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Preparations of Pure ISeCN, ISCN, and INCO

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Pure INCO, ISCN, and the hitherto unknown molecule ISeCN have been prepared in the HeI photoelectron spectrometer (PES) by the heterogeneous reactions of ICl gas with AgNCO, AgSCN at room temperature, and AgSeCN at −9 (±1) °C, respectively. They were characterized on line by PES experiments and OVGF calculations. The well-matched results between the PES experiments and OVGF calculations not only show that the new reaction is a good reaction to prepare pure INCO and pure ISCN, but also that the new compound prepared by passing the ICl gas over the freshly AgSeCN powder at −9(±1) °C is the hitherto unknown ISeCN.

Introduction

It is well-known that XNCO, XSCN, and XSeCN (X = Cl, Br) have been first prepared in the gas phase by heterogeneous reactions of the chlorine gas and bromine vapor with corresponding silver salts AgNCO, AgSCN, and AgSeCN, respectively, and also characterized on line by their respective PES in combination with sophisticated quantum chemical calculations.[1−3] That is, the PES technique can be also used to prepare some short-lived compounds by a gas−solid reaction.

By a procedure analogous to the preparation of BrNCO, iodine isocyanate (INCO) was also prepared by passing I_2 vapor at low pressure over heated and dried AgNCO at ∼190 °C, and its PE spectrum was recorded, but it was also pointed out that "Spectra completely free of I_2 were never obtained".[1] Similarly, gaseous iodine thiocyanate (ISCN) was prepared at 140 °C, and its PE spectra were also reported,[4] but there are some byproducts in the PE spectrum. No further reports on either INCO or ISCN have been published, and there is no previous report on the preparation of selenocyanate (ISeCN).

In order to investigate extensively both the physical and chemical properties of INCO, ISCN, and the hitherto unknown ISeCN, an improved preparation for the pure compounds is needed, and this new reaction should easily be performed.

Our laboratory has demonstrated the ability to generate a continuous flowing beam of radicals via the pyrolysis of well-selected compounds, allowing us to perform PES studies on short-lived species.[5−10] Recently, pure XN_3 (X = F, Cl, Br, I) compounds have been prepared in the gas phase by heterogeneous reactions of solid NaN_3/AgN_3 with gaseous F_2, Cl_2, Br_2, and I_2, respectively, and were characterized on line by the PES technique combined with the outer valence green function (OVGF) calculations.[11] In this paper, a new reaction to prepare pure gas-phase INCO, ISCN, and the hitherto unknown ISeCN is reported. The compounds are also characterized by the PES technique in combination with OVGF calculations.

Experimental Section

The precursor ICl was synthesized according to a previously reported method,[12] and its PE spectrum is identical with that

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Table 1. Optimized Geometrical Structures of ISeCN, ISCN, and INCO at 6-311++G(2df,pd) Basis Set Level with Four Different Methods

species		B3P86	B3LYP	B3PW91	MP2
ISeCN	R_{I-Se}/Å	2.4757	2.5056	2.4798	2.4593
	R_{Se-C}/Å	1.8272	1.8390	1.8299	1.8233
	R_{C-N}/Å	1.1548	1.1550	1.1555	1.1759
	∠ISeC/°	97.7	98.0	97.7	96.7
	∠SeCN/°	177.2	177.0	177.1	177.6
	∠ISeCN/°	180.0	180.0	180.0	180.0
ISCN	R_{I-S}/Å	2.3589	2.3876	2.3619	2.3460
	R_{S-C}/Å	1.6790	1.6867	1.6811	1.6853
	R_{C-N}/Å	1.1561	1.1563	1.1568	1.1766
	∠ISC/deg	100.9	101.3	100.9	99.3
	∠SCN/deg	175.9	175.9	175.9	176.4
	∠ISCN/deg	180.0	180.0	180.0	180.0
INCO	R_{I-N}/Å	1.9639	1.9813	1.9663	1.9644
	R_{N-C}/Å	1.2111	1.2124	1.2122	1.2231
	R_{C-O}/Å	1.1601	1.1628	1.1607	1.1698
	∠INC/deg	130.5	130.2	130.4	128.4
	∠NCO/deg	173.6	173.7	173.6	173.0
	∠INCO/deg	180.0	180.0	180.0	180.0

recorded previously.[13] AgNCO and AgSCN were bought from the ACROS Company, and their purity was better than 99%.

AgSeCN, prepared by the reaction between $AgNO_3$ and KSeCN in aqueous solution, was filtered, washed, dried under vacuum, and stored in the dark in a desiccator over P_2O_5.

The AgNCO, AgSCN, and freshly prepared AgSeCN powders were loosely filled into the quartz inlet tube and supported on quartz wool. The unstable INCO, ISCN, and ISeCN molecules are prepared by passing the ICl gas over AgNCO, AgSCN at room temperature, and freshly prepared AgSeCN at −9 (±1) °C, respectively.

The PE spectra of the INCO, ISCN, and ISeCN molecules were recorded on a double-chamber UPS machine, which was built specifically to detect transient species as described elsewhere[14] at a resolution of about 30 meV, as indicated by the Ar^+ ($^2P_{3/2}$) photoelectron band. Experimental vertical ionization energies (Iv in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

Outer Valence Green Functional (IVGF) Calculations. In order to assign the PES bands of the INCO, ISCN, and ISeCN molecules, outer valence green functional (OVGF) calculations have been performed. The geometries of INCO, ISCN, and ISeCN molecules were optimized at 6-311++G (2df,pd) basis set level with four different methods (see Table 1). The calculations of the ionization energies used the geometries optimized by B3lYP method, because no experimental geometries have been reported until now, and the agreement of the results in the geometry optimization using the four different methods is good for INCO, ISCN, and ISeCN. The calculations of the OVGF method are all at the 6-311++G (2df,pd) level.

Results and Discussion

The PE spectrum of the product obtained by the heterogeneous reaction of ICl gas with solid AgNCO at room temperature is given in Figure 1c, which is in accord with the previously reported PE spectrum of the INCO[1] as far as positions and structures of the PES bands are concerned, except for the signals of the I_2 impurity in the latter spectrum.

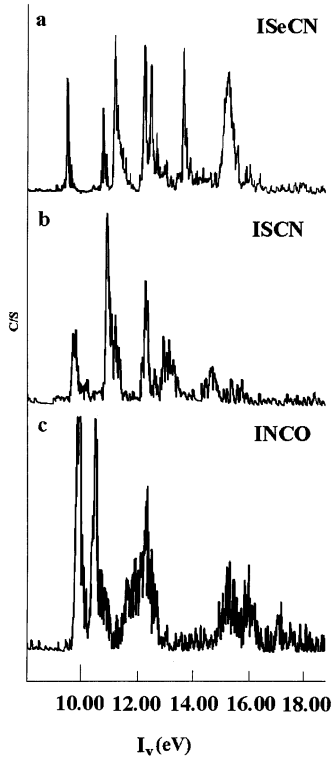

Figure 1. PE spectra of ISeCN (a), ISCN (b), and INCO (c).

This fact shows that pure INCO can easily be prepared at room temperature by the following reaction:

$$AgNCO(s) + ICl(g) \rightarrow INCO(g) + AgCl(s) \qquad (1)$$

Furthermore, an X-ray diffraction analysis showed that the solid residue in the reactor inlet tube was AgCl.[15]

Pure ISCN is also prepared at room temperature by a reaction analogous to that described above for INCO:

$$AgSCN(s) + ICl(g) \rightarrow ISCN(g) + AgCl(s) \qquad (2)$$

Figure 1b gives the PE spectrum of ISCN, which is of much better quality than the one reported,[4] because there are no signals of impurities and it exhibits a much better signal-to-noise ratio. This fact again shows that ICl is a good precursor to prepare pure INCO and ISCN by the heterogeneous reaction of ICl(g) with AgNCO and AgSCN, respectively. ICl is also a good precursor for the preparation of the hitherto unknown molecule ISeCN by a reaction analogous to that discussed for INCO and ISCN

$$AgSeCN(s) + ICl(g) \rightarrow ISeCN(g) + AgCl(s) \qquad (3)$$

but the reaction temperature is −9 (±1) °C, because the thermal stability of ISeCN is lower than those of INCO and ISCN.

Figure 1a gives the PE spectrum of the ISeCN generated by the heterogeneous reaction of ICl gas with solid AgSeCN. Furthermore, an X-ray diffraction analysis showed that the solid residue in the reactor inlet tube is AgCl(s).[15]

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Table 2. Observed and Calculated PES Vertical Ionization Energies (Iv in eV) and Ionization Energies (Ev in eV) for ISeCN, ISCN, and INCO[a]

I_V (eV) this work	E_v(eV) by OVGF	MO	character	reference
		ISeCN		
9.58	9.739	14a″(50)	π_{I-Se}	
10.80	10.909	36a′(49)	n_I	
11.27	11.593	13a″(48)	π_{I-Se}	
12.36	12.379	35a′(47)	$\pi_{I-Se}\pi_{C-N}$	
12.62	13.577	34a′(46)	$n_I\sigma_{Se-C}$	
12.85	13.602	12a″(45)	π_{Se-C-N}	
13.80	14.043	33a′(44)	$\pi_{I-Se-C-N}$	
15.44	16.519	32a′(43)	σ_{I-Se}	
		ISCN		
9.74	9.907	11a″(41)	π_{I-S}	9.75[b]
11.10	11.024	30a′(40)	n_I	11.48[b]
11.34	11.785	10a″(39)	π_{I-S}	11.86[b]
12.55	12.396	29a′(38)	σ_{I-S}	11.98[b]
13.36	13.736	9a″(37)	$n_I\pi_{S-C-N}$	12.79[b]
15.26	14.069	28a′(36)	σ_{S-C}	
	14.523	27a′(35)	π_{S-C-N}	
	17.044	26a′(34)	$n_S n_I \sigma_{S-C}$	
		INCO		
9.87	10.113	10a"(37)	$n_I\pi_{N-C}$	9.89 [c]
10.57	10.380	27a′(36)	n_I	10.58[c]
12.17	12.691	9a″(35)	σ_{I-N}	12.16[c]
12.55	12.823	26a′(34)	π_{I-N}	12.53[c]
15.68	16.540	25a′(33)	$n_I\sigma_{I-N}$	15.60[c]
16.41	16.663	8a″(32)	π_{N-C-O}	16.39[c]
17.63	16.682	24a′(31)	π_{N-C-O}	17.55[c]

[a] The geometries were optimized at the B3LYP/6-311++G (2df,pd) level, and the calculation of OVGF method was done with a 6-311++G (2df,pd) basis set. [b] Reference 4. [c] Reference 1.

The assignment of the observed PE spectrum of the unstable species ISeCN is supported by the OVGF calculations. Table 2 gives the PES vertical ionization energies (Iv in eV) and the ionization energies (Ev in eV) calculated by the OVGF method for the ISeCN molecule. For comparison, the PES experimental and the OVGF calculated ionization energies for INCO and ISCN are also listed in Table 2. From Table 2, it can clearly be seen that the PES ionization energies of INCO, ISCN, and ISeCN match very well with the corresponding values calculated by the OVGF method. This demonstrates that pure INCO and ISCN can be prepared by the new reactions and that the PE spectrum given in Figure 1a is that of ISeCN.

Further support for the PES assignment of ISeCN is derived from the comparison with the PE spectra of ClSeCN and BrSeCN,[3] because they exhibit similar band structures and a regular reduction of their ionization energies.

In summary, ICl is a good precursor to prepare pure INCO, ISCN, and the hitherto unknown molecule ISeCN by the heterogeneous reactions of ICl with AgNCO(s), AgSCN(s) at room temperature, and prepared AgSeCN(s) at $-9(\pm1)$ °C. The ionization energies of ISeCN, ISCN, and INCO are assigned from the PES experiment and the OVGF calculations. The agreement between the PES experiments and the OVGF calculations for INCO, ISCN, and ISeCN show that the new reaction is a good preparative method for not only pure INCO and pure ISCN, but also for the new compound ISeCN. The discovery of this new reaction can promote the investigations of these compounds and also might be extended to the preparation of similar compounds.

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