The energies of dissociation of the N—O bonds in pyridine 1-oxide derivatives

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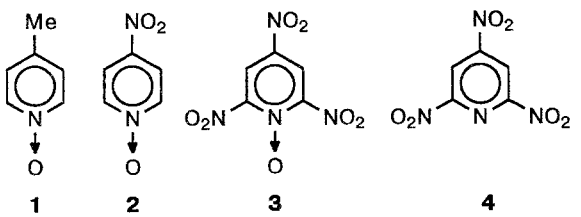
The enthalpies of combustion of some pyridine derivatives in the solid state have been measured by precision bomb calorimetry, and their enthalpies of formation have been calculated. The enthalpies of sublimation of these compounds have been determined from the experimental temperature dependences of saturated vapor pressure using the Clausius—Clapeyron equation. The enthalpies of combustion, formation, and sublimation are the following (kJ mol^{-1}): −3360.9±2.1, −0.5±2.1, and 79.1±1.3, respectively, for 4-methylpyridine 1-oxide; −2551.0±1.7, 11.7±1.7, and 89.1±2.5, respectively, for 4-nitropyridine 1-oxide; −2355.6±1.3, 102.1±1.3, and 106.3±2.9 for 2,4,6-trinitropyridine 1-oxide; and −2287.6±1.3, 34.3±1.3, and 101.7±2.9 for 2,4,6-trinitropyridine. The enthalpies of formation in the solid state and the enthalpies of sublimation of pyridine derivatives obtained together with the literature data allowed the energies of dissociation of the donor-acceptor N—O bond in pyridine 1-oxides to be calculated.

Key words: enthalpies of formation; enthalpies of sublimation; dissociation energy; pyridine 1-oxides; calorimetry.

Thermochemical studies of heterocyclic compounds containing an N—O bond involving the nitrogen atom of a heterocyclic ring indicate that the energy of dissociation of this bond varies over wide limits.[1—7] The present work is devoted to a determination of the dissociation energies of the donor-acceptor N—O bonds in pyridine 1-oxide derivatives and an evaluation of the effects of the chemical natures and positions of functional groups on these values.

At this time only pyridine 1-oxide[7] has been studied by the thermochemical method. The dissociation energy of the N—O bond in this compound was found to be 301.7 kJ mol^{-1}.



We experimentally determined the thermochemical properties of 4-methylpyridine 1-oxide (**1**), 4-nitropyridine 1-oxide (**2**), 2,4,6-trinitropyridine 1-oxide (**3**), and 2,4,6-trinitropyridine (**4**).

The resulting thermochemical data were used to evaluate the dissociation energies of the N—O bonds in compounds **1—3**.

Experimental

The compounds were specially synthesized for the thermochemical studies and were chromatographically pure.

The heats of combustion of these compounds were measured on two precision microcalorimeters with an isothermal shell and a static calorimetric bomb.[8—9]

The calorimeters were calibrated by the combustion of the reference K-1 benzoic acid having a heat of combustion of 26434.9±4.5 J g^{-1}. The combustion of compound **1** was carried out on a calorimetric unit with a heat number of 4225.50 J (condit. deg.)$^{-1}$, and compounds **2—4** were burned on a unit with a heat number of 1042.44 J (condit. deg.)$^{-1}$. The heat numbers of the calorimeters obtained were checked by the combustion of secondary reference compounds, succinic and hippuric acids.

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The initial oxygen pressure was 3 MPa for the combustion of all of the compounds; prior to an experiment, 1.0 mL of water was introduced in the calorimetric bomb. To ensure the complete combustion of compounds **1—3**, they were burned together with an auxiliary compound, the reference benzoic acid.

Ignition was carried out by a dosed current pulse from a special device through a platinum wire. The procedure used in this work, which takes into account the peculiarities of the combustion of nitrogen- and oxygen-containing organic compounds, have been described in detail previously.[4—10] The necessary corrections for the thermal effect of the formation of nitric acid, for heat evolution due to the auxiliary compounds, and for the heat exchange between the calorimetric vessel and the shell, *etc.* were applied in the calculations.

The heats of combustion were measured for the following reactions.

$$\underset{\mathbf{1}}{C_6H_7ON\ (s.)} + 7.25\ O_2\ (g.) \longrightarrow 6\ CO_2\ (g.) + 3.5\ H_2O\ (l.) + 0.5\ N_2\ (g.) \quad (1)$$

$$\underset{\mathbf{2}}{C_5H_4O_3N_2\ (s.)} + 4.5\ O_2\ (g.) \longrightarrow 5\ CO_2\ (g.) + 2.0\ H_2O\ (l.) + N_2\ (g.) \quad (2)$$

$$\underset{\mathbf{3}}{C_5H_2O_7N_4\ (s.)} + 2.0\ O_2\ (g.) \longrightarrow 5\ CO_2\ (g.) + H_2O\ (l.) + 2.0\ N_2\ (g.) \quad (3)$$

$$\underset{\mathbf{4}}{C_5H_2O_6N_4\ (s.)} + 2.5\ O_2\ (g.) \longrightarrow 5\ CO_2\ (g.) + H_2O\ (l.) + 2.0\ N_2\ (g.) \quad (4)$$

After introducing the Washbern corrections and the work of gas expansion, the enthalpies of combustion under standard conditions were determined (Table 1).

Based on Eqs. (1—4) for combustion in oxygen using the enthalpies of the formation of CO_2(g.) and H_2O(l.), equal to[11] -393.51 ± 0.13 and -285.830 ± 0.040 kJ mol^{-1}, respectively, we found the enthalpies of formation of the compounds studied (see Table 1).

The enthalpies of sublimation of the pyridine derivatives were determined from the Clausius—Clapeyron equation using the experimentally obtained temperature dependences of the saturated vapor pressure.

In the calculations, we neglected the volume of the condensed phase and considered the vapor to be ideal at low pressures.

The pressure of the saturated vapor of 4-methylpyridine 1-oxide was studied by the effusion Knudsen method based on the measurement of the rate by weight of the outflow of vapor from the chamber through a hole in the membrane (the thickness of the membrane l was 0.05 mm, and the diameter of the hole d was 0.518 mm), and the vapor pressures of other compounds were studied by free evaporation *in vacuo* (the Langmuir method). The measurements were carried out using procedures specially developed for studying heavy organic compounds.[12]

To verify the reliability of the procedures used, we determined the parameters of sublimation of the standard K-1 benzoic acid. The enthalpy of sublimation calculated for this compound was in good agreement with the reference book data.[13]

The temperature intervals of the measurements, the temperature dependences of the vapor pressure, and the enthalpies of sublimation and formation of the compounds in the gas state are listed in Table 2.

Results and Discussion

The experimental values for the enthalpies of formation of the pyridine derivatives in the condensed state and the enthalpies of their sublimation obtained in this work, together with the literature data, allowed us to calculate the energies of dissociation of the donor-acceptor nitrogen—oxygen bonds in pyridine 1-oxides.

The energies of dissociation of N—O bonds in compounds **1—3** were calculated from the equations presented below using the Δ_fH°(g.) values for 4-methylpyridine (**5**) and 4-nitropyridine (**6**).

$$D_1(\text{N—O}) = \Delta_fH^\circ(\text{g.})\ [\mathbf{5}] + \Delta_fH^\circ(\text{g.})\ [\text{O}] - \Delta_fH^\circ(\text{g.})\ [\mathbf{1}] \quad (5)$$

$$D_2(\text{N—O}) = \Delta_fH^\circ(\text{g.})\ [\mathbf{6}] + \Delta_fH^\circ(\text{g.})\ [\text{O}] - \Delta_fH^\circ(\text{g.})\ [\mathbf{2}] \quad (6)$$

Table 1. The energies of combustion ($-\Delta U_b'$), the enthalpies of combustion ($-\Delta_cH^\circ$(s.)), and the enthalpies of formation ($-\Delta_fH^\circ$(s.)) of pyridine derivatives in the condensed state

Compound	The number of runs	$-\Delta U_b'$ /J g^{-1}	$-\Delta_cH^\circ$(s.) /kJ mol^{-1}	$-\Delta_fH^\circ$(s.) /kJ mol^{-1}
1	6	30800.2±19.3	3360.9±2.1	−0.5±2.1
2	8	18252.7±11.7	2551.0±1.7	11.7±1.7
3	6	10309.8±5.4	2355.6±1.3	102.1±1.3
4	6	10756.6±5.4	2287.6±1.3	34.3±1.3

Table 2. The temperature dependence of the vapor pressure, the enthalpy of sublimation ($-\Delta_sH^\circ$), and the standard enthalpy of formation in the gas phase ($-\Delta_fH^\circ$(g.)) of pyridine derivatives

Compound	ΔT/K	$\log(p/\text{Pa}) = A - B/T$	Δ_sH° /kJ mol^{-1}	Δ_fH°(g.) /kJ mol^{-1}
1	316—341	$\lg p = 12.215 - 4124/T$	79.1±1.3	78.6±2.5
2	311—335	$\lg p = 12.198 - 4663/T$	89.1±2.5	100.8±3.0
3	377—403	$\lg p = 11.771 - 5561/T$	106.3±2.9	208.4±3.2
4	335—357	$\lg p = 12.823 - 5302/T$	101.7±2.9	136.0±3.2

$$D_3(\text{N—O}) = \Delta_f H^\circ(\text{g.})\ [4] + \\ + \Delta_f H^\circ(\text{g.})\ [\text{O}] - \Delta_f H^\circ(\text{g.})\ [3] \qquad (7)$$

The calculations were carried out with $\Delta_f H^\circ$(g.) [O] = 249.18±0.10 kJ mol^{-1} (see Ref. 11), $\Delta_f H^\circ$(g.) [5] = 104.1±0.9 kJ mol^{-1} (see Ref. 14). The enthalpy of formation of 4-nitropyridine in the gas state has been evaluated by the known methods[12,15] and amounted to $\Delta_f H^\circ$(g.) [6] = 126.4 kJ mol^{-1}.

The following magnitudes of the energies of dissociation of the nitrogen—oxygen donor-acceptor bonds (D(N—O)/kJ mol^{-1}) in the pyridine 1-oxides studied were obtained: 301.7 (pyridine 1-oxide),[7] 274.7 (**1**), 274.8 (**2**), 176.8 (**3**).

The energies of dissociation for compounds **1—3** in the gas state vary over the 176.8—301.7 kJ mol^{-1} interval. The greatest value was found for unsubstituted pyridine 1-oxide. The introduction of substituents of various natures, *viz.*, electron acceptors or donors, in position 4 results in a decrease in the energy of dissociation to 274.8 kJ mol^{-1}.

The substantial decrease in the dissociation energy (to 176.8 kJ mol^{-1}) in 2,4,6-trinitropyridine 1-oxide is due to the effect of the nitro groups in positions 2 and 6 of the pyridine ring.

The numerical values for the thermochemical characteristics and for the energies of dissociation of *N*-oxides of heterocyclic compounds obtained in the present work and in other studies may serve as a base for various calculations and for predicting the properties of compounds of these classes.[16]

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