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THE STANDARD ENTHALPY OF FORMATION OF SILVER ACETYLIDE

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ABSTRACT

The standard enthalpy of formation of crystalline silver(I) acetylide at 298.15 K has been determined as 357.6 ± 5.0 kJ mol^{-1} by solution-reaction calorimetry.

INTRODUCTION

The literature on the chemistry of silver(I) acetylide prior to 1949 has been fully summarised by Vestin and Ralf [1]. Although complexes such as $Ag_2C_2 \cdot AgNO_3$ and $Ag_2C_2 \cdot 6AgNO_3$ can be formed when acetylene reacts with neutral or acidic solutions of silver nitrate, only silver acetylide is precipitated from ammoniacal solutions. This compound, like many other acetylides, is treacherously unstable and is liable to spontaneous detonation when dry or subjected to mechanical stimulus [2].

Thermodynamic data are sparse and are not concordant. Berthelot and Delépine [3] determined the enthalpy of formation from calorimetric measurements on the precipitation of silver acetylide from ammoniacal solutions of silver nitrate, and Stadler [4] also determined this quantity by means of its explosive decomposition to its elements in a bomb, but there is a disparity of 70 kJ mol^{-1} between the two results. Vestin and Somersalo [5] determined $\Delta G^{\ominus}$ by an electrochemical method for the reaction $Ag_2C_2(cr) + 2H^+ \rightarrow C_2H_2(g) + 2Ag^+$. In this paper we report three consistent and reliable values for the standard enthalpy of formation of silver acetylide using solution-reaction calorimetry.

EXPERIMENTAL

Materials

Silver acetylide was prepared from aqueous ammoniacal silver nitrate (B.D.H., AnalaR) and an aqueous acetone solution of acetylene. The white

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precipitate was filtered on a sintered glass crucible, washed with water followed by acetone, dried to constant mass and stored over silica gel in an evacuated desiccator. Silver acetylide is dangerously explosive and manipulations were conducted with due care and in small quantities (< 0.2 g). Samples were analysed titrimetrically using Volhard's method with the following result: Ag, 89.5% (calculated for Ag_2C_2, 90.0%).

The silver nitrate used in the calorimetric experiments was obtained from Aldrich and the mass fraction purity was found to be 0.9964 by titrimetry against standard chloride solution.

Acetylene (B.O.C. Ltd) and potassium cyanide (B.D.H. Chemicals Ltd, AnalaR) were both used without further purification.

Calorimetry

A twin-vessel isoperibolic system, constructed in this laboratory and fully described elsewhere [6], was used. The precision and accuracy were regularly checked, before and after runs involving silver acetylide, using the neutralisation of tris(hydroxymethylamino)methane (THAM) with excess 0.100 M hydrochloric acid as a test reaction. Results were: $\Delta H^\ominus = -29.83 \pm 0.14$ kJ mol^{-1} ($5204 < n < 13913$, mean of 6 runs); literature value [7], $\Delta H^\ominus = -29.76 \pm 0.03$ kJ mol^{-1}, $n = 1345$, where n denotes the mole ratio of water to THAM. The enthalpy of dilution of THAM hydrochloride is negligible [8].

Throughout this paper uncertainty intervals are reported at the 95% confidence level.

Three independent solution calorimetric methods, based on the following equations, were investigated

$$2AgNO_3 + 2NH_3 + C_2H_2 \rightarrow Ag_2C_2 + 2NH_4NO_3 \qquad (1)$$

$$Ag_2C_2 + 2HCl \rightarrow 2AgCl + C_2H_2 \qquad (2)$$

$$Ag_2C_2 + 4KCN + 2H_2O \rightarrow 2KAg(CN)_2 + 2KOH + C_2H_2 \qquad (3)$$

Reaction (1)

Preliminary experiments confirmed the stoichiometry of this reaction by duplicate gravimetric determinations of the silver acetylide produced under conditions identical to those employed in the calorimetric procedure. The ratio of the mass found to the calculated mass was 1.003 : 1. The results are summarised in Table 1.

Assuming that the enthalpies of solution of NH_3(g), C_2H_2(g) and NH_4NO_3(cr) in aqueous acetone (concentration 0.14 M) are the same as in pure water, ignoring the enthalpies of mixing of the reactants and products (but assigning a nominal uncertainty of ± 2 kJ mol^{-1} to allow for this

TABLE 1

Enthalpies of precipitation of silver acetylide from an ammoniacal aqueous acetone (A) solution[a] of acetylene at 298.15 K

$$\mathrm{AgNO_3(cr)} + [(q+0.5)\mathrm{C_2H_2} + (p+1)\mathrm{NH_3}](m\mathrm{H_2O} + n\mathrm{A})(\mathrm{sln})$$
$$\rightarrow 0.5\mathrm{Ag_2C_2(cr)} + [\mathrm{NH_4NO_3} + p\mathrm{NH_3} + q\mathrm{C_2H_2}](m\mathrm{H_2O} + n\mathrm{A})(\mathrm{sln})$$

$m(\mathrm{AgNO_3})$ (g)[b]	m	$-\Delta H$ (kJ $\mathrm{mol^{-1}}$)[c]
0.23360	8074	63.76
0.19503	9671	63.89
0.19090	9880	63.62
0.18790	10038	63.61
0.18510	10190	62.99
0.18305	10304	63.72
0.16366	11525	63.77

[a] Reaction conditions were $m/(p+1) = 302.7$; $m/n = 410.4$; and $m/(q+0.5) = 7310$.
[b] Masses corrected for buoyancy using $\rho(\mathrm{AgNO_3}) = 4.35$ g $\mathrm{cm^{-3}}$.
[c] $\langle \Delta H \rangle = -63.62 \pm 0.27$ kJ $\mathrm{mol^{-1}}$.

assumption) and ignoring the enthalpy of dilution of $\mathrm{C_2H_2}$ in aqueous acetone, the reaction equation reduces to

$$\mathrm{AgNO_3(cr)} + 0.5\mathrm{C_2H_2(aq)} + [(p+1)\mathrm{NH_3} + m\mathrm{H_2O}](\mathrm{aq})$$
$$\rightarrow 0.5\mathrm{Ag_2C_2(cr)} + \mathrm{NH_4NO_3(aq)} + p\mathrm{NH_3(aq)} + m\mathrm{H_2O(l)} \qquad (4)$$

Using the ancillary data listed in Table 2, $\Delta H_f^{\ominus}(\mathrm{Ag_2C_2}$, cr, 298.15 K$) = +354.5 \pm 2.7$ kJ $\mathrm{mol^{-1}}$.

Reaction (2)

This reaction depends on the quantitative conversion of (insoluble) silver acetylide (moistened with about 1 $\mathrm{cm^3}$ of water to avoid explosion in the

TABLE 2

Ancillary thermodynamic data[a]

Species	$\Delta H_f^{\ominus}$ (kJ $\mathrm{mol^{-1}}$)	Reference
$\mathrm{AgNO_3(cr)}$	−124.39	9
$\mathrm{NH_3}$, $300\mathrm{H_2O}$	−80.21	9
$\mathrm{C_2H_2(aq)}$	211.46	9
$\mathrm{NH_4NO_3}$, $10000\mathrm{H_2O}$	−339.75	9
AgCl(cr)	−127.07	9
HCl, $12.3\mathrm{H_2O}$	−162.27	9
KCN, $200\mathrm{H_2O}$	−101.3	9
KOH, $20000\mathrm{H_2O}$	−482.28	9
$\mathrm{KAg(CN)_2(aq)}$	18.0	9
$\mathrm{H_2O(l)}$	-285.83 ± 0.04	10

[a] An arbitrary uncertainty of ±0.5 kJ $\mathrm{mol^{-1}}$ was attached to the data from ref. 9 in the calculation of enthalpies of formation.

TABLE 3

Enthalpies of dissolution of crystalline silver acetylide in excess aqueous hydrochloric acid [a] at 298.15 K

$[Ag_2C_2(cr) + nH_2O(l)] + [(p+2)HCl + mH_2O](aq)$

$\rightarrow 2AgCl(cr) + [C_2H_2 + pHCl + (m+n)H_2O](sln)$

$m(Ag_2C_2)$ (g) [b]	m	$-\Delta H$ (kJ mol^{-1})	$-\Delta H'$ (kJ mol^{-1}) [cd]
0.03450	77153	77.85	77.55
0.04309	61773	77.4	77.1
0.05865	46986	77.7	77.4
0.08701	30592	78.8	78.5
0.08306	32058	78.1	77.8
0.06002	44348	78.9	78.6

[a] Reaction conditions were $m/(p+2) = 12.33$; and $153 < n < 383$.

[b] Mass corrected for buoyancy using $\rho(Ag_2C_2) = 4.4$ g cm^{-3}.

[c] $\Delta H'$ is the enthalpy change corrected for dilution of HCl(aq) by the water in the ampoule (nH_2O).

[d] $\langle \Delta H' \rangle = -77.8 \pm 0.6$ kJ mol^{-1}.

ampoule) to solid silver chloride. The stoichiometry of this reaction was confirmed by two methods. (i) A weighed amount of silver chloride, prepared under calorimetric conditions, was dissolved in an ammoniacal solution of ammonium chloride, potassium cyanide and nickel(II) chloride. Silver was determined by titration against 0.01 M EDTA solution using murexide as indicator. The yield of AgCl was 99.1 ± 0.8%, based on four experiments. (ii) The mass of precipitated AgCl was determined gravimetrically and yields in excess of 98% of the calculated values were obtained. The calorimetric results are summarised in Table 3.

Assuming that the enthalpy of mixing of HCl(aq) and C_2H_2(aq) is negligible (but assigning a nominal uncertainty of ± 2 kJ mol^{-1} to allow for this assumption) and after correcting for the enthalpy of dilution of HCl(aq) by the water in the ampoule ($\Delta H = -0.29 \pm 0.02$ kJ mol^{-1}, based on five determinations), the reaction equation reduces to

$$Ag_2C_2(cr) + [(p+2)HCl + mH_2O](aq) \rightarrow 2AgCl(cr) + C_2H_2(aq) + pHCl(aq) + mH_2O(l) \qquad (5)$$

Using the ancillary data from Table 2, we obtain $\Delta H_f^\ominus(Ag_2C_2$, cr, 298.15 K$) = +359.7 \pm 1.6$ kJ mol^{-1}. The maximum concentration of C_2H_2 liberated in these experiments was 0.0016 M, well below the aqueous solubility [11] at 25°C, 0.038 M.

Reaction (3)

Ampoules were loaded with solid silver acetylide, moistened with about 1 cm^3 of water to avoid explosion. The reaction was quantitative, slower than

TABLE 4

Enthalpies of reaction of crystalline silver acetylide with excess aqueous potassium cyanide [a] at 298.15 K

$$[Ag_2C_2(cr) + nH_2O(l)] + [(p+4)KCN + (m+2)H_2O](aq)$$
$$\rightarrow [2KAg(CN)_2 + 2KOH + C_2H_2 + pKCN + mH_2O](sln)$$

$m(Ag_2C_2)$ (g) [b]	m	$-\Delta H$(kJ mol^{-1}) [c]
0.09516	27972	98.7
0.07223	36851	98.1
0.06211	42856	98.75
0.07512	35434	98.3
0.08892	29934	98.0

[a] Reaction conditions were $(m+2)/(p+4) = 370.1$; and $104 < n < 214$.

[b] masses corrected for buoyancy (see Table 3).

[c] $\langle \Delta H \rangle = -98.4 \pm 0.4$ kJ mol^{-1}.

reactions (1) and (2), but substantially complete within about 3 min. The results are summarised in Table 4.

The maximum concentration of the C_2H_2 produced, 0.002 M, was again well below the solubility in water at 25 °C, 0.038 M. The enthalpy of dilution by the water in the ampoule was shown to be negligible. Assuming that the enthalpy of mixing of the products is 0 ± 2 kJ mol^{-1} and that the enthalpies of solution are the same as in pure water, the reaction equation reduces to

$$Ag_2C_2(cr) + [(p+4)KCN + (m+2)H_2O](aq)$$
$$\rightarrow 2KAg(CN)_2(aq) + 2KOH(aq) + C_2H_2(aq) + pKCN(aq) + mH_2O(l) \tag{6}$$

Using the ancillary data in Table 2, we obtain $\Delta H_f^\ominus(Ag_2C_2$, cr, 298.15 K$) = 358.2 \pm 3.2$ kJ mol^{-1}.

RESULTS AND DISCUSSION

The three values for the enthalpy of formation of Ag_2C_2(cr) at 298.15 K are in quite good agreement, and from which is obtained a weighted mean (each weighted according to the reciprocal of its variance) of +357.6 kJ mol^{-1}. Because the uncertainty intervals associated with the enthalpies of formation calculated from the reaction enthalpies already include arbitrary assignments of uncertainties for unknown heats of mixing, we prefer also to make an arbitrary estimate of the uncertainty of the weighted mean as ±5.0 kJ mol^{-1}.

The mean value differs by only 8.8 kJ mol^{-1} from that obtained by Berthelot and Delépine [3] 348.8 kJ mol^{-1}, when their experimental results are recalculated using modern ancillary data. This early work was based on only four determinations of the enthalpy of the reaction between gaseous acetylene and ammoniacal silver nitrate solution which ranged over 4.5 kJ (mol Ag_2C_2)$^{-1}$. The value $\Delta H_f^\ominus(Ag_2C_2, \text{cr}, 298.15) = 294.1$ kJ mol^{-1}, obtained by detonation calorimetry [4], cannot be reconciled with the results of the present study or the earlier work of Berthelot and Delépine.

From the value $pK = 3.46$ at 25°C determined by Vestin and Somersalo [5] for the reaction

$$Ag_2C_2(cr) + 2H^+ \rightarrow C_2H_2(g) + 2Ag^+ \quad (7)$$

and the standard electrode potential of Ag^+ (0.7991 V) [12], we obtain $\Delta G^\ominus = -114.7$ kJ mol^{-1} for the reaction

$$Ag_2C_2(cr) + H_2(g) \rightarrow C_2H_2(g) + 2Ag(cr) \quad (8)$$

Using values of $\Delta G_f^\ominus(C_2H_2$, g, 298.15 K), $S^\ominus$(C, graphite, 298.15 K) and $S^\ominus$(Ag, cr, 298.15K) taken from ref. 9, the standard entropy of silver acetylide has been calculated as $S^\ominus(Ag_2C_2$, cr, 298.15 K) = 210 J mol^{-1} K^{-1}.

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REFERENCES

1 R. Vestin and E. Ralf, Acta Chem. Scand., 3 (1949) 101.
2 T. Ya. Kosolapova, Carbides, Plenum Press, New York, 1971.
3 M. Berthelot and M. Delépine, Ann. Chim. Phys., 19 (1900) 5.
4 R. Stadler, Z. Gesamte Schiess. Sprengstoffwes., 33 (1938) 334.
5 R. Vestin and A. Somersalo, Acta Chem. Scand., 3 (1949) 125.
6 S.J. Peake, Ph.D. Thesis, University of London, 1976.
7 E.J. Prosen and M.V. Kilday, J. Res. Natl. Bur. Stand. Sect. A, 77 (1973) 581.
8 R.J. Irving and I. Wadsö, Acta Chem. Scand., 18 (1964) 195.
9 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Supplement 2.
10 J.D. Cox, D.D. Wagman, and V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
11 A. Seidell, Solubilities of Organic Compounds, van Nostrand, New York, 3rd edn., 1941.
12 A.J. de Bethune and N.A.S. Loud, Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C, C.A. Hampel, Stokie, Ill., 1964.