Catalysis by Iodine in the Solvolysis of Tertiary Alkyl Halides

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Solvolysis of t-butyl and t-amyl iodides in aqueous ethanol and aqueous hexafluoropropan-2-ol is catalysed by iodine. The same effect, but to a smaller extent, is also found for t-butyl bromide in aqueous ethanol; the strongest catalysis by iodine was found for the aqueous ethanolysis of 1-adamantyl iodide. The catalytic constants for aqueous ethanolysis of t-butyl iodide decrease less steeply than the rate constants of the uncatalysed reactions as the proportion of ethanol in the medium is increased. The results are accommodated by a mechanism involving pre-association of iodine with the alkyl halide superimposed upon a general mechanism for solvolysis the rate-determining step of which may be ionization, ion-pair separation, or reaction of reversibly formed intimate ion-pairs with the solvent according to the nature of the alkyl halide and the solvolytic medium.

It is well known that alkyl iodides gradually decompose upon storage with the liberation of iodine. It has also been observed that kinetic measurements upon the more reactive alkyl iodides are commonly not reproducible. Whilst investigating the apparent increase in solvolytic reactivity of t-amyl iodide with time elapsed following purification, we have identified iodine as a catalyst in solvolysis reactions. Soft Lewis acids such as Ag^+ and Hg^{2+} have long been known to catalyse solvolysis of some alkyl halides [1a] as also have some salts with non-nucleophilic anions such as lithium perchlorate.[2,3,4a] There have also been reports of halogen exchange between alkyl halides and bromine and iodine.[1b,c] These reactions were carried out under non-solvolytic conditions but ion-pair mechanisms were proposed which are closely related to the ones we invoke here for the solvolytic analogues.

The rate laws of reactions catalysed by *e.g.* Ag^+ are frequently complicated and not always amenable to simple interpretation, but it is commonly assumed that the cationic electrophile complexes with the incipient leaving group and facilitates heterolysis of the carbon–halogen bond. In contrast, catalysis by anions such as perchlorate is usually held to be due to a reduction in the extent of ion-pair return as the halide anion of an intermediate ion-pair is replaced by the more weakly nucleophilic anion. In a broad sense, this latter mechanism of catalysis is the converse of common-ion rate depression [4b,5] (an enhancement of ion-pair return by increased activity of the anionic leaving group in the solution).

Both common-ion rate depression and rate acceleration by *e.g.* ClO_4^- are part of a substantial body of experimental evidence in support of a general mechanistic scheme for the solvolysis of alkyl halides involving ion-pairs and an initial ionization which may be reversible.[3,4] Catalysis of the solvolysis of alkyl halides by iodine also fits into this general mechanistic scheme in a predictable way and thereby constitutes further supportive evidence of the general mechanism.

Experimental

Solvents.—Ethanol was purified by fractional distillation from magnesium ethoxide.[6] Aqueous ethanol was made by mixing the appropriate volumes of anhydrous ethanol and distilled water. Hexafluoropropan-2-ol (HFIP) was purified by fractional distillation from barium oxide;[7] 97% aqueous hexafluoropropan-2-ol (97 HFIP) was made by mixing 97 parts by weight of HFIP with 3 parts of water.

Substrates.—t-Butyl bromide, and t-butyl and t-amyl iodides were commercially available. The purity of t-amyl iodide was improved (as indicated by g.l.c.) by treatment with aqueous sodium thiosulphate followed by desiccation, but this had no significant effect upon the observed solvolysis rates in the absence of iodine, which were in good agreement with literature results.[8]

1-*Adamantyl Iodide.*[9]—Adamantan-1-ol (1.0 g) and concentrated hydriodic acid (AnalaR grade; *d* 1.7; 55% HI) were heated on a boiling water-bath for 1.5 h under a partially stoppered reflux condenser. The solution was cooled to 0 °C, diluted with water, and extracted twice with pentane. The combined pentane solution was washed with aqueous sodium thiosulphate and saturated sodium hydrogen carbonate; it was then dried over magnesium sulphate, filtered, and evaporated. The residual crystals comprised a single compound by t.l.c. A sample for identification and kinetics was recrystallized from methanol at −70 °C, m.p. 75—76 °C (lit.,[9] 75.3—76.4 °C).

Kinetics.—All reactions were carried out at 25 °C except the solvolysis of t-butyl iodide in 97 HFIP in the presence of iodine which was investigated at 20 °C. Each alkyl halide was introduced by syringe either as the neat liquid or as a concentrated solution in n-pentane to give a solution in the concentration range 5×10^{-5}—2×10^{-4} mol dm^{-3}. The iodine, when present, was in large excess (*ca.* 4×10^{-4}—1×10^{-2} mol dm^{-3}) and pseudo-first-order kinetics were always observed by monitoring the increase in the conductance of the solutions, normally over 6—8 half-lives.

Results

The observed kinetics are described by equations (i) and (ii)

$$RX + SH \xrightarrow[k_e]{SH,\ I_2} RS + H^+X^- \qquad (i)$$

$$k_e = k_0 + k_1[I_2] \qquad (ii)$$

where SH = the solvent, RX = the alky halide, k_e = the observed pseudo-first-order rate constant, k_0 = the first-order rate constant of the uncatalysed solvolysis, k_1 = the second-order catalytic constant for the reaction catalysed by iodine, and $[I_2]$ = the concentration of free iodine.

The reactions of t-butyl and t-amyl iodides in all solvents were cleanly first order and the rates were such that reactions could be conveniently monitored conductometrically at 25 °C with adequate precision. A slow reaction between iodine and ethanol (presumably oxidation–reduction) was also detected in the aqueous ethanol in the absence of alkyl

Table 1. t-Amyl iodide [a] in 80 vol % ethanol–water at 25 °C

$10^4[I_2]$ [b]/mol dm^{-3}	10^2k_e/s^{-1}
0	0.156 (± 0.005) [c]
3.36	0.40
5.70	0.718
7.70	0.876
14.4	1.70
16.4	1.84
23.1	2.64
25.1	2.94
31.8	3.66
33.8	3.76
40.5	4.31
42.5	4.35
60.3	6.33
62.3	6.58
64.3	6.26
105.8	10.2
107.8	10.4

[a] [t-Amyl iodide] *ca.* 2 × 10^{-4} mol dm^{-3}. [b] Average concentration during reaction. [c] Mean of five results with [t-amyl iodide] 2.0 × 10^{-4}—4.0 × 10^{-3} mol dm^{-3}; k_1 9.53 dm^3 mol^{-1} s^{-1} (*r* 0.998).

Table 2. t-Butyl iodide [a] in 60 vol % ethanol–water at 25 °C

$10^4[I_2]$ [b]/mol dm^{-3}	10^3k_e/s^{-1}
0	7.12 (±0.25) [c]
3.61	15.6
7.47	24.1
11.4	32.5
15.2	38.1
18.8	46.2
19.1	47.2

[a] [t-Butyl iodide] *ca.* 5 × 10^{-5} mol dm^{-3}. [b] Average concentration during reaction. [c] Mean of four results; k_1 20.5 dm^3 mol^{-1} s^{-1} (*r* 0.999).

Table 3. t-Butyl iodide [a] in 80 vol % ethanol–water at 25 °C

$10^4[I_2]$ [b]/mol dm^{-3}	10^3k_e/s^{-1}
0	0.913 (±0.01) [c]
10.9	6.39
34.3	18.2
57.8	30.7

[a] [t-Butyl iodide] 1.5 × 10^{-4} mol dm^{-3}. [b] Average concentration during reaction. [c] Mean of two results; k_1 5.15 dm^3 mol^{-1} s^{-1} (*r* 0.9999).

Table 4. t-Butyl iodide [a] in 95 vol % ethanol–water at 25 °C

$10^4[I_2]$ [b]/mol dm^{-3}	10^4k_e/s^{-1}
0	0.619 (±0.004) [c]
4.5	2.85
9.9	5.56
21.5	10.9
32.8	17.1
41.8	22.8
52.5	28.3 (±0.3) [c]

[a] [t-Butyl iodide] 1.5 × 10^{-4} mol dm^{-3}. [b] Average concentration during reaction. [c] Mean of two determinations; k_1 = 0.528 dm^3 mol^{-1} s^{-1} (*r* 0.999).

Table 5. t-Butyl iodide [a] in 97 wt % hexafluoropropan-2-ol–water at 20 °C

$10^4[I_2]$ [b]/mol dm^{-3}	10^3k_e/s^{-1}
0	7.18 (±0.25) [c]
2.5	7.43
6.1	8.20
13.4	8.94
24.4	9.80
35.4	11.0

[a] [t-Butyl iodide] 2.3 × 10^{-4} mol dm^{-3}. [b] Average concentration during reaction. [c] Mean of two determinations; k_e 11.5 (±0.4) × 10^{-3} s^{-1} at 25 °C; k_1 1.05 dm^3 mol^{-1} s^{-1} (*r* 0.99).

Table 6. Effect of I^- on iodine-catalysed solvolysis of t-butyl iodide [a] in 80 vol % ethanol–water at 25 °C

$10^3[I_2]$/mol dm^{-3}	$10^3[I^-]$/mol dm^{-3}	10^3k_e/s^{-1}
5.00	0.00	25.4
5.00	1.04	18.2
5.00	2.08	12.8
5.00	3.12	7.9
5.00	4.15	4.4
0.00	3.12	0.83

[a] [t-Butyl iodide] 1.5 × 10^{-4} mol dm^{-3}.

Table 7. t-Butyl bromide in 80 vol % ethanol–water at 25 °C

$[I_2]$/mol dm^{-3}	10^4k_e/s^{-1}
0	3.35 (±0.1)
5.0 × 10^{-3}	4.58
0.1	6.03

halide which caused a linear increase in conductance with time. This increase in background conductance during a solvolytic run was equivalent to not more than a few percent of the total for t-butyl and t-amyl iodides and was allowed for in calculating the rate constants. The second-order catalytic constants, k_1, given in Table 8, were calculated by least-squares fitting of the sets of k_e and $[I_2]$ data (Tables 1–7) to equation (ii); the correlation coefficient, *r*, is given in parentheses. In calculating k_1/k_0, the experimental k_0 value was used rather than the extrapolated value obtained in the calculation of k_1.

Equation (ii) was further tested by carrying out a series of reactions using t-butyl iodide in 80E at constant total iodine concentration and adding different concentrations of potassium iodide. The results fit equation (ii) quantitatively when allowance is made for the reduction in the free iodine concentration by the formation of tri-iodide according to equation (iii). For the much slower reactions of t-butyl bromide and

$$I_2 + I^- \overset{K_{I_3^-}}{\rightleftharpoons} I_3^- \qquad \text{(iii)}$$

1-adamantyl iodide, the increase in background conductance was proportionately greater and led to a lower precision in the rate constants for these two compounds. However, as the results for t-butyl bromide indicate (Table 7), the low precision does not affect the conclusion that, for this compound, iodine has only a very small effect indeed upon the rate of solvolysis in aqueous ethanol.

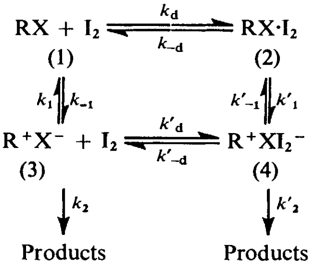
A second complication was observed in the reaction of 1-iodoadamantane in 80E. Somewhere between 50 and 75%

Table 8. Collected results for t-alkyl iodides at 25 °C

R in RI	Solvent	10^4k_0/s^{-1}	k_1/dm^3 mol^{-1} s^{-1}	(k_1/k_0)/dm^3 mol^{-1}
t-Amyl	80E	15.6 [a]	9.53	6 100
t-Butyl	97HFIP	115		
	97HFIP [b]	72	1.05	150
	60E	71	20.5	2 900
	80E	9.1 [c]	5.15	5 600
	95E	0.62	0.53	8 500
1-Adamantyl	80E	8.5×10^{-3} [d]	2.6×10^{-2}	3×10^4

[a] Lit.,[8] 18.9×10^{-4} s^{-1}. [b] 20 °C. [c] Lit.,[8] 9.3×10^{-4} s^{-1}. [d] Result taken from ref 9.

completion a rapid increase in conductance occurred to give a value corresponding to complete reaction. Our catalytic constant for this reaction, k_1 *ca.* 2.6×10^{-2} dm^3 mol^{-1} s^{-1}, is based upon estimates of the half-life of the reaction ($t_{\frac{1}{2}}$ *ca.* 45 min at [I_2] 0.01 mol dm^{-3} and 90 min at 0.005 mol dm^{-3}). The cause of the sudden increase in conductance was not investigated further. As the results in Table 8 show, the iodine-catalysed process of 1-adamantyl iodide is so much faster than the uncatalysed reaction (k_0 8.5×10^{-7} s^{-1}) [9] that the absolute error in the catalytic constant is not significant, and the ratio k_1/k_0 *ca.* 3×10^4 dm^3 mol^{-1} is by far the largest in the series of compounds investigated.



Scheme.

Discussion

Since iodine forms structurally varied complexes with diverse molecular and ionic compounds [10-12] a range of potential mechanisms for catalysis of solvolysis of alkyl halides is available. On the grounds that 1-adamantyl iodide shows the largest susceptibility to catalysis in aqueous ethanol and is the one substrate which is quite incapable of a rear-side bimolecular displacement process, we may discount mechanisms involving initial rate-determining formation of iodonium ions through rear-side attack of iodine at the alkyl residue [reaction (iv)]. And since Wiberg [1b] and Noyes [1c] were able to

$$I_2 + R{-}X \longrightarrow I{-}\overset{+}{I}{-}R\ X^- \longrightarrow \text{further reaction} \qquad \text{(iv)}$$

rule out free-radical mechanisms for comparable reactions in non-polar solvents, we may be confident that such processes do not intervene under solvolytic conditions. The Scheme includes two general routes through Lewis acid–base reaction of iodine with the halide residue. Both involve the ion-pair $R^+ XI_2^-$ (4) as the crucial intermediate in the catalytic route.

One reaction path [reaction (v)] involves unassisted initial

$$(1) \longrightarrow (3) \longrightarrow (4) \longrightarrow \text{Products} \qquad \text{(v)}$$

heterolysis of the alkyl halide followed by combination of the simple ion-pair with iodine to give the complex ion-pair (4). By this route, the iodine does not affect ionization but acts exclusively by eliminating or reducing the extent of ion-pair return. It could only account for the observed rate increases if a subsequent reaction of the ion-pair (3) were rate-determining in the uncatalysed reaction (vi) (which, in itself, seems very unlikely throughout the range of solvents considered and argues against this mechanism) and was faster than the direct route, (vii). k'_d May be close to the diffusion-controlled limit

$$(3) \xrightarrow{I_2} (4) \longrightarrow \text{Products} \qquad \text{(vi)}$$

$$(3) \longrightarrow \text{Products} \qquad \text{(vii)}$$

for a second-order reaction ($k'_d \leqslant 10^{10}$ dm^3 mol^{-1} s^{-1}) [10a] and the equilibrium constant for the formation of (4) from (3) and I_2 should be large in aqueous ethanol and increase as the proportion of ethanol increases.[10b,11,13] Assuming a value of k'_d/k'_{-d} *ca.* 8 000 dm^3 mol^{-1} for 80% aqueous ethanol, then $k'_{-d} \leqslant 1.3 \times 10^6$ s^{-1}. This is almost certainly smaller than k'_{-1}, the rate constant for collapse of the ion-pair (4) (estimated from results for more stable, *i.e.* less reactive, carbonium ions [14,15]) to give the pre-associated complex (2) of the alternative route to (4). So if (4) $\longrightarrow$ (2) $\longrightarrow$ (1) is the lowest-energy back reaction of (4), it must also be the most favourable route by which (4) is produced from (1).[15,16] The formation of (4), therefore, involves a pre-association mechanism enforced by its own instability.

An independent argument based upon the reactivity of the t-butyl cation also rules out route (v) as the catalytic process. The reaction of t-butyl cation with nucleophiles and nucleophilic solvent molecules is not very discriminating [17] and, by extrapolation from results for other carbocations, very fast.[14,15] So even if the ion-pair (3) reacts with I_2 at the diffusion limit,[10a] the low concentration of I_2 (compared with solvent molecules) means that only a minute proportion of (3) could possibly be captured by I_2. For these several reasons, therefore, route (v) need be considered no further as a catalytic mechanism.

In the second reaction path (viii) of the Scheme which involves pre-association of RX and I_2, the source of catalysis

$$(1) \longrightarrow (2) \longrightarrow (4) \longrightarrow \text{Products} \qquad \text{(viii)}$$

is one (or both) of two effects: (a) enhancement of the rate of heterolysis of the R–X bond by complexation of RX with iodine and (b) faster subsequent step(s) of the complex ion-pair (4), compared [in both (a) and (b)] with the corresponding processes of the uncatalysed route (ix).

$$(1) \longrightarrow (3) \longrightarrow \text{Products} \qquad \text{(ix)}$$

(1) *t-Butyl Iodide in Aqueous Ethanol.*—t-Butyl halides (with the exception of the fluoride) are generally agreed to undergo solvolysis in ionizing nucleophilic media with rate-limiting ionization (with or without nucleophilic solvent assistance)

followed by rapid capture of the t-butyl cation by the solvent.[3,4,18]

From equation (i) and the Scheme, $k_0 = k_1$ and, assuming that the pre-association of iodine and alkyl iodide is rapid,[10a] $k_1 = k_dk'_1/k$d-, therefore equation (x) applies. According to

$$\frac{k_1}{k_0} = \frac{k_d}{k_{-d}} \cdot \frac{k'_1}{k_1} \qquad \text{(x)}$$

this mechanism, therefore, catalysis is the consequence of two effects: (1) a favourable equilibrium between covalent alkyl iodide and iodine, and (2) I_3^- being a better leaving group than I^-. Iodine forms complexes with diverse σ-donor molecules [12] including alkyl halides. If the trend in the equilibrium constants for such complexes parallels those for other iodine complexes,[10,11,13] their values will increase with the proportion of ethanol in the aqueous ethanol and the trend of k_1/k_0 which we have found could be due largely to this effect. [However, (2), with its more polarizable and better leaving group, is expected to have a lower m value [19] than (1) and this would also contribute to k_1/k_0 increasing as the proportion of ethanol in the aqueous ethanol increases.] Correspondingly, the very much smaller catalysis found for t-butyl bromide in aqueous ethanol is due principally to the anticipated smaller equilibrium constant between iodine and the alkyl bromide.[10b,11,12]

(2) 1-*Adamantyl Iodide in* 80% *Aqueous Ethanol*.—The substantially greater catalytic effect for 1-adamantyl iodide compared with t-amyl and t-butyl iodides in 80E (k_1/k_0 *ca.* 3×10^4 dm^3 mol^{-1} compared with 6 100 and 5 600 dm^3 mol^{-1}, respectively) argues against a common mechanism, rate-determining ionization. We have argued,[7,20] along with others,[21] that 2-adamantyl arenesulphonates undergo solvolysis with rate-determining ion-pair separation following reversible ionization. We expect 1-adamantyl iodide to react in the same way. Application of the steady-state approximation to (4) in the Scheme with the assumption of $k_{-1} > k_2$ *and* $k'_{-1} > k'_2$ leads to expression (xi). This differs from equation

$$k_1/k_0 = \frac{k'_1}{k_1} \cdot \frac{k_{-1}}{k'_{-1}} \cdot \frac{k_d}{k_{-d}} \cdot \frac{k'_2}{k_2} \qquad \text{(xi)}$$

(x) by having two extra factors, k'_2/k_2 and k_{-1}/k'_{-1}. The former expresses the effect of the less basic, more weakly nucleophilic anion I_3^- compared with I^- upon ion-pair separation of the ion-pairs (3) and (4). The latter expresses the same effect upon internal return. Both of these quotients in equation (xi) should be greater than unity. This satisfactorily accounts for the larger catalytic effect of I_2 upon 1-adamantyl iodide compared with the acyclic t-butyl and t-amyl analogues in aqueous ethanol.

(3) *t-Butyl Iodide in* 97HFIP.—The small ratio k_1/k_0 150 dm^3 mol^{-1} in the highly ionizing, weakly nucleophilic medium 97HFIP compared with the much higher values for the same compound in aqueous ethanol is particularly intriguing. But since the catalytic effect is so much smaller than that found for 1-adamantyl iodide (admittedly in a different solvent), it seems unlikely that catalysis is being expressed in the same elementary step of the reaction, rate-determining ion-pair separation. A second possibility is that the mechanism is as for the same compound in the more nucleophilic aqueous ethanolic mixtures (rate-determining ionization) and the lower catalytic effect is simply due to a much smaller equilibrium constant for the pre-association in the different solvent.

Equilibrium constants for reactions such as (xii) increase

$$K^+I^- + I_2 \rightleftharpoons K^+I_3^- \qquad \text{(xii)}$$

appreciably as ethanol is added to an aqueous solution,[13] and values in non-ionizing non-aqueous media are very large.[10,11] However, in highly ionizing, non-nucleophilic media such as hexafluoropropan-2-ol, the equilibrium constant may be smaller and values for iodine complexes with non-ionic compounds may be very small. This is a matter for further investigation.

A third alternative involving rate-determining nucleophilic capture of the carbonium ion (or proton abstraction) by the solvent may be derived from the general overall mechanism encapsulated in the Scheme. According to this mechanism, k_1/k_0 is given by equation (xi) where k_2 and k'_2 now refer to the weighted mean elementary rate constants for nucleophilic capture–proton abstraction in uncatalysed and catalysed reactions. The ratio k'_2/k_2 is probably close to unity since these steps involve direct basic–nucleophilic interaction between only solvent and carbonium ion and are unlikely to be affected appreciably by a change in the counter-anion (I^- replaced by I_3^-). Consequently, we have equation (xiii). The present

$$k_1/k_0 \sim \frac{k'_1}{k_1} \cdot \frac{k_{-1}}{k'_{-1}} \cdot \frac{k_d}{k_{-d}} \qquad \text{(xiii)}$$

catalysis results do not allow us to distinguish between this mechanism and the one involving rate-determining ionization (both require k_d/k_{-d} to be lower in the highly ionizing media). However, earlier β-deuterium kinetic isotope effect determinations [22] for t-butyl chloride in aqueous trifluoroethanol are strong evidence that, indeed, t-butyl substrates do react *via* rate-determining reaction of the carbonium ion with solvent following reversible initial ionization in solvents which are highly ionizing but of low nucleophilicity–basicity, and our present results are compatible with such a mechanism.

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