Heats of Formation and Bond Dissociation Energies of Some Simple Sulfur- and Halogen-Containing Molecules

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The heats of formation and bond dissociation energies of some simple sulfur- and halogen-containing molecules are derived from information found in the literature. These thermochemical quantities are useful in determining the energetically favorable reactions that may occur between the sulfur and halogen chemical cycles of the stratosphere.

Chlorine (*17*), bromine (*22*), and fluorine (*17*, *18*) chemistry play an important role in the chemistry of the stratosphere. Sulfur compounds are also known to be important constituents of the atmosphere, and chemistry involving sulfur species (e.g., S, SO, SO_2, SO_3) is of vital importance in the formation of aerosols in photochemical smog and in the Jungle layer of the lower stratosphere (*4*, *7*, *9*, *12*). These sulfur and halogen cycles have thus far been considered independent of one another; however, chemical reactions between these cycles may occur.

In order to determine which reactions are thermodynamically favorable, the change in Gibbs free energy is required. At 0 K, $\Delta G = \Delta H_0°$ and therefore the change in enthalpy was

Table I. Heats of Formation and Bond Dissociation Energies of Some Gaseous Sulfur- and Halogen-Containing Molecules

Species	$\Delta H_{f0}°$, kcal/mol	Ref	$D_0°$(X–Y), kcal/mol	Ref
O	58.983	21		
O_3	34.74	21	$(O_2\text{–}O)$ 24.2 ± 0.5	11
F	18.36 ± 0.4	19		
Cl	28.68	21		
ClO	24.33	11	63.3	This work[a]
Cl_2	0	21	57.3 ± 0.1	5
S	66.1	21		
S_2	30.8 ± 0.2	19	101.5 ± 1.5	5
SO	1.5	21	123.6 ± 2	5
SO_2	−70.336	21	(OS–O) 130.8 ± 2.0	5
SCl	19 ± 3[b]	16	76 ± 4	16, This work[c]
SCl_2	−5.3	3	(ClS–Cl) 53 ± 4	16, This work[d]
S_2Cl_2	−7.7	3	(ClS–SCl) 46 ± 7	This work[e]
			(ClSS–Cl) 53 ± 1	16
S_2Cl	17 ± 2	This work[f]	(ClS–S) 68 ± 5	This work[g]
			(SS–Cl) 42 ± 3	16, This work[h]
$OSCl_2$	−50.0 ± 0.2	21	(OClS–Cl) 58 ± 2	16
			$(Cl_2S\text{–}O)$ 104 ± 2	This work[i]
OSCl	−21 ± 3	This work[j]	(OS–Cl) 51 ± 4	This work[k]
			(O–SCl) 99 ± 6	This work[l]
O_2SCl_2	−83.3 ± 0.5	1	$(O_2ClS\text{–}Cl)$ 46 ± 4	16, This work[m]
			$(Cl_2OS\text{–}O)$ 92 ± 2	2, This work[n]
O_2SCl	−66 ± 4	This work[o]	$(O_2S\text{–}Cl)$ 24 ± 4	This work[p]
			(ClOS–O) 104 ± 7	This work[q]
OSF_2	−129 ± 25	1		
O_2SF_2	−179.3 ± 2	1	$(O_2FS\text{–}F)$ 81 ± 2	23
			$(OF_2S\text{–}O)$ 109 ± 27	This work[r]
O_2SF	−117 ± 5	This work[s]	$(O_2S\text{–}F)$ 65 ± 5	This work[t]
O_2SClF	−131.2 ± 5	1	$(O_2FS\text{–}Cl)$ 43 ± 10	This work[u]
			$(O_2ClS\text{–}F)$ 84 ± 10	This work[v]
$OSBr_2$	−29.6 ± 0.6[w]	6		
O_2SBrF[x]				

[a] Calculated using eq 2 and the heats of formation of Cl, O, and ClO. [b] Observation of the sixth vibrational level of HCl in the reaction $H + SCl_2 \rightarrow HCl + SCl$ requires $\Delta H_{f0}°(SCl) = 22$ kcal/mol; the seventh vibrational level may also be produced which would give $\Delta H_{f0}°(SCl) = 19$ kcal/mol. If the difference, $D(S\text{–}S) - D(HS\text{–}SH)$, is the same for $D(S\text{–}S) - D(ClS\text{–}SCl)$, then $\Delta H_{f0}°(SCl) = 16$ kcal/mol is needed (*16*). [c] Calculated using eq 2 and the heats of formation of S, Cl, and SCl. [d] Calculated using eq 2 and the heats of formation of Cl, SCl, and SCl_2. [e] Calculated using eq 2 and the heats of formation of SCl and S_2Cl_2. The bond dissociation energy of RS–SR is 68 ± 6 kcal/mol when R = Me, Et, *n*-Pr, *n*-Bu, and *t*-Bu (*14*, *15*). [f] Calculated using eq 2, the bond dissociation energy of ClSS–Cl, and the heats of formation Cl and S_2Cl_2. [g] Calculated using eq 2 and the heats of formation of S, SCl, and S_2Cl. The bond dissociation energy of RS–SR is 68 ± 6 kcal/mol when R = Me, Et, *n*-Pr, *n*-Bu, and *t*-Bu (*14*, *15*). [h] Calculated using eq 2 and the heats of formation of S_2, Cl, and S_2Cl. [i] Calculated using eq 2 and the heats of formation of O, SCl_2, and $OSCl_2$. [j] Calculated using eq 2, the bond dissociation energy of OClS–Cl, and the heats of formation of Cl and $OSCl_2$. [k] Calculated using eq 2 and the heats of formation of SO, Cl, and OSCl. [l] Calculated using eq 2 and the heats of formation of O, SCl, and OSCl. [m] Calculated using eq 2 and the heats of formation of Cl, O_2SCl, and O_2SCl_2. [n] Calculated using eq 2 and the heats of formation of O, $OSCl_2$, and O_2SCl_2. [o] Estimated using heats of formation for Cl, Cl_2, and O_2SCl_2 and heat of reaction $\Delta H° = -11.5 \pm 2.5$ kcal/mol for $Cl + O_2SCl_2 \rightarrow Cl_2 + O_2SCl$ at 300 °C (*20*). [p] Calculated using eq 2 and the heats of formation of SO_2, Cl, and O_2SCl. [q] Calculated using eq 2 and the heats of formation of O, OSCl, and O_2SCl. [r] Calculated using eq 2 and the heats of formation of O, OSF_2, and O_2SF_2. [s] Calculated using eq 2, the bond dissociation energy of O_2FS–F, and the heats of formation of F and O_2SF_2. [t] Calculated using eq 2 and the heats of formation of SO_2, F, and O_2SF. [u] Calculated using eq 2 and the heats of formation of O_2SF, Cl, and O_2SClF. [v] Calculated using eq 2 and the heats of formation of F, O_2SCl, and O_2SClF. [w] At 25 °C. [x] The following thermodynamic properties for O_2SBrF have been reported at 25 °C: $(H° - E°)/T = 12.3764$, $-(G° - E_0°)/T = 63.0424$, $S° = 75.4188$, $C_p° = 17.7014$ (all in cal/(deg mol)) (*8*).

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evaluated at 0 K for each reaction. This was accomplished by using eq 1 where ΔH_{f0}° represents the heat of formation of

$$\Delta H_0^\circ = \sum_{P} \nu_P(\Delta H_{f0}^\circ)_P - \sum_{R} \nu_R(\Delta H_{f0}^\circ)_R \qquad (1)$$

reactants, R, and products, P, and ν_P and ν_R are the stoichiometric coefficients of the products and reactants, respectively. An equivalent method is to sum the bond dissociation energies, D_0°, of the bonds that are broken and subtract from this total the bond energies of the bonds formed in the reaction. Unfortunately, few values for the heats of formation and bond dissociation energies of sulfur- and halogen-containing molecules have been reported in standard reference tables (*1*, *5*, *10*, *11*, *13*). These data (Table I) were therefore derived by making use of eq 2 and information found in the literature. As an

$$D_0^\circ(\text{X-Y}) = \Delta H_{f0}^\circ(\text{X}) + \Delta H_{f0}^\circ(\text{Y}) - \Delta H_{f0}^\circ(\text{XY}) \qquad (2)$$

example of the use of Table I the exothermicities of four chemical reactions involving sulfur- and chlorine-containing species are listed below:

$$\text{S(g)} + \text{Cl(g)} + \text{M(g)} \rightarrow \text{SCl(g)} + \text{M(g)} \quad \Delta H_0^\circ = -76 \text{ kcal/mol} \qquad (3)$$

M in reaction 3 refers to the third body involved in this termolecular reaction.

$$\text{S(g)} + \text{ClO(g)} \rightarrow \text{SCl(g)} + \text{O(g)} \quad \Delta H_0^\circ = -12 \text{ kcal/mol} \qquad (4)$$

$$\text{SCl(g)} + \text{O}_3\text{(g)} \rightarrow \text{OSCl(g)} + \text{O}_2\text{(g)} \quad \Delta H_0^\circ = -75 \text{ kcal/mol} \qquad (5)$$

$$\text{OSCl(g)} + \text{O}_3\text{(g)} \rightarrow \text{O}_2\text{SCl(g)} + \text{O}_2\text{(g)} \quad \Delta H_0^\circ = -80 \text{ kcal/mol} \qquad (6)$$

It is also interesting to note that abstraction of a Cl atom from $CFCl_3$ or CF_2Cl_2 by an S atom is slightly exothermic since the C–Cl bond energies in these molecules are approximately 70–75 kcal/mol (*17*).

$$\text{S(g)} + \text{CF}_x\text{Cl}_{4-x}\text{(g)} \rightarrow \text{SCl(g)} + \text{CF}_x\text{Cl}_{3-x}\text{(g)} \qquad (7)$$

The corresponding reactions of $S(^1D_2)$ and $S(^1S_0)$, which are formed from photolysis of SCO in the stratosphere (*4*), are 26.4 and 63.4 kcal/mol, respectively, more exothermic than reactions involving ground-state S atoms.

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Thermodynamic Quantities for the Ionization of Water in Sodium Chloride Media to 300 °C

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The thermodynamic quantities at the saturation pressure for the dissociation of water at rounded temperatures from 0 to 300 °C and ionic strengths to 5 *m* in NaCl media are presented in tabular form. The thermodynamic parameters were derived by computer from analytical expressions representing $Q_w = [H^+][OH^-]$ presented in an earlier paper. The small difference in the effect of NaCl over KCl on the ionization of water is briefly discussed.

Data have been previously reported (*1*, *3*) which precisely define the ionization behavior of water, $H_2O(l) = H^+ + OH^-$, in both NaCl and KCl media at the saturation vapor pressure of water to 300 °C. In the study of aqueous equilibria involving hydrogen ion or hydroxide ion dissociation it is often desirable to examine the thermodynamic quantities for the processes. However, the analytical expressions representing $Q_w \equiv [H^+][OH^-]$ as a function of temperature, pressure, and ionic strength are sufficiently complex to require the use of computers for routine derivation of the thermodynamic parameters. These calculations have already been reported for the KCl media but not for the NaCl media (*3*).

In this brief paper we have employed the results from ref 3 to fix the parameters describing the infinite dilution and the

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