] = 0.1764$, $[HBr] = 0.0482$, $[AgBr] = 0.01$, $[H_2O] = 2.7778$.

(4) $[Bu^\gamma Br] = 1.163$, $[HBr] = 0.0000$, $[H_2O] = 5.5556$.

t.	[HBr].	x.	10^4k.	t.	x.	10^4k.	t.	x.	10^4k.	t.	x.	10^3k.
0.43	0.1613	0.0140	678	0.30	0.0074	510	0.30	0.0085	702	0.11	0.1280	196
0.85	0.1748	0.0275	710	0.72	0.0171	510	0.72	0.0197	588	0.22	0.2491	205
1.34	0.1875	0.0402	688	1.13	0.0263	513	1.13	0.0308	612	0.33	0.3560	205
1.83	0.1987	0.0514	668	1.63	0.0380	536	1.63	0.0422	640	0.45	0.4584	209
2.3	0.2065	0.0592	630	2.3	0.0511	539	2.3	0.0514	636	0.62	0.5475	197
2.83	0.2141	0.0668	603	2.8	0.0611	551	2.8	0.0615	633	0.85	0.6220	181
				3.3	0.0695	552	3.3	0.0710	633	24.5	0.9784	—
				3.97	0.0805	558	3.97	0.0788	624			

TABLE VIII.

$[Pr^\beta OH] = 0.1000$, $[HBr] = 0.1004$, $[H_2O] = 1.1111$, $[HgBr_2] = 0.0000$.

$[Pr^\beta OH] = 0.1000$, $[HBr] = 0.1011$, $[H_2O] = 1.1111$, $[HgBr_2] = 0.0100$.

t.	[HBr].	x.	$k \times 10^5$.	t.	[HBr].	x.	$k \times 10^6$.
196	0.0660	0.0338	210	432	0.0860	0.0151	379
265	0.0573	0.0431	213	600	0.0818	0.0193	357
336	0.0487	0.0517	217	714	0.0778	0.0233	372
432	0.0398	0.0606	216	907	0.0731	0.0280	362
504	0.0344	0.0660	214				
			Mean 214				Mean 368

Examination of the Reaction Products.—*From* tert.-*butyl bromide.* *tert.*-Butyl bromide (27.4 g.), water (20 g.), and mercuric bromide (3.6 g.) in acetone (200 ml.) were kept at 50° for 1⅓ hours; excess of powdered chalk was added, and the liquid filtered. To test for *iso*butylene the liquid was then refluxed, and any vapours from liquids of b. p. <20° were passed through a vessel containing ice–salt at *ca.* − 20° and finally through standard aqueous bromine. A trace of liquid collected in the vessel, but there was negligible absorption of bromine both during the refluxing and afterwards, on passing the vapour of this liquid, which had the odour of acetone, through the standard bromine. The reaction liquid was then distilled without having been previously dried. The distillate was extracted with ether, washed with water, and dried over potassium carbonate. Distillation of the ethereal liquid gave fractions : (i) b. p. 75—80°, 4.2 g.; (ii) b. p. 80—85°, 8.5 g.; (iii) 85—97.5°, 2.6 g. Fraction (ii) was dried over sodium and redistilled, giving a solid (6.4 g.) of m. p., and mixed m. p. with *tert.*-butyl alcohol, 23.5°. (The theoretical yield of *tert.*-butyl alcohol would have been 14.8 g.)

From isopropyl bromide. *iso*Propyl bromide (24.2 g.), water (20 g.), and mercuric bromide

(22 g.) in acetone (200 ml.) were kept at 50° for 90 hours and then treated exactly as above, but no propylene was obtained. From the ethereal extract were obtained the fractions : (i) b. p. 74—78°, 5·2 g. ; (ii) b. p. 78—85°, 7·7 g. ; (iii) b. p. 85—99°, 3·1 g. 0·79 G. of fraction (ii) gave a 3 : 5-dinitrobenzoate (2·15 g.), m. p. 120—121°, so it was mainly *iso*propyl alcohol, the theoretical yield of which would have been 12·0 g.

Attempted Catalytic Hydrogenation of Alkyl Halides in Dry Inert Solvents containing no Dissolved Base.—The attempts are summarised in Table IX. The usual type of hydrogenation apparatus was employed (" Organic Syntheses," 1928, **8**, 10), the pressure throughout being approximately 2 atm. Solvents such as water, alcohol, and acetic acid which would themselves react with alkyl halides were excluded, as also were soluble bases.

TABLE IX.

Expt.	Catalyst.	Alkyl halide.	Solvent.	Temp.	Time, hrs.	Result.
1	Adams's Pt (0·015 g.) dried over H_2SO_4	Maleic acid (0·32 g.) for control of catalyst	Aqueous 95% EtOH (50 ml.)	20°	1	Quantitative absorption of H; product was succinic acid, m. p. 183°
2	As in (1) with dry $CaCO_3$ (from A.R. materials) in 12-fold excess on weight of halide	$Pr^\beta Br$ (0·55 g.)	Dioxan (50 ml.), Na-dried	20	1½	No reduction
3	As in (2)	$Bu^\gamma Cl$ (3 g.)	Et_2O (50 ml.), Na-dried	30	7	No reduction
4*	As in (2) with trace of Fe	$Bu^\gamma Cl$ (3 g.)	Et_2O (20 ml.), Na-dried	30	6	No reduction
5	Pd–$CaCO_3$ (0·375 g.) (Busch and Stove, *loc. cit.*) (free from Cl' and dried over H_2SO_4)	$Bu^\gamma Cl$ (0·5 g.)	As in (2)	20	¼	No reduction
6	As in (5)	$PhCH_2 \cdot CH_2 Br$	As in (2)	20	3	No reduction
7	Pd (0·01 g.)–$CaCO_3$ (2·5 g.)	$Pr^\beta Br$ (0·55 g.)	As in (2)	20	19	No reduction
8	As in (7)	As in (7)	As in (2)	50	3	No reduction
9	As in (7)	As in (7)	Et_2O (50 ml.), Na-dried	20	21	No reduction
10	As in (7)	$Bu^\gamma Cl$ (3 g.)	As in (2)	50	20	No reduction
11	As in (7) (double quantities)	As in (10)	Et_2O (10 ml.), Na-dried	20	21	No reduction
12†	Pd–$ZnCO_3$ (2·5 g.)	As in (10)	$CH_3 \cdot CO_2 Et$ (20 ml.)	20	23	No reduction
13	As in (12)	As in (10)	Dioxan (20 ml.)	20	22	No reduction
14‡	Pd–$CaCO_3$ (2·5 g.) with trace of Fe	As in (10)	As in (13)	20	6	No reduction
15§	Zn–Cu (2·5 g.)	As in (10)	As in (13)	20	22	No reduction
16	As in (15)	As in (10)	As in (12)	20	19	No reduction
17	As in (7)	$Bu^\gamma Cl$ (5 ml.)	No solvent, but irradiated with U.V. light	20	22	No reduction
18	As in (7)	$Pr^\beta Br$ (5 g.)	Ether (20 ml.), irradiated	20	6	No reduction
19	As in (7)	MeBr (5 g.)	Dioxan (20 ml.), irradiated	20	4	No reduction
20	$HgBr_2$ (1·8 g.)	$Bu^\gamma Br$ (5 g.)	Dioxan (50 ml.), irradiated	20	20	Yellow colour; very little HBr developed
21	As in (20)	As in (20)	Dioxan (50 ml.), no irradiation	20	21	As in (20)

* Adams's PtO_2 (0·0213 g.) and $CaCl_2,6H_2O$ (11·67 g.) were dissolved in water (500 ml.) containing $N/10$-$FeCl_3$ (1 ml.). To this was added a solution of Na_2CO_3 (5·65 g.) in water (500 ml.) with vigorous shaking. The fine ppt. was washed with water and dried with alcohol–ether.
† A solution of Na_2CO_3 (6·36 g.) in water (500 ml.) was added to a solution of $ZnSO_4,7H_2O$ (17·22 g.) and 1% $PdCl_2$ (2·4 ml.) in water (500 ml.). The ppt. was washed and dried as before.
‡ A solution of Na_2CO_3 (6·36 g.) in water (500 ml.) was added to a solution of $CaCl_2,6H_2O$ (13·14 g.), 1% $PdCl_2$ (2·4 ml.), and $N/10$-$FeCl_3$ (1 ml.) in water (500 ml.). The fine ppt. was washed and dried as before.
§ Zinc dust (8 g.) was stirred with 1·5% copper sulphate solution (165 ml.), and the couple treated as before.