Evidence for Reaction of Hydrogen Iodide Dimers with Fluorine

Sir:

Six-center reactions of halogens and halogen halides to form interhalogens have been recently observed by two different techniques. Schweitzer and Noyes[1] found evidence for a third-order reaction, $Br_2 + 2I_2 \rightarrow 2IBr + I_2$, in 96% aqueous sulfuric acid. Using a supersonic nozzle source, King, Dixon, and Herschbach[2] generated dimeric chlorine. Under single collision conditions they observed two reactions involving one free molecule and one van der Waals molecule:

$$(Cl_2)_2 + Br_2 \rightarrow Cl_2 + 2BrCl \qquad \Delta H = 1 \text{ kcal mol}^{-1} \tag{1}$$

$$(Cl_2)_2 + HI \rightarrow Cl_2 + HCl + ICl \qquad \Delta H = -25 \text{ kcal mol}^{-1} \tag{2}$$

Reactants and products were monitored by a mass spectrometer equipped for time-of-flight velocity analysis.

We wish to report another example of a reaction involving a weakly bound complex. Infrared emission from hydrogen fluoride formed by one of the following reactions

$$F_2 + (HI)_2 \rightarrow HF + HI + IF \qquad \Delta H = -93 \text{ kcal mol}^{-1} \tag{3}$$

and/or

$$F_2 + (HI)_2 \rightarrow HF + HI + I + F \qquad \Delta H = -26 \text{ kcal mol}^{-1} \tag{4}$$

was observed with a Digilab Model 296 Michelson interferometer. The apparatus has been discussed in detail by Moehlmann et al.[3] Dimeric hydrogen iodide, a weakly bound van der Waals molecule with a dissociation energy of 1 kcal mol^{-1} (assumed similar to $(Cl_2)_2$, as the dipole moment of HI is small), is formed as an impurity in concentrations as high as 5% in a supersonic beam of HI. HI, obtained from Linde Specialty Gases, was chilled to 77 K and degassed to remove residual H_2. A sintered glass disk was mounted in the inlet line, 80 mm from the nozzle, to filter out dirt or solid iodine particles. The cylindrical 0.3-mm internal diameter Pyrex nozzle, with an aspect ratio of approximately 3:1, was cooled by radiation from the liquid nitrogen cooled reaction chamber and resistively heated with a chromel wire to maximize the dimer concentration. This occurred at 230 K and at relatively high pressure, between 0.5 and 2 atm. Fluorine entered the reaction chamber effusively from a copper tube, 4-mm i.d., intersecting the HI beam about 30 mm in front of the nozzle (50 mm inside the reaction chamber). The fluorine flow rate was typically adjusted to attenuate the HI dimer beam by 75%. A quadrupole mass spectrometer, mounted opposite the beam source, was used to monitor the reagent flows and dimer concentration. Pressure in the reaction chamber was kept below 5×10^{-5} Torr to minimize vibrational relaxation.

Infrared emission was observed from the first, second, and third excited vibrational levels of HF. The procedure for converting integrated line intensities into populations of individual rotational-vibrational states has been presented elsewhere.[4,5] Uncertainty in the HF populations caused by radiative relaxation of the hot HF during the course of the typical 0.3 ms residence time (1-12%) was less than the uncertainty in the intensity measurement (15%). Figure 1 shows the rotational populations for the three levels. Relative vibrational populations are 0.50, 0.34, and 0.16 for V = 1, 2, and 3, respectively. The relative population of the V = 0 level cannot be determined by the infrared chemiluminescence technique because it only samples information from the excited states. In some cases it is possible to extrapolate the desired information from the known values for the higher vibrational levels, but in this case it is not clear whether the vibrational distribution is peaked at V = 1, as has been observed for other systems,[6] or has its maximum at V = 0.

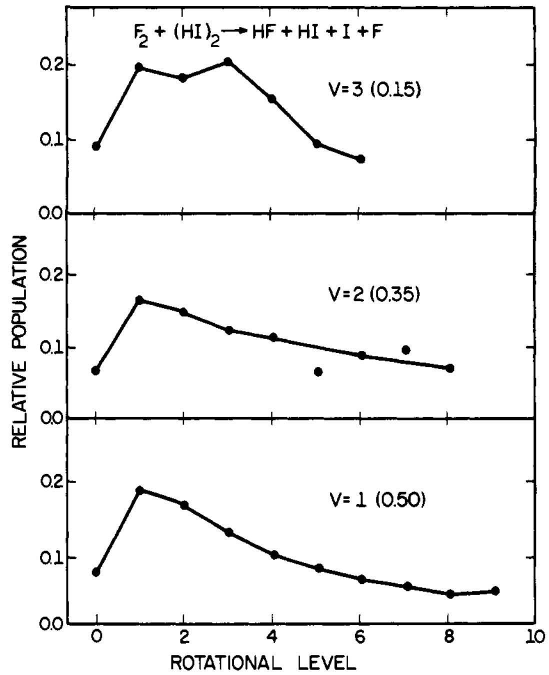

Figure 1. Relative rotational populations of HF for the $F_2 + (HI)_2$ reaction normalized such that $\sum_J N_{V,J} = 1$ for each V state. The relative vibrational populations are indicated by the numbers in the parentheses.

No emission was observed from IF as it is out of the frequency range of the instrument. Any HI emission, due to vibrational energy exchange within the complex or by collisions, would be too weak to be detected owing to its small transition probabilities. Thus, it is impossible to determine the relative distribution of the available energy among the three molecules. The third vibrational level is at the exothermic limit for reaction 4, while reaction 3 would be expected to show higher vibrational states, possibly as high as V = 10. From our measurements, it appears likely that reaction 4 predominates.

Other possible reactions include

$$F_2 + HI \rightarrow + F + I \qquad \Delta H = -27 \text{ kcal mol}^{-1} \tag{5}$$

$$F_2 + HI \rightarrow HF + IF \qquad \Delta H = -94 \text{ kcal mol}^{-1} \tag{6}$$

If the dimers are removed from the reaction, either by heating the nozzle above 340 K or reversing the reagent sources, no HF emission is observed. Therefore, it appears reactions 5 and 6 are not responsible for the observed emission. A secondary reaction of fluorine atoms formed from the dissociation of IF is possible:

$$F + HI \rightarrow HF + I \qquad \Delta H = -65 \text{ kcal mol}^{-1} \tag{7}$$

The observed vibrational energy distribution does not show any evidence of HF being formed in higher vibrational levels as is the case in (7).

Great care was taken to remove any traces of H_2, minimizing the possibility of the reactions:

$$F_2 + H_2 \rightarrow 2HF \qquad \Delta H = -129 \text{ kcal mol}^{-1} \tag{8}$$

$$F + H_2 \rightarrow HF + H \qquad \Delta H = -32 \text{ kcal mol}^{-1} \tag{9}$$

Reaction 8 would result in a large amount of vibrational excitation, not observed, while the peaked vibrational distribution usually associated with reaction 9 was not evident.[4,5,7]

A final possibility, reactions of $(HI)_n$ with $n \geq 3$, cannot be completely excluded, as some trimers and tetramers were present, although they appeared to be much less common (by a factor of 5 to 20) than the dimers.

Reaction 2 was tried under a variety of beam conditions with $(Cl_2)_2$ concentrations as high as 10%, but no emission from HCl was observed. It is possible that not enough energy is imparted to the HCl to significantly populate the first vibrational level.

References and Notes

(1) P. Schweitzer and R. M. Noyes, *J. Am. Chem. Soc.*, **93**, 3561 (1971).
(2) D. L. King, D. A. Dixon, and D. R. Herschbach, *J. Am. Chem. Soc.*, **96**, 3328 (1974); D. A. Dixon and D. R. Herschbach, *ibid.*, **97**, 6268 (1975).
(3) J. G. Moehlmann, J. T. Gleaves, J. W. Hudgens, and J. D. McDonald, *J. Chem. Phys.*, **60**, 4790 (1974).
(4) H. W. Chang and D. W. Setser, *J. Chem. Phys.*, **58**, 2298 (1973).
(5) J. K. Cashion and J. C. Polanyi, *Proc. R. Soc. London, Ser. A*, **258**, 529, 564 (1960).
(6) J. G. Moehlmann and J. D. McDonald, *J. Chem. Phys.*, **62**, 3061 (1975).
(7) J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.*, **57**, 1574 (1972).

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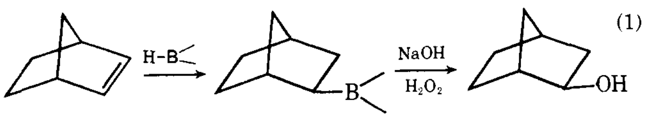
Consistent Inversion in the Base-Induced Reaction of Iodine with Organoboranes. A Convenient Procedure for the Synthesis of Optically Active Iodides

Sir:

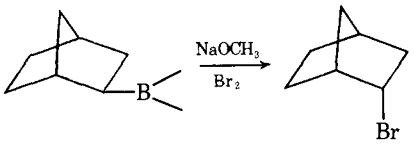
The base induced reaction of iodine with diisopinocampheyl-2-butylborane produces optically active 2-iodobutane of high optical activity with configuration opposite to that of the 2-butanol produced in the oxidation of the borane by alkaline hydrogen peroxide. Similarly, the products from the corresponding reactions of iodine with tri-*exo*-norbornylborane and *B*-methoxy-9-borabicyclo[3.3.1]nonane (B-MeO-9-BBN) reveal that the reaction involves inversion of configuration at carbon. It is therefore evident that this reaction, in contrast to the large majority of reactions of organoboranes, involves *substitution* of the boron-carbon bond with clean inversion.

The great majority of the reactions of organoboranes involving rupture of the carbon-boron bond proceed with retention[1] (eq 1). We recently observed that the reaction of



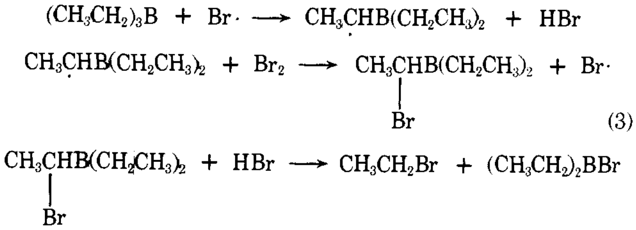
(1)

bromine with tri-*exo*-norbornylborane in the presence of sodium methoxide yielded a product that was predominantly *endo*-bromonorbornane[2] (eq 2).



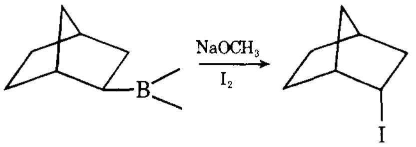
(2)

The question arose as to whether this unexpected stereochemistry of substitution was a consequence of some unique feature of the norbornyl system,[3,4] or a consequence of the exceptional tendency of bromine to engage in free radical reactions.[5] For example, we had previously observed that the apparent heterolytic reaction of bromine with organoboranes, $R_3B + Br_2 \rightarrow RBr + R_2BBr$, actually proceeds through a free radical bromination[6] (eq 3). Accordingly, we decided to investigate the reaction of iodine with organoboranes as a means of avoiding such ambiguities. Free-radical chain reactions involving iodine are rare.[7]



$$\begin{aligned}&(CH_3CH_2)_3B + Br\cdot \longrightarrow CH_3\underset{\cdot}{C}HB(CH_2CH_3)_2 + HBr\\&CH_3\underset{\cdot}{C}HB(CH_2CH_3)_2 + Br_2 \longrightarrow CH_3\underset{\substack{|\\ Br}}{C}HB(CH_2CH_3)_2 + Br\cdot \qquad (3)\\&CH_3\underset{\substack{|\\ Br}}{C}HB(CH_2CH_3)_2 + HBr \longrightarrow CH_3CH_2Br + (CH_3CH_2)_2BBr\end{aligned}$$

The reaction of iodine with tri-*sec*-alkylborane in the presence of sodium methoxide in methanol proceeds with the conversion of two of the three alkyl groups to the corresponding iodide.[8] Tri-*exo*-norbornylborane, obtained via the hydroboration of norbornene, behaves similarly, giving a 70% yield of 2-iodonorbornane. The product proved to be largely *endo*-norbornyl iodide in the initial stages of the reaction. However, with extended treatment, considerable isomerization to exo occurs. The hitherto unreported *endo*-norbornyl iodide could be obtained by running the reaction to the approximate utilization of one group, followed by removal of the small amount of exo isomer by selective solvolysis (eq 4). Consequently, the earlier result involving bromine[2] is not exceptional.



(4)

The following procedure is representative. A dry, nitrogen-flushed 400-ml flask with the usual accessories[9] was charged with 29.25 g of norbornene (0.300 mol) in 200 ml of dry tetrahydrofuran (THF) and hydroborated by the dropwise addition of 41 ml of 2.45 M borane-THF (0.100 mol) at 0°. After 1 h at 25°, 1 ml of methanol was added to destroy traces of residual hydride. The flask was wrapped in aluminum foil,[10] and cooled to 0°. Then 56 g of iodine (0.220 mol) was added (under nitrogen), followed by 46.5 ml of a 4.72 M solution of sodium methoxide in methanol over 10 min. Excess iodine was decolorized with 10 ml of saturated aqueous sodium thiosulfate. Extraction with pentane (3 × 50 ml) and distillation yielded 17.2 g (78% based on one norbornyl group) of 2-iodonorbornane (bp 54-55° at 1.8 mm). Analysis by ^1H NMR[11] revealed the mixture to be 80% *endo*- and 20% *exo*-iodonorbornane. Refluxing the isomeric mixture in 200 ml of 80% aqueous methanol (v/v) containing 5 g of potassium carbonate for 3 h selectively destroyed the exo isomer. Extraction with pentane and distillation gave 12.0 g of pure *endo*-iodonorbornane (bp 51.5-52.0° at 1.2 mm, $n^{20}D$ 1.5650).

Treatment of B-MeO-9-BBN in the presence of methanolic sodium methoxide with iodine at 25° results in the disappearance of the iodine color over 1-2 h. Following oxidation by alkaline hydrogen peroxide, 9-oxabicyclo[3.3.1]nonane, IV, was formed in 60-85% yields by GLC analysis (eq 5). Oxidation of I must produce the *trans*-5-iodocyclooctanol II, readily converted into 9-oxabicyclo[3.3.1]nonane.[13] Indeed, it proved possible to isolate the postulated intermediate I as the crystalline diethanolamine derivative, III,[14] mp 148-153° dec.

Both B-MeO-9-BBN and tri-*exo*-norbornylborane in-