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Enthalpies of combustion of 2,4,6-trimethylbenzonitrile, 2,4,6-trimethylbenzonitrile *N*-oxide, 2,6-dimethylbenzonitrile, 2,4,6-trimethoxybenzonitrile, and 2,4,6-trimethoxybenzonitrile *N*-oxide: the dissociation enthalpies of the (N–O) bonds

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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 the following aromatic nitriles and aromatic nitrile *N*-oxides:

2,4,6-Trimethylbenzonitrile	5530.7 ± 0.9	82.9 ± 1.6
2,4,6-Trimethylbenzonitrile *N*-oxide	5563.1 ± 0.8	77.5 ± 3.7
2,4,6-Trimethoxybenzonitrile	5150.0 ± 0.9	112.6 ± 2.0
2,4,6-Trimethoxybenzonitrile *N*-oxide	5187.1 ± 1.6	91.9 ± 1.9
2,6-Dimethylbenzonitrile	4890.1 ± 1.0	83.9 ± 2.8

From the standard molar enthalpies of formation of the gaseous compounds, the molar dissociation enthalpies of the (N–O) bonds were derived: $D(\mathrm{N{-}O})/(\mathrm{kJ \cdot mol^{-1}})$: trimethylbenzonitrile *N*-oxide, (222.2 ± 4.6); trimethoxybenzonitrile *N*-oxide, (232.8 ± 3.8).

1. Introduction

The dissociation enthalpy of the $\mathrm{N^+{-}O^-}$ dative covalent bond shows large variations depending on the molecular environment in the immediate vicinity of the

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bond. The present paper reports the values of $D(\mathrm{N{-}O})$ in two aromatic nitrile *N*-oxides, $\mathrm{Ar{-}C{\equiv}N^{+}{-}O^{-}}$. The $D(\mathrm{N{-}O})$ values were derived from the standard molar enthalpies of formation of the gaseous *N*-oxides and the corresponding nitriles, 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

2,6-Dimethylbenzonitrile (DMeBzCN), 2,4,6-trimethylbenzonitrile (TMeBzCN), (Frinton Laboratories), and 2,4,6-trimethoxybenzonitrile (TMeOBzCN) (Aldrich) were recrystallized several times from methanol and (benzene + hexane). Subsequently, repeated sublimation *in vacuo* was required to purify TMeBzCN as the recrystallized sample gave unacceptable low carbon-dioxide recoveries on combustion. TMeBzCNO and TMeOBzCNO were prepared by the procedures reported by Grundmann and Dean,(1) and Beltrame *et al.*(2) Hydroxylamine hydrochloride was added to a hot solution of 2,4,6-trimethylbenzaldehyde (or 2,4,6-trimethoxybenzaldehyde) in methanol and the resulting aldoxime was converted to the nitrile *N*-oxide with sodium hypobromite. Both compounds were recrystallized three times from (benzene + hexane): for TMeOBzCNO, approximately 10 g of the synthesized material was supplemented with 4 g of a commercial sample (Frinton Laboratories) before recrystallization. Elemental analyses on the purified samples were in excellent agreement with calculated values: for TMeBzCNO, mass percentages found: C, 74.58; H, 6.94; N, 8.62; calculated: C, 74.51; H, 6.88; N, 8.69; for TMeOBzCNO found: C, 57.36; H, 5.34; N, 6.61; calculated: C, 57.41; H, 5.30; N, 6.70. The densities ρ of the samples and 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 were:

TMeBzCN: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.15$, (0.9985 ± 0.0001);
TMeBzCNO: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.12$, (0.9994 ± 0.0001);
TMeOBzCN: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.36$, (1.0000 ± 0.0001);
TMeOBzCNO: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.26$, (1.0011 ± 0.0002);
DMeBzCN: $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.47$, (1.0000 ± 0.0001).

The static-bomb calorimeter, subsidiary apparatus, and technique have been described.(3,4) The energy equivalent of the calorimeter was determined from the combustion of benzoic acid, NBS SRM 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 $\mathrm{cm^3}$ 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 $\mathrm{CH_{1.686}O_{0.843}}$, $-\Delta_c u^\circ/(\mathrm{J \cdot g^{-1}}) = 16250$.(5) 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 $\mathrm{H_2O(l)}$.(6)

Corrections for carbon formation were based on $-33\ \mathrm{kJ \cdot g^{-1}}$ for the specific energy of combustion of C(cr).(5) 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. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced. For each compound, $\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.*(5) and the molar masses used were those recommended by the IUPAC Commission.(7)

The standard molar enthalpies of sublimation, except for TMeOBzCNO, were measured by the "vacuum sublimation" drop-microcalorimetric method.(8) 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.*(9) The microcalorimeter was calibrated *in situ* for these experiments by making use of the reported enthalpy of sublimation of naphthalene: $(72.51 \pm 0.01)\ \mathrm{kJ \cdot mol^{-1}}$.(10)

TMeOBzCNO decomposed under the conditions employed in the drop microcalorimetric method. The enthalpy of sublimation was derived from the variation of vapour pressure with temperature using a Knudsen-type cell placed in a Calvet Standard Microcalorimeter as reported by Yang Meng-Yan and Pilcher.(11) On applying high vacuum to the cell, heat was absorbed to sublime solid to replace that vapour lost by effusion, and in a steady-state, the rate of heat absorption was directly proportional to the rate of effusion and hence could be related to the vapour pressure. The apparatus was calibrated in the range 298 K to 388 K using the reported vapour pressure of naphthalene,(10) benzoic acid,(12) and anthraquinone.(13)

The derived vapour-pressure equations were:

$$\text{TMeOBzCN (350 K to 373 K): } \ln(p/\mathrm{Pa}) = (34.426 \pm 0.019) - (13480 \pm 250)(\mathrm{K}/T),$$

$$\text{TMeOBzCNO (358 K to 373 K): } \ln(p/\mathrm{Pa}) = (28.417 \pm 0.009) - (10919 \pm 200)(\mathrm{K}/T).$$

The enthalpies of sublimation at the mean temperatures were corrected to 298.15 K using $\Delta^g_{cr} C^\circ_p = -2R$,(14) giving $\Delta^g_{cr} H^\circ_m(\mathrm{TMeOBzCNO})/(\mathrm{kJ \cdot mol^{-1}}) = (91.9 \pm 1.9)$ and $\Delta^g_{cr} H^\circ_m(\mathrm{TMeOBzCN})/(\mathrm{kJ \cdot mol^{-1}}) = (113.1 \pm 2.1)$; for the latter the drop-microcalorimetric method gave $(112.0 \pm 1.9)\ \mathrm{kJ \cdot mol^{-1}}$, hence we accept the mean value $(112.6 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$.

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 ε(calor); ΔU_Σ is the correction to the standard state; the remaining terms are as previously described.(5) As samples were ignited at (298.150 ± 0.001) K, $\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(\mathrm{H_2O, l})\Delta m(\mathrm{H_2O}) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\mathrm{ign})$; where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. The individual values of $-\Delta_c u^\circ$ together with the mean and its

TABLE 1. Typical combustion results at 298.15 K ($p^\circ = 0.1$ MPa)

	TMeBzCN	TMeBzCNO	TMeOBzCN	TMeOBzCNO	DMeBzCN
$m(\mathrm{CO_2}$, total)/g	1.70496	2.46611	1.87858	1.94033	2.63951
m(cpd.)/g	0.56157	0.90204	0.82304	0.92126	0.87297
m(fuse)/g	0.00237	0.00215	0.00232	0.00240	0.00220
ΔT_{ad}/K	1.37862	2.00906	1.41735	1.47548	2.09930
$\varepsilon_{\mathrm{f}}/(\mathrm{J \cdot K^{-1}})$	13.5	13.7	13.5	13.6	13.7
$\Delta m(\mathrm{H_2O})$/g	0.4	0.5	0.3	−0.1	0.8
$-\Delta U$(IBP)/J	21444.9	31253.4	22046.8	22948.8	32659.9
$\Delta U(\mathrm{HNO_3})$/J	37.0	99.7	61.5	65.7	93.8
ΔU(ign)/J	1.1	1.1	1.1	1.1	1.1
ΔU(carbon)/J	8.6	—	—	14.5	—
ΔU_{Σ}/J	10.4	16.4	14.0	15.4	17.2
$-m\Delta_{\mathrm{c}}u^\circ$(fuse)/J	38.5	34.9	37.7	39.0	35.7
$-\Delta_{\mathrm{c}}u^\circ(\mathrm{cpd.})/(\mathrm{J \cdot g^{-1}})$	38049.8	34480.1	26649.5	24795.6	37244.3

standard deviation are given in table 2. 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 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. 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.(17)

TABLE 2. Individual values of $-\Delta_{\mathrm{c}}u^\circ$ at 298.15 K ($p^\circ = 0.1$ MPa)

TMeBzCN	TMeBzCNO	TMeBzCN	TMeOBzCNO	DMeBzCN
		$-\Delta_{\mathrm{c}}u^\circ/(\mathrm{J \cdot g^{-1}})$		
38049.8	34480.1	26649.5	24795.6	37244.3
38060.0	34488.8	26645.6	24793.5	37236.5
38052.3	34483.2	26644.5	24787.8	37238.2
38050.4	34481.1	26652.5	24790.9	37251.2
38045.2	34483.5	26645.4	24784.6	37251.9
38046.6	34480.3	26642.6	24797.6	37250.6
		$\langle -\Delta_{\mathrm{c}}u^\circ/(\mathrm{J \cdot g^{-1}}) \rangle$		
38050.7 ± 2.1	34482.8 ± 1.3	26646.7 ± 1.5	24791.7 ± 2.0	37245.5 ± 2.8

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

	$\frac{-\Delta_{\mathrm{c}}U^\circ_{\mathrm{m}}(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{-\Delta_{\mathrm{c}}H^\circ_{\mathrm{m}}(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta^{\mathrm{g}}_{\mathrm{cr}}H^\circ_{\mathrm{m}}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{g})}{\mathrm{kJ \cdot mol^{-1}}}$
TMeBzCN	5525.1 ± 0.9	5530.7 ± 0.9	23.5 ± 1.6	82.9 ± 1.6	106.4 ± 2.3
TMeBzCNO	5558.7 ± 0.8	5563.1 ± 0.8	55.9 ± 1.5	77.5 ± 3.7	133.4 ± 4.0
TMeOBzCN	5148.2 ± 0.9	5150.0 ± 0.9	−357.2 ± 1.6	112.6 ± 2.0	−244.6 ± 2.6
TMeOBzCNO	5186.5 ± 1.6	5187.1 ± 1.6	−320.1 ± 2.1	91.9 ± 1.9	−228.2 ± 2.8
DMeBzCN	4885.7 ± 1.0	4890.1 ± 1.0	62.3 ± 1.5	83.9 ± 2.8	146.2 ± 3.2

The enthalpies of combustion and of sublimation of TMeBzCN were reported by Meier *et al.*:(18) $-\Delta_c H^\circ_m/(\mathrm{kJ \cdot mol^{-1}}) = (5513.6 \pm 2.8)$ and $\Delta^g_{cr} H^\circ_m/(\mathrm{kJ \cdot mol^{-1}}) = (78.0 \pm 1.2)$ in disagreement with the values reported here. Meier *et al.* based their result on the mass of compound, whereas our value was based on the CO_2 produced. Even after repeated sublimation *in vacuo*, the CO_2 recovery ratio for this compound was (0.9985 ± 0.0001), and this could account for the Meier *et al.* value of $-\Delta_c H^\circ_m$ being about 0.2 per cent lower than our value.

Because of the difficulty of purification of TMeBzCN, DMeBzCN was measured to provide the possibility of estimating $\Delta_f H^\circ_m$(TMeBzCN, g): fortunately this was not required. The increment in $\Delta_f H^\circ_m(g)$ for substitution of a methyl group into the benzene ring *para* to a substituent X, depends on whether X is electron donating or electron withdrawing with respect to the benzene ring. Values of $-\Delta\{\Delta_f H^\circ_m(g)\}/(\mathrm{kJ \cdot mol^{-1}})$ for substituting methyl *para* to X in the benzene ring are: OH, (29.0 ± 1.8);(19) H, (32.8 ± 0.4);(19) NO_2, (36.6 ± 4.0);(19) and CN, (39.8 ± 3.9). Examination of such trends are important in improving methods for estimation of $\Delta_f H^\circ_m(g)$ of substituted benzenes.

The dissociation enthalpies of the (N–O) bonds are derived from the enthalpy of the reaction: $\mathrm{Ar{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O}(g) = Ar{-}C{\equiv}N(g) + O(g)}$, requiring $\Delta_f H^\circ_m(\mathrm{O, g})/(\mathrm{kJ \cdot mol^{-1}}) = (249.17 \pm 0.10)$.(17) The $D(\mathrm{N{-}O})/(\mathrm{kJ \cdot mol^{-1}})$ values are for TMeBzCNO, (222.2 ± 4.6) and for TMeOBzCNO, (232.8 ± 3.8). As the electron-donating power of the methoxy group is greater than that for methyl, an increase in the electron density in the benzene ring in the trimethoxy compound could account for the increased D(N–O) in TMeOBzCNO.

These D(N–O) values are the smallest reported as far for organic N-oxides and do not correlate with bond lengths. $r(\mathrm{N{-}O})/\mathrm{pm} = 124.9$ has been reported by Shiro *et al.*(20) in 4-methoxy-2,6-dimethylbenzonitrile N-oxide, a derivative similar to those studied here. We may compare the values:

	$D(\mathrm{N{-}O})/(\mathrm{kJ \cdot mol^{-1}})$	$r(\mathrm{N{-}O})/\mathrm{pm}$
trans-Azoxybenzene	321.5 ± 2.9(4)	127.9(21)
cis-Azobenzene dioxide	262.8 ± 3.3(22)	126.8(23)
Pyridine N-oxide	301.7 ± 2.8(24)	135(25)
Phenazine N-oxide	280.7 ± 5.6(26)	124(27)
Benzofuroxan	250.9 ± 3.0(26)	123.5(28)
TMeBzCNO	$222.2 + 3.8$	124.9(20)

In nitrile N-oxides, the (N–O) bond will assume some double-bond character because of resonance structures of the form: $\mathrm{Ar{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O}}$, $\mathrm{Ar{-}\overset{-}{C}{=}\overset{+}{N}{=}O}$, and on dissociation the (C–N) bond will revert to its full triple-bond character, thus causing reduction in D(N–O). Shiro *et al.*(20) state that in aromatic nitrile N-oxides there is no evidence that the (C–N) bond is lengthened by the formation of the (N–O) bond; however, the effect may be small and within the limits of experimental uncertainty.

A reaction scheme due to Holm and his colleagues,(29, 30) orders oxygenated species, including N-oxides, in terms of their abilities to transfer oxygen atoms in Mo(IV) to Mo(VI) conversions by considering the enthalpy of the reaction:

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

The arylnitrile *N*-oxides are the first *N*-oxides to give a positive enthalpy of reaction. The *N*-oxides may be ordered: TMeBzCNO, (27.0 ± 4.6) kJ · mol^{-1}; TMeOBzCNO, (17.4 ± 3.8) kJ · mol^{-1}; benzofuroxan, −(1.7 ± 3.0) kJ · mol^{-1}; $C_6H_5CH{=}N(O)C_6H_5$, −(15.7 ± 3.0) kJ · mol^{-1}; phenazine *N*-oxide, −(31.5 ± 5.6) kJ · mol^{-1}; $C_6H_5CH{=}N(O)C(CH_3)_3$, −(46.7 ± 3.6) kJ · mol^{-1}; pyridine *N*-oxide, −(52.7 ± 2.8) kJ · mol^{-1}; $C_6H_5N{=}N(O)C_6H_5$, −(72.7 ± 2.9) kJ · mol^{-1}. 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.

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