Thermochemistry of the Reaction of Hydrogen Sulfide with Iodine and the Heat of Formation of HSI—a New Sulfur Compound

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Abstract: Gas-phase equilibrium constants K for the reaction $H_2S + I_2 \rightleftarrows HSI + HI$ have been measured spectrophotometrically over the temperature range 519–596 K. From the measured values of K, $\Delta H°_{558} = 6.19 \pm 0.57$ kcal/mol and $\Delta S°_{558} = 1.6 \pm 1.0$ eu are obtained. When corrected to room temperature by using an estimated value $\Delta C_p° = -0.3 \pm 0.2$ gibbs/mol, these become $\Delta H°_{298} = 6.28 \pm 0.67$ kcal/mol and $\Delta S°_{298} = 1.8 \pm 1.2$ eu. This yields values of $\Delta H_f°_{298}(HSI,g) = 10.08 \pm 0.67$ kcal/mol and $S°_{298}(HSI,g) = 64.3 \pm 1.2$ eu when combined with known values for H_2S, I_2, and HI. The above value of entropy agrees well with the estimated value. A tenfold slower secondary reaction leads to the formation of a new product which is probably SI_2 or HS_2I.

Introduction

Although no stable compounds of the type RSI seem to be known, a recent survey of the thermochemistry of sulfur compounds[6] has suggested that compounds containing divalent S–I bonds should be stable thermodynamically. In condensed phases such compounds may tend to disproportionate to the slightly more stable polysulfides + I_2.

$$2RSI \rightarrow R_2S_2 + I_2$$

A large driving force for this reaction is the heat of condensation of I_2, and so we conjectured that it might be easier to observe such compounds in gas-phase reactions where this behavior is not possible. To the best of our knowledge, no stable compounds have been reported which contain the RS–I bond. We chose for our study the reaction of I_2 with H_2S, which was calculated to occur in a convenient range of temperatures and pressures and which could be followed spectrophotometrically.

Applicable photometric techniques have been elucidated by Benson and co-workers,[1,2] who have determined the kinetic parameters and equilibrium constants of reactions in the temperature range 250–400 °C of the type $RH + I_2 \rightleftharpoons RI + HI$ where R is an organic radical. The extent of reaction is small and the equilibria are well to the left. Rodgers and co-workers[3] have recently studied the effect of fluorine on bond dissociation energies of organic fluorides employing the same technique. We wish to extend this technique to sulfur-containing compounds to provide thermochemical data on sulfur-containing molecules and radicals. The work presented here concerns the equilibrium constant for the case where R is the SH radical and thus yields values for the heat of formation and entropy of HSI.

Experimental Section

Matheson hydrogen sulfide (99.5%) and hydrogen iodide (98%), both further purified by distillation under vacuum, and reagent grade resublimed iodine were used.

Experiments were carried out in a 700-cm^3 cylindrical quartz vessel which was closed at each end by two pairs of Suprasil windows (2.5 cm in diameter) situated parallel to each other. One pair of windows was 18.7 cm apart, while the other pair was 3.9 cm apart, providing an alternate optical path length. The vessel was placed in a uniformly heated and well-insulated aluminum block furnace. The temperature was maintained to within 0.1 °C during any experiment (as indicated by a copper–constantan thermocouple situated in a well in the center of the vessel) by an electronic process proportional controller. The temperature variation along the length of the vessel was less than 1 °C.

The vessel could be isolated from the gas-handling system (evacuated to 10^{-5} Torr) by a heated stopcock at a point which left a dead space of <10 cm^3. The stopcock and the glass lead into the vessel were kept at ~ 140 °C. Gases were admitted to the vessel through glass tubing of 8-cm^3 volume (kept at 90–100 °C) which included a sensitive Validyne DP7 differential pressure transducer used as a null device for pressure measurement. Total range was ±5 Torr with a sensitivity of ±0.001 Torr.

The vessel and oven were placed vertically above the sample compartment of a Beckman Model 25 double-beam spectrophotometer which had been modified so that the sample beam passed through the light path of the vessel. All the necessary external optics were enclosed by a light-tight casing. In order to compensate for the loss of the light energy in the sample beam due to the long light path, the reference beam was attenuated by an iris diaphragm.

At each experimental temperature, the extinction coefficients of I_2 were determined at 500, 490, and 480 nm. Other extinction coefficients at 280, 270, and 260 nm for HI were also determined for the experimental temperatures. Absorbance readings vs. pressure of reagents gave excellent Beer's law plots up to 1.0 absorbance.

In general, I_2 was admitted into the reaction vessel and its pressure measured; then H_2S was expanded into the vessel and its pressure obtained by difference. Equilibrium pressures were determined from the absorbance of I_2 at 490 and 500 nm. The total pressure was again measured after reaction and no significant change was observed (±0.02 Torr). The entire system which attained equilibrium was quickly frozen by means of a liquid nitrogen trap, bathing a U tube.

UV absorption of the system was also checked in some experiments. HI appearance could not be measured spectrophotometrically since a broad peak with fine structure (spacing was 2.75 nm) between 260 and 320 nm was observed after the reaction was started. This peak, as shown in Figure 1, was presumably caused by the other reaction product, i.e., HSI. The large excess of hydrogen sulfide used in the reaction showed a strong absorption in the region below 260 nm and observed HI in this region.

The unreacted iodine and hydrogen sulfide were removed from the reaction mixture by trap-to-trap distillation under vacuum. The fraction which passed a −16 °C bath and condensed in a −78 °C bath was a dark, brownish liquid at room temperature. However, this liquid was not stable enough to be analyzed. The liquid became a black solid and a yellow deposit on the glass wall was observed during spectroscopic analysis. The mass spectrum showed that this fraction contained mass peaks corresponding to sulfur, iodine, and hydrogen iodide, while the infrared spectrum (gas phase) indicated weak absorptions at 2460, 1260, and 1080 and 810 cm^{-1}.

Some inhibition experiments were also carried out at 312 °C by adding HI to the I_2 vapor ($P_{HI}:P_{I_2} = 1.67:1$) before H_2S was introduced into the reaction vessels. Observations showed no iodine consumption and no new absorption peak such as that attributed to HSI.

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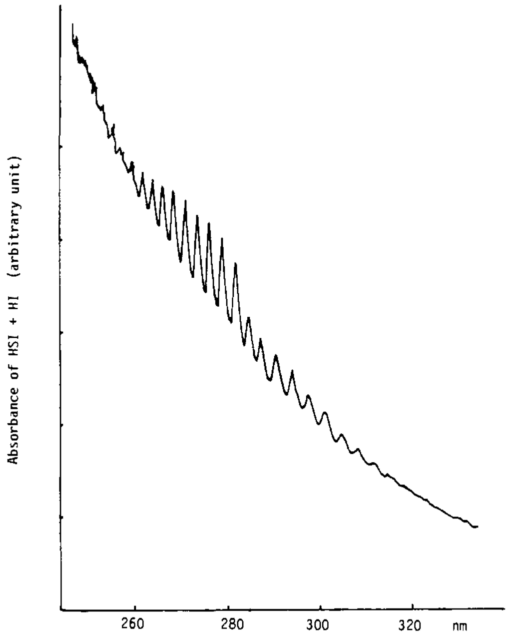

Figure 1. UV spectrum of HSI + HI.

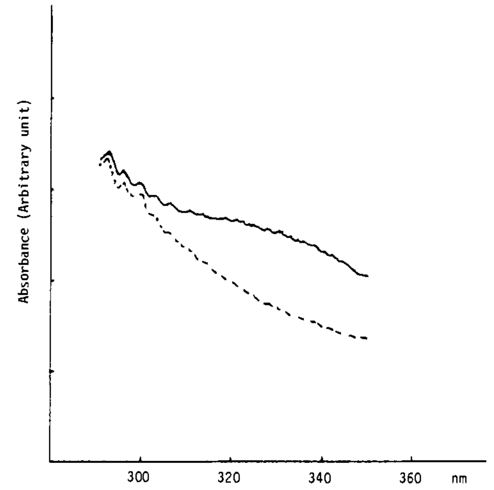

Figure 2. Absorption spectrum between 300 and 350 nm (i) for 30 min (dotted line); (ii) for 3 h (solid line).

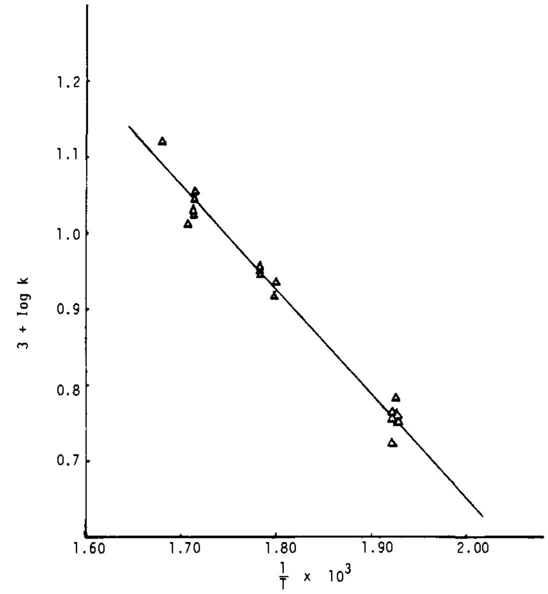

Figure 3. Plot of log k vs. $1/T$ for the reaction $H_2S + I_2 \rightleftarrows HSI + HI$.

Table I. Equilibrium Data for the Gas System[a] $H_2S + I_2 \rightleftarrows HSI + HI$

temp, K	$(I_2)_0$	$(H_2S)_0$	$(I_2)_{eq}$	$(H_2S)_{eq}$	$(HSI)_{eq}$	$(HI)_{eq}$	$K \times 10^3$
520.6	2.76	34.7	2.14	34.1	0.62	0.62	5.27
520.6	3.00	51.3	2.20	50.5	0.80	0.80	5.76
520.7	2.90	32.3	2.26	31.7	0.64	0.64	5.71
519.5	10.6	23.5	9.52	22.4	1.11	1.11	5.78
519.3	9.85	57.1	8.18	55.4	1.66	1.66	6.08
519.5	8.16	83.1	6.54	81.4	1.74	1.74	5.70
560.5	3.29	31.1	2.48	30.3	0.81	0.81	8.79
560.6	3.07	22.5	2.39	21.8	0.68	0.68	8.87
560.6	3.55	44.5	2.55	43.5	1.00	1.00	9.02
555.5	2.30	78.6	1.35	77.7	0.95	0.95	8.62
556.0	1.51	90.7	0.76	90.0	0.75	0.75	8.23
585.5	3.60	63.0	2.37	61.8	1.23	1.23	10.2
583.5	3.88	19.8	3.07	19.0	0.81	0.81	11.3
582.0	3.35	38.8	2.38	37.8	0.97	0.97	10.5
583.7	3.32	39.3	2.34	38.3	0.98	0.98	10.7
583.7	3.17	30.9	2.30	30.0	0.87	0.87	11.0
595.2	3.00	45.0	1.94	43.9	1.06	1.06	13.2

[a] All pressures in torr.

If the entire system after attaining apparent equilibrium (~10–30 min) was observed spectrophotometrically for a period of 3–24 h, a small, slow decrease in iodine concentration (~10–15% of equilibrium value) and a new, weak absorption between 300 and 350 nm were observed (as shown in Figure 2).

Results and Discussion

In order to test the apparatus, it was first used to determine the equilibrium constant for the reaction

$$i\text{-}C_4H_{10} + I_2 \rightleftarrows i\text{-}C_4H_8 + 2HI$$

The equilibrium constant for this reaction has been measured[4] over the temperature range 252–310 °C and the results with this apparatus, obtained at 252–320 °C, were within ~10% of Benson and Teranishi's values.

The reaction of I_2 with H_2S gave rise to products we believe to be HI and HSI.

$$I_2 + H_2S \rightleftarrows HI + HSI \qquad (1)$$

The formation of HSI is based on the following evidence: (1) The characteristic UV absorption between 260 and 320 nm was observed but no such absorption was observed in HI inhibition experiments. (2) A dark, brownish liquid was formed at room temperature. (3) Mass spectrum showed that this liquid product contained iodine and sulfur even though it decomposed during analysis. (4) The weak infrared absorptions at 2460 and 1080 cm^{-1} may be attributed to the S–H group. (5) No significant pressure change was observed. This is in accord with the stoichiometric relation $I_2 + H_2S \rightleftarrows HSI + HI$. (6) H_2S_2, HS_2I, or SI_2, which might be formed as secondary products after extended reaction times, were not observed at the end of the normal reaction time (30 min). (7) The thermochemical data determined from the equilibrium constant were in good agreement with the estimated values[5] from the stoichiometry mentioned above. This will be discussed in the following.

The equilibrium measurements were made over the range 519.3–595.2 K and the results are summarized in Table I. The equilibrium constants shown in Table I are calculated from the equilibrium partial pressure of I_2 by assuming that $-\Delta P(I_2) = -\Delta P(H_2S) = \Delta P(HI) = \Delta P(HSI)$.

The plot of log K vs. $1/T$ gives a line with reasonable linearity as shown in Figure 3. From the slope and intercept of the solid line (determined by a computed least-squares fit) values of $\Delta H°_{558} = 6.19 \pm 0.57$ kcal/mol and $\Delta S°_{558} = 1.6 \pm 1.0$ eu are determined. $C_p°$ of HSI is estimated[5] by assuming $\sim$400 cm^{-1} as S-I stretching frequency and $\sim$1350 cm^{-1} as deformation frequency of HSI. The contribution from the S-H stretch (2600 cm^{-1}) to $C_p°$ is very small at temperatures considered. Thus, $C_p°_{558}$(vib) and $C_p°_{298}$(vib) of HSI are 2.6 ± 0.2 and 1.6 ± 0.2 gibbs/mol, respectively. Adding 8 gibbs/mole for translational and rotational contributions (assuming a nonlinear molecular for HSI), $C_p°_{558} = 10.6 \pm 0.2$ gibbs/mol and $C_p°_{298} = 9.6 \pm 0.2$ gibbs/mol are obtained. $\Delta H°_{298} = 6.28 \pm 0.67$ kcal/mol and $\Delta S°_{298} = 1.8 \pm 1.2$ eu can be obtained by using a value of $\Delta C_p°\,[= (\Delta C_p°_{298} + \Delta C_p°_{558})/2]$ of -0.3 ± 0.2 gibbs/mol. Combining these with the well-known values of $\Delta H_f°_{298}$ and $S°_{298}$ for I_2, H_2S, and HI[5] leads to values of $\Delta H_f°_{298}(\text{HSI,g}) = 10.08 \pm 0.67$ kcal/mol and $S°_{298}(\text{HSI,g}) = 64.3 \pm 1.2$ eu.

The entropy value of HSI obtained here is in good agreement with the value of $S°_{298} = 64.0 \pm 1.0$ eu estimated from bond additivity.[5] This lends support to the values obtained. If known values of $\Delta H_f°_{298}(\text{SH}) = 34 \pm 1$ kcal/mol[5,6] and $\Delta H_f°_{298}(\text{I}) = 25.5$ kcal/mol[5] are adopted, the bond dissociation energy of HS-I is calculated as 49.4 ± 2 kcal/mol. This is the first quantitative report of a bond strength of a divalent S, RS-I bond.[6]

The secondary reactions are somewhat ambiguous. Plausible secondary products in the system are SI_2, H_2S_2, and HSSI. Reactions for their formation would be

$$HSI + I_2 \rightleftarrows SI_2 + HI \qquad (2)$$

$$2H_2S + I_2 \rightleftarrows H_2S_2 + 2HI \qquad (3)$$

$$H_2S + I_2 + HSI \rightleftarrows HSSI + 2HI \qquad (4)$$

The equilibrium constants for reaction 3 can be calculated from known data[5] ($\Delta S_{300} = 0$; $\Delta H_{300} = 21.7$ kcal/mol) and shown to lead to negligible H_2S_2 production under the reaction conditions ($K_{(580K)} = 10^{-8.2}$). It is difficult, however, to decide between the remaining two candidate reactions 2 or 4. If SI_2 follows bond additivity then we can estimate $K_2 \approx K_1 \approx 10^{-2}$ and this would account for about 1% further depletion of I_2, which is a factor of 10 from the observed value. A decrease in ΔH_2 from bond additivity of 2.5 kcal, which would be quite plausible,[7] could account for the secondary reactions.

However, the same type of estimates (somewhat weaker) could be made for reaction 4 so that no definite choice can be made between them from present observations. A choice could be made if we had even crude measurements of the dependence of the fraction of secondary reaction to H_2S pressure. Reaction 4 would be strongly affected by this while reaction 2 would not.

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Preparation and Characterization of [*rac*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazocyclotetradecane]copper(II) *o*-Mercaptobenzoate Hydrate, $[Cu(tet\ b)(o\text{-}SC_6H_4CO_2)]\cdot H_2O$, a Complex with a CuN_4S (Mercaptide) Chromophore

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Abstract: The synthesis, crystal structure, electronic spectra, magnetic susceptibility, and ESR data are reported for the title complex. Dark green crystals were obtained in the monoclinic space group $P2_1/n$ with $a = 8.387$ (3) Å, $b = 21.16$ (1) Å, $c = 14.677$ (5) Å, $\beta = 90.92$ (3)°, $d_{obsd} = 1.32$ (1) g/cm^3, $d_{calcd} = 1.322$ g/cm^3, $Z = 4$. Least-squares refinement of 1870 reflections having $F^2 \geq 2\sigma$ gave a conventional R factor of 0.079 and $R_{wF} = 0.095$. The structure consists of Cu(II) monomers with distorted trigonal bipyramidal N_4S ligand donor sets. Structural parameters within the triangular fragment include Cu-S, 2.359 (4) Å; Cu-N, 2.193 (10) and 2.132 (9) Å; S-Cu-N, 120.8 (3) and 135.4 (3)°; and N-Cu-N, 103.5 (4)°. The coordination geometry is completed by two apical Cu-N bonds (2.028 (9), 1.997 (10) Å). Both the X-band ESR spectra ($g_1 = 2.074$, $g_2 = 2.086$ (poorly resolved), $g_3 = 2.117$) and the measured magnetic moment (2.02 (5) μ_B at 293 K) of the polycrystalline complex support its formulation as a Cu(II) N_4S(mercaptide) species. Structural and electronic-spectral data are compared with those reported for analogous CuN_4X (X = Cl, CN) species. The title complex exhibits absorptions at $\sim$590 (poorly resolved), 730 ($\epsilon \sim$900), and $\sim$920 nm (shoulder), which are assigned as ligand field transitions. Additional spectral features at 360, 418, and 430 nm which are not exhibited by either free $^-SC_6H_4CO_2^-$ or a reference $Zn(tet\ b)(o\text{-}^-SC_6H_4CO_2^-)\cdot H_2O$ complex are attributed to S → Cu(II) charge transfer.

Introduction

Because of inherent interest in these compounds and their possible usefulness as models for the blue copper proteins, a number of attempts to prepare Cu^{II}-mercaptide complexes have been reported recently.[2] However, since nearly all known Cu^{II}-mercaptide systems revert to Cu(I) and disulfide rapidly

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