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Enthalpies of combustion of phenazine *N*-oxide, phenazine, benzofuroxan, and benzofurazan: the dissociation enthalpies of the (N–O) bonds

M. LUISA P. LEITÃO,[a] G. PILCHER,

Department of Chemistry, University of Manchester.
Manchester M13 9PL, U.K.

W. E. ACREE Jr., ANITA I. ZVAIGZNE, SHERYL A. TUCKER,

Department of Chemistry, University of North Texas,
Denton, TX 76203-5068, U.S.A.

and MARIA D. M. C. RIBEIRO DA SILVA

Departamento de Química, Faculdade de Ciências,
Universidade do Porto, P-4000 Porto, Portugal

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The standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion at 298.15 K were measured by static-bomb calorimetry and the standard molar enthalpies of sublimation at 298.15 K were measured by microcalorimetry for phenazine, benzofurazan, and their corresponding *N*-oxides:

	$-\Delta_c H_m^\circ(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$	$\Delta_{cr}^{g} H_m^\circ/(\mathrm{kJ \cdot mol^{-1}})$
Phenazine	6102.4 ± 1.2	91.8 ± 2.1
Phenazine *N*-oxide	6062.7 ± 4.5	100.0 ± 1.3
Benzofurazan	3168.5 ± 1.1	64.4 ± 1.6
Benzofuroxan	3151.6 ± 1.2	79.6 ± 1.7

From the standard molar enthalpies of formation of the gaseous compounds, the molar dissociation enthalpies of the (N–O) bonds were derived: $D(\mathrm{N{-}O})/(\mathrm{kJ \cdot mol^{-1}})$: phenazine *N*-oxide, 280.7 ± 5.6; benzofuroxan, 250.9 ± 3.0.

1. Introduction

The dissociation enthalpy of the $\overset{+}{\mathrm{N}}{-}\overset{-}{\mathrm{O}}$ dative covalent bond shows large variations depending on the molecular environment in the immediate vicinity of the bond. Values of $D(\mathrm{N{-}O})/(\mathrm{kJ \cdot mol^{-1}})$ have been reported for $C_6H_5N{=}N(O)C_6H_5$, (321.5 ± 2.9);(1) $C_6H_5CH{=}N(O)C_6H_5$, (264.9 ± 3.0);(1) $C_6H_5CH{=}N(O)C(CH_3)_3$, (285.9 ± 3.6);(2) and in pyridine *N*-oxide, (301.7 ± 2.8).(3) The present paper reports the

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[a] Departamento de Química, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal.

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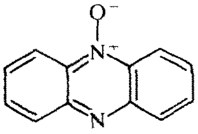
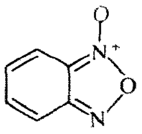
values of D(N–O) in the quite different molecular environments in phenazine N-oxide (I) and in benzofuroxan (II):


(I)


(II)

The D(N–O) values were derived from the standard molar enthalpies of formation of the gaseous compounds and the corresponding compounds minus the oxygen atoms, from measurements of the molar enthalpies of combustion of the crystalline compounds by static-bomb calorimetry and the molar enthalpies of sublimation measured by microcalorimetry.

2. Experimental

Phenazine (PHEN) (Aldrich) was purified by repeated zone-melting. Phenazine N-oxide (PHENO) was synthesized by the method of Pachter and Kloetzel(4) for 2-chlorophenazine 5-oxide, except that nitrobenzene replaced 4-chloronitrobenzene as a starting reagent.(5) Additional samples of this compound were obtained from two commercial sources (Aldrich and Frinton Laboratories). All samples were recrystallized several times from (benzene + hexane), but it proved impossible to purify phenazine N-oxide effectively by crystallization. Mixed crystals of phenazine and phenazine N-oxide have been reported by Glazer.(6) It was assumed that the sole impurity in the sample was phenazine, and from the amount of carbon dioxide produced in the combustion experiments, the proportion of phenazine in the sample was determined. The different sources led to samples with a mass percentage of phenazine ranging from 4.5 to 15.2 and after making the appropriate corrections, the derived energies of combustion were consistent. Benzofuroxan (BFNO) was prepared by dissolving 2-nitroaniline in ethanolic potassium hydroxide followed by the slow addition of 5 mass per cent aqueous sodium hypochlorite as described by Jarrar.(7) The resulting precipitate was initially recrystallized from ethanol and further purified by repeated recrystallizations from (benzene + hexane). Benzofurazan (BFN) was prepared by the reduction of benzofuroxan with hydroxylamine using the procedure reported by Gaughran *et al.*(8) and the sample was purified by steam distillation followed by repeated zone-melting. The average ratios of the mass of carbon dioxide produced by the sample in the combustion experiments to that calculated from its mass with uncertainties of twice the standard deviation of the mean together with the densities of the samples were: PHEN: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.303$, $(1.0000 + 0.0001)$; BFN: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.40, 0.9995 \pm 0.0002)$; BFNO: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.48$, (1.0001 ± 0.0002). The static-bomb calorimeter, subsidiary apparatus, and technique have been described.(1,9) The energy equivalent of the calorimeter was determined from the combustion of benzoic acid, NBS standard reference material 39i, for which under standard bomb conditions, $-\Delta_c u/(\mathrm{J \cdot g^{-1}}) = (26434 \pm 3)$. From 12 calibration experiments, $\varepsilon(\mathrm{calor}) = (15540.98 \pm 0.47)\ \mathrm{J \cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. The solid samples, in pellet form, were ignited at (298.150 ± 0.001) K in oxygen at 3.04 MPa with 1 cm^3 of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a 1281 μF capacitor when discharged from 40 V through the platinum ignition wire. For the cotton-thread fuse, empirical formula $\mathrm{CH}_{1.686}\mathrm{O}_{0.843}$, $-\Delta_c u^\circ/(\mathrm{J \cdot g^{-1}}) = 16250$.(10) Corrections for nitric-acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$ for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2}$, $\mathrm{O_2}$, and $\mathrm{H_2O(l)}$.(11) The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced. For each compound, $-(\partial u/\partial p)_T$ at 298.15 K was assumed to be $0.1\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$, a value typical for most organic solids. For each compound, $\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.*(10) and the molar masses used were those recommended by the IUPAC Commission.(12)

The standard molar enthalpies of sublimation were measured by the "vacuum sublimation" drop-microcalorimetric method.(13) Samples (about 5 mg) of each compound in a thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter and then removed from the hot-zone by vacuum sublimation. The observed standard molar enthalpies of sublimation $\{H^\circ_m(\mathrm{g}, T) - H^\circ_m(\mathrm{cr}, 298.15\ \mathrm{K})\}$ were corrected to 298.15 K using $\Delta^{T}_{298.15\,\mathrm{K}} H^\circ_m(\mathrm{g})$ estimated by applying a group method based on the values of Stull *et al.*(14) The microcalorimeter was calibrated *in situ* for these experiments by making use of the reported enthalpy of sublimation of naphthalene: $(72.51 \pm 0.01)\ \mathrm{kJ \cdot mol^{-1}}$.(15) The method was tested by measuring $\Delta^{\mathrm{g}}_{\mathrm{cr}} H^\circ_m(\mathrm{I_2})/(\mathrm{kJ \cdot mol^{-1}}) = (62.3 \pm 0.3)$ in agreement with the CODATA value $(62.4 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$.(16)

3. Results and discussion

Results for a typical combustion experiment on each compound are given in table 1. $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 2897.0 g, the mass assigned for $\varepsilon(\mathrm{calor})$; $\Delta U(\mathrm{carbon})$ was based on $-33\ \mathrm{kJ \cdot g^{-1}}$ for the specific energy of combustion of C(cr);(10) ΔU_Σ is the correction to the standard state; the remaining terms are as previously described.(10) As samples were ignited at (298.150 ± 0.001) K,

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(\mathrm{H_2O, l})\Delta m(\mathrm{H_2O}) + \varepsilon_f\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign}),$$

where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. For phenazine *N*-oxide, the amount of phenazine impurity was determined from the mass of carbon dioxide produced. The mass of sample was corrected for the presence of this impurity and the energy of combustion of the impurity was calculated using $-\Delta_c u^\circ$(phenazine, cr). The individual values of $-\Delta_c u^\circ$ together with the mean and its standard deviation are given in table 2. For phenazine *N*-oxide the mass percentage of the phenazine impurity is also listed. Table 3 lists the derived standard molar enthalpies of combustion and of formation in the crystalline and gaseous states. In accordance with normal thermochemical practice, the

TABLE 1. Typical combustion experiments ($p^\circ = 0.1$ MPa)

	PHEN	PHENO	BFN	BFNO
$m(\mathrm{CO_2}$, total$)/\mathrm{g}$	2.96468	2.66157	1.75071	2.14023
$m(\mathrm{cpd})/\mathrm{g}$	1.01001	0.93870[a]	0.79491	1.10192
$m(\mathrm{fuse})/\mathrm{g}$	0.00294	0.00282	0.00202	0.00288
$\Delta T_{\mathrm{ad}}/\mathrm{K}$	2.20861	1.97146	1.35734	1.64814
$\varepsilon_{\mathrm{f}}/(\mathrm{J\cdot K^{-1}})$	13.3	13.1	12.6	13.3
$\Delta m(\mathrm{H_2O})/\mathrm{g}$	0.0	0.1	0.0	0.1
$-\Delta U(\mathrm{IBP})/\mathrm{J}$	34352.2	30664.0	21110.4	25635.2
$\Delta U(\mathrm{HNO_3})/\mathrm{J}$	97.9	94.3	85.4	57.3
$\Delta U(\mathrm{carbon})/\mathrm{K}$	—	0.7	1.3	19.8
$\Delta U(\mathrm{ign})/\mathrm{J}$	1.1	1.1	1.1	1.1
$\Delta U_{\Sigma}/\mathrm{J}$	21.2	19.7	12.5	18.0
$-m(\mathrm{fuse})\Delta_{\mathrm{c}}u^\circ/\mathrm{J}$	47.8	45.8	32.8	46.8
$-\Delta U(\mathrm{phenazine})/\mathrm{J}$	—	1506.9	—	—
$-\Delta_{\mathrm{c}}u^\circ(\mathrm{cpd})/(\mathrm{J\cdot g^{-1}})$	33846.5	30891.7	26394.2	23171.3

[a] Sample mass after correction for phenazine impurity of 0.04452 g.

uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. For phenazine *N*-oxide, the additional uncertainty arising from the correction for impurity has been arbitrarily allowed for by trebling the conventional uncertainty. To derive $\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}$ from $\Delta_{\mathrm{c}}H^\circ_{\mathrm{m}}$ the standard molar enthalpies of formation: for $\mathrm{H_2O(l)}$: $-(285.83 \pm 0.04)\ \mathrm{kJ\cdot mol^{-1}}$ and for $\mathrm{CO_2(g)}$: $-(393.51 \pm 0.13)\ \mathrm{kJ\cdot mol^{-1}}$, were used.(16)

Comparison with previous measurements is made in table 4. For benzofurazan there is agreement with Arshadi(18) for both the molar enthalpy of combustion and of sublimation but for phenazine there is disagreement with Arshadi for both quantities, but agreement with McEachern *et al.*(19) for the enthalpy of sublimation. Arshadi purified phenazine by sublimation, McEachern *et al.* by crystallization, whereas we have used zone-melting, and the discrepancies probably arise from differences in purity of the samples.

TABLE 2. Values of $-\Delta_{\mathrm{c}}u^\circ$ at 298.15 K ($p^\circ = 0.1$ MPa); mass fraction w of impurity in phenazine *N*-oxide

PHEN	PHENO		BFN	BFNO
		$-\Delta_{\mathrm{c}}u^\circ/(\mathrm{J\cdot g^{-1}})$		
	$10^2\,w$			
33846.5	15.20	30896.0	26394.2	23171.3
33848.9	14.35	30902.9	26395.2	23159.5
33843.6	5.63	30878.9	26380.4	23169.2
33844.1	4.53	30891.7	26406.0	23181.5
33852.1	14.80	30891.7	26378.6	23170.0
33859.8	14.53	30898.3	26383.4	23188.4
		$-\langle\Delta_{\mathrm{c}}u^\circ\rangle/(\mathrm{J\cdot g^{-1}})$		
33849.2 ± 2.5		30893.3 ± 3.4	26389.6 ± 4.3	23173.3 ± 4.2

TABLE 3. Derived molar values at 298.15 K ($p^\circ = 0.1$ MPa)

	$\frac{-\Delta_c U^\circ_m(\mathrm{cr})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{-\Delta_c H^\circ_m(\mathrm{cr})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_f H^\circ_m(\mathrm{cr})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta^g_{cr} H^\circ_m}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta_f H^\circ_m(\mathrm{g})}{\mathrm{kJ\cdot mol^{-1}}}$
PHEN	6099.9 ± 1.2	6102.4 ± 1.2	237.0 ± 2.0	91.8 ± 2.1	328.8 ± 2.9
PHENO	6061.5 ± 4.5	6062.7 ± 4.5	197.3 ± 4.6	100.0 ± 1.3	297.3 ± 4.8
BFN	3169.7 ± 1.1	3168.5 ± 1.1	235.8 ± 1.4	64.4 ± 1.6	300.2 ± 2.1
BFNO	3154.1 ± 1.2	3151.6 ± 1.2	218.9 ± 1.4	79.6 ± 1.7	298.5 ± 2.2

The dissociation enthalpies of the (N–O) bonds are derived from the enthalpies of reactions such as

$$\mathrm{R{-}\overset{+}{N}{-}\overset{-}{O}(g) = R{-}N(g) + O(g)},$$

requiring $\Delta_f H^\circ_m(\mathrm{O, g})/(\mathrm{kJ\cdot mol^{-1}}) = (249.17 \pm 0.10)$.(16) The derived D(N–O)/(kJ·mol^{-1}) values are for phenazine N-oxide; (280.7 ± 5.6); and for benzofuroxan: (250.9 ± 3.0).

A reaction scheme has been employed by Holm and his colleagues(20, 21) to order various oxygenated species including N-oxides in terms of their abilities to transfer oxygen atoms in molybdenum(IV) to molybdenum(VI) conversions, by considering the enthalpy of reaction:

$$\mathrm{RN(g) + \tfrac{1}{2}O_2(g) = RN^+{-}O^-(g)}.$$

These particular transfers are important in the biological chemistry of molybdenum complexes, and the order of decreasing enthalpy of reaction provides a method for predicting the feasibility of such conversions. Limited enthalpies of formation have restricted the scale to a few select compounds. The N-oxides so far studied give negative values for this enthalpy of reaction in decreasing order: benzofuroxan $-(1.7 \pm 3.0)$ kJ·mol^{-1}; $C_6H_5CH{=}N(O)C_6H_5$, $-(15.7 \pm 3.0)$ kJ·mol^{-1}; phenazine N-oxide, $-(31.5 \pm 5.6)$ kJ·mol^{-1}; $C_6H_5CH{=}N(O)C(CH_3)_3$, $-(46.7 \pm 3.6)$ kJ·mol^{-1}; pyridine N-oxide, $-(52.7 \pm 2.8)$ kJ·mol^{-1}; and $C_6H_5N{=}N(O)C_6H_5$ $-(72.7 \pm 2.9)$ kJ·mol^{-1}.

The (N–O) bond lengths in these and related molecules have been reported: r(N–O)/pm: phenazine N-oxide, 124;(22) benzofuroxan, 123.5;(23) and pyridine N-oxide, 135.(24) Interestingly, these bond lengths do not correlate with the D(N–O)

TABLE 4. Comparison with previous measurements

	$-\Delta_c H^\circ_m(\mathrm{cr})/(\mathrm{kJ\cdot mol^{-1}})$	$\Delta^g_{cr} H^\circ_m/(\mathrm{kJ\cdot mol^{-1}})$	Reference
Phenazine	6112.8 ± 6.3		17
	6109.1 ± 1.7	99.9 ± 2.5	18
		90.3 ± 1.6	19
	6102.4 ± 1.2	91.8 ± 2.1	This work
Benzofurazan	3168.5 ± 0.4	64.9 ± 1.7	18
	3168.5 ± 1.1	64.4 ± 1.6	This work

values, but such correlations would require that removal of the oxygen atom from the various *N*-oxides did not alter neighbouring (C–H), (C–C), *etc.* bond lengths or affect strain energies. Crystallographic results rarely locate hydrogen atoms with great accuracy. In phenazine *N*-oxide the van der Waals radii of the 4,6-H atoms overlap that of the O atom attached to the 5-N atom.(25) Upon dissociation there may be reduction of steric strain-energy resulting in diminution of *D*(N–O) compared with that for pyridine *N*-oxide, where the 2,6-H atoms point away from the dative covalent (N–O) bond. *D*(N–O) for benzofuroxan is considerably smaller than the values determined so far for *N*-oxides, and further demonstrates the large effect that the molecular environment has on the (N–O) bond. The electronegative oxygen atom adjacent to the dative (N–O) bond may withdraw electron density from the bond causing reduction in the dissociation enthalpy. More convincing consideration of these dissociation enthalpies must await further measurements or theoretical calculations.

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