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Optical Spectra of the Dibromide and Diiodide Ions in the Matrix-Isolated $M^+Br_2^-$ and $M^+I_2^-$ Species

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Abstract: The products of argon matrix reactions of alkali metal atoms and bromine and iodine have been studied optically in thin films on a sapphire window at 17 K. The bromine reaction produced a strong band near 360 and a weak band near 640 nm, depending upon the alkali reagent, and the reactions with iodine gave a strong absorption near 380 and a medium intensity absorption near 680 nm. These bands are due to $\sigma \rightarrow \sigma^*$ and $\pi^* \rightarrow \sigma^*$ transitions, respectively, of the dihalide anions in the $M^+X_2^-$ species. The small alkali metal effect on the transition energies is in accord with an ionic model of polarizable ion pairs, with the exception of cesium, which is capable of inner shell bonding and red-shifting the transitions from their expected positions. In addition, a very strong 227 nm absorption in bromine and a strong 254, 286 nm doublet in iodine experiments are attributed to molecular halogen aggregates.

The dibromide and diiodide radical anions were first proposed in 1933 as intermediates in photoreactions involving aqueous solutions of the halide, halogen, and oxalates.[2] Subsequent work of Taube in 1948 on the oxidation of bromide ion in aqueous solution provided mechanistic evidence for an intermediate complex between atomic bromine and bromide ion.[3] Radiolysis of the alkali halide salt[4a] or solutions[4b] and mercury arc photolysis of NaBr and NaI glasses containing oxidizers[5] at low temperatures have provided ESR spectroscopic evidence for the Br_2^- and I_2^- species.

Of particular interest to this work, flash photolysis of Br^- and I^- in aqueous solutions has produced transient absorptions near 350 and 370 nm, which have been attributed to the Br_2^- and I_2^- species, respectively.[6] Pulse radiolysis of aqueous KBr solutions yielded a strong transient absorption at 360 nm which disappeared in 100 μs and a new 270 nm absorption appeared which was stable for 2 min; these absorptions were assigned to Br_2^- and Br_3^-, respectively.[7] In similar studies of aqueous KI, a strong absorption was observed at 380 nm for I_2^-.[8] γ-Irradiation of NaBr-H_2SO_4 glasses at 77 K produced 355-nm absorption which was replaced by a 270-nm band upon warming to room temperature, and a like investigation using NaI gave strong I_3^- absorption and a weak new absorption at 380 nm.[9] After x-raying solid KBr at 77 K with impurity ions such as Tl^+ present, the optical spectrum revealed a strong absorption at 385 nm and a weak band at 750 nm which were assigned to the Br_2^- color center.[10] Analogous studies on KI produced a strong 400 nm absorption and a medium-intensity 800-nm band which were attributed to I_2^- and assigned to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ and ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transitions, respectively.[10,11] Flash photolysis studies of dilute KI in ethanol have shown that, in addition to the strong near-ultraviolet I_2^- absorption, there is residual 750-nm absorption which cannot be due to solvated electrons, and accordingly, the red absorption is also associated with I_2^-.[12]

Laser Raman studies of the products of alkali metal atom–iodine matrix reactions found a resonance Raman progression using 647.1-nm excitation with a strong 114-cm^{-1} fundamental and five overtones which was attributed to the diiodide anion in the $M^+I_2^-$ species.[13] The present optical experiments were done to observe the red absorption band which was responsible for the resonance Raman spectrum. Similar laser-excitation studies of the alkali metal–bromine reaction produced Raman fundamentals near 157 cm^{-1} which are believed to be due to Br_2^-.[14] Absorption spectra of these reaction products will help understand the chemistry and identify the product species.

In addition, gas-phase absorption spectra of bromine and iodine vapors[15-17] have shown temperature dependent bands which were assigned to $(Br_2)_2$ and $(I_2)_2$. The present matrix-isolation study observed these bands which supports the dimer assignments. Here follows an optical absorption study of alkali metal bromine and iodine matrix reaction products.

Experimental Section

The vacuum system, cryogenic apparatus, spectrophotometer, and experimental technique were the same as discussed in the previous paper.[18] Bromine (B.D.H. Chemicals, Ltd.) was frozen, outgassed, thawed, refrozen, and evacuated before use. Iodine (Mallinckrodt, reagent) crystals were placed in a Pyrex finger, evacuated, and allowed to reach equilibrium vapor pressure (0.25 mm at 23 °C), in a 2-l. Pyrex bulb; 100 Torr of argon was added giving an

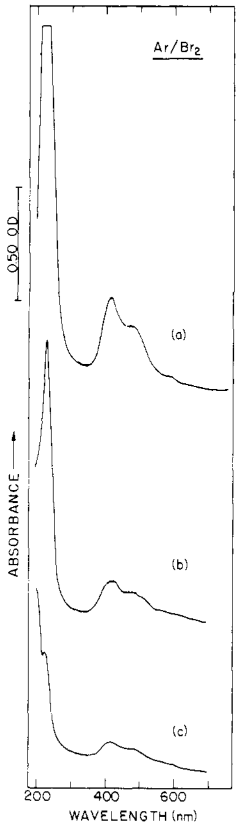

Figure 1. Visible and ultraviolet spectra of bromine in solid argon at 17 K. (a) Ar/Br$_2$ = 200/1, later scan, and (b) earlier scan. (c) Ar/Br$_2$ = 600/1.

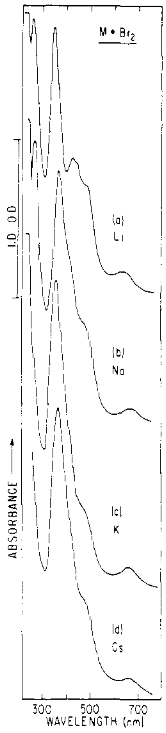

Figure 2. Optical spectra in the 300-700-nm region for the products of alkali metal atom matrix reactions with bromine, Ar/Br$_2$ = 200/1: (a) Li, (b) Na, (c) K, and (d) Cs.

Table I. Absorption Band Maxima (nm) for the $M^+Br_2^-$ and $M^+I_2^-$ Species[a]

	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
Br_2^-	351	368	363	364	365
	635 ± 2	665 ± 2	660 ± 2	667 ± 2	660 ± 2
I_2^-	366	382	377	379	382
	675	695 ± 2	686	686	686
				980 ± 10	

[a] Wavelength accuracy is ±1 nm unless otherwise noted. Rubidium experiments were done on a Cary 17 at Virginia and the data were added in proof.

approximate Ar/I$_2$ ratio of 400/1. Argon-bromine samples were prepared using standard techniques. In addition to alkali metal matrix reactions, cesium bromide (Orion Chemical Co., Reagent) vapor at 440 °C was codeposited with an argon-bromine sample and cesium iodide (Harshaw Chemical Co., Optical) vapor at 438 °C was also allowed to react with iodine in argon matrices. The salts were heated under vacuum above these temperatures before use.

Results

Alkali metal atom matrix reactions with bromine and iodine have produced new absorptions which will be presented for each halogen.

Bromine. Two optical spectra of an argon-bromine sample (Ar/Br$_2$ = 200/1) are shown at the top of Figure 1. A very strong, sharp absorption was observed at 227 ± 1 nm along with the strong bromine absorption at 415 nm with a 480-nm shoulder, the latter in excellent agreement with the gas phase spectrum.[15] The bottom spectrum for an Ar/Br$_2$ = 600/1 sample shows that the 227-nm band is concentration dependent. The 227/415 band intensity ratio of 5/1 in the 200/1 sample is reduced to 1/1 at 600/1.

Lithium atoms were deposited with an argon-bromine sample for 2.5 h, and the resulting spectrum is shown in Figure 2a. The dominant new feature in the spectrum appeared at 351 ± 1 nm (1.2 OD) (optical density) with a 420-nm shoulder due to unreacted bromine. Additional new bands were observed at 262 ± 1 nm (0.4 OD) and 635 ± 2 nm (0.08 OD). A 5-min operation of the Cary 14 tungsten lamp to photolyze the sample reduced the 351-nm band to 0.8 OD and the 635-nm absorption to 0.05 OD.

Sodium experiments were done with several bromine samples. The spectrum from the best Ar/Br$_2$ = 200/1 experiment contained a very strong new band at 368 ± 1 nm (1.4 OD) and weaker absorptions at 450 (0.15 OD), 635 (0.10 OD), and 264 (0.20 OD). After exposing the sample to the tungsten lamp for 10 min the spectrum shown in Figure 2b revealed a reduction in the 368-nm band, 635 nm was replaced by a weaker 665-nm band (0.06), 264 nm was unchanged, and 450 nm was destroyed. The 635-nm band was due to aggregated sodium, as revealed by a number of experiments with excess sodium, and the sharp 450-nm band is attributed to Na$_2$ owing to its proximity to the gas-phase bands.[19]

The third trace in Figure 2 shows the potassium-bromine reaction where no interference is present from metal absorptions. A very strong band appeared at 363 ± 1 nm (1.2 OD) and a weak band was found at 660 ± 2 nm (0.07 OD). A 10-min W lamp exposure reduced both bands to half of their initial intensities.

The absorption spectrum of cesium-bromine reaction products is illustrated in Figure 2d. The very strong band at 365 ± 1 nm (1.1 OD) and the weak 660 ± 2 nm feature (0.05 OD) were reduced by 20% upon a 10-min exposure to the W lamp. The absorption peaks for the products of alkali metal-bromine reactions are listed in Table I.

Finally, cesium bromide vapor was deposited with an Ar/Br$_2$ = 200/1 sample for 3 h. A very strong new absorption was observed at 268 nm.

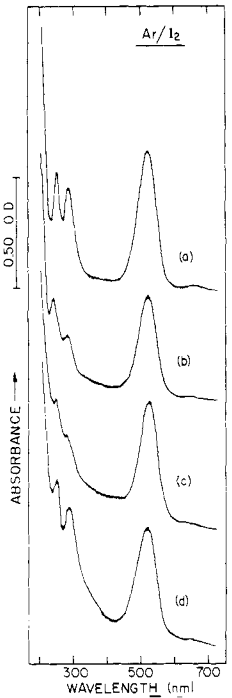

Figure 3. Visible and ultraviolet spectra of iodine in solid argon at 17 K. (a) $Ar/I_2 \approx 400/1$, (b) $Ar/I_2 \approx 800/1$, (c) $Ar/I_2 \approx 2000/1$, and (d) after warming the $Ar/I_2 \approx 2000/1$ sample to 40 K and recooling to 17 K.

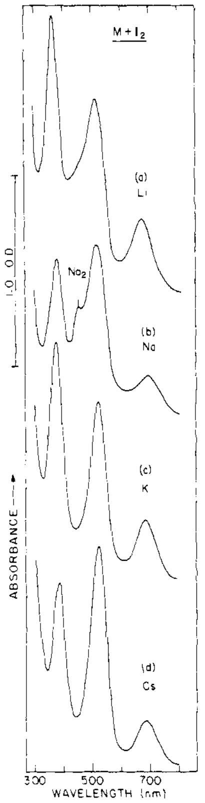

Figure 4. Optical spectra in the 300–800-nm region for the alkali metal atom–iodine matrix reaction product, $Ar/I_2 \approx 400/1$: (a) Li, (b) Na, (c) K, and (d) Cs.

Iodine. Several blank experiments were run with argon iodine samples and spectra were recorded between 750 and 200 nm. The first trace in Figure 3 shows the spectrum of an $Ar/I_2 \approx 400/1$ sample. In addition to the dominant iodine band at 520 nm, a strong doublet appeared at 254 and 286 ± 2 nm and a weak feature was observed at 670 nm. When the iodine concentration was reduced to $Ar/I_2 \approx 800/1$, the intensity of the ultraviolet doublet was markedly reduced relative to the visible iodine band as Figure 3b illustrates. Further sample dilution to $Ar/I_2 \approx 2000/1$ reduced the ultraviolet absorptions to weak shoulders while the visible band remained prominent in Figure 3c. Finally, warming this sample to 40 K to allow limited diffusion of the trapped iodine and recooling to 17 K produced marked growth of the ultraviolet bands at 254 and 286 nm as the last spectrum in Figure 3 shows.

Lithium atoms were codeposited with an $Ar/I_2 \approx 400/1$ sample for 2 h; the absorption spectrum is shown in Figure 4a. A very strong new band was observed at 366 ± 1 nm (1.5 OD) along with a strong band at 675 ± 1 nm (0.45 OD). These bands grew with a 3/1 relative intensity during reagent deposition and decreased with the same relative intensity following 10-, 30-, and 50-min exposures to the tungsten lamp.

Three sodium-iodine reactions were examined spectroscopically; an early scan in the first experiment using $Ar/I_2 \approx 400/1$ is shown in Figure 4b. New product bands appeared at 382 ± 1 and 695 ± 2 nm along with the iodine precursor absorption at 522 nm and the Na_2 shoulder at 450 nm. Another experiment using excess iodine ($Ar/I_2 \approx 250/1$) produced the red band at 693 ± 2 nm (0.28 OD) and the violet band at 382 ± 1 nm (0.73 OD); exposure to the tungsten lamp for 20 min halved these absorptions. The final experiment using insufficient iodine ($Ar/I_2 \approx 800/1$) produced the product bands at 385 and 695 nm (0.45 and 0.15 OD, respectively) along with a strong Na_2 absorption at 450 nm.

Potassium atoms were allowed to react with an $Ar/I_2 \approx 400/1$ sample. Figure 4c shows the new product bands at 377 ± 1 and 686 ± 1 nm (0.91 and 0.28 OD, respectively). In this experiment, the first scan after 26 min of K atom deposition with the I_2 sample showed the red band (0.08 OD) and the violet band (0.28 OD), and the final scan taken after a 120-min period exhibited 0.40 and 1.3 OD bands. After 10 min of W lamp photolysis, the bands were reduced markedly and shifted slightly to 375 (0.44 OD) and 690 nm (0.15 OD). Ten more minutes of tungsten photolysis reduced the absorptions a little more to 0.38 and 0.12 OD, respectively.

The experiment with cesium employed a slightly higher iodine concentration ($Ar/I_2 \approx 320/1$) to minimize the possibility of excess cesium. After 138 min of reaction, new product bands were observed at 686 ± 1 and 382 ± 1 nm with 0.20 and 0.64 OD, respectively, which is shown in Figure 4d. A 17-min exposure to W light reduced these bands only 20% to 0.16 and 0.50 OD, respectively.

The final reactions were done with CsI and I_2 using dilute samples to minimize the ultraviolet iodine doublet. In the first experiment using $Ar/I_2 \approx 800/1$, a new band appeared at 366 nm (0.35 OD) when the CsI sample was warm (370–380 °C) but *before* the sliding door to the Knudsen cell was opened. After opening the door and depositing CsI for 2 h, the 366-nm band continued to grow (0.87 OD) and a strong absorption appeared at 273 nm (0.86 OD). The tungsten lamp (5 min) reduced the 366-nm band to 0.47 OD while the 273-nm absorption was reduced to 0.70 OD. Sample warming to 37 K and recooling increased the 273-nm band to 1.0 OD while the 366-nm band was unchanged. The sample was faint pink in color, owing to unreacted I_2, however, warming to 50 K changed it to mustard yellow.

Discussion

The present observations provide information on bromine and iodine dimers, the dibromide and diiodide radical anions, and bonding interactions between cation and anion in ionic molecules.

Bromine and Iodine Aggregates. Figure 1 shows a strong absorption at 227 nm whose intensity relative to the bromine absorption at 415 nm is favored at the higher bromine concentration. From the matrix data, this band can be assigned to bromine aggregates $(Br_2)_n$. The assignment of a broad, temperature dependent 210-nm band to $(Br_2)_2$ in the gas phase[15] suggests that the sharp 227-nm band in solid argon may be due to $(Br_2)_2$.

In the iodine spectrum the very weak 670-nm band is due to the X → A absorption of I_2 which has been observed very weakly at approximately 660–690 nm in the gas phase.[20] The I_2 absorption at 270 nm in the gas phase is so very weak that it must be obscured by the ultraviolet doublet at 254 and 286 nm in solid argon. The concentration dependence and growth of the ultraviolet doublet on sample warming shown in Figure 3 indicate that both of these bands are due to iodine aggregate species $(I_2)_n$. The broad temperature dependent band at 245 or 265 nm assigned by two groups[16,17] to $(I_2)_2$ is in agreement with the 245- and 286-nm argon matrix assignments to molecular aggregates which could be dimers of different structural arrangements.

Dibromide and Diiodide Anions. The strong ultraviolet absorptions near 360 and 380 nm depending upon the alkali reagent can be assigned to Br_2^- and I_2^-, respectively, in the $M^+Br_2^-$ and $M^+I_2^-$ species for the following reasons: (a) the bands follow the pattern established in the previous paper for $M^+F_2^-$ and $M^+Cl_2^-$, (b) the absorptions agree with the pulse radiolysis and flash-photolysis assignments to the transient Br_2^- and I_2^- species in aqueous solution,[6-8] and (c) the strong bands are due to primary reaction products of eq 1 and 2 since alkali atoms were required for their formation and the bands were *not* produced with the CsBr and CsI reagents.

$$M + Br_2 \longrightarrow M^+Br_2^- \longrightarrow MBr + Br \qquad (1)$$

$$M + I_2 \longrightarrow M^+I_2^- \longrightarrow MI + I. \qquad (2)$$

The secondary reactions were studied for the CsBr and CsI salts, reactions 3 and 4

$$CsBr + Br_2 \longrightarrow Cs^+Br_3^- \qquad (3)$$

$$CsI + I_2 \longrightarrow Cs^+I_3^- \qquad (4)$$

The strong bands produced in these experiments at 268 and 273 nm are due respectively to the products of reactions 3 and 4. The bands at 262 and 264 nm in Figure 2 (a and b) are, respectively, due to $Li^+Br_3^-$ and $Na^+Br_3^-$, which were produced by secondary reaction of the MBr product of reaction 1 with each metal.

Ultraviolet absorptions due to alkali bromides and iodides are very weak,[21] and the quantities of these salts produced and studied here do not make an appreciable contribution to the absorption spectrum.

The red absorptions near 640 nm in four different alkali metal bromine reactions maintain a constant relative intensity with the strong 360-nm absorptions; the intensity ratios 360 nm/640 nm were (18 ± 3)/1 for the four reactions studied. The bands are both photobleached by W light at the same rate. Likewise the red bands near 680 nm in four alkali-iodine studies maintain a constant intensity ratio within 10% with the strong 380-nm absorptions; the intensity ratios 380 nm/680 nm were 3/1 for the four alkali metal species. The two alkali-iodine product bands were destroyed at the same rate by the W lamp. These data indicate that the red and violet bands in each halogen reaction are due to the same species. In fact the W photolysis data link the red and violet $M^+I_2^-$ bands; since an order of magnitude more W lamp output is available in the red as compared to the violet, more of the $M^+I_2^-$ photolysis is affected by absorption in the red band, but, since the red and violet bands belong to the same molecular species, they decrease at the same rate.

In the x-ray studies of solid KBr and KI, near-infrared bands at 750 and 800 nm have been assigned to Br_2^- and I_2^-, respectively.[10,11] These latter bands correspond to the red 640 and 680 nm absorptions of the matrix-isolated $M^+Br_2^-$ and $M^+I_2^-$ species.

Band Assignments. The strong ultraviolet bands at 360 and 380 nm for Br_2^- and I_2^- continue in the series of 300 and 340 nm established by F_2^- and Cl_2^-. Accordingly, these absorptions are assigned to the $\sigma \rightarrow \sigma^*$ valence electron transition in each dihalide anion in the corresponding $M^+X_2^-$ species.

The red bands are assigned to one of the $\pi^* \rightarrow \sigma^*$ transitions. As the schematic energy level diagram in Figure 4 of the previous paper indicates, the presence of an intimately bonded M^+ removes the degeneracy of the π and π^* orbitals with presumably the lower energy π orbital in the MX_2 plane. The 640 and 680 nm absorptions for Br_2^- and I_2^- probably arise from the $\pi_x^* \rightarrow \sigma^*$ transition, since the $\sigma \rightarrow \sigma^*$ energy for $Na^+I_2^-$ is 75 kcal/mol and the red absorption requires 42 kcal/mol which appears to be too much energy for promotion of an electron from the uppermost π^* orbital. The very weak 980 ± 10 nm absorption of I_2^- in $Rb^+I_2^-$ (see Table I), which is a factor of 60 weaker than the 686-nm band, is probably due to the $\pi_y^* \rightarrow \sigma^*$ transition of I_2^-. The analogous absorption has been observed for I_2^- in solid KI at 1150 nm.[10]

The intensity of the $\pi^* \rightarrow \sigma^*$ transition increases relative to the strong $\sigma \rightarrow \sigma^*$ transition intensity with increasing atomic weight in the matrix-isolated $M^+X_2^-$ species, as was found for the X_2^- color centers.[10] This trend may be due to a mixing of the $^2\Sigma_g^+$ and $^2\Pi_g$ electronic states due to increased spin-orbit coupling. A similar trend has been noted for the $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions of Br_3^- and I_3^- in solution.[22]

Bonding. As was pointed out in the previous paper,[18] the $\sigma \rightarrow \sigma^*$ energy for Cl_2^- is about half that for Cl_2. Likewise, these energies for Br_2^- and I_2^- are approximately 28 000 and 26 300 cm^{-1}, respectively, and 54 200 and 49 800 cm^{-1} for Br_2 and I_2.[23] Again, the anion electron raises the energies of the valence orbitals and decreases the orbital energy separation as compared to the neutral halogen molecule. The same effect is noted for the $\pi^* \rightarrow \sigma^*$ transition on Br_2 (415 nm) as compared to Br_2^- (640 nm) and I_2 (520 nm) as compared to I_2^- (680 nm).

The effect of M^+ on the X_2^- transition energies is also of interest. Figure 5 of the previous paper displays the trend of $\sigma \rightarrow \sigma^*$ wavelength increasing (energy decreasing) Li^+ to Na^+ then decreasing to K^+ and on to Cs^+ for the $M^+F_2^-$ species. This trend is consistent with the ionic model of polarizable ion pairs[24] with the maximum ionic character and lowest $\sigma \rightarrow \sigma^*$ energy for $Na^+F_2^-$. The trend holds for Cl_2^-, Br_2^-, and I_2^- with the exception of Cs^+ whose effect becomes more pronounced with increasing halogen size. The somewhat anomalous effect of Cs^+ can be explained by inner shell bonding of the 5p orbitals of cesium with the halogen valence orbitals.[25] The $(n - 1)$p orbitals of cesium are higher enough in energy to interact slightly with the valence X_2^- orbitals and this interaction is stronger with the larger halogen. The interaction forces the $\sigma(a_1)$ orbital to higher energy more than the $\sigma^*(b_1)$ orbital causing a red shift in the $\sigma \rightarrow \sigma^*$ transition energy. The same effect is noted for the $\pi_x^*(b_1)$ orbital which is also forced higher in energy more than $\sigma^*(b_1)$ giving again a red shift from the trend in $\pi^* \rightarrow \sigma^*$ energies expected from the ionic model. The $\pi_y^*(a_2)$ orbital is not of the proper symmetry to interact with the cesium 5p orbitals and its energy would not be affected by inner shell bonding in C_{2v} symmetry.

Finally, there is a red shift for each Br_2^- and I_2^- transition, and the Cl_2^- and F_2^- transitions,[18] on going from the argon matrix-isolated $M^+X_2^-$ species to the X_2^- color center in the solid alkali halide lattice.[10] The largest difference was found for the $\sigma \rightarrow \sigma^*$ transition of F_2^-. These differences in dihalide radical anion spectra must be attributed to the different types and symmetries of the immediate X_2^- ion environments in the two cases. It may also be possible that charge transfer to the halogen molecule in the $M^+X_2^-$ species is not quite as complete as for the X_2^- color center, owing to the induced dipole moment on the intimately involved M^+ ion in the $M^+X_2^-$ species.

Matrix Reaction Chemistry. Although the tungsten lamp photolysis data are not as quantitatively accurate for $M^+Br_2^-$ and $M^+I_2^-$ as compared to the lighter species due to overlapping Br_2 absorption and a steeply rising background, a general statement can be made. The two heavier $M^+X_2^-$ species photodecompose more readily than $M^+Cl_2^-$; however, they are clearly more stable than $M^+F_2^-$. Again, the Cs^+ compounds appear to be the most stable.

It is of considerable interest that the $M^+X_2^-$ intermediates are trapped in the matrix reaction experiments. In earlier crossed-molecular beam work, evidence has been presented for an electron transfer mechanism forming $M^+\cdots X_2^-$, which decomposed readily to give the final products of reactions 1 and 2. The role of the X_2^- ion in these reactions has been described by Herschbach.[26]

Finally, the salt-molecule reactions (3 and 4) proceed readily under the conditions of these experiments. In fact these products increase on sample warming which indicates that reactions 3 and 4 have very little activation energy. This is in accord with the observation of a collision complex in the crossed-molecular beam reaction of CsI and Cl_2 which persisted for many vibrational periods and then decomposed to give CsCl and ICl.[27]

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A New Class of Nickel Hydrides. $HNiL_3CN$

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Abstract: Addition of HCN to phosphorus complexes of zerovalent nickel of the type NiL_4 gives a new class of five-coordinate nickel hydride complexes $HNiL_3CN$, which have been characterized in solution by ^1H and ^{31}P NMR and ir. ^1H NMR line shape analysis of $HNi(PEt_3)_3CN$ solutions indicates that PEt_3 exchanges by a dissociative process with $\Delta G_{300}^{\ddagger} = 12.0$ kcal/mol. The four-coordinate $HNiL_2CN$ intermediates can be observed in solution if the ligands L have sufficient steric bulk.

Earlier papers reported that addition of strong acids, such as H_2SO_4, to NiL_4 complexes (L = phosphorus ligand) causes protonation at the nickel to give cationic five-coordinate hydride complexes $HNiL_4^+$.[1,2] Crystalline salts of $HNi[Ph_2PCH_2CH_2PPh_2]_2^+$ and $HNiL_4^+$ (L = cyclic or bicyclic phosphite) have been isolated.[3] We now wish to report that addition of the weak acid HCN to NiL_4 (or NiL_3) complexes gives a new class of five-coordinate nickel hydride complexes of the type $HNiL_3CN$.

Addition of HCN to solutions of NiL_4 (or NiL_3) complexes usually causes the solutions to change color rapidly to yellow or orange. Proton NMR spectra at −25° in non-