Thermochemical properties of the salts of picric and dinitrobenzoic acids

T. S. Kon'kova and Yu. N. Matyushin*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156. E-mail: gks@chph.rc.ac.ru

The enthalpies of formation and dissolution of the ammonium and guanidinium picrates and dinitrobenzoate were determined by precision calorimetry. On the basis of the data obtained, the enthalpies of formation of the anions of the acids in indefinitely diluted aqueous solutions were calculated and the enthalpy of formation of potassium picrate was estimated.

Key words: thermochemistry, calorimetry, combustion, dissolution, ions, nitrocompounds, salts of organic acids.

Estimation of the enthalpies of ion formation, in particular organic anions in indefinitely diluted solutions, is one of the most important problems of the thermochemistry of solutions.

Combining the techniques of burning calorimetry and dissolution calorimetry, one can estimate not only the enthalpies of formation of novel ions but also correct the values determined previously. This is important in those cases where the purity grade of a substance under study cannot be established. Since the enthalpy of formation of a salt is unambiguously connected to the enthalpies of formation of its constituent ions in indefinitely diluted aqueous solutions by the enthalpy of dissolution (Eq. (1)), the coincidence of the values of the enthalpy of ion formation based on the data for two or more compounds containing this ion is a reliable guarantee for correctness of the estimation of enthalpies of formation of the substances studied:

$$\Delta H^\circ_f(\mathrm{CatAn})_{cr} + \Delta H^\circ_{sol}(\mathrm{CatAn})_{cr} = \Delta H^\circ_f(\mathrm{Cat}^+)_{aq} + \Delta H^\circ_f(\mathrm{An}^-)_{aq}, \qquad (1)$$

where $\Delta H^\circ_f(\mathrm{CatAn})_{cr}$ and $\Delta H^\circ_{sol}(\mathrm{CatAn})_{cr}$ are the enthalpies of formation and dissolution of the salt in the crystalline state (cr); $\Delta H^\circ_f(\mathrm{Cat}^+)_{aq}$ and $\Delta H^\circ_f(\mathrm{An}^-)_{aq}$ are the enthalpies of formation of a cation and an anion of a salt in an indefinitely diluted solution (aq).

Experimental

The enthalpies of combustion of organic salts were determined on an AKS-3 automatic calorimeter according to the procedure described previously.[1] In some cases, the enthalpy was measured on an automatic calorimeter with an isothermic jacket designed[2] by the N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences. The calorimeters were calibrated with the use of standard benzoic acid of K-1 grade produced by the D. I. Mendeleev Research Institute of Metrology. The absence of a fixed error in the measurements was verified by combustion of the second standard, hippuric acid.[3]

The salts in the form of pressed pellets were burned in a bomb under a standard oxygen pressure of 30 atm. The ignition was induced by a current pulse from a capacitor through a platinum coil with a wire diameter of 0.1 mm which was put on the pellet. The energy of ignition in the AKS-3 calorimeter was determined from the initial and final voltages of the capacitor. In the case of the calorimeter with an isothermic jacket, the capacitor was discharged to zero; the energy of ignition remained constant as in the calibration experiments.

Some measurements were carried out in parallel on two calorimeters. For these cases, the change in the resistance of the thermometer (R) for the calorimeter with an isothermic jacket and the number of pulses of the integrator (N) for the AKS-3 calorimeter are shown in the tables.

The enthalpies of dissolution were measured on a hermetically sealed swinging reaction calorimeter with an isothermic jacket.[4] The accuracy of measurements on the reaction calorimeter was verified by the heats of dissolution of KCl in water. At a KCl : H_2O ratio equal to 1 : 1100, the heat of dissolution of KCl was 4190.0±2.4 cal mol^{-1}, which is in good agreement with the recommended[5] value of 4191.2±2.2 cal mol^{-1}. The error is expressed hereafter in the form of twice the root-mean-square deviation from the average value with a confidence interval of 0.95. The calorimeter was calibrated by the current before and after dissolution of the substance. The average value of the energy equivalent was taken for calculations.

Prior to dissolution, substances were placed in preweighed thin-walled glass ampules with ground-glass joints. The ampules were attached to a high-vacuum system and placed into thermostatted furnaces. After drying off the substance at the corresponding temperature, the ampules were sealed with a thin flame of a gas burner with the use of a gadget protecting the substance from overheating. Prior to burning and dissolution, the substances were weighed on a Bunge balance with an accuracy of $2 \cdot 10^{-6}$ g.

Tables 1—4 present the experimental data on the energies of combustion and the enthalpies of dissolution of the salts studied.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2467—2470, December, 1998.

Table 1. The energies of combustion ($-\Delta U'_B$) of the salts of picric acids

m_0	$\Delta T/N$	q_B	q_{ign}	q_N	Q	$-\Delta U'_B$
			Ammonium picrate			
0.093360	3.5991	634.50		2.07	895.06	2768.8
0.100425	3.6564	629.09		1.93	909.30	2771.1
0.223874	78.19		1.01	1.59	622.61	2769.5
0.221996	47.54		1.01	1.12	617.44	2771.7
0.107905	82.01	340.65	1.01	1.23	641.82	2770.3
						2770.3±1.1
			Guanidinium picrate			
0.181157	66.77		1.01	2.73	531.68	2914.2
0.192578	71.12		1.01	3.23	566.31	2918.7
0.177389	65.41		1.01	2.79	520.85	2914.8
0.189061	70.89		1.01	1.93	554.79	2918.9
0.197867	74.22		1.00	2.40	580.85	2918.4
						2917.0±2.0

Notes. m is the weighed portion of a substance reduced to weight in vacuum, g; ΔT is the change in temperature during the run, arbitrary degrees (the change in the voltage on the resistance thermometer); N is the number of pulses on the AKS-3 integrator; q_B is the heat of combustion of the auxiliary substance, benzoic acid, cal; q_{ig} is the heat of ignition in the AKS-3, cal; q_N is the correction for the formation of nitric acid, cal; Q is the overall heat release during the run, cal; $\Delta U'_B$ is the energy of combustion in the bomb, cal g^{-1}.

Table 2. The enthalpies of dissolution (ΔH°_{sol}) of the salts of picric acid

m_0	$-\Delta T$	Q	q_v	ΔH°_{sol}	C_m
		Ammonium picrate			
0.153193	0.15590	7.0029	0.0081	11.24	0.006
0.089144	0.09106	4.0903	0.0089	11.27	0.003
0.077088	0.07876	3.5263	0.0087	11.23	0.003
0.150541	0.15303	6.8810	0.0086	11.24	0.006
0.078990	0.08090	3.6377	0.0087	11.31	0.003
				11.25±0.02	
		Guanidinium picrate			
0.006980	0.00803	0.3616	0.0091	14.55	0.0002
0.007099	0.00821	0.3696	0.0088	14.65	0.0002
0.009340	0.01093	0.4920	0.0091	14.59	0.0003
0.011017	0.01280	0.5762	0.0085	14.71	0.0004
				14.63±0.07	
		Potassium picrate			
0.151074	0.1492	3.0792	0.0092	11.89	0.003
0.081874	0.0811	4.6629	0.0090	11.93	0.004
0.217154	0.2146	5.7737	0.0091	12.00	0.005
0.207385	0.2065	3.6217	0.0086	11.96	0.003
				11.87±0.03	

Notes. q_v is the correction for the water evaporation into a free volume of the ampule in the calorimeter for dissolution, cal; ΔH°_{sol} is the enthalpy of dissolution of the salt, kcal mol^{-1}; C_m is the molality of the solution, mol (1000 g of a solvent)$^{-1}$. For other designations, see Table 1.

Table 3. The energies of combustion ($-\Delta U'_B$) of the salts of 3,5-dinitrobenzoic acid

m_0	N	q_{ign}	q_N	Q	$-\Delta U'_B$
		Ammonium 3,5-dinitrobenzoate			
0.129079	55.16	1.18	1.08	431.62	3326.3
0.112580	48.10	1.19	1.05	376.37	3323.3
0.119391	50.93	1.18	1.01	398.52	3319.6
0.120668	51.57	1.19	1.08	403.52	3325.2
0.125054	53.44	1.19	1.15	418.16	3325.1
					3323.9±1.2
		Guanidinium 3,5-dinitrobenzoate			
0.127983	55.83	1.19	0.88	436.86	3397.3
0.139543	60.87	1.02	1.28	476.30	3396.7
0.115492	50.39	1.20	1.10	394.29	3394.1
0.117335	51.23	1.19	1.16	400.87	3396.4
					3396.1±1.4

Note. For designations, see Table 1.

Table 4. The enthalpies of dissolution (ΔH°_{sol}) of the salts of 3,5-dinitrobenzoic acid

m_0	$-\Delta T$	Q	q_{ign}	ΔH°_{sol}	C_m
		Ammonium 3,5-dinitrobenzoate			
0.035202	0.03011	1.255	0.0091	8.11	0.002
0.041310	0.03534	1.473	0.0100	8.11	0.002
0.034726	0.02970	1.238	0.0100	8.10	0.002
				8.11±0.01	
		Guanidinium 3,5-dinitrobenzoate			
0.026004	0.02496	1.0204	0.0089	10.55	0.001
0.061505	0.05879	2.4034	0.0086	10.56	0.002
0.053182	0.05095	2.0829	0.0090	10.58	0.002
0.044605	0.04277	1.7485	0.0085	10.60	0.002
				10.57±0.02	

Note. For designations, see Tables 1 and 2.

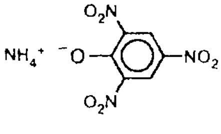
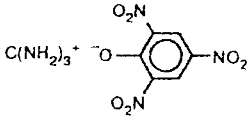
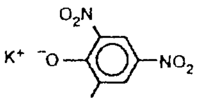
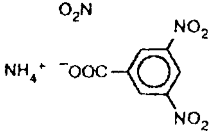
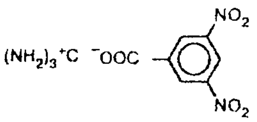
Corrections for the reduction of the energy of combustion to the standard conditions were used during calculation of the enthalpy of combustion. The enthalpies of formation of CO_2 (in the gaseous phase) and H_2O in the liquid state were accepted to be −94.051 and −68.315 kcal mol^{-1}, respectively.[6]

Results and Discussion

The enthalpies of formation of the compounds under study were calculated on the basis of the experimental data on the enthalpies of combustion with the use of the equations of the reactions; the enthalpies are shown in Table 5. The enthalpies of combustion and dissolution are also shown in Table 5. Estimation of the enthalpies of dissolution allowed one to calculate not only the enthalpies of formation of organic anions in an indefinitely diluted aqueous solution but also to evaluate the reliability of the enthalpies of formation found.

According to Eq. (1), which correlates the enthalpies of formation and dissolution of a salt with the enthalpies of formation of ions, the enthalpy of formation of an ion

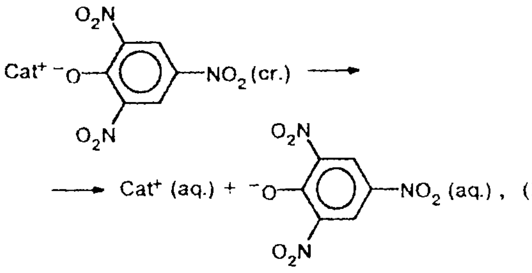
Table 5. Thermochemical characteristics of the salts studied (kcal $\mathrm{mol^{-1}}$)

Compound	$-\Delta H^\circ_c$[a]	ΔH°_{sol}[b]	ΔH°_f[c]
	679.09± ±0.25	11.25± ±0.02	−90.16± ±0.25
	836.83± ±0.59	14.63± ±0.07	−94.79± ±0.59
	—	11.87± ±0.03	−119.17± ±0.26
	759.09± ±0.27	8.11± ±0.01	−138.37± ±0.27
	917.98± ±0.38	10.57± ±0.02	−141.85± ±0.38

[a] Standard enthalpy of combustion of the compound.
[b] Enthalpy of dissolution of the salt.
[c] Standard enthalpy of formation of the compound.

in an indefinitely diluted solution obtained from thermochemical data for various salts containing this ion should be the same within the limits of experimental error.

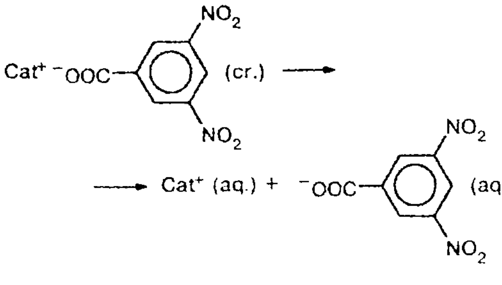
The enthalpies of dissolution of the salts of picric acid relate to the following equation:



(2)

where $\mathrm{Cat^+ = NH_4^+, K^+, (NH_2)_2C{=}NH^+_2}$.

The enthalpies of dissolution of the salts of 3,5-dinitrobenzoic acid relate to the equation



(3)

Solutions with a molar concentration less than 0.05 can be treated as indefinitely diluted solutions.[7] Therefore, all the enthalpies of dissolution measured can be assigned to indefinite dilution, because the molality of the solutions studied was varied from 0.006 to 0.0003; the two-to-threefold change in the concentration of the substance within the accuracy of measurements (0.01—0.03 kcal $\mathrm{mol^{-1}}$) did not affect the value of the enthalpy of dissolution. In addition, corrections for the reduction to indefinite dilution calculated according to the Debye—Hückel equation[8] are within the accuracy of measurements.

The enthalpy of formation of ammonium picrate was calculated from the experimental data on the energy of burning under the bomb conditions according to the equation

$$\mathrm{C_6H_6N_4O_7\ (cr.) + 4\ O_2\ (g.) \longrightarrow 6\ CO_2\ (g.) + 3\ H_2O\ (l.) + 3\ N_2\ (g.)}, \quad (4)$$

where g. and l. correspond to the gaseous and liquid states, respectively. The following values were obtained: $\Delta H^\circ_c = -679.09\pm0.25$ kcal $\mathrm{mol^{-1}}$; $\Delta H^\circ_f = -90.16\pm0.25$ kcal $\mathrm{mol^{-1}}$.

The enthalpy of combustion of guanidinium picrate was calculated according to the equation

$$\mathrm{C_7H_8N_6O_7\ (cr.) + 5.5\ O_2\ (g.) \longrightarrow 7\ CO_2\ (g.) + 4\ H_2O\ (l.) + 3\ N_2\ (g.)} \quad (5)$$

and is equal to $\Delta H^\circ_c = -836.83\pm0.59$ kcal $\mathrm{mol^{-1}}$; $\Delta H^\circ_f = -94.79\pm0.59$ kcal $\mathrm{mol^{-1}}$.

The enthalpy of combustion of ammonium 3,5-dinitrobenzoate was obtained according to Eq. (6) and is equal to -759.09 ± 0.27 kcal $\mathrm{mol^{-1}}$:

$$\mathrm{C_7H_7N_3O_6\ (cr.) + 5.75\ O_2\ (g.) \longrightarrow 7\ CO_2\ (g.) + 3.5\ H_2O\ (l.) + 1.5\ N_2\ (g.)} \quad (6)$$

The standard enthalpy of formation of this salt is equal to -138.37 ± 0.27 kcal $\mathrm{mol^{-1}}$.

The enthalpy of combustion of guanidinium 3,5-dinitrobenzoate was determined according to Eq. (7) and is equal to -917.98 ± 0.38 kcal $\mathrm{mol^{-1}}$:

$$\mathrm{C_8H_9N_5O_6\ (cr.) + 7.25\ O_2\ (g.) \longrightarrow 8\ CO_2\ (g.) + 4.5\ H_2O\ (l.) + 2.5\ N_2\ (g.)} \quad (7)$$

The standard enthalpy of formation of this salt is equal to -141.85 ± 0.39 kcal $\mathrm{mol^{-1}}$.

With the use of the values of enthalpies of formation and dissolution of ammonium and guanidinium picrates, we obtained nearly the same values of the enthalpy of formation of picrate ion (-47.06 ± 0.26 and -46.92 ± 0.63 kcal $\mathrm{mol^{-1}}$, respectively). Statistical treatment of these data taking into account the weighed errors[9] gives the value of the enthalpy of formation of picrate ion equal to -47.04 ± 0.24 kcal $\mathrm{mol^{-1}}$.

Similarly, two values of the enthalpy of formation of dinitrobenzooate anion were obtained from the thermochemical properties of ammonium and guanidinium dinitrobenzooates (−98.41±0.28 and −98.16±0.40 kcal mol^{-1}). Taking into account the weighted errors, we accepted −98.33±0.23 kcal mol^{-1} as the recommended value of the enthalpy of formation of dinitrobenzoate anion. Enthalpies of formation of ammonium and guanidinium ions equal to −31.85±0.06 kcal mol^{-1} and −33.24±0.21 kcal mol^{-1}, respectively,[6,10] were taken for calculations.

The estimation of the enthalpies of formation of organic anions extends the possibilities of experimental thermochemistry, because it allows one to obtain the enthalpies of formation of salts of these anions with various cations. Thus, the enthalpy of formation of potassium picrate was determined on the basis of the enthalpy of dissolution.

The literature data on the enthalpies of formation of two salts, potassium and ammonium picrates, are available. The enthalpy of formation of potassium picrate has been estimated[11] previously from the heat of combustion equal to −116.5 kcal mol^{-1}. The enthalpy of combustion of ammonium picrate measured[12] previously was 2762.1 cal g^{-1} under the bomb conditions. When the corrections were taken into account, this value gave an enthalpy of formation equal to −92.2 kcal mol^{-1}. Thus, the enthalpies of formation of these salts were refined.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32254a).

References

1. Yu. N. Matyushin, T. S. Kon'kova, Yu. A. Lebedev, V. Ya. Rosolovskii, and K. V. Titova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 498 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
2. Yu. N. Matyushin, T. S. Kon'kova, and A. B. Vorob'ev, USSR Inventor's Certificate 1221568, *Byul. Izobret.* [*Invent. Bull.*], 1986, No. 12 (in Russian).
3. Yu. N. Matyushin, T. S. Kon'kova, K. V. Titova, and V. Ya. Rosolovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 498 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
4. Yu. N. Matyushin, A. B. Vorob'ev, and T. S. Kon'kova, USSR Inventor's Certificate 726442, *Byul. Izobret.* [*Invent. Bull.*], 1980, No. 13 (in Russian).
5. R. L. Montgomery, *J. Chem. Thermodynamics*, 1977, **9**, 915.
6. *CODATA, Key Values for Thermodynamics*, Eds. J. D. Cox, D. D. Wagman, and V. A. Medvedev, Hemisphere, New York, 1989.
7. A. F. Vorob'ev, D. Sc. (Chem.) Thesis, Moscow State Univ., Moscow, 1971, 321 pp. (in Russian).
8. P. Debye and E. Huckel, *Phys. Z.*, 1923, **24**, 185.
9. B. N. Oleinik, *Tochnaya kalorimetriya* [*Precision Calorimetry*], Izd. Standartov, Moscow, 1973 (in Russian).
10. Yu. N. Matyushin, T. S. Kon'kova, K. V. Titova, and V. Ya. Rosolovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 787 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 713 (Engl. Transl.)].
11. E. Sarrau and P. Vieille, *Comptes Rendus*, 1881, **93**, 269.
12. L. Medard and M. Thomas, *Mem. Poudres*, 1949, **31**, 173.

Received January 13, 1998;
in revised form April 15, 1998