Thermochemistry of Ammonium Metavanadate and Sodium Metavanadate

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Appropriate ΔH values obtained by means of solution calorimetry lead to ΔH_f° = −251.7 kcal. per mole for $NH_4VO_3(c)$ and ΔH_f° = −274.2 kcal. per mole for $NaVO_3(c)$. These values are compared with results in the literature and used for calculation of ΔG_f° values for both compounds.

RECENT calorimetric measurements (*1*) that led to ΔH_f° of aqueous pervanadyl ion (VO_2^+) were carried out partly to provide a path for convenient determination of ΔH_f° values for several solid compounds of vanadium as reported in this paper for $NH_4VO_3(c)$ and $NaVO_3(c)$.

EXPERIMENTAL

The calorimetric apparatus used for these measurements was patterned after one previously described (*7*). The calorimeter consists of a Dewar vessel suspended in a brass can submerged in a water bath maintained at constant temperature. Temperatures in the calorimetric system were determined with a nickel resistance thermometer connected to a Leeds & Northrup Mueller G-2 bridge and a Beckman Model 14 breaker amplifier. The resistance thermometer and the calibration heater were contained in a glass spiral filled with mineral oil. Stirring was effected by means of a glass stirrer that passed through the center of the glass spiral. A fragile glass bulb attached to the end of the stirrer contained the weighed calorimetric sample, which was introduced to the solution by depressing the stirrer and breaking the bulb. All of the calorimetric data reported here were obtained with 950 ml. of 0.595*M* perchloric acid solution in the Dewar at 25.0° ± 0.1° C.

Samples of ammonium metavanadate and sodium metavanadate from both Fisher and McKay were recrystallized from aqueous ethanol, washed with ether, and dried under vacuum for several days. These samples showed less than 0.05% V(IV) and a purity of 100.0 ± 0.2% by permanganate titration after reduction with bisulfite. Analysis of ammonium metavanadate by weight loss on thermal decomposition to V_2O_5 showed a purity of 99.7 ± 0.2%.

RESULTS AND CALCULATIONS

The results of our calorimetric measurements are shown in Table I, where the symbol (sol) indicates that the preceding species is dissolved in 0.595*M* $HClO_4$ solution. Each value listed is the average of at least three independent measurements. The ΔH value for Reaction 1 was determined in the previous study (*1*) and confirmed during the course of this investigation.

We represent the enthalpy change for the reaction

$$\tfrac{1}{2}\,V_2O_5(c) + 4.895\,H_2O(liq) + NH_4Cl(c) = NH_4VO_3(c) + HCl\cdot 4.395\,H_2O(liq) \qquad (8)$$

by ΔH_8 and calculate the desired value as

$$\Delta H_8 = \Delta H_1 - \Delta H_2 + \Delta H_4 - \Delta H_6 + \Delta H_7 = +6.05 \text{ kcal.}$$

Combination of this value for ΔH_8 with heats of formation for H_2O, NH_4Cl, and $HCl\cdot 4.395\,H_2O$ from Wagman *et al.* (*9*) and ΔH_f° = −370.6 kcal. per mole of V_2O_5 from the work of Mah and Kelley (*5*) leads to ΔH_f° = −251.7 kcal. per mole of $NH_4VO_3(c)$. Entropy data from Kelley and King (*3*) have been used with this ΔH_f° in calculating ΔG_f° = −212.3 kcal. per mole for $NH_4VO_3(c)$.

Matignon's data (*6*) for a poorly defined reaction at 15° are the basis for several ΔH_f° values that have been calculated for NH_4VO_3. Bichowsky and Rossini (*2*) list ΔH_f° = −283.5 kcal. per mole for NH_4VO_3. This value was based on ΔH_f° = −437 kcal. per mole for V_2O_5 and other ΔH_f° values that have subsequently been shown to require revision. Rossini *et al.* (*8*) cite ΔH_f° = −251.2 kcal. per mole for NH_4VO_3. The apparent agreement of this ΔH_f° with our value above is illusory, since this value is based on ΔH_f° = −373 kcal. per mole for V_2O_5. Our recalculations with the best available auxiliary data (*5, 8, 9*) lead to ΔH_f° = −250 (± more than 1.0 kcal.) for NH_4VO_3. The uncertainty in our ΔH_f° = −251.7 kcal. per mole of $NH_4VO_3(c)$ amounts to no more than ±0.1 kcal. from our calorimetric uncertainties plus about ±0.25 kcal. from the ΔH_f° of V_2O_5 and very small contributions from uncertainties in other auxiliary data.

We represent the enthalpy change for the reaction

$$\tfrac{1}{2}\,V_2O_5(c) + 4.895\,H_2O(liq) + NaCl(c) = NaVO_3(c) + HCl\cdot 4.395\,H_2O(liq.) \qquad (9)$$

by ΔH_9 and calculate the desired value as

$$\Delta H_9 = \Delta H_1 - \Delta H_3 + \Delta H_5 - \Delta H_6 + \Delta H_7 = +6.74 \text{ kcal.}$$

Combination of this ΔH_9 with auxiliary data (*5, 9*) leads to ΔH_f° = −274.2 kcal. per mole for $NaVO_3(c)$. Kohler (*4*) has earlier reported ΔH_f° = −274.9 kcal. per mole for $NaVO_3$, based on ΔH_f° = −373 kcal. per mole for V_2O_5. Recalculation in terms of the more recent (*5*) ΔH_f° = −370.6 kcal. per mole for V_2O_5 leads to ΔH_f° = −273.7 kcal. per mole for $NaVO_3(c)$. The discrepancy between this value and our value is barely within the sum of the estimated experimental uncertainties associated with the two independent investigations. Our work was done with acidic solutions, while the earlier work was done with alkaline solutions. We suggest adoption of ΔH_f° = −273.9 kcal. per mole for $NaVO_3(c)$. Combination of this value with entropies from Kelley and King (*3*) leads to ΔG_f° = −254.4 kcal. per mole for $NaVO_3(c)$.

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Table I. Heats of Reactions

Reaction	ΔH, Kcal./Mole	Reaction
$\frac{1}{2}V_2O_5(c) + H^+(sol) = VO_2^+(sol) + \frac{1}{2}H_2O(sol)$	-3.94 ± 0.02	(1)
$NH_4VO_3(c) + 2\,H^+(sol) = VO_2^+(sol) + NH_4^+(sol) + H_2O(sol)$	-3.61 ± 0.02	(2)
$NaVO_3(c) + 2\,H^+(sol) = VO_2^+(sol) + Na^+(sol) + H_2O(sol)$	-6.69 ± 0.25	(3)
$NH_4Cl(c) = NH_4^+(sol) + Cl^-(sol)$	$+3.41 \pm 0.01$	(4)
$NaCl(c) = Na^+(sol) + Cl^-(sol)$	$+1.02 \pm 0.04$	(5)
$HCl \cdot 4.395\,H_2O(liq) = H^+(sol) + Cl^-(sol) + 4.395\,H_2O(sol)$	-2.94 ± 0.04	(6)
$4.895\,H_2O(liq) = 4.895\,H_2O(sol)$	$+0.03 \pm 0.01$	(7)

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Displacement Reactions of 3-(2-Chloroethyl)-2-oxazolidinones with Phenoxides and Mercaptides

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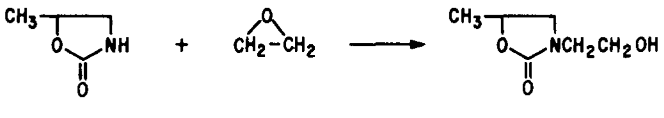
Condensation of 2-oxazolidinones with alkylene oxides at about 130° C. produces 3-(2-hydroxyalkyl)-2-oxazolidinones in excellent yields. The 3-(2-chloroethyl) derivatives react with phenoxides or mercaptides to produce the corresponding ethers or thioethers in fair to excellent yields.

THE REACTION of 3-(2-chloroethyl)-2-oxazolidinone with alkali metal alkoxides (*1, 3, 4*) or hydroxides (*1*) to produce *N*-vinyl-2-oxazolidinone has been reported. As part of a program aimed at preparing and studying derivatives of 2-oxazolidinones, the author investigated several reactions of 3-(2-chloroethyl)-2-oxazolidinones with nucleophiles such as phenoxide, mercaptide, or other divalent sulfur nucleophiles.

The required 3-(2-hydroxyalkyl)-2-oxazolidinones have been prepared by reaction of a dialkanolamine with diethyl carbonate (*6*), ethyl trichloroacetate (*9*), or carbon dioxide (*10*) or by reaction of a dialkanolamine sulfate ester with bicarbonate (*11*).

A convenient synthesis involves the direct condensation of a 2-oxazolidinone with an alkylene oxide at about 100° to 140° C. and 50 to 60 p.s.i. to give the hydroxyalkyl derivatives in excellent yield—e.g.,



Ethylene-, propylene-, or 1,2-butylene oxides all reacted.

Conversion of the *N*-(2-hydroxyalkyl)-derivatives to the chlorides was straightforward (*3, 4*). A variety of phenoxides reacted with the chlorides to give the corresponding phenyl ethers in low to moderate yields. Prolonged refluxing in ethanol (12 to 24 hours) was required. In addition to the displacement product, some dehydrochlorination product, *N*-vinyl-5-methyl-2-oxazolidinone, was obtained. Infrared analysis of the crude product indicated no hydroxyl band, demonstrating the lack of any significant amounts of C-alkylated product (*7, 8*).

Mercaptans and dithiocarbamates reacted readily to give excellent yields of products. In neither case did dehydrochlorination appear to be a factor. All of these sulfur derivatives with two methylene groups between the nitrogen and sulfur had a strong, sharp band at 7.90 to 7.95 microns in the infrared whereas in alkylthio derivatives of the type N—CH—SR this band is shifted to 8.05 microns (*5*).

EXPERIMENTAL

Materials. The phenols used were commercial materials sold by Dow Chemical Co. The thiols and sodium diethyl dithiocarbamate were obtained from Eastman.

3-(2-Hydroxyethyl)-2-oxazolidinone was prepared from diethanolamine and diethyl carbonate by the method of Homeyer (*6*), n_D^{25} 1.4830. It could not be distilled without decomposition, so the product was used without purification.