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Abstract

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STANDARD ENTHALPIES OF FORMATION OF CERTAIN PICRATES*

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The absence of reliable literature data for the enthalpies of formation of sodium, potassium, lithium, and ammonium picrates led to the need for an experimental determination of these quantities.

For this determination, the route adopted was to calculate them by the following system of thermochemical equations $(= \mathrm{K, Na, Li, NH_4})^{**}$.

1. $C_6H_2(NO_2)_3O\ _{[\ ]} + [xH_2O] = C_6H_2(NO_2)_3O\ _{[\text{p−p } C_6H_2(NO_2)_3O\ \cdot xH_2O]};\quad \Delta H_1$
2. $C_6H_2(NO_2)_3OH_{[\ ]} +\ OH_{[\text{p−p }\ OH\cdot xH_2O]} =$
   $C_6H_2(NO_2)_3O\ _{[\text{p−p } C_6H_2(NO_2)_3O\ \cdot xH_2O]} + H_2O_{[\text{p−p } C_6H_2(NO_2)_3O\ \cdot xH_2O]};\quad \Delta H_2$
3. $6C_{[\text{graphite}]} + 1^1/_2H_{2[\text{gas}]} + 1^1/_2N_{2[\text{gas}]} + 3^1/_2O_{2[\text{gas}]} = C_6H_2(NO_2)_3OH_{[\ ]};\quad \Delta H_3$
4. $_{[\ ]} + {}^1/_2O_{2[\text{gas}]} + {}^1/_2H_{2[\text{gas}]} + [xH_2O] =\ OH_{[\text{p−p }\ OH\cdot xH_2O]};\quad \Delta H_4$
5. $H_{2[\text{gas}]} + {}^1/_2O_{2[\text{gas}]} + [\text{p} - \text{p } C_6H_2(NO_2)_3O\ \cdot xH_2O] = H_2O_{[\text{p−p } C_6H_2(NO_2)_3O\ \cdot xH_2O]};\quad \Delta H_5$

6. $6C_{[\text{graphite}]} + H_{2[\text{gas}]} + 1^1/_2N_{2[\text{gas}]} + 3^1/_2O_{2[\text{gas}]} +\ _{[\ ]} =$
   $C_6H_2(NO_2)_3O\ _{[\ ]};\quad \Delta H_6$

$$\Delta H_6 = \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1 - \Delta H_5.$$

A review of the literature data on the enthalpies of the reactions entering into this system of equations showed that, for the determination of the enthalpies of solution of sodium and lithium picrates, there is a single paper (^{1}); for the enthalpies of solution of potassium and ammonium picrates and the enthalpies of neutralization, there are no literature data. The values of the enthalpy of formation of picric acid obtained in different works differ by approximately 2 kcal/mole.

Consequently, we experimentally measured the enthalpies of solution of all four picrates, the enthalpies of neutralization of solid picric acid by solutions of the corresponding hydroxides, and also, in order to refine the value, the enthalpy of combustion of picric acid. The remaining quantities needed for the calculation were estimated with sufficient reliability from literature data.

Preparations of picrates and picric acid were recrystallized three times from bidistilled water, after which they were carefully dehydrated in vacuo with heating. Thermochemical determinations were carried out with samples recrystallized twice and three times. In all cases the measurement results fell into a single series, which indicated sufficient purity of the preparations used. All operations with sodium and lithium picrates, which are readily hydrated in air, were carried out in a dry chamber. With picric acid and potassium and ammonium picrates, one could—but had to be handled in air. In determining the enthalpies of solution and neutralization, samples of picrates or picric acid were introduced into the calorimetric vessel in thin-walled glass ampoules hermetically sealed with fused stoppers made of a picein–paraffin alloy.

The enthalpy of combustion of picric acid was measured in a liquid calorimeter with a self-sealing bomb. Attempts to burn picric acid showed that the completeness of its combustion depends on many details. Apparently, incomplete combustion of picric acid in individual experiments, as well as its insufficient purity, caused the considerable scatter in the literature data. After testing various alternatives, we selected conditions ensuring complete combustion of picric acid. The picric acid sample was placed in the bomb in a thin-walled platinum crucible. The bomb was filled with a mixture of oxygen (12–14 atm) and argon (23–25 atm). No water was introduced into the bomb before the experiment. It was verified that combustion of picric acid under these conditions does not lead to the formation of carbon monoxide (analysis by means of an ammoniacal solution of $PdCl_2$, $(NH_4)_2SO_4$, $(NH_4)_2MoO_4$).

After introduction of all the necessary corrections, the enthalpy of combustion of picric acid was found to be -615.65 ± 0.32 kcal/mole, and the standard enthalpy of formation -51.14 ± 0.32 kcal/mole.

The results of determining the enthalpies of formation of the picrates, as well as intermediate quantities, are given in Table 1.

Table 1

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* O. G. Talakin took part in the experimental part of the work.

** In the case of ammonium, in reaction equations 4 and 6, instead of $_{[\ ]}$, there should appear $^1/_2 N_{2[gas]} + 2H_{2[gas]}$.

<table>
<tr><th>Cation</th><th>Picrate concentration in solution and neutralization</th><th>ΔH of solution of picrate, kcal/mole</th><th>ΔH of neutralization, kcal/mole</th><th>ΔH of formation of hydroxide solution, kcal/mole</th><th>ΔH of formation of picrate, kcal/mole</th></tr>
<tr><td>Na^+</td><td>1 : 2000 H_2O</td><td>4.84$±0.04|− 8.32±0.05|− 112.39±0.05|− 118.45±0.33||K^{+}$</td><td>1 : 3500 H_2O</td><td>12.17$±0.05|− 8.22±0.04|− 115.24±0.05|− 108.37±0.33||Li^{+}$</td><td>1 : 1000 H_2O</td></tr>
</table>

To clarify the reasons for the sharp difference between the enthalpies of solution of sodium and lithium picrates obtained by us and in work (^{1}), the enthalpy of solution of sodium picrate monohydrate was determined. To obtain sodium picrate monohydrate, a weighed portion of anhydrous picrate was kept for several days in an atmosphere saturated with water vapor at room temperature. The increase in weight of the substance corresponded to the stoichiometric ratio calculated for the monohydrate.

As a result of comparing the value obtained by us for the enthalpy of solution of sodium picrate monohydrate (8.34 ± 0.02 kcal/mole) with the data of work (^{1}) (7.66 kcal/mole), it may be asserted that the results obtained in work (^{1}) refer to an almost entirely hydrated sample of sodium picrate. An analogous situation apparently also holds for lithium picrate.

In the present work the relation 1 cal = 4.1840 abs. J has been adopted. All errors are expressed as twice the "standard deviation."

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named after M. V. Lomonosov

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CITED LITERATURE

1. F. Askew et al., J. Chem. Soc., 1934, 1368.

Note: Figure translations are in progress. See original paper for figures.