Combined study of thermochemical properties of nitroform and its salts

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A combined method for determination of the standard enthalpies of formation of nitroform and its salts was proposed. The enthalpies of dissolution of nitroform and its ammonium, hydrazinium, guanidinium, and potassium salts in water were measured. The enthalpy of combustion of hydrazinium salt of nitroform was determined by a combustion calorimetry, and its standard enthalpy of formation was calculated. The enthalpy of formation of trinitromethyl anion in indefinitely diluted aqueous solution, −24.94±0.79 kJ mol^{-1}, was calculated on the basis of the data obtained for enthalpies of formation and dissolution of ammonium and hydrazinium salts of nitroform. Standard enthalpies of formation of nitroform and its salts were calculated.

Key words: thermochemistry, enthalpy of formation, enthalpy of dissolution, calorimetry, combustion; nitroform, ammonium salt, hydrazinium salt, guanidinium salt, potassium salt.

Nitroform, $CH(NO_2)_3$, holds a special position among nitro compounds. It participates in replacement, condensation, nitration, and other reactions. A number of reactions involve trinitromethyl anion, but the thermodynamics of these reactions is still not clearly understood.

Data on the enthalpy of formation of nitroform available in the literature are contradictory. Thus, an enthalpy of formation equal to −77.82 kJ mol^{-1} has been estimated from a single experiment on combustion;[1] based on other data,[2] it is equal to −25.9 kJ mol^{-1}. According to the findings of one work,[3] the enthalpy of formation of liquid nitroform is equal to −21.3 kJ mol^{-1}, but it is equal to −9.2 kJ mol^{-1} according to another work.[2] The enthalpies of formation of solid and liquid nitroform have been found[4] to be equal to −48.5±2.1 kJ mol^{-1} and −33.1±1.7 kJ mol^{-1}, respectively.

The enthalpies of formation of only two compounds of nitroform are known, ammonium (−197.90±0.88 kJ mol^{-1})[4] and hydrazinium (−71.96 kJ mol^{-1})[5] salts. They were calculated from the energies of burning.

The aim of this study is determination of the enthalpies of formation of nitroform and its salts, $NH_4C(NO_2)_3$, $N_2H_5C(NO_2)_3$, $[(NH_2)_2{-}C{=}NH_2]C(NO_2)_3$, and $KC(NO_2)_3$.

Calorimetric measurements of the energies of combustion of nitro compounds, unlike hydrocarbons, present considerable difficulties,[6] because these compounds explode on exposure to heat or mechanical attack. Their heats of combustion are lower than those for hydrocarbons, and handling considerable amounts of the substance is dangerous because of the change from combustion to detonation.

The enthalpy of formation estimated from the energies of combustion is a small difference of two great values, the enthalpy of combustion and the sum of the enthalpies of formation of the products of combustion. Therefore, the accuracy of the enthalpies of combustion determines the accuracy of the enthalpy of formation obtained. Reliability of the enthalpy of formation found is due to the presence of admixtures and moisture in the sample studied even when precision calorimetric equipment is used and the findings are well reproduced. The enthalpy of formation for a salt can easily be determined from the enthalpy of dissolution, when the enthalpy of formation of the corresponding ions is known. The enthalpy of dissolution can be measured with a high accuracy, and it slightly depends on the content of admixtures. The accuracy of estimation and the reliability of the enthalpies of formation of salts is determined by the accuracy and reliability of the enthalpies of formation of the ions used.

It is well known[7] that the enthalpy of formation of ions in indefinitely diluted aqueous solution is independent of the nature of other ions which are present in this solution. In addition, the enthalpy of formation of the ion studied that is estimated from the enthalpy of formation and dissolution of any salts containing this ion, should be the same within the accuracy of measurements. The enthalpy of formation for salts containing ions with C, H, N, and O atoms can be estimated from the energies of their combustion. The enthalpy of formation of the ion can be determined from the enthalpies of dissolution of the salts containing this ion. Coincidence of the enthalpies of formation of the ion studied will provide evidence for the reliability of the enthalpies of formation measured by the burning technique.

A combined method, burning calorimetry and reaction calorimetry, was used in this work to determine the thermodynamic characteristics.

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This approach allows one to estimate the enthalpies of formation of the compounds by the two independent methods, to refine the values both available in the literature and obtained in this work, and to establish more reliable values of the thermochemical characteristics of the compounds.

Experimental

The sample of nitroform had m.p. 299.4 K. The weighed portions for the runs were prepared as follows. Preweighed thin-walled spherical glass ampules sealed with ground-glass joints and a test tube with nitroform were connected to a high-vacuum bench. Water was removed by multiple freezing and evacuation, and then nitroform was condensed into the ampules which were sealed with the use of a gear protecting the specimen from the flame attack. The values of the enthalpy of dissolution were independent of the sequence of filling the ampules, indicating complete removal of moisture from the sample.

Table 1. The enthalpy of dissolution (ΔH°_{sol}) of nitroform and its salts in water

m_0	ΔT	Q	q	ΔH°_{sol}	C
		$HC(NO_2)_3$			
0.11422	0.00968	15.093	0.1113	19.79	1 : 7500
0.08301	0.00699	10.899	0.0975	19.66	1 : 10200
0.06819	0.00577	8.997	0.0979	19.71	1 : 12500
0.12280	0.01029	16.040	0.0958	19.62	1 : 7000
				19.71±0.08	
		$NH_4C(NO_2)_3$			
0.07703	0.01322	18.405	0.0326	40.00	1 : 12100
0.04797	0.00821	11.407	0.0356	39.83	1 : 19400
0.14724	0.02525	35.084	0.0272	40.00	1 : 6300
0.03608	0.00618	8.587	0.0368	39.83	1 : 25900
0.04718	0.00806	11.199	0.0377	39.75	1 : 19700
				39.87±0.08	
		$N_2H_5C(NO_2)_3$			
0.10495	0.018397	28.808	0.0494	50.17	1 : 9700
0.10440	0.018226	28.540	0.0456	49.96	1 : 9700
0.12123	0.02113	33.087	0.0448	49.92	1 : 8400
0.05218	0.00915	14.325	0.0498	50.08	1 : 19500
0.05223	0.00915	14.328	0.0410	50.08	1 : 19460
				50.04±0.08	
		$CN_3H_6C(NO_2)_3$			
0.11942	0.01785	27.930	0.0435	49.08	1 : 9700
0.11267	0.01681	26.303	0.0515	48.95	1 : 10400
0.11310	0.01689	26.428	0.0448	48.99	1 : 10300
0.11635	0.01738	27.187	0.0448	48.99	1 : 10000
0.12114	0.01813	28.369	0.0431	49.12	1 : 9600
0.06057	0.00906	14.177	0.0452	49.04	1 : 19200
				49.04±0.04	
		$KC(NO_2)_3$			
0.11489	0.02486	38.980	0.0477	64.10	1 : 9100
0.10821	0.02340	36.685	0.0481	64.02	1 : 9700
0.12077	0.02621	41.097	0.0439	64.31	1 : 8700
0.11966	0.02589	40.595	0.0439	64.10	1 : 8700
0.12347	0.02670	41.866	0.0381	64.06	1 : 8500
0.06194	0.01340	21.011	0.0397	64.02	1 : 17000
				64.10±0.08	

Notes. m_0 is the weighed portion of a substance under study, g; ΔT is the corrected signal of the temperature rise in the run, arbitrary degree; Q is the quantity of heat measured in the run, J; q is the correction for evaporation of water into the free volume of the ampule, J; ΔH°_{sol} is the enthalpy of dissolution of the test substance, kJ mol^{-1}; C is the concentration of the solution, salt mol (mol of water)$^{-1}$.

The nitroform salts studied were placed into the thin-walled ampules and dried in a high vacuum. Then the ampules were sealed to prevent contact of the substance with atmosphere. Ammonium salt of nitroform was dried for 1 h at 313 K, the hydrazinium salt for 1 h at 323 K, the guanidinium salt for 30 min at 343 K, and the potassium salt for 1.5 h at 353 K.

The enthalpy of dissolution was measured on a precision hermetically sealed swinging calorimeter with an isothermal jacket.[8] The procedure of calorimetric measurements and that of experiments have been described in detail previously.[9] Table 1 presents the experimental data on the enthalpy of dissolution of nitroform and its salts in water.

Dissolution of nitroform and its salts can be presented by the stoichiometric equation

$$CatC(NO_2)_3\ (cr.) \xrightarrow[H_2O]{\Delta H^\circ_{sol}} Cat^+\ (aq.) + C(NO_2)_3^-\ (aq.), \quad (1)$$

where $Cat^+ = H^+, NH_4^+, N_2H_5^+, (NH_2)_2C{=}NH_2^+, K^+$, cr. and aq. are the crystalline state and aqueous solution, respectively.

The combustion energies of the test substances were measured on a precision automatic calorimeter with an isothermal jacket designed[10] by the N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences. The calorimeter was calibrated with the use of standard benzoic acid of K-1 grade produced by the D. I. Mendeleev Research Institute of Metrology. The O_2 initial pressure during combustion of all the substances was 3.0 MPa. Before the run, 1.0 mL of water was introduced in the calorimetric bomb. The ignition was induced by a cotton filament which in turn was ignited by incandescence of the platinum wire by the dosed current pulse. The energy of combustion of a cotton filament was measured in a series of seven runs and was found to be equal to 16601±6.6 J g^{-1}. Corrections for the heat effects during the formation of HNO_3, the heat exchange between the calorimetric vessel with an isothermal jacket, and for the energy of combustion of an auxiliary substance and a cotton filament were taken into account. The energy of combustion of hydrazinium salt of nitroform under conditions of the calorimetric bomb is shown in Table 2.

The combustion of this salt is described by the stoichiometric equation

$$\begin{aligned} N_2H_5C(NO_2)_3\ (cr.) \longrightarrow\ & CO_2\ (g.) + 2.5\ H_2O\ (l.)\ + \\ & + 2.5\ N_2\ (g.) + 0.75\ O_2\ (g.), \quad (2) \end{aligned}$$

where g. and l. correspond to the gaseous and liquid states, respectively.

Results and Discussion

According to the stoichiometry of reaction (2), the enthalpy of formation of hydrazinium salt of nitroform

Table 2. The energies of combustion ($-\Delta U'_B$) of hydrazinium salt of nitroform

m_0	ΔT	Q	q_{fil}	q_N	q_B	$-\Delta U'_B$
0.49582	2.678	4184.0	50.62	18.41	1282.0	5713.7
0.79931	2.972	4643.0	38.07	45.19		5700.3
0.79248	2.955	4616.6	71.55	27.61		5700.3
0.81176	3.024	4722.1	67.78	30.12		5696.5
0.80749	3.000	4686.9	58.58	26.78		5698.6
						5702.0±5.9

Notes. q_{fil} is the energy of combustion of a cotton filament, J g^{-1}; q_B is the energy of combustion of benzoic acid, J; q_N is the correction for the formation of HNO_3, J; $\Delta U'_B$ is the energy of combustion of a substance under conditions of the bomb, J. For the other designations, see Table 1.

was calculated from the energy of combustion equal to -1031.23 ± 1.13 kJ mol^{-1}:

$$\Delta H^\circ_f[N_2H_5C(NO_2)_3\ (cr.)] \longrightarrow \longrightarrow \Delta H^\circ_f[CO_2\ (g.)] + 2.5\ \Delta H^\circ_f[H_2O\ (l.)] - \Delta H^\circ_c, \quad (3)$$

where $\Delta H^\circ_f[N_2H_5C(NO_2)_3$ (cr.)] is the enthalpy of formation of hydrazinium salt of nitroform, ΔH°_c is the standard enthalpy of combustion of the compound, $\Delta H^\circ_f[CO_2$ (g.)], $\Delta H^\circ_f[H_2O$ (l.)] are the standard enthalpies of formation of CO_2 (g.) and H_2O (l.) equal[11] to -393.51 ± 0.13 and -285.83 ± 0.04 kJ mol^{-1}, respectively.

The enthalpy of formation of hydrazinium salt of nitroform was found to be -76.86 ± 1.13 kJ mol^{-1}.

The enthalpy of formation of this compound is related to the enthalpies of dissolution and those of formation of the ions by the following equation:

$$\Delta H^\circ_f[N_2H_5C(NO_2)_3\ (cr.)] + \Delta H^\circ_{sol} \longrightarrow \longrightarrow \Delta H^\circ_f[N_2H_5^+\ (aq.)] + \Delta H^\circ_f[C(NO_2)_3^-\ (aq.)], \quad (4)$$

where $\Delta H^\circ_f[N_2H_5]^+$ (aq.) and $\Delta H^\circ_f[C(NO_2)_3]^-$ (aq.) are the enthalpies of formation of hydrazinium and trinitromethyl ions, respectively, in an indefinitely diluted solution.

The enthalpy of formation of hydrazinium ion was obtained from the experimental values of the enthalpies of combustion and dissolution of hydrazinium nitrate and is equal to -1.46 ± 1.05 kJ mol^{-1}. The enthalpy of formation of trinitromethyl anion calculated according to Eq. (4) is equal to -25.32 ± 1.54 kJ mol^{-1}.

The enthalpy of formation of trinitromethyl anion was also determined from the thermochemical data for a salt of nitroform according to Eq. (5) and was found to be -24.77 ± 0.92 kJ mol^{-1}. The enthalpy of formation of ammonium salt of nitroform that is required for calculation was taken from the previous work[4] (-197.90 ± 0.88 kJ mol^{-1}), and the enthalpy of formation of ammonium cation was accepted to be[11] -133.26 ± 0.25 kJ mol^{-1}:

Table 3. Thermochemical properties of trinitromethane and its salts (kJ mol^{-1})

Compound	ΔH°_{sol}	ΔH°_f
$HC(NO_2)_3$	19.71±0.08	−44.65±1.13
$NH_4C(NO_2)_3$	39.87±0.08	−197.90±0.88
$N_2H_5C(NO_2)_3$*	50.04±0.08	−76.86±1.13
$CN_3H_6C(NO_2)_3$	49.12±0.04	−213.14±1.18
$KC(NO_2)_3$	64.10±0.08	−341.18±0.80

* $\Delta H^\circ_c = -1031.23$ kJ mol^{-1}.

$$\Delta H^\circ_f[NH_4C(NO_2)_3\ (cr.)] + \Delta H^\circ_{sol} \longrightarrow \longrightarrow \Delta H^\circ_f[NH_4^+\ (aq.)] + \Delta H^\circ_f[C(NO_2)_3^-\ (aq.)] \quad (5)$$

The enthalpies of formation of trinitromethyl anion obtained on the basis of independent thermochemical data are in good agreement. The weighted mean value of the enthalpy of formation of trinitromethyl anion is equal to -24.94 ± 0.79 kJ mol^{-1}.

With the use of the value found and the enthalpies of dissolution of guanidinium and potassium salts of trinitromethane determined experimentally, the enthalpies of formation of these salts were calculated (Table 3). The enthalpies of formation of guanidinium and potassium cations required for calculations were accepted to be -139.08 ± 0.88 [12] and -252.14 ± 0.08 [11] kJ mol^{-1}, respectively.

Thus, the combined method of thermochemical studies proposed and realized allows one to obtain the precision thermochemical data on both the enthalpies of formation of compounds and the enthalpies of formation of organic anions.

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