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Acidity, Basicity, and Gas-Phase Ion Chemistry of Hydrogen Selenide by Ion Cyclotron Resonance Spectroscopy

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Reaction pathways, product distributions, and rate constants have been determined for the gas-phase ion–molecule reactions of H_2Se by ion cyclotron resonance spectroscopy. Hydrogen selenide fragment ions condense with neutral H_2Se, expel H_2, and generate ions containing two atoms of selenium. No condensation reactions involving negative ions were observed. The gas-phase acidity, $PA(HSe^-) = 339 \pm 5$ kcal/mol, and basicity, $PA(H_2Se) = 170 \pm 3$ kcal/mol, of H_2Se have been determined by studying the course of proton-transfer reactions in binary mixtures of H_2Se with appropriate molecules. Comparisons of the chemical reactivity and thermochemical properties of H_2Se with H_2S and H_2O are presented.

Introduction

In order to provide a more complete understanding of the gas-phase ion chemistry and thermochemical properties of the binary hydrides, an investigation of hydrogen selenide (H_2Se) by ion cyclotron resonance spectroscopy (icr) was undertaken. Although mass spectrometric studies of both the positive and negative ions[1,2] derived from H_2Se have been reported, the gas-phase ion–molecule chemistry has not previously been investigated. Using icr techniques we have systematically studied the ion–molecule reactions of H_2Se, where possible kinetic and thermodynamic data have been determined including the acidity and basicity of H_2Se. In the Discussion the gas-phase ion chemistry of H_2Se, H_2S, and H_2O are compared and contrasted to elucidate the important factors determining the chemical reactivity and thermochemical properties of these interesting species.

Experimental Section

H_2Se was generated *in vacuo* by transferring H_2O onto excess aluminum selenide (Al_2Se_3).[3] Purification was achieved by bulb-to-bulb fractionation at −63° to eliminate excess H_2O followed by freeze–pump–thaw cycles with liquid nitrogen. No impurities greater than 0.1% were detected in the 70-eV mass spectrum.

The icr instrumentation and various experimental techniques have been described in great detail.[4,5] A flat cell with overall dimensions of 2.54 × 1.27 × 12.7 cm was employed. Pressure measurements were made with an MKS Model 90 H 1-E capacitance manometer.[5] Electron energies were measured with a Heath EU-805A digital voltmeter.

Spectral intensities reported in figures and tables were converted to approximate ion abundance by dividing the measured single-resonance peak heights by ion mass. Binary mixtures were prepared manometrically and agreed to within 25% with compositions calculated from the measured total ionization current.[5]

Results

Mass Spectrometry of H_2Se.—Analysis of the 70-eV mass spectrum of H_2Se (Figure 1) is complicated by the presence of five isotopes of selenium. The relative ion abundancies at 70 eV for one isotope are 39% for H_2Se^+, 18% for HSe^+, and 43% for Se^+ in fair agreement with the values reported by Neuert and Clasen.[6] The appearance potentials for HSe^+ (13.8 ± 0.2 eV) and Se^+ (12.6 ± 0.1 eV) were determined by the method of extrapolated voltage differences relative to the appearance potential of H_2Se^+ which has previously been determined to be 9.90 ± 0.03 eV by photoionization methods.[7-9] These values are in good agreement with those reported by Neuert and Clasen.[6]

Gas-Phase Ion Chemistry of H_2Se.—The positive ion chemistry of H_2Se in the gas phase is relatively straightforward. Single-resonance spectra of H_2Se at 70 eV and at three pressures are given in Figure 2. At low pressure only the three primary ions formed by electron impact are observed (Figure 2a). As the pressure is increased, ion–molecule reactions lead to the formation of the protonated parent H_3Se^+ as well as the condensation products Se_2^+ and HSe_2^+ (Figure 2b). At high pressure, these product ion peaks become prominent in the spectrum (Figure 2c). Condensation products containing three selenium atoms were not observed.

Analysis of the single-resonance spectrum as a function of electron energy allows the elucidation of individual reaction processes.[5] At low electron energy (12.0 eV) only the parent ion is formed. With increasing pressure H_2Se^+ reacts to form H_3Se^+ (reaction 1). At 14 eV the ion Se^+ is present and leads to the formation of Se_2^+ as the pressure is raised (reaction 2).

$$H_2Se^+ + H_2Se \longrightarrow H_3Se^+ + HSe \qquad (1)$$

$$Se^+ + H_2Se \longrightarrow Se_2^+ + H_2 \qquad (2)$$

At 15 eV HSe^+ is observed and leads to the formation of HSe_2^+ with increasing pressure (reaction 3). The occurrence of reactions 1–3 was verified by double-resonance experiments.

$$HSe^+ + H_2Se \longrightarrow HSe_2^+ + H_2 \qquad (3)$$

Several determinations of the rate constant for reaction 1 utilizing Buttrill's analysis[10] and iterative computer techniques yielded the average value $(4 \pm 1) \times 10^{-10}$ cm^{-3} molecule^{-1} sec^{-1} with the major source of error being due to pressure measurement. Using the

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[1] H. Neuert, *Z. Naturforsch. A*, **8**, 459 (1953).

[2] O. Rosenbaum and H. Neuert, *ibid.*, *A*, **9**, 990 (1954).

[3] The authors gratefully acknowledge the gift of a sample of Al_2Se_3 from Rocky Mountain Research, Inc., Denver, Colo.

[4] J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

[5] D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970), and references cited therein.

[6] H. Neuert and H. Clasen, *Z. Naturforsch. A*, **7**, 410 (1952).

[7] K. Watanabe, J. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

[8] W. C. Price, S. P. Feegan, and A. D. Walsh, *Proc. Roy. Soc., Ser. A*, **201**, 600 (1950).

[9] J. Delwiche, P. Natalis, and J. E. Collin, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 443 (1970).

[10] S. E. Buttrill, Jr., *J. Chem. Phys.*, **50**, 4125 (1969).

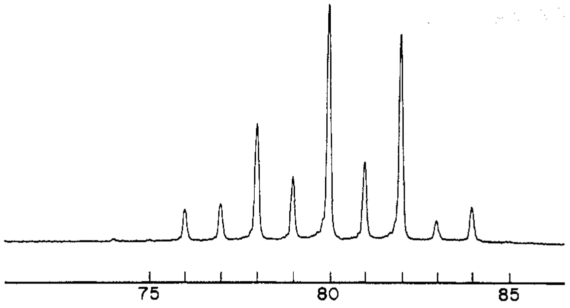

Figure 1.—Single-resonance spectrum of H_2Se at 70 eV and 4×10^{-7} Torr.

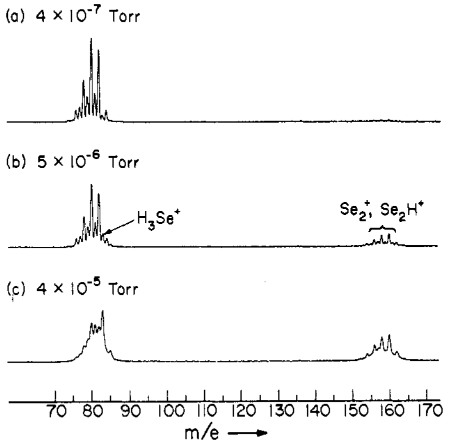

Figure 2.—Single-resonance spectra of H_2Se at 70 eV and various pressures.

analysis previously described,[5] the rate constants for reactions 2 and 3 were determined relative to the rate constant measured for reaction 1. The results are summarized in Table I.

TABLE I

GAS-PHASE ION–MOLECULE REACTIONS AND RATE CONSTANTS OF THE GROUP VI HYDRIDES

Reaction	Rate constant ($k \times 10^{10}$ cm^3 molecule^{-1} sec^{-1}) Se	S	O
$H_2X^+ + H_2X \rightarrow H_3X^+ + HX$	4 ± 1^a	$7^{c,d}$	16^c
$HX^+ + H_2X \rightarrow HX_2^+ + H_2$	3 ± 1^a	$\ldots^e$	$\ldots^e$
$X^+ + H_2X \rightarrow X_2^+ + H_2$	4 ± 1^a	1.9^d	$\ldots^e$
$HX^+ + H_2X \rightarrow H_3X^+ + X$	$\ldots^{a,b}$	$9^{c,d}$	15^c

[a] This work. [b] Reaction not observed. [c] S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967). [d] W. E. W. Ruska and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 221 (1969). [e] Reaction not reported in the literature.

The negative ion chemistry of H_2Se was briefly investigated. The only negative ion detected in abundance, HSe^-, was not observed to react with H_2Se at high pressure.

Basicity of Hydrogen Selenide.—A quantitative measure of the basicity of a species M is its proton affinity (PA), defined as the enthalpy change of the gas-phase reaction $MH^+ \rightarrow M + H^+$. Relative basicities can be determined by examining the course of proton-transfer processes occurring in binary mixtures as generalized in reaction 4.[5,11,12] Sufficient reference data are available to permit the determination of absolute proton affinities to within ±5 kcal/mol.

$$M_1H^+ + M_2 \rightleftharpoons M_2H^+ + M_1 \qquad (4)$$

Mixtures of H_2O, H_2S, HCN, and AsH_3 with H_2Se were prepared and the proton-transfer reactions generalized in reaction 4 were investigated. The results of a typical experiment are illustrated in Figure 3 for the mixture of H_2O with H_2Se. With increasing pressure, the parent ions decrease concomitantly with the formation of both protonated parent ions. At the highest pressures examined it is observed that the abundance of H_3Se^+ increases relative to that of H_3O^+ indicating reaction 5 and implying PA(H_2Se) ≥ PA (H_2O) = 164 kcal/mol. Double-resonance experiments confirmed the occurrence of reaction 5 in the direction indicated. Results for other mixtures are summarized in Table II and lead to an estimate of 170 ± 3 kcal/mol for PA(H_2Se) corresponding to $\Delta H_f(H_3Se^+) = 183$ kcal/mol. It should be mentioned that in mixtures of H_2Se with H_2S and H_2Se with HCN no tendency for proton transfer to occur preferentially in either direction was observed at high pressure. Double-resonance experiments were consistent with the above results showing that the proton-transfer reactions of interest occurred at comparable rates in both directions. These results imply that the proton affinities of H_2Se, H_2S, and HCN are approximately equal.

$$H_3O^+ + H_2Se \rightarrow H_3Se^+ + H_2O \qquad (5)$$

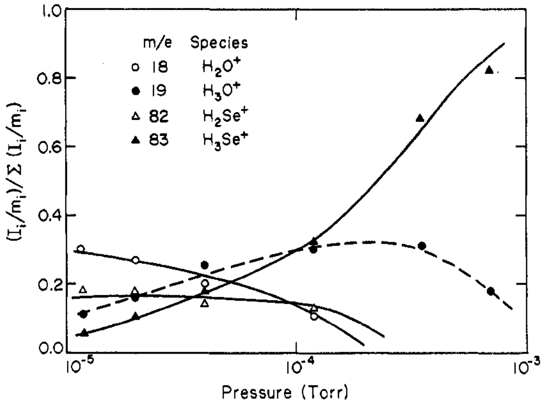

Figure 3.—Variation of ion densities (reported as mass-corrected single-resonance intensities normalized to unity) with pressure for a 2:1 mixture of H_2O and H_2Se at 12 eV.

TABLE II

PROTON-TRANSFER REACTIONS TO DETERMINE THE RELATIVE BASICITY OF H_2Se

Reaction	PA(H_2Se), kcal/mol	Ref
$H_3Se^+ + AsH_3 \rightarrow AsH_4^+ + H_2Se$	≤175	*b*
$H_3Se^+ + H_2S \rightleftarrows H_3S^+ + H_2Se$	170[a]	*c*
$H_3Se^+ + HCN \rightleftarrows H_2CN^+ + H_2Se$	170[a]	*c*
$H_3O^+ + H_2Se \rightarrow H_3Se^+ + H_2O$	≥164	*c*

[a] No preferential tendency for reaction to occur in either direction. [b] R. Wyatt, D. Holtz, and J. L. Beauchamp, unpublished results. [c] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73,** 4329 (1969).

Acidity of Hydrogen Selenide.—The gas-phase acidity of a species MH is in principle determined in the same manner as the gas-phase basicity. The

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(11) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

(12) D. Holtz, J. L. Beauchamp, W. G. Henderson, and R. W. Taft, *Inorg. Chem.*, **10**, 201 (1971).

enthalpy of the reaction $MH \rightarrow M^- + H^+$ is the proton affinity of the anion, M^-, and is a measure of the acidity of MH. An investigation of the proton-transfer reactions between negative ions of H_2Se with species of known acidity leads to a bracketing of the proton affinity of HSe^-. The proton affinities of negative ions have not been as extensively studied as those of the parent neutrals, and it remains difficult to determine these interesting quantities to better than ±5 kcal/mol.

In order to determine the gas-phase acidity of H_2Se, mixtures with HCl, H_2S, and HCN were examined. A typical result is illustrated in Figure 4 for the mixture of H_2Se with HCl at an electron energy of 2.1 eV. Only the ions Cl^- and HSe^- were observed at low pressure. With increasing pressure, Cl^- is observed to increase in abundance relative to HSe^- suggesting reaction 6 and implying $PA(HSe^-) \geq PA(Cl^-)$. Since

$$HSe^- + HCl \longrightarrow Cl^- + H_2Se \tag{6}$$

the *lower* proton affinity corresponds to the *stronger* acid, the acidity of HCl is greater than or equal to the acidity of H_2Se. Results for other mixtures[13] are summarized in Table III and lead to an estimate of 339 ± 5 kcal/mol for $PA(HSe^-)$.

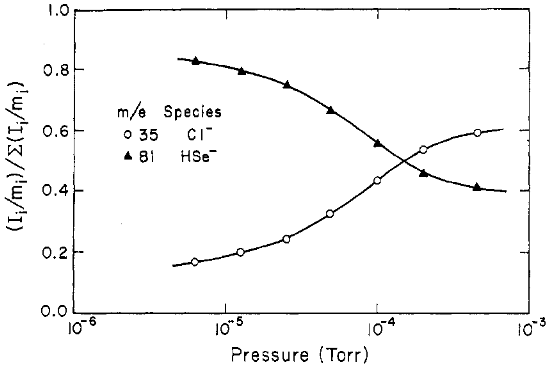

Figure 4.—Variation of negative ion densities (reported as mass-corrected single-resonance intensities normalized to unity) with pressure for a 3.5:1 mixture of H_2Se and HCl at 2.1 eV.

TABLE III

PROTON-TRANSFER REACTIONS TO DETERMINE THE RELATIVE ACIDITY OF H_2Se

Reaction	$PA(HSe^-)$,[a] kcal/mol
$HS^- + H_2Se \rightarrow HSe^- + H_2S$	≤350
$CN^- + H_2Se \rightarrow HSe^- + HCN$	≤344
$HSe^- + HCl \rightarrow Cl^- + H_2Se$	≥333

[a] Proton affinity values taken from ref 5.

Discussion

Ion Chemistry of H_2Se.—The ion chemistry of H_2Se is relatively straightforward. The results of this study serve, however, to clarify general features of the gas-phase ion chemistry of the simple hydrides. The appearance potentials for the group VI hydrides are given in Table IV. For the oxygen system, the appearance potentials increase in the order H_2X^+, HX^+, and X^+. In contrast, for the sulfur and selenium systems, an inversion occurs, the order being H_2X, X^+, and HX^+. Thus the elimination of molecular rather than atomic hydrogen from the parent ion H_2X^+ becomes thermodynamically favored as the atomic number increases. A similar trend is observed for the group V hydrides.[5,14]

TABLE IV

APPEARANCE POTENTIALS FOR THE GROUP VI HYDRIDES[a]

Species	Appearance Potential, eV O	S	Se
H_2X^+	12.6	10.4	9.88[b,d]
HX^+	18.3	14.4	13.8[c,d]
X^+	18.9	13.5	12.6[c,d]

[a] Except where noted appearance potentials have been taken from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. T. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [b] References 7 and 8. [c] This work. [d] Neuert and Clasen[6] reported values of 10.1, 13.9, and 12.8 for H_2X^+, HX^+, and X^+, respectively.

The gas-phase ion molecule chemistry of H_2Se is somewhat simpler than that observed for the other group VI hydrides (Table I). For example, all of the condensation reactions in which H_2Se participates occur with the elimination of H_2. As noted above the expulsion of H_2 instead of H becomes thermodynamically more favorable with increasing atomic number for both the group V[14] and the group VI hydrides due to the decrease in the X–H bond strength. Further, in contrast to the reactions of the fragment ions OH^+ and SH^+ with their parent neutrals, HSe^+ does not undergo reaction 7 to form the protonated parent H_3Se^+ even

$$HSe^+ + H_2Se \not\rightarrow H_3Se^+ + Se \tag{7}$$

though the process is calculated to be exothermic. A similar effect is observed for the group V hydrides where the protonated parent comes from both NH_2^+ and NH_3^+ in the ammonia system but only from the parent ions in the phosphine and arsine systems. Finally, it is interesting to note that ion–molecule reaction rate constants of the group VI hydrides decrease by approximately a factor of 2 as one proceeds from H_2O to H_2S to H_2Se. A similar effect is observed for the group V hydrides.[5,14]

Acidity of H_2Se.—The acidities of the group V, VI, and VII hydrides exhibit an entirely periodic behavior which can be interpreted in terms of fundamental molecular parameters. The gas-phase acidity of a molecule can be divided into three thermodynamic components: bond dissociation energy (to a radical and a hydrogen atom), ionization potential of the hydrogen atom (to a proton), and electron affinity of the radical (to an anion). The thermodynamic cycle is illustrated in eq 8. Therefore, the gas-phase acidity of

$$\begin{tikzcd} MH \arrow[r, "PA(M^-)"] \arrow[d, "D(MH)"'] & M^- + H^+ \\ M\cdot + H\cdot \arrow[r, "IP(H\cdot)"] & M\cdot + H^+ \arrow[u, "-EA(M\cdot)"'] \end{tikzcd} \tag{8}$$

MH, $PA(M^-)$, is given by eq 9. The thermochemical

$$PA(M^-) = D(MH) + IP(H\cdot) - EA(M\cdot) \tag{9}$$

properties related to the acidity of the group V, VI, and VII hydrides are presented in Table V. One notes

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[13] Ethyl nitrite was added to the H_2S–H_2Se mixture to enhance negative ion formation by means of the general process $C_2H_5O^- + MH \rightarrow C_2H_5OH + M^-$. See ref 5.

[14] R. Wyatt, D. Holtz, and J. L. Beauchamp, unpublished results.

TABLE V

SOME THERMOCHEMICAL QUANTITIES RELATED TO THE ACIDITY OF THE GROUP V, VI, AND VII HYDRIDES[a,b]

Species	Bond strength	EA(radical)	PA(anion)
NH_3	109	17[c]	(405)
PH_3	84	29[c]	(368)
AsH_3	(72)	29[c]	356[d]
H_2O	119	42	(390)
H_2S	90	53	(350)
H_2Se	76[e]	(50)	339[f]
HF	136	79	(370)
HCl	103	83	(333)
HBr	88	78	(323)
HI	71	71	(313)

[a] All quantities in kcal/mol. Except as noted, data are taken from J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [b] Values in parentheses are calculated by means of eq 9. [c] J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *J. Amer. Chem. Soc.*, **93**, 6360 (1971). [d] R. Wyatt, D. Holtz, and J. L. Beauchamp, unpublished results. [e] Authors' estimate. [f] This work.

that *within a given group* electron affinities remain approximately constant; bond strengths are thus the major factor affecting acidity.[5]

Basicity of H_2Se.—The trends in basicity in the group V, VI, and VII hydrides can be interpreted in terms of fundamental molecular parameters. From thermochemical consideration, the proton affinity of X is defined as

$$PA(X) = HA(X^+) + IP(H) - IP(X) \qquad (10)$$

The hydrogen affinity, $HA(X^+)$, is the bond strength of the X^+–H bond and can be physically interpreted as the bond-forming ability of the ion X^+. The ionization potential, IP(X), is a direct measure of the n-donor ability of the base. *Therefore, as indicated by eq 10 the proton affinity, the basicity, depends on two factors: the electron-donating ability of a molecule and the bond-forming ability of its corresponding molecular ion.* The proton affinities, hydrogen affinities, and ionization potentials for the group V, VI, and VII hydrides are tabulated in Table VI.

The proton affinities of the group VI hydrides are approximately equal since differences in the hydrogen affinities and ionization potentials approximately cancel. Water has the strongest bond-forming ability but is the weakest electron donor; the effects work in opposite directions to give it the lowest proton affinity of the group VI hydrides. Similar cancelation effects are observed in H_2S and H_2Se. The group V hydrides have nearly equal ionization potentials. Therefore, changes in the proton affinity parallel changes in the hydrogen affinities which decrease regularly with increasing atomic number. For the group VII hydrides, the trend is reversed with the dominant effect being the large decrease in ionization potential with increasing atomic number. Therefore, the proton affinities of the hydrogen halides increase with increasing atomic number.

TABLE VI

PROTON AND HYDROGEN AFFINITIES OF THE GROUP V, VI, AND VII HYDRIDES[a]

Species	IP, eV	PA, kcal/mol	HA, kcal/mol
NH_3	10.15	207	128
PH_3	9.98	185	102
AsH_3	10.03	175[b]	93
H_2O	12.60	164	143
H_2S	10.42	170	97
H_2Se	9.98	170[c]	85
HF	15.77	131	182
HCl	12.74	140	121
HBr	11.62	141	96
HI	10.38	145	71

[a] Except as noted, data are taken from J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [b] R. Wyatt, D. Holtz, and J. L. Beauchamp, unpublished results. [c] This work.

Although H_2Se is both a strong acid and a strong base in the gas phase, it is interesting to note that 169 kcal/mol would still have to be supplied to allow autoprotolysis reaction 11 to occur. The endothermicity

$$H_2Se + H_2Se \longrightarrow H_3Se^+ + HSe^- \qquad (11)$$

of the gas-phase autoprotolysis reaction is much larger for most other hydrides (Table VII).

TABLE VII

HEATS OF REACTION FOR GAS-PHASE AUTOPROTOLYSIS REACTIONS[a,b]

Species	ΔH	Species	ΔH	Species	ΔH
NH_3	198	H_2O	226	HF	239
PH_3	183	H_2S	180	HCl	193
AsH_3	181	H_2Se	169	HBr	182
				HI	168

[a] Endothermicity of the general reaction $MH + MH \rightarrow MH_2^+ + M^-$ calculated from data in Tables V and VI. [b] All values in kcal/mol.

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