Ligand Coupling Mechanism of Nucleophilic Vinylic Substitution of Iodonium Salts with Hypervalent 10-I-3 and 12-I-4 Intermediates

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Reaction of 2-bromo-1-decenyl iodonium salt with bromide ion in acetonitrile results in nucleophilic substituion with complete retention. Observed rate constants show unexpected dependence on the bromide concentration, conforming with a mechanism involving ligand coupling within a bromoiodane 10-I-3 intermediate.

We have previously reported that (*E*)-1-decenyl(phenyl)-iodonium salt (**1a**) gives a completely inverted substitution product in the reaction with halide ions[1] while the reaction of the 2-bromo derivative, (*Z*)-2-bromo-1-decenyl(phenyl)iodonium salt (**1b**), leads to exclusively a product of retention of configuration.[2] Kinetics of the reaction of **1b** with bromide ion are now examined. The observed rate constants show unexpected dependence on the bromide concentration [Br$^-$], which is accommodated with a mechanism involving hypervalent 10-I-3 (**I$_1$** or **I$_1$'**) and 12-I-4 (**I$_2$**) intermediates as shown in Scheme 1. The main reaction of **1b** (X = Br) is ligand coupling within the intermediate bromoiodane **I$_1$'** to give (*Z*)-1,2-dibromo-1-decene (**2b**) with retention in contrast to that of **1a** (X = H) occurring as a bimolecular reaction of the iodane **I$_1$** with external bromide ion to lead to inversion of configuration.

Reaction of **1b**[3] was carried out in acetonitrile solution containing tetrabutylammonium bromide at 60 °C, maintaining the ionic strength at 0.20 with added tetrabutylammonium perchlorate. When the stock solution of **1b** was added to the bromide solution, a new absorption immediately developed in the region of 250-270 nm, which gradually disappeared following the pseudo-first-order kinetics. The initial absorbance A_i at 265 nm was measured by extrapolation to the time of addition. The absorbance A_i increases with [Br$^-$] following a saturation curve.

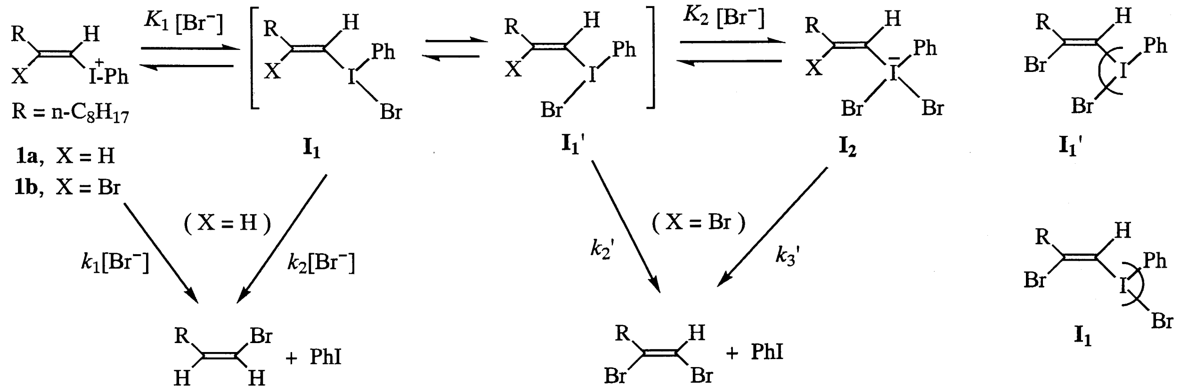
The pseudo-first-order rate constants k_{obsd} were calculated from the time-dependent decrease of the absorbance and are plotted against [Br$^-$] in Figure 1. The rate decreases with [Br$^-$] following a sharp increase from 0 to 0.01 mol dm^{-3} of bromide passing the maximum value at about 0.01 mol dm^{-3}. This curvature for **1b** is quite contrasting to that observed for **1a** (k_{obsd} obtained at 50 °C are shown in Figure 1)[4] that increases monotonously but concave downward with [Br$^-$].

The saturation curve for the initial absorbance and characteristic kinetic curves seem to be accommodated with preequilibrium formation of complex(es), and that the retardation curve for **1b** suggests formation of an unreactive complex at higher concentrations of bromide. This unreactive complex would be a 12-I-4 iodate **I$_2$**[5] and Scheme 1 is proposed. Scheme 1 provides relationships expressed by eq. 1. All the curves both for rates and absorbance can be simulated by a non-linear least-squares method[7] according to eq. 1 and with the parameters given in Table 1.

$$y = (ax + bx^2)/(1 + cx + dx^2) \qquad (1)$$

where y = ΔA (= A_i - A_0) or k_{obsd}, x = [Br$^-$], $a = \Delta A_1 K_1$ or $k_1 + k_2' K_1$, $b = \Delta A_2 K_1 K_2$ or $k_2 K_1 + k_3' K_1 K_2$, $c = K_1$, and $d = K_1 K_2$. All the equilibrium and kinetic parameters have usual meanings illustrated in Scheme 1, and **I$_1$** and **I$_1$'** are not kinetically differentiated.

The curves for ΔA and k_{obsd} are reasonably reproducible by using the same equilibrium constants, K_1 and K_2, according to Scheme 1. The rate curves for **1a** and **1b** look quite differently but conform with the rate equation of the same form (eq. 1). The difference is in bimolecular and unimolecular reactions involved for **1a** and **1b**, respectively. That is, the nucleophilic vinylic substitution of **1a** with exclusive inversion is consistent with the bimolecular S$_N$2 mechanism while the vinylic substitution of **1b** with stereospecific retention is reasonably explained by the ligand coupling within a hypervalent iodane intermediate as illustrated in Scheme 1. The ligand coupling is assumed to occur more readily between the apical and equatorial ligands of a trigonal-bipyramidal hypervalent species with retention of configuration



Scheme 1.

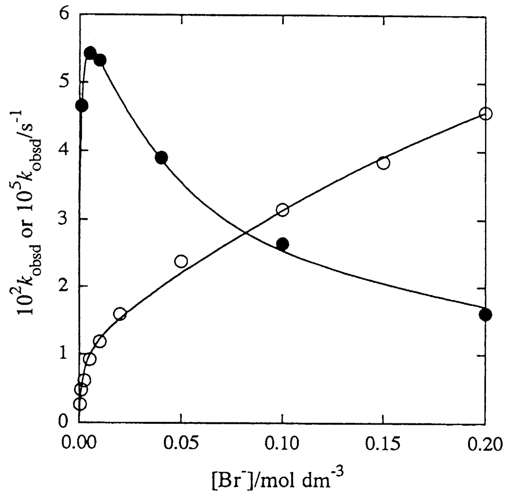


Figure 1. Observed rate constants for the reactions of **1a** (○, 10^2k_{obsd}, 50 °C) and **1b** (●, 10^5k_{obsd}, 60 °C) with bromide ion in acetonitrile at the ionic strength of 0.20.

than between the two equatorial ligands.[8,9] This is a new type of pathway of nucleophilic vinylic substitution in addition to those summarized by Rappoport.[10]

The red-shifted UV absorption band was previously observed in nonaqueous solutions of diphenyliodonium halides and was ascribed to the charge-transfer interaction between iodonium and halide ions.[11] The present spectral observations are similar, but strong absorbance ($\varepsilon > 10^4$) and large association constants ($K_1 > 500$) seem to be incompatible with the charge-transfer band. The observed absorption bands are assumed to be due to the hypervalent species. The association constants obtained from absorption are consistent with those from kinetics. That is, the spectroscopically observed complexes are kinetically significant. However, charge-transfer complexes are difficult to imagine how to participate in the nucleophilic substitution reaction. The 1 : 2 complex is also reasonably assumed to be a second hypervalent 12-I-4 species.

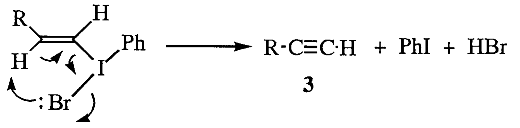
Equilibrium and kinetic parameters summarized in Table 1 are compatible with the mechanisms proposed. The 2-bromo substituent of **1b** increases the association constants probably by stabilizing the hypervalent bonding as a more electonegative apical ligand. The 10-I-3 species ($\mathbf{I_1}$) is more than 10 times as reactive as the 12-I-4 species ($\mathbf{I_2}$) derived from **1b**.

Scheme 1 shows only the main reactions of **1a** and **1b** for simplicity. However, the side reactions are also involved and they are very suggestive of the overall mechanisms. The by-products of the reaction of **1b** are a pair of (*Z*)-2-bromo-1-iodo-1-decene (**3**) and bromobenzene.[2] These products are reasonably accounted for by the ligand coupling within the isomeric iodane $\mathbf{I_1}$ (Scheme 1) occurring as a couterpart of the main reaction within $\mathbf{I_1}'$. The conformational interchanges between $\mathbf{I_1}$ and $\mathbf{I_1}'$ must occur readily by pseudorotation and they cannot kinetically be differentiated. The product ratio of (*Z*)-**2b** : **3** is about 10 : 1 in a range of [Br⁻], 0.01-0.2 mol dm⁻³, probably reflecting the ratio of $\mathbf{I_1}'/\mathbf{I_1}$. Other conformations of $\mathbf{I_1}$ may also be possible but the electronegative ligand (Br) tends to occupy one of the apical positions.

Table 1. Parameters used for the curve fittings

	1a (50 °C)	**1b** (60 °C)
K_1/mol⁻¹dm³	600	2700
K_2/mol⁻¹dm³	2.0	18
a/mol⁻¹dm³s⁻¹	7.14	0.173
b/mol⁻²dm⁶s⁻¹	158	0.20

The by-product of the reaction of **1a** is 1-decyne (**4**) formed via β elimination[1] and this reaction must occur intramolecularly within the intermediate $\mathbf{I_1}'$ or $\mathbf{I_2}$ (eq. 2).[12] When X = H, *syn* β elimination takes place more smoothly than the possible, kinetically equivalent ligand coupling. Apparent reactivity of **1a** under the reaction conditions is more than 10^3 times greater than that of **1b**. The ligand coupling reaction will show up when both S_N2 and β elimination are inhibited for some reasons.



(2)

$\mathbf{I_1}'$

In conclusion, reactions of vinyl iodonium salt with bromide ion involve hypervalent 10-I-3 and 12-I-4 species. Although simple 1-alkenyliodonium salt undergoes bimolecular vinylic S_N2 reaction with inversion, the reaction of the unreactive 2-halo derivative results in unimolecular ligand coupling within hypervalent iodane intermediates to give a retained product of nucleophilic substitution. The reactions with chloride ion showed similar results.

References and Notes

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3 The tetrafluoroborate salt of **1b** as well as the bromide salt was obtained as described previously.[2] The UV spectra were recorded on a spectrometer Shimadzu UV-2200.

4 Details of the reactions of **1a** will be presented elsewhere.

5 Similar 12-I-4 species were assumed to be intermediates for ligand exchange of some 10-I-4 iodanes.[6]

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12 With a normal base like carboxylate and amine, **1a** undergoes bimolecular α elimination to give the same product **4**.