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Note

Enthalpy of formation of sodium bromite

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The thermodynamic properties of the oxyhalogen ions are reasonably well known, with the exception of the bromite ion. The object of this note is to report briefly a calorimetric determination of the enthalpy of the reaction in aqueous solution.

$$NaBrO_2 + 2Na_2SO_3 \rightarrow NaBr + 2Na_2SO_4$$

This is a rapid reaction, apparently free from side reactions. From this, and available thermodynamic data, the enthalpy of formation of aqueous sodium bromite can be calculated. An indirect determination of this quantity has been made by one of the present authors from the kinetics of decomposition of aqueous sodium bromite[1] and sodium hypobromite[2]. The enthalpy of solution of sodium sulphite was also measured as a value of this was needed for the concentration used in the experiments.

EXPERIMENTAL

The calorimeter used was that described earlier[3], with some improvements, particularly the use of a 40 junction thermocouple of copper and constantan, giving about 1.5 mV deg^{-1}. The temperature rise in the experiments was about 0.5°C, and the voltage could be read to the nearest microvolt. The calorimeter was, as usual, calibrated by electrical heating, and it was estimated from the sensitivity of the timer, and of the galvanometer to measure the current or the voltage, that the precision of the calibration was about 0.06%.

Chemicals

Sodium bromite. Crystals of $NaBrO_2 \cdot 3H_2O$ were supplied by La Société d'Études Chimiques pour l'Industrie et l'Agriculture of Argenteuil, France, to whom we are much indebted. These were supplied immersed in a saturated solution, and small amounts of sodium bromide crystals were also present. A stock solution was made by dissolving these crystals in 0.12 M sodium hydroxide. Since sodium bromite decomposes slowly, the stock solution was analysed as required by the methods of ref. 1. A typical analysis gave: $NaBrO_2$ 0.06635 M, NaBrO 0.00175 M, $NaBrO_3$ 0.02213 M, NaBr 0.01927 M, NaOH 0.120 M.

Sodium sulfite. Fisher Certified reagent was used, after two recrystallisations; iodometric analysis gave purity of over 99.5%. It was assumed that the remainder was water.

Sodium bromate and bromide. Fisher Scientific Reagent Grades were used.

RESULTS

The enthalpy of solution of sodium sulfite was in a solution containing sodium bromate, bromide and hydroxide at the same concentrations as were present in the calorimeter at the end of the runs with sodium bromite. The concentration of sodium sulfite, after dissolving, was 0.0305 M, or in a molar ratio to water of 1:1820. The initial temperature was 25.0 °C. Results were −17.50, −17.66 kJ: mean −17.58 kJ.

In the runs with sodium bromite and sodium sulfite, 1.60 g of sodium sulfite (crystals) were added to the stock solution diluted twenty times (total volume 420 ml). The initial temperature was between 24.4 and 24.5 °C. The resultant heat evolved was corrected for the part arising from the reaction of sodium hypobromite and sodium sulfite, which is also a fast reaction: $NaBrO + Na_2SO_3 \rightarrow NaBr + Na_2SO_4$. Data[4,5] on enthalpies of formation make ΔH° equal to −304 kJ for this reaction. This correction was about 1.2% of the total heat evolved.

The calorimetric results for the reaction of sodium bromite and sodium sulphite in aqueous solution at 25 °C were −650.1, −651.5, −647.1 kJ: mean −549.6 kJ. The final solution was 0.0115 M in 1:1 salts (sodium bromide, bromate and hydroxide), and 0.0302 M in 1:2 salts (sodium sulfite and sulfate); that is, the ionic strength was 0.102 M. If we take data for very dilute aqueous solution from ref. 4, 5, and allow for the enthalpies of dilution from solutions at approximately the final ionic strength to infinite dilution from data in ref. 6, the enthalpies of formation of the various substances are: NaBr −361.3, Na_2SO_3 −1107.9 and Na_2SO_4 −1388.9 kJ. Hence the enthalpy of formation of aqueous sodium bromite is −273.7 kJ.

If we take −240.1 kJ as the conventional enthalpy of formation of the aqueous sodium ion[4], then the conventional enthalpy of formation of the bromite ion is −33.6 kJ. This may be compared with the series: Br^- −121.5, BrO^- −94.1, BrO_3^- −83.7, BrO_4^- +12.1 kJ[6], showing the relative instability of the bromite ion (and also, of course, of perbromate), which is reflected in its general chemistry. In the chlorine compounds, the chlorite ion also has a less negative ΔH_f^0, but to a much lesser extent; while the corresponding IO_2^- ion seems to be too unstable to occur in a crystalline compound.

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