Enthalpies of combustion of four N-phenylmethylene benzenamine N-oxide derivatives, of N-phenylmethylene benzenamine, and of *trans*-diphenyldiazene N-oxide: the dissociation enthalpy of the (N–O) bonds

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The standard ($p^\circ = 101.325$ kPa) molar enthalpies of combustion at 298.15 K were measured by static-bomb calorimetry and the standard molar enthalpies of sublimation were measured by microcalorimetry for four N-phenylmethylene benzenamine N-oxide derivatives, for N-phenylmethylene benzenamine, for for *trans*-diphenyldiazene N-oxide:

	$-\Delta_c H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{sub}} H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
$C_6H_5CH{=}N(O)C_6H_5$	6835.7 ± 1.0	115.0 ± 0.8
$4\text{-}CH_3OC_6H_4CH{=}N(O)C_6H_5$	7346.1 ± 1.2	130.6 ± 1.2
$4\text{-}(CH_3)_2CHC_6H_4CH{=}N(O)C_6H_5$	8780.0 ± 1.5	127.2 ± 1.7
$2\text{-}HOC_6H_4CH{=}N(O)C_6H_5$	6625.1 ± 1.1	116.5 ± 1.4
$C_6H_5CH{=}NC_6H_5$	6872.7 ± 1.1	93.7 ± 0.9
$C_6H_5N{=}N(O)C_6H_5$	6394.7 ± 1.5	98.6 ± 0.9

From the standard molar enthalpies of formation of the gaseous compounds, the dissociation enthalpies of the (N–O) bonds were derived, in N-phenylmethylene benzenamine N-oxide, $D(\text{N–O})/(\text{kJ} \cdot \text{mol}^{-1}) = (264.9 \pm 3.0)$ and in *trans*-diphenyldiazene N-oxide, $D(\text{N–O})/(\text{kJ} \cdot \text{mol}^{-1}) = (321.5 \pm 2.9)$. The intramolecular hydrogen-bond enthalpy in N-2-hydroxyphenylmethylene benzenamine N-oxide was assessed as (30 ± 7) kJ $\cdot$ mol^{-1}.

1. Introduction

Organic compounds containing the imino N-oxide function, such as nitrones, azoxy compounds, and heterocyclic N-oxides, generally exhibit photochemical reactivity. Photoprocesses which have been reported include syntheses of oxaziridines and

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oxazepines, initiation of cross-linking of polymeric materials, and the use of imino N-oxides as enzyme-mimicking photochemical oxidizers.[1] Despite the importance of the imino N-oxide group in photochemical reactions, very few precise thermochemical quantities are available for compounds which contain the dative covalent bond ($\geqslant \overset{+}{N} - \overset{-}{O}$). Byström[2] reported the standard molar enthalpies of formation of di-*n*-propyldiazene N-oxide and of di-*t*-butyldiazene N-oxide which contain the azoxy group [$-N=N(O)-$]. The present paper reports the standard molar enthalpy of combustion and the standard molar enthalpy of sublimation of four N-phenylmethylene benzenamine N-oxide derivatives which contain the nitrone group [$-CH=N(O)-$], of N-phenylmethylene benzenamine which contains the imine group [$-CH=N-$], and of *trans*-diphenyldiazene N-oxide which contains the azoxy group. From the standard molar enthalpies of formation of the gaseous compounds, the dissociation enthalpy of the (N−O) bond present in the nitrone group can be derived and compared with the dissociation enthalpy of the (N−O) bond present in the azoxy group in the dialkyldiazene N-oxides and in *trans*-diphenyldiazene N-oxide.

2. Experimental

The preparation and purification of the samples were carried out at Kent State University and the calorimetric measurements were made at Manchester University. The phenylmethylene benzenamine N-oxide derivatives were prepared by the condensation of N-phenylhydroxylamine with the appropriate aldehyde according to the method of Wheeler and Gore.[3] No attempt was made to maximize the yields which varied between 40 and 70 per cent. The compounds were crystallized at least four times from (benzene + *n*-hexane) to yield products with melting temperatures within 1 K of values reported in the literature. N-phenylmethylene benzenamine was prepared by the condensation of benzaldehyde with aniline.[4] The product was purified by three crystallizations from light petroleum. *Trans*-diphenyldiazene N-oxide (Lancaster Syntheses) was purified by repeated crystallization from methanol followed by sublimation *in vacuo*. For convenience, the names of the compounds have been abbreviated: N-phenylmethylene benzenamine N-oxide by NIT; N-4-methoxyphenylmethylene benzenamine N-oxide by 4MeONIT; N-4-isopropylphenylmethylene benzenamine N-oxide by 4IPRNIT; N-2-hydroxy-phenylmethylene benzenamine N-oxide by 2OHNIT; N-phenylmethylene benzenamine by BENZAN; and *trans*-diphenyldiazine N-oxide by AZOX. Table 1 lists the microanalysis results for each sample and the densities used to calculate the mass from the apparent mass in air. The average ratios of the mass of carbon dioxide produced by the sample in the combustion experiment to that calculated from its mass were: NIT, (1.0000 ± 0.0001); 4MeONIT, (1.0001 ± 0.0001); IPRNIT, (1.0001 ± 0.0001); 2OHNIT, (1.0002 ± 0.0001); BENZAN, (0.9996 ± 0.0001); AZOX, (1.0003 ± 0.0003).

The static-bomb calorimeter, subsidiary apparatus, and technique have been described.[5] The platinum resistance thermometer has been replaced by a quartz thermometer (Hewlett-Packard HP2804) interfaced to a Commodore 8096

TABLE 1. Mass-percentage analyses, densities at 298.15 K, and molar masses

	$\rho/(\text{g}\cdot\text{cm}^{-3})$	C	H	N	C	H	N	$M/(\text{g}\cdot\text{mol}^{-1})$
			found			expected		
NIT	1.32	79.25	5.51	7.02	79.17	5.62	7.10	197.2360
4MeONIT	1.30	73.95	5.68	6.20	73.99	5.77	6.16	227.2622
4iPRNIT	1.32	80.29	7.22	5.79	80.30	7.16	5.85	239.3164
2OHNIT	1.35	73.28	5.31	6.45	73.23	5.20	6.57	213.2354
BENZAN	1.11	86.20	6.30	7.75	86.15	6.12	7.73	181.2366
AZOX	1.16	72.80	5.10	14.01	72.71	5.08	14.13	198.2238

microcomputer programmed to compute the adiabatic temperature change. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid, NBS standard reference sample 39i, having a specific energy of combustion under standard bomb conditions of $-(26434\pm3)$ $\text{J}\cdot\text{g}^{-1}$. From six calibration experiments, $\varepsilon(\text{calor} = (15537.87\pm0.68)$ $\text{J}\cdot\text{K}^{-1}$, 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 across a 1281 μF capacitor when discharged from about 40 V through the platinum ignition wire. For the cotton thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^\circ = 16250$ $\text{J}\cdot\text{g}^{-1}$.[6] The corrections for nitric acid formation were based on -59.7 $\text{kJ}\cdot\text{mol}^{-1}$ for the molar energy of formation of 0.1 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 from N_2, O_2, and $H_2O(l)$.[7] The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse; $\Delta_c u^\circ$ for each compound was calculated by the procedure given by Hubbard et al.[6] For each compound, $(\partial u/\partial p)_T$ was assumed to be -0.1 $\text{J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$, a value typical for most organic solids. The relative atomic masses used were those recommended by the IUPAC commission.[8]

The standard molar enthalpies of sublimation were measured by the "vacuum sublimation" drop microcalorimetric method.[9] Samples (about 5 mg) of each compound contained in a small thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter held at 414 K, and then removed from the hot-zone by vacuum sublimation. The observed standard molar enthalpies of sublimation $\{H_m^\circ(\text{g}, 414\text{ K})-H_m^\circ(\text{cr}, 298.15\text{ K})\}$ were corrected to 298.15 K using $\{H_m^\circ(\text{g}, 414\text{ K})-H_m^\circ(\text{g}, 298.15\text{ K})\}$ for the gaseous compounds estimated by applying a group method based on the data of Stull et al.[10] The microcalorimeter was calibrated in situ for these experiments at 414 K by making use of the reported enthalpy of sublimation of naphthalene.[10]

3. Results and discussion

Results for a typical combustion experiment on each compound are given in table 2; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from

TABLE 2. Typical combustion experiments ($p° = 101.325$ kPa)

	NIT	4MeONIT	4IPRNIT	2OHNIT	BENZAN	AZOX
$m(CO_2$, total)/g	2.76674	2.49345	2.77295	2.86635	2.91268	2.53662
m'(cpd.)/g	0.95211	0.91802	0.94100	1.06645	0.92103	0.95020
m'''(fuse)/g	0.00304	0.00282	0.00259	0.00308	0.00319	0.00313
ΔT_{ad}/K	2.12992	1.91584	2.22686	2.14006	2.25371	1.98174
$\varepsilon_f/(J \cdot K^{-1})$	13.7	13.7	14.1	13.8	13.8	13.4
$\Delta m(H_2O)$/g	0.0	0.0	−0.1	−0.7	−0.2	−2.1
$-\Delta U$(IBP)/J	33123.6	29794.3	34631.1	33275.2	35047.1	30801.2
$\Delta U(HNO_3)$/J	75.0	72.4	76.1	81.0	70.7	92.5
ΔU(ign)/J	1.1	1.1	1.1	1.1	1.1	1.1
ΔU_Σ/J	20.4	18.4	19.2	22.2	20.6	17.6
$-\{m'''\Delta_c u°$(fuse)$\}$/J	49.4	45.8	42.1	50.0	51.8	50.8
$-\{\Delta_c u°$(cpd.)$\}/(J \cdot g^{-1})$	34636.4	32305.0	36655.3	31057.2	37895.5	32245.0

2897.0 g, the mass assigned for ε(calor); ΔU_Σ is the correction to the standard state; the remaining terms are as previously defined.[5] As samples were ignited at (298.150 ± 0.001) K, $-\Delta U$(IBP) $= -\{\varepsilon$(calor)$+c_p(H_2O$, l)$\Delta m(H_2O)$ $+\varepsilon_f\}\Delta T_{ad}$. The individual values of $-\Delta u°$ together with the mean and standard deviation of the mean are given in table 3. Table 4 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 of formation are twice the overall standard deviations of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_f H_m°$ from $\Delta_c H_m°$ the standard molar enthalpies for formation: for H_2O(l): $-(285.83 \pm 0.04)$ kJ $\cdot$ mol^{-1} and for CO_2(g): $-(393.51 \pm 0.13)$ kJ $\cdot$ mol^{-1}, were used.[11]
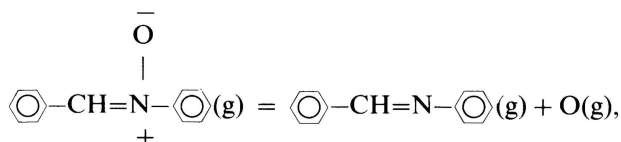
The only recently reported value for any of the compounds studied in this paper was for N-phenylmethylene benzenamine by Coates and Sutton[12] who gave $-\Delta_c H_m°$(cr) $= (6855.5 \pm 7.1)$ kJ $\cdot$ mol^{-1}, lower than the value reported here, (6872.7 ± 1.1) kJ $\cdot$ mol^{-1}. Coates and Sutton did not use calorimetric equipment designed for high-precision measurements and their value was based on the mass of

TABLE 3. Values of $-\Delta_c u°$ at 298.15 K ($p° = 101.325$ kPa)

NIT	4MeONIT	4IPRNIT	2OHNIT	BENZAN	AZOX
		$-\Delta_c u°/(J \cdot g^{-1})$			
34635.7	32302.5	36655.3	31054.8	37887.6	32241.9
34636.4	32300.5	36659.7	31049.4	37885.1	32258.4
34636.6	32305.0	36650.3	31058.0	37892.6	32243.6
34631.6	32310.0	36653.5	31051.9	37892.0	32240.3
34634.4	32305.8	36647.6	31057.2	37889.6	32245.0
34637.5	32307.8	36658.2	31058.3	37895.5	32256.4
		$-\langle\Delta_c u°\rangle/(J \cdot g^{-1})$			
34635.4 ± 0.9	32305.3 ± 1.4	36654.1 ± 1.9	31054.9 ± 1.5	37890.4 ± 1.5	32247.6 ± 3.2

sample burned and not on the carbon dioxide produced. Kharasch[13] gave for trans-diphenyldiazene N-oxide, $-\Delta_c H_m^\circ(cr) = 6416.6$ kJ · mol⁻¹ from measurements made in the last century and this differs from the value reported here, (6394.7 ± 1.5) kJ · mol⁻¹.

The dissociation enthalpy of the (N—O) bond in N-phenylmethylene benzenamine N-oxide is given by the enthalpy of the reaction:

$$\underset{+}{\underset{|}{\overset{\overset{\displaystyle\bar{O}}{|}}{\bigcirc\!\!-CH\!=\!N\!-\!\bigcirc}}}(g) \;=\; \bigcirc\!\!-CH\!=\!N\!-\!\bigcirc(g) + O(g),$$

for which the derivation requires $\Delta_f H_m^\circ(O, g)/(kJ \cdot mol^{-1}) = (249.17 \pm 0.10)$.[11] $D(N—O)$ for the other diphenylnitrones was derived by estimating the molar enthalpies of formation of the appropriate $R—\bigcirc—CH\!=\!N\!-\!\bigcirc$ gaseous molecules using the Cox scheme,[14] i.e. assuming the enthalpy increment of substitution for R into $C_6H_5CH=NC_6H_5$ to be the same as for substitution of R into benzene. To calculate these enthalpy increments the following standard molar enthalpies of formation were used: benzene(g), (82.9 ± 0.3); methoxybenzene(g), $-(68.0 \pm 1.1)$; isopropylbenzene(g), (4.0 ± 1.0); and phenol(g), $-(96.3 \pm 0.8)$ kJ · mol⁻¹.[15] The derived values of $D(N—O)$ are given in table 5, where the uncertainties include an additional ± 5 kJ · mol⁻¹ arising from the estimation procedure.
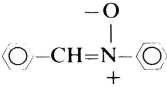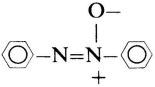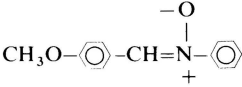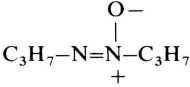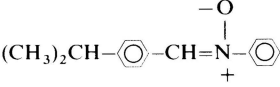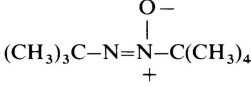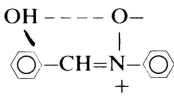
The $D(N—O)$ values in the diphenylnitrones are unaffected by substitution in the 4-position. The increase in $D(N—O)$ for N-2-hydroxyphenylmethylene benzenamine N-oxide is due to intramolecular hydrogen bonding as suggested by Wheeler and Core[3] from spectroscopic evidence: the increase, (30 ± 7) kJ · mol⁻¹, can be ascribed to the intramolecular hydrogen-bond enthalpy.

$D(N—O)$ in trans-diphenyldiazene N-oxide was derived using for trans-diphenyldiazene, $\Delta_f H_m^\circ(cr)/(kJ \cdot mol^{-1}) = (320.5 \pm 1.7)$,[16] and $\Delta_{sub} H_m^\circ/(kJ \cdot mol^{-1}) = (93.8 \pm 0.1)$.[17] Table 5 also lists the $D(N—O)$ values in di-n-propyldiazene N-oxide and in di-t-butyldiazene N-oxide derived from the standard molar enthalpies of formation of these gaseous N-oxides: $-(31.0 \pm 1.4)$ kJ · mol⁻¹ and

TABLE 4. Derived standard molar values at 298.15 K ($p^\circ = 101.325$ kPa)

	$\dfrac{-\Delta_c U_m^\circ(cr)}{kJ \cdot mol^{-1}}$	$\dfrac{-\Delta_c H_m^\circ(cr)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_f H_m^\circ(cr)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_{sub} H_m^\circ}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_f H_m^\circ(g)}{kJ \cdot mol^{-1}}$
NIT	6831.3 ± 1.0	6835.7 ± 1.0	148.0 ± 2.0	115.0 ± 0.8	263.0 ± 2.1
4MeONIT	7341.8 ± 1.2	7346.1 ± 1.2	-20.9 ± 2.2	130.6 ± 1.2	109.7 ± 2.5
4IPRNIT	8771.9 ± 1.5	8780.0 ± 1.5	54.3 ± 2.6	127.2 ± 1.7	181.5 ± 3.1
2OHNIT	6622.0 ± 1.1	6625.1 ± 1.1	-62.6 ± 2.0	116.5 ± 1.4	53.9 ± 2.4
BENZAN	6867.1 ± 1.1	6872.7 ± 1.1	185.0 ± 2.0	93.7 ± 0.9	278.7 ± 2.2
AZOX	6392.2 ± 1.5	6394.7 ± 1.5	243.4 ± 2.2	98.6 ± 0.9	342.0 ± 2.4

TABLE 5. D(N—O) values at 298.15 K

Structure	D(N—O)/(kJ·mol^{-1})	Structure	D(N—O)/(kJ·mol^{-1})
⟨C$_6$H$_5$⟩—CH=N$^+$(—O$^-$)—⟨C$_6$H$_5$⟩	264.9 ± 3.0	⟨C$_6$H$_5$⟩—N=N$^+$(O$^-$)—⟨C$_6$H$_5$⟩	321.5 ± 2.9
CH$_3$O—⟨C$_6$H$_4$⟩—CH=N$^+$(—O$^-$)—⟨C$_6$H$_5$⟩	267.5 ± 6.1	C$_3$H$_7$—N=N$^+$(O$^-$)—C$_3$H$_7$	331.5 ± 3.8
(CH$_3$)$_2$CH—⟨C$_6$H$_4$⟩—CH=N$^+$(—O$^-$)—⟨C$_6$H$_5$⟩	267.3 ± 6.4	(CH$_3$)$_3$C—N=N$^+$(O$^-$)—C(CH$_3$)$_4$	321.2 ± 4.2
⟨C$_6$H$_4$(OH)⟩—CH=N$^+$(—O$^-$ ···· HO)—⟨C$_6$H$_5$⟩	294.8 ± 6.0		

$-(107.6 \pm 2.1)$ kJ·mol^{-1}, respectively, as reported by Byström,[2] and of the corresponding diazenes: di-*n*-propyldiazene(g),[18] (51.3 ± 3.5) kJ·mol^{-1} and di-*t*-butyldiazene(g),[19] $-(35.6 \pm 3.6)$ kJ·mol^{-1}. D(N—O) is about 10 kJ·mol^{-1} less in di-*t*-butyldiazene *N*-oxide than in di-*n*-propyldiazene *N*-oxide consistent with steric strain energy in the former molecule as shown by a molecular mechanics study by Byström.[20]

D(N—O) in *trans*-diphenyldiazene *N*-oxide is of similar magnitude to that in the dialkyldiazene *N*-oxides but is approximately 60 kJ·mol^{-1} greater than that in the diphenylnitrones. Hiberty *et al.*[21,22] reported valence-bond treatments of some 1,3-dipoles including the structures >C=N̶—O and ⎯N=N̶—O, but as the main purpose of these calculations was to derive weights of structural formulae, including both ionic and diradical structures, the results can be used only to give qualitative explanations. The calculations showed that the structural weight [⎯N̲—N̶̲$^+$=O], 0.134 was almost double that of [⎯C̲H—N̶$^+$=O], 0.074. This suggests that the double-bond character of the (N—O) bond will be greater in azoxy compounds than in nitrones and it is reasonable to expect this to be an important factor in the strengthening of the (N—O) bond in azoxy compounds relative to nitrones. Because of the large number of possible contributing structures in these compounds, a quantitative theoretical calculation would be probably so complex that an explanation of the difference in D(N—O) between azoxy compounds and nitrones in simple terms may not be available.

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