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PROTON AFFINITIES OF SULFATE AND BISULFATE IONS

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The decomposition of $(NH_4)_2SO_4(s)$ has been studied by DSC. The decomposition takes place in two steps to produce $NH_3(g)$ and $NH_4HSO_4(s)$ in the first and $NH_3(g)$ and $H_2SO_4(g)$ in the second. Enthalpies for these reactions are 195 and 169 kJ/mole, respectively. These values permit calculation of the proton affinities of SO_4^{2-} and HSO_4^-, and the values found are 1847 and 1338 kJ/mole, respectively.

The proton affinity of a species provides a valuable measure of the gas phase basicity of that species. Proton affinities have been measured for numerous anions and neutral molecules [1]. Most of the neutral molecules are the various organic bases. Proton affinities of anions, particularly polyatomic ions, are lacking. Previously, the proton affinities of the carbonate and bicarbonate ions were found to be 2261 kJ/mol and 1318 kJ/mol, respectively [2]. These values were obtained by making use of the heats of decomposition of the ammonium compounds and other thermochemical data. In particular, the lattice energies of the compounds must be available. In the case of the ammonium salts, the Kapustinskii equation was used to determine the lattice energies. In the present study, we have determined the heats of decomposition of ammonium sulfate and ammonium bisulfate and have used these data with other appropriate thermodynamic quantities to determine the proton affinities of the sulfate and bisulfate ions.

Experimental

Reagent grade ammonium sulfate was used without further treatment. Decomposition of ammonium sulfate was studied using a Perkin–Elmer differential scanning calorimeter, model DSC-2. Procedures used were similar to those previously described [3].

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Results and discussion

Ammonium sulfate was found to decompose in two steps:

$$(NH_4)_2SO_4(s) \rightarrow NH_3(g) + NH_4HSO_4(s) \tag{1}$$

$$NH_4HSO_4(s) \rightarrow NH_3(g) + H_2SO_4(g) \tag{2}$$

The first reaction takes place in the range 257–362° while the second occurs in the range 367–467°. The enthalpies for these processes were determined to be 195 kJ/mol and 169 kJ/mol, respectively.

In order to calculate the proton affinity of SO_4^{2-}, the following thermochemical cycle was used.

$$\begin{tikzcd}
(NH_4)_2SO_4(s) \arrow[r, "\Delta H_1"] \arrow[d, "U_1"] & NH_3(g) + NH_4HSO_4(s) \\
2NH_4^+(g) + SO_4^{2-}(g) \arrow[d, "PA_{NH_3}"] & \\
NH_4^+(g) + NH_3(g) + H^+(g) + SO_4^{2-}(g) \arrow[r, "-PA_{SO_4^{2-}}", "NH_4^+(g)"'] & + HSO_4\,(g) + NH_3(g) \arrow[uu, "-U_2"']
\end{tikzcd}$$

In this cycle, U_1 is the lattice energy of $(NH_4)_2SO_4$, U_2 is the lattice energy of NH_4HSO_4, PA_{NH_3} is the proton affinity of ammonia, $PA_{SO_4^{2-}}$ is the proton affinity of the sulfate ion. Combining the thermochemical quantities from the cycle yields,

$$PA_{SO_4^{2-}} = U_1 + PA_{NH_3} - \Delta H_1 - U_2. \tag{3}$$

The measured enthalpy of decomposition is ΔH_1 and this was determined to be 195 kJ/mol. The lattice energies of $(NH_4)_2SO_4$ and NH_4HSO_4 can be calculated by making use of the Kapustinskii equation,

$$U\,(\text{kcal/mol}) = \frac{287.2 Z_a Z_c m}{(r_a + r_c)}\left(1 - \frac{0.345}{r_a + r_c}\right) + 2.5m \tag{4}$$

where Z is an ionic charge, r is an ionic radius, and m is the number of ions in the formula. For this calculation, the following ionic radii were used: NH_4^+, 143 pm; SO_4^{2-}, 230 pm; and HSO_4^-, 206 pm [4]. Accordingly the lattice energy for $(NH_4)_2SO_4$ is found to be 1817 kJ/mol. Similarly, the lattice energy for NH_4HSO_4 is 641 kJ/mol. Since the proton affinity of ammonia is 866 kJ/mol [1], the proton affinity of SO_4^{2-} is determined to be 1847 kJ/mol.

This value is somewhat lower than those of other -2 ions. For example, for some -2 ions the reported proton affinities are as follows: 0^{2-}, 2318; S^{2-}, 2300; Se^{2-}, 2200; NH^{2-}, 2565; and CO_3^{2-}, 2261 kJ/mol [1, 3]. However, all of these ions are distinctly basic and their conjugate acids are all very weak acids. On the other hand, the HSO_4^- ions is acidic, so it is expected that the proton affinity of SO_4^{2-} would be lower than the 2200–2300 kJ/mol expected for a -2 ion. The S—O bond distance is short enough so that some $d_\pi - p_\pi$ bonding occurs. Accordingly, this ion is stabilized by the contributions from several resonance structures. Since adding a proton decreases the extent of electron delocalizaton, some loss in resonance energy could occur making the addition of the proton less favorable. Also, the delocalization reduces the negative charge on each oxygen atom thereby reducing the attraction for the proton that might be expected for a -2 ion (overall charge). Because of these factors, the proton affinity would be considerably lower than expected for a -2 ion, as is observed.

The enthalpy of decomposition of ammonium bisulfate permits the determination of the proton affinity of HSO_4^- using the following cycle.

$$\begin{tikzcd}
NH_4HSO_4(s) \arrow[r, "\Delta H_2"] \arrow[d, "U_2"] & NH_3(g) + H_2SO_4(g) \\
NH_4^+(g) + HSO_4^-(g) \arrow[r, "PA_{NH_3}"] & NH_3(g) + H^+(g) + HSO_4^-(g) \arrow[u, "-PA_{HSO_4^-}"']
\end{tikzcd}$$

From this cycle, it is clear that,

$$PA_{HSO_4^-} = U_2 + PA_{NH_3} - \Delta H_2 \tag{5}$$

In this case, ΔH_2 was found to be 169 kJ/mol, and U_2 was calculated from Eq. (3) as 641 kJ/mol. Accordingly, the calculated proton affinity for HSO_4^- is 1338 kJ/mol.

Reported proton affinities for -1 ions range from 1309 kJ/mol for I^- to 1695 kJ/mol for CH_3^- with most values being about 1400–1450 kJ/mol [1]. There is, however, frequently rather large disagreement between the values for the same ion reported by different workers. On this basis, the 1338 kJ/mol for HSO_4^- appears to be quite reasonable, and it is almost identical with the 1318 kJ/mol found for HCO_3^- [2]. Adding a second proton would again hinder delocalization of electron density, but not to as great an extent as in the case of SO_4^{2-}. Accordingly, if the proton affinity for HSO_4^- is somewhat lower than those for most other -1 ions, this may be one of several reasons. It is also true that HSO_4^- is the conjugate base of a stronger acid than are the other -1 ions so that its proton affinity could be expected to be lower.

The ΔH values measured in this work are accurate to within perhaps 5% (about 10 kJ/mol) and the proton affinity of NH_3 is probably accurate to within a similar magnitude (±10 kJ/mol). The greatest error involved in determining $PA_{SO_4^{2-}}$ and $PA_{HSO_4^-}$ is in calculating the lattice energies of $(NH_4)_2SO_4$ and NH_4HSO_4. In general, thermochemical radii are not highly accurate. Realistically, the radii sum is probably no more accurate than ±0.05 Å, which for $(NH_4)_2SO_4$ would result in calculated lattice energies of 1796 and 1838 kJ/mol at the upper and lower limits. Since lattice energies for both $(NH_4)_2SO_4$ and NH_4HSO_4 are used in the calculation of $PA_{SO_4^{2-}}$ it is likely that the error resulting from lattice energies could be 40–50 kJ/mol. Considering the additional probable errors in ΔH_1 and PA_{NH_3}, the value for $PA_{HSO_4^-}$, is probably correct to within ±60–80 kJ/mol. In the case of $PA_{HSO_4^-}$, only one lattice energy is involved, that of NH_4HSO_4, so that the resulting value calculated for $PA_{HSO_4^-}$ is probably more accurate than that for $PA_{SO_4^{2-}}$. A reasonable estimate is ±30–60 kJ/mol. These magnitudes are similar to the uncertainties in other proton affinities [1].

References

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Zusammenfassung — Die Zersetzung von $(NH_3)_2SO_4(s)$ wurde mittels DSC untersucht. Sie läuft in zwei Stufen ab, wobei während der ersten $NH_3(g)$ und $NH_4HSO_4(s)$ und während der zweiten $NH_3(g)$ und $H_2SO_4(g)$ gebildet werden. Die Enthalpien für diese Reaktionen belaufen sich auf 195 bzw. 169 kJ/mol. Diese Angaben ermöglichen die Errechnung der Protonenaffinität von SO_4^{2-} und HSO_4^-, deren Werten 1847 bzw. 1338 kJ/mol betragen.

Резюме — Методом ДСК изучено разложение твердого сульфата аммония. Разложение протекает в две стадии с образованием на первой стадии газообразного аммиака и твердого кислого сернокислого аммония, а на второй стадии — газообразных аммиака и серной кислоты. Энтальпии этих реакций равны, соответственно, 195 и 169 кдж/моль, что позволило вычислить сродство к протону сульфат- и гидросульфат-ионов и которое, соответственно, равнялось 1847 и 1338 кдж/моль.