The Dissociation Enthalpies of Terminal (N–O) Bonds in Organic Compounds

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Dissociation enthalpies of terminal (N–O) bonds, $DH°(N–O)$, in amine N-oxides, nitrile N-oxides, pyridine N-oxides, quinoxaline 1,4-dioxides, furoxans, nitrones, azoxy-derivatives, azo-N,N-dioxides, nitro compounds, nitramines, and alkyl nitrates are calculated from published enthalpy of formation, enthalpy of sublimation, and enthalpy of vaporization data. For each class of organic compounds, the calculated $DH°(N–O)$ values are critically evaluated. The derived $DH°(N–O)$ values can be used to estimate enthalpies of formation of other molecules in each of these classes of organic compounds. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1851531]

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1. Introduction

Organic compounds that contain terminal (N–O) bonds have the potential to act as oxidizing agents, which leads to a variety of applications. As an example, the use of C-nitroso compounds (–C–N=O) as spin traps is well known for the indirect detection of short-lived free radicals, R·, which has justified much interest in their properties especially those related to spectroscopic, photochemical, and kinetic studies. The spin-trapping technique[1–4] involves an addition reaction of such a radical to an efficient scavenger (spin trap) to form a long-lived radical (spin adduct). C-nitroso compounds react rapidly and irreversibly with many radicals according to Eq. (1)

$$RNO + R· = RR·NO. \qquad (1)$$
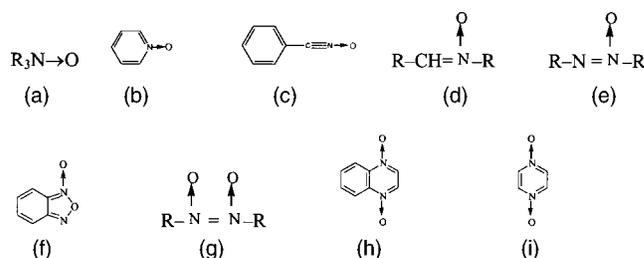
FIG. 1. Structural formula of different types of compound containing a terminal (N–O) bond [(a) amine N-oxide; (b) pyridine N-oxide; (c) benzonitrile N-oxide; (d) nitrone; (e) azoxy compound; (f) furoxan; (g) azo-N,N-dioxide; (h) quinoxaline 1,4-dioxide; (i) pyrazine 1,4-dioxide].

The product is easily detected and its esr spectrum contains information about the radical R·. Thermochemical measurements on C-nitroso compounds will assist in prediction of their spin trapping potential.

As a second application, compounds containing terminal (N–O) bonds such as nitrones [Fig. 1(d)], azoxy compounds [Fig. 1(e)], and heterocyclic N-oxides generally exhibit photochemical activity resulting in syntheses of oxaziridines and oxazepines, initiation of cross-linking of polymeric materials, and the use of imino-N-oxides as enzyme-mimicking photochemical oxidizers.[5] Heterocyclic N-oxides have also been shown capable of oxidative demethylation of N,N-dimethylamine to afford N-monomethylaniline. Here the photochemical oxygen transfer is reported to occur via a single-electron process. Product yield and ease of reaction depend significantly on the nature of the N-oxide employed.[6] The determination of the dissociation enthalpies of the (N–O) bonds will assist in understanding these processes.

Recently, some compounds containing terminal (N–O) bonds have assumed pharmacological importance, in particular, some heterocyclic di-N-oxides appear to be promising candidates for selective biological activities as "hypoxic modifiers."[7–10] The oxygenation status of clonogenic cells in solid tumors is believed to be a major factor affecting tumors response to radiotherapy. The presence of hypoxia in human tumors influences the treatment and some studies suggest that hypoxic cells may be refactory to certain chemotherapeutic drugs. The concept of bireductive activation of drugs in hypoxia cells to produce more toxic compounds has been reviewed and one of the general classes of such agents are 1,2,4-benzotriazine-1,4-dioxide derivatives. The importance of the (N–O) bonds for the selective activity suggests the design of new heterocyclic di-N-oxides to explore their activities. It has been suggested that the more negative the reduction potential the greater the hypoxic selectivity to the point at which enzymes can no longer reduce the compound. The formation of such di-N-oxide derivatives for their pharmacological application is of current interest[11,12] and the determination of the energetics of the (N–O) bonds has importance in the development of these pharmacological treatments.

As compounds containing terminal (N–O) bonds have the potential to act as oxidizing agents, it is desirable to be able

to place them in order, together with other oxygenated species, in terms of their abilities to transfer oxygen atoms in chemical and biochemical conversions. Holm *et al.*[13,14] introduced a simple reactivity scale for primary oxo transfer reactions, compiling the values of the enthalpies of reaction in a decreasing order. Holm's scale is analogous to that of a table of standard reduction in view of the prediction of the direction of the oxo transfer reaction. The enthalpy changes of the Reactions (2) and (3) involving generalized acceptor/donor couples oxygen atom, X/XO or Y/YO, may be obtained as the difference in the standard molar enthalpies of formation of products and reactants

$$X + \tfrac{1}{2}O_2(g) = XO, \qquad (2)$$

$$Y + \tfrac{1}{2}O_2(g) = YO. \qquad (3)$$

If $|T\Delta_r S_m| \langle\langle \Delta_r H_m$, and $\Delta_r H_m(1) \rangle \Delta_r H_m(2)$, the following reaction is thermodynamically favorable:

$$XO + Y = X + YO. \qquad (4)$$

For an oxidized molecule such as XO, the bond dissociation enthalpy is the enthalpy of the following reaction:

$$XO(g) = X(g) + O(g). \qquad (5)$$
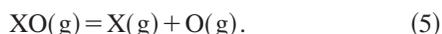
The terminal (N–O) bonds in various compounds can be of differing types. The (N–O) dative–covalent bond, written as $(-N^+ - O^-)$ or as $(N \rightarrow O)$ is present in a large number of different types of compound, e.g., amine oxides, pyridine *N*-oxides; nitrile *N*-oxides, nitrones, azoxy compounds, furoxans, azo-*N,N*-dioxides, quinoxaline 1,4-dioxides, and pyrazine 1,4-dioxide, as it is represented in Fig. 1. (N–O) double bonds are present in C-nitroso compounds, R–N=O and in organic nitrites R–O–N=O. A canonical form for the structure of organic nitro compounds

$$R \!-\! N \overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}}$$

and nitrates

$$R \!-\! O \!-\! N \overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}}$$
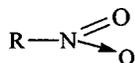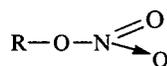
show both a double bond and a dative-covalent link but the two terminal (N–O) bonds in these compounds are equivalent. The description of these bonds as dative-covalent or as double bonds is oversimplified as the bond order can be modified by interaction with the immediate environment of the bond.

There have been many investigations of the thermochemistry of compounds containing terminal (N–O) bonds since the excellent reviews by Batt and Robinson[15] in 1982 and by Liebman *et al.*[16,17] in 1996 and 1997. The reviews compiled available thermochemical data, and critically evaluated published values for selected compounds. The main effort has been in measuring enthalpies of formation in the condensed state, usually by combustion calorimetry and enthalpies of vaporization or sublimation to derive the standard molar enthalpies in the gaseous state. From these results and those of related compounds, the dissociation enthalpies of the (N–O)

bond have been derived. As expected, the dissociation enthalpies vary depending on the nature of the compound and on the immediate molecular environment of the bond. Such results assist in understanding the chemical behavior of these compounds particularly as oxidizing agents and enable the ordering of these compounds on Holm's reactivity scale. As there are many compounds for which the molar enthalpies of formation in the gaseous state are known, there is the potential for developing procedures for obtaining reliable estimated values for gaseous molar enthalpies of formation using either the group method of Benson and Buss[18] which is most satisfactory for aliphatic compounds or by using enthalpy increments for substitution into aromatic compounds as developed by Cox.[19]

The bond dissociation energy, D_o°, is defined as $\Delta_r U_m^{\circ}$ at $T/K = 0$ for the following reaction, where (A–B), A and B are in their ground state vibrational states: D_o° is generally derived from spectroscopic measurements:

$$(A-B)(g) = A(g) + B(g). \qquad (6)$$

The bond dissociation, $DH_{298.15\,K}^{\circ}$, is $\Delta_r H_m^{\circ}$ for the above reaction (6) at $T/K = 298.15$ and can be derived from equilibrium studies, measurement of activation energies, and for the majority of the compounds in this review, from thermochemical measurements. The difference between D_o° and $DH_{298.15\,K}^{\circ}$ is usually small and Cottrell[20] has shown that the maximum difference would be $\sim$10 kJ mol^{-1} for the dissociation of a polyatomic molecule if none of the vibrational degrees of freedom lost on dissociation are excited at $T/K = 298.15$. Improvements in experimental methods have resulted in reductions in experimental uncertainties so that, particularly for small molecules, the difference between D_o° and $DH_{298.15\,K}^{\circ}$ is larger than the combined uncertainties, e.g.,

	D_o° (kJ·mol^{-1})	$DH_{298.15\,K}^{\circ}$ (kJ·mol^{-1})	Δ (kJ·mol^{-1})
(N–O)	627.88±0.18[21]	631.62±0.18	3.74±0.25
(ON–O)	300.55±0.41[21]	306.24±0.41	5.69±0.58

Hence it is unacceptable to confuse these two quantities and call them both dissociation energies, a common practice carried out in the past. In this paper we will deal exclusively with $DH_{298.15\,K}^{\circ}$ and will omit the temperature descriptor unless the temperature is other than $T/K = 298.15$.

The DH°(N–O) values are derived from the enthalpy of the following reaction, at $T/K = 298.15$, with the reactants and products in their standard states:

$$RN-O(g) = RN(g) + O(g). \qquad (7)$$
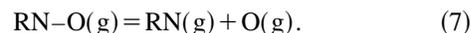
Required is $\Delta_f H_m^{\circ}(O,g)/(kJ \cdot mol^{-1}) = 249.17 \pm 0.10.$[22] Then $DH^{\circ}(N-O) = \Delta_f H_m^{\circ}(RN,g) + \Delta_f H_m^{\circ}(O,g) - \Delta_f H_m^{\circ}(RN-O,g).$

2. Amine-*N*-Oxides

The sole reliable thermochemical measurement on an amine-*N*-oxide is the enthalpy of combustion of

trimethylamine-*N*-oxide [Fig. 1(a) with R＝CH$_3$] by Steele *et al.*[23] To protect this hygroscopic compound from water vapor in the combustion bomb, a polythene cover was placed over the pellet in the crucible and sealed from the atmosphere by a small quantity of oil. The recovery of CO$_2$ from the combustion was 99.97%±0.02% percent. The measurements yielded $\Delta_f H_m^\circ((CH_3)_3NO,cr)/kJ\cdot mol^{-1}=-(109.6\pm 0.5)$ for the standard enthalpy of formation of crystalline trimethylamine-*N*-oxide. Unfortunately, no measurement of the enthalpy sublimation is available but a reasonable estimate would be [80±5] kJ mol^{-1}, leading to $\Delta_f H_m^\circ((CH_3)_3NO,g)/kJ\cdot mol^{-1}=-(30\pm 5)$. With $\Delta_f H_m^\circ((CH_3)_3N,g)/kJ\cdot mol^{-1}=-(23.7\pm 0.7)$,[24] then for $(CH_3)_3NO$, $DH^\circ(N-O)=(260\pm 5)$ kJ mol^{-1}. In the same study, Steele *et al.* measured the enthalpy of combustion of pyridine-*N*-oxide (this compound is discussed in Sec. 3). Support for these combustion measurements has been provided by Haaland *et al.*[25] who made *ab initio* calculations of the energy of the following gaseous reaction and obtained $\Delta_r H_m^\circ/kJ\cdot mol^{-1}=-(7.1\pm[5.0])$; the combustion measurements, albeit with an estimated enthalpy of sublimation, yield $-([10]\pm[6])$ kJ·mol^{-1}, in agreement:

$$(CH_3)_3NO(g)+c-C_5H_5N(g)$$

$$=(CH_3)_3N(g)+c-C_5H_5NO(g). \tag{8}$$
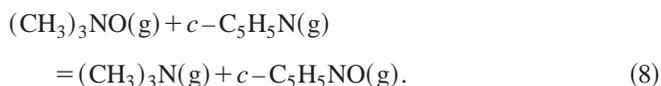
A reaction–solution calorimetric method was used by Airoldi and Gonçalves[26] for triethyl- and tributylamine-*N*-oxides by determining the enthalpy of thermochemical reactions such as the following reaction, by measuring the enthalpies of solution of the reactants and separately of the products into $(0.08\ mol\cdot dm^{-3}\ TiCl_3+5.6\ mol\cdot dm^{-3}\ HCl)$ so that the final solutions from the dissolution of the reactants and that from the products were the same:

$$3(C_2H_5)_3NO(cr)+KCl(cr)$$

$$=KClO_3(cr)+3(C_2H_5)_3N(l). \tag{9}$$
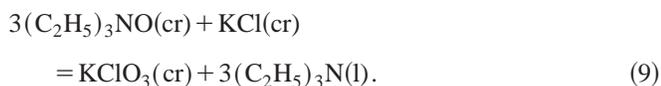
This method was used by Li Shaofeng and Pilcher[27] for pyridine *N*-oxide but the combustion results of Steele *et al.*[23] have shown this reaction–solution calorimetric result was in error by (35.5 ± 2.4) kJ·mol^{-1}. For triethyl- and tributylamine *N*-oxides, it is straightforward to show that the reaction–solution calorimetric results to be erroneous.

For $(C_2H_5)_3NO(cr)$, $\Delta_f H_m^\circ/(kJ\cdot mol^{-1})$ was given as (9.0 ± 0.8) and with an estimated enthalpy of sublimation of [80±5] kJ·mol^{-1}, then $\Delta_f H_m^\circ((C_2H_5)_3NO,g)/(kJ\cdot mol^{-1})=(89\pm 5)$ and as $\Delta_f H_m^\circ((C_2H_5)_3N,g)/(kJ\cdot mol^{-1})=-(92.8\pm 0.6)$,[24] then for $(C_2H_5)_3NO$, $DH_m^\circ(N-O)=(67\pm 5)$ kJ·mol^{-1}, an extraordinary small value when compared with that for $(CH_3)_3NO$, (260 ± 5) kJ·mol^{-1}. For $(C_4H_9)_3NO(cr)$, $\Delta_f H_m^\circ/(kJ\cdot mol^{-1})$ was given as (16.0 ± 1.1) and with an estimated enthalpy of sublimation of [80±5] kJ·mol^{-1}, then $\Delta_f H_m^\circ((C_4H_9)_3NO,g)/(kJ\cdot mol^{-1})=(96\pm 5)$ and as $\Delta_f H_m^\circ((C_4H_9)_3N,g)/(kJ\cdot mol^{-1})=-(226.8\pm 2.0)$,[24] then for $(C_4H_9)_3NO$, $DH^\circ(N-O)=-(74\pm 6)$ kJ·mol^{-1}, and a negative dissociation enthalpy is not possible. These DH° values are unacceptable.

In fairness, it should be noted that enthalpies of formation of 2-methylpyridine *N*-oxide,[28] 3-methylpyridine *N*-oxide,[28] 4-methylpyridine *N*-oxide,[28] and 2,2′-bipyridine di-*N*-oxide[29] have also been determined by the solution–reaction calorimetric method. For 4-methylpyridine *N*-oxides, the reaction–solution based value of $\Delta_f H_m^\circ(cr)$ is in reasonable agreement with combustion calorimetric measurement (12.9 ± 0.9) kJ·mol^{-1} versus (5.6 ± 2.1) kJ·mol^{-1}.[30] Bond dissociation enthalpies of 2-methylpyridine *N*-oxide $(DH^\circ(N-O)/(kJ\ mol^{-1})=259.9\pm 2.4)$ and of 3-methylpyridine *N*-oxide $(DH^\circ(N-O)/(kJ\ mol^{-1})=264.6\pm 2.6)$ are also reasonable, and are comparable in magnitude to values of several other substituted pyridine *N*-oxides that were determined from combustion calorimetric measurements. Bond dissociation enthalpies of the pyridine *N*-oxides will be discussed in the next section. There is no *a prior* way of knowing whether or not the $\Delta_f H_m^\circ$ values determined from the TiCl$_3$ reduction method are correct, and no results arising from the TiCl$_3$ reduction method are included in this review.

3. Pyridine *N*-Oxide Derivatives, a Quinoline *N*-Oxide Derivative, and Phenazine *N*-Oxide

Table 1 lists the most reliable thermochemical results for pyridine *N*-oxide [Fig. 1(b)] derivatives and for comparison 6-methoxyquinoline *N*-oxide. Except for 2-carboxypyridine *N*-oxide, 2-hydroxypyridine *N*-oxide, 2,4,6-trinitropyridine *N*-oxide, and the two amide substituted pyridine *N*-oxides, the $DH^\circ(N-O)$ values lie between 266 and 253 kJ·mol^{-1}. Hence, in the absence of any special stabilizing effect or steric hindrance, $DH^\circ(N-O)$ in pyridine *N*-oxide derivatives should lie in the region of (260 ± 10) kJ·mol^{-1} providing a method for estimating $\Delta_f H_m^\circ(g)$ for other pyridine *N*-oxides from $\Delta_f H_m^\circ(g)$ of the corresponding pyridine derivative. This approximate constancy of $DH^\circ(N-O)$ in pyridine *N*-oxides arises because the effect on $\Delta_f H_m^\circ(g)$ of substitution into pyridine *N*-oxide is fairly closely matched by the corresponding effect of substitution into pyridine. Tables 2 and 3 show the effect of substitution into pyridine *N*-oxide and pyridine, respectively, compared with substitution into benzene. The general pattern of effects is similar in each case so that values given in Table 3 could assist in prediction of the enthalpies of formation of the corresponding pyridine *N*-oxide derivatives.

The crystal structure of 2-carboxypyridine *N*-oxide determined by Laing and Nicholson[39] showed a very short intramolecular hydrogen bond with the (O---O) distance of 239 pm, whereas the (N–O) bond length was normal, 134 pm, the same as in pyridine *N*-oxide, 135 pm.[40] The increase in $DH^\circ(N-O)$ in 2-carboxypyridine *N*-oxide is only 20 kJ·mol^{-1} over the $DH^\circ(N-O)$ in the 3- and 4-carboxypyridine *N*-oxides and is much smaller than would be expected for such a short hydrogen bond. From self-consistent field-configuration interaction calculations, Shahawy *et al.*[41] showed that 2-carboxypyridine also has an intramolecular hydrogen bond so that the difference of 20

TABLE 1. Standard molar enthalpies of formation of gaseous substituted pyridine N-oxide and pyridine compounds and calculated $DH°$(N–O) values

| | Pyridine N-oxide derivative | | | Pyridine Deriv. | |
	$\Delta_f H_m°$(cr) (kJ·mol^{-1})	$\Delta_{cr}^g H_m°$ (kJ·mol^{-1})	$\Delta_f H_m°$(g) (kJ·mol^{-1})	$\Delta_f H_m°$(g) (kJ·mol^{-1})	$DH_m°$(N–O) (kJ·mol^{-1})
c-C$_5$H$_5$NO	44.1±0.5[23]	80.6±1.8[27]	124.7±1.9	140.4±0.5[24]	264.9±2.0
4-H$_3$C-c-C$_5$H$_4$NO	5.6±2.1[30]	85.3±2.6[30]	90.9±3.3	103.8±0.9[24]	262.1±3.4
3-NC-c-C$_5$H$_4$NO	170.9±1.4[30]	101.9±2.0[30]	272.8±2.4	277.9±2.0[31]	254.3±3.1
4-NC-c-C$_5$H$_4$NO	162.8±1.4[30]	104.4±4.3[30]	267.2±4.5	283.5±1.1[31]	265.5±4.6
2-HO-c-C$_5$H$_4$NO	−198.7±1.7[32]	89.4±0.9[32]	−109.3±1.9	−79.7±1.7[33]	278.8±2.3
3-HO-c-C$_5$H$_4$NO	−171.3±1.0[30]	121.8±4.4[30]	−49.5±4.5	−43.7±1.7[33]	255.0±5.0
2-HO$_2$C-c-C$_5$H$_4$NO	−364.1±1.8[30]	94.4±4.0[30]	−269.7±4.4	−243.0±2.6[30]	275.9±5.1
3-HO$_2$C-c-C$_5$H$_4$NO	−377.4±1.1[34]	152.3±1.9[34]	−225.1±1.5	−221.5±1.5[31,35]	252.8±2.7
4-HO$_2$C-c-C$_5$H$_4$NO	−381.2±1.3[30]	136.1±1.2[30]	−245.1±1.8	−234.8±4.7[30]	259.5±5.0
4-O$_2$N-c-C$_5$H$_4$NO	17.1±0.8[34]	108.9±0.3[34]	126.0±0.9	[135.3±5.2][34]	258.5±5.3
3-H$_3$C-4-O$_2$N-c-C$_5$H$_5$NO	−19.5±3.4[30]	106.7±2.0[30]	87.2±3.9	[101.4±6.0][30]	263.4±7.1
2,4,6-(O$_2$N)$_3$-c-C$_5$H$_2$NO	102.1±1.3[36]	106.3±2.9[36]	208.4±3.2	136.0±3.2[36]	176.8±4.5
3-H$_2$NOC-c-C$_5$H$_4$NO	−199.2±2.1[37]	119.2±2.3[37]	−80.0±3.1	−28.9±3.7[37]	300.3±5.0
4-H$_2$NOC-c-C$_5$H$_4$NO	−198.8±2.1[37]	125.3±1.8[37]	−73.5±2.8	−34.1±2.1[37]	288.6±3.7
6-CH$_3$O-quinoline N-oxide	−85.6±3.7[38]	117.9±1.0[38]	32.3±3.8	52.3±3.2[38]	269.2±5.0

kJ·mol^{-1} can be regarded as the increase in energy of the intramolecular hydrogen bond in 2-carboxypyridine N-oxide over that in 2-carboxypyridine. The N–O bond dissociation enthalpy in 2-hydroxypyridine N-oxide is also likely increased as the result of intramolecular hydrogen bond formation. The reduction of $DH°$(N–O) in 2,4,6-trinitropyridine N-oxide can be ascribed to steric interference of the nitro-groups in the 2,6 positions.

The larger $DH°$(N–O) values for the carboxyamide pyridine N-oxides are surprising. It is apparent from Table 2 that pyridine N-oxide substituted with −CONH$_2$ is stabilized relative to that substituted by −CO$_2$H. It suggests that the carboxyamide derivatives have an increased double bond character in the (N–O) bond possibly due to the negative charge on the oxygen atom in the (N–O) bond being partially distributed to the −CONH$_2$ group. Table 4 lists the increments in $\Delta_f H_m°$ for substitution of the group −CO$_2$H by −CONH$_2$, and surprisingly, this increment appears to be constant in the crystalline state but not in the gaseous state.

Further measurements and theoretical studies will be needed to provide an explanation of the larger $DH°$(N–O) values in the carboxyamide pyridine N-oxides.

Leitão et al.[42] studied phenazine N-oxide and phenazine, with the results in kJ·mol^{-1}, for phenazine N-oxide $\Delta_f H_m°$(cr)=(197.3±4.6), $\Delta_{cr}^g H_m°$=(100.0±1.3), hence $\Delta_f H_m°$(g)=(297.3±4.8), and for phenazine $\Delta_f H_m°$(cr)=(237.0±2.0), $\Delta_{cr}^g H_m°$=(91.8±2.1), hence $\Delta_f H_m°$(g)=(328.8±2.9) leading to $DH°$(N–O)=(280.7±5.6) kJ·mol^{-1}, about 20 kJ·mol^{-1} greater than in pyridine N-oxide.

The (N–O) bond will not be purely dative-covalent but will possess some double bond character. In pyridine N-oxide (a) there will be contributions from the forms (b), (c) and (d), represented in Fig. 2, where the negative charge on the oxygen atom is being partially distributed to carbon atoms.

In phenazine N-oxide, the negative charge on the oxygen can be partially transferred to a nitrogen atom as it is represented in Fig. 3. As nitrogen is more electronegative than

TABLE 2. Standard molar enthalpy changes for comparison of substitution into pyridine N-oxide with benzene

| R−c-C$_5$H$_4$NO(g)+C$_6$H$_6$(g)=c-C$_5$H$_5$NO(g)+R-C$_6$H$_5$(g) | | | |
| | $\Delta_r H_m°$(g)/kJ·mol^{-1} Position of substituent | | |
R	2	3	4
−CH$_3$			0.3±3.6
−CO$_2$H	17.7±5.3	−26.9±3.7	−6.9±3.5
−CONH$_2$		21.2±3.9	14.7±3.7
−CN		−16.2±3.4	−10.7±5.1
−OH	55.0±2.8	−4.8±5.0	
−NO$_2$			−17.7±1.7

Note: The $\Delta_r H_m°$ values were calculated using auxiliary data for C$_6$H$_6$(g) and R−C$_6$H$_5$(g) listed by Pedley.[24]

TABLE 3. Standard molar enthalpy changes for comparison of substitution into pyridine with benzene

| R−c-C$_5$H$_4$N(g)+C$_6$H$_6$(g)=c-C$_5$H$_5$N(g)+R-C$_6$H$_5$(g) $\Delta_r H_m°$(g)/kJ·mol^{-1} Position of substituent | | | |
R	2	3	4
−CH$_3$	9.1±1.3	1.9±1.4	4.2±1.4
−CO$_2$H	6.7±3.5	−14.8±2.8	−1.5±5.3
−CN	−7.1±2.7	−4.3±3.0	−9.9±2.5
−OH	41.1±1.9	5.1±2.0	2.2±2.4
−NH$_2$	26.8±1.7	0.7±2.1	15.0±1.9
−NO$_2$			−10.1±5.3

Note: The $\Delta_r H_m°$ values were calculated using auxiliary data for C$_6$H$_6$(g) and R−C$_6$H$_5$(g) listed by Pedley.[24]

TABLE 4. Increments in $\Delta_f H_m^\circ$ (298.15 K), $\Delta(\Delta_f H_m^\circ)$, for substitution of the group $-CO_2H$ by $-CONH_2$

	Crystalline state		
	$\Delta_f H_m^\circ/kJ \cdot mol^{-1}$		
Compound	$R-CO_2H$	$R-CONH_2$	$\Delta(\Delta_f H_m^\circ)/kJ\ mol^{-1}$
C_6H_5-R	-385.2 ± 0.5	-202.6 ± 1.1	182.6 ± 1.2
$3R-c-C_5H_4NO$	-377.4 ± 1.1	-199.2 ± 2.1	178.2 ± 2.4
$4R-c-C_5H_4NO$	-381.2 ± 1.3	-198.8 ± 2.1	182.4 ± 2.5
	Gaseous state		
	$\Delta_f H_m^\circ/kJ \cdot mol^{-1}$		
C_6H_5-R	-294.1 ± 2.2	-100.9 ± 1.2	193.2 ± 2.5
$3R-c-C_5H_4NO$	-225.1 ± 1.5	-80.0 ± 3.1	145.1 ± 3.4
$4R-c-C_5H_4NO$	-245.1 ± 1.8	-73.5 ± 2.8	171.6 ± 3.3

Note: Values calculated making use of auxiliary data listed by Pedley.[24]

carbon, it is expected that the double bond character in the (N–O) bond in phenazine *N*-oxide will be greater than that in pyridine *N*-oxide accounting for the larger DH°(N–O) value. The (N–O) bond length in phenazine *N*-oxide is 124 pm[43] shorter than that in pyridine *N*-oxide, 135 pm.[40]

4. Nitrile *N*-Oxides

Table 5 lists the known thermochemical results for nitrile *N*-oxides. As the electron donating power of the methoxy group is greater than that for methyl, an increase in the electron density in the benzene could account for the increased DH°(N–O) in 2,4,6-trimethoxybenzonitrile *N*-oxide over that in the trimethyl derivative.

The (N–O) bond length in 4-methoxy-2,6-dimethylbenzonitrile *N*-oxide, a compound similar to those in Table 5, was reported by Shiro *et al.*[46] to be 124.9 pm so it is surprising that the DH°(N–O) values are so low. If we consider the possibility of double bond character with canonical structures of the form $Ar-C\equiv N^+-O^-$ and $Ar-C^-=N^+=O$, then on dissociation the (C–N) bond will revert to its full triple bond character causing reduction in DH°(N–O). Shiro *et al.*[46] state that in aromatic nitrile *N*-oxides, there is no evidence that the (C–N) is lengthened by the formation of the (N–O) bond but the effect may be small and within the limits of experimental uncertainty.

The average DH°(N–O) in dicyanobenzene di-*N*-oxide is close to DH°(N–O) in 2,4,6-trimethylbenzenenitrile *N*-oxide, suggesting the successive bond dissociation enthalpies will be nearly equal, which is to be expected because in this compound the (N–O) bonds are far apart and should have little influence on each other.

5. Nitrones

Table 6 lists the most reliable results for nitrones, R–CH =N(O)R and the corresponding benzylidene derivatives with the estimated values in brackets [ ]. For both the *N*-phenylmethylene benzenamine derivatives, R–C$_6$H$_4$CH
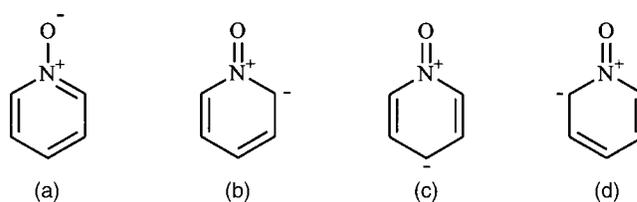
FIG. 2. Structural valence formulas for pyridine *N*-oxide.

=N–C$_6$H$_5$ and for benzylidene *tert*-butylamine derivatives, R–C$_6$H$_4$CH=N–C(CH$_3$)$_3$, estimations of $\Delta_f H_m^\circ$(g) were made using the Cox scheme[19] by assuming that the enthalpy increment in $\Delta_f H_m^\circ$(g) for substitution into the benzene ring was the same as for substitution into benzene, using thermochemical data from Pedley.[24]

Recently, Lebedev *et al.*[49] reported enthalpies of combustion and sublimation for some of the compounds listed in Table 6. Recalculation of their results was made because of some minor printing errors in this publication. Their results yielded $\Delta_f H_m^\circ$(g)/(kJ·mol^{-1}) values for 2-HOC$_6$H$_4$CH =N(O)C$_6$H$_5$, (65.3±3.3), C$_6$H$_5$CH=N(O)C(CH$_3$)$_3$ (10.9 ±6.8), and 2-HOC$_6$H$_4$CH=NC$_6$H$_5$ (55.7±3.3). These values differ by more than the sums of experimental uncertainties from the values in Table 6, in particular, the value for the benzylidene derivative differs by (41.8±6.5) kJ·mol^{-1}. The values in Table 6 are preferred, especially in view of the difficulty in preparing a benzylidene derivative in the high state of purity required for high precision enthalpy of combustion measurements.

It is apparent that for both sets of nitrones that DH°(N–O) is unaffected by substitution in the 4 position. The increase in DH°(N–O) for *N*-2-hydroxyphenyl-methylenebenzenamine *N*-oxide is due to an intramolecular hydrogen bond as suggested by Wheeler and Gore[50] from spectroscopic evidence. The increase in DH°(N–O) of (30±7) kJ·mol^{-1} can be ascribed to the intramolecular hydrogen bond enthalpy.

DH°(N–O) for the benzylidene *tert*-butylamine *N*-oxides are approximately 20 kJ·mol^{-1} larger than for the *N*-phenylmethylenebenzamine *N*-oxides. The inductive effect of the *tert*-butyl group is greater than that of the phenyl group so replacing phenyl by *tert*-butyl on the nitrogen atom should result in increased electron density of the (N–O) bond causing an increase in its dissociation enthalpy.

6. Azoxy Derivatives

Table 7 lists the available thermochemical results for azoxy compounds: the estimated values in [ ] were calcu-
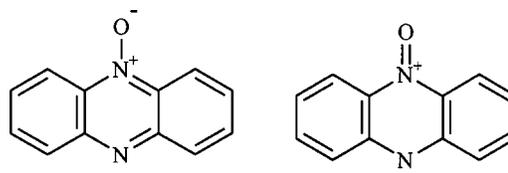
FIG. 3. Structural valence formulas for phenazine *N*-oxide.

TABLE 5. Standard molar enthalpies of formation of gaseous benzonitrile N-oxide and nitrile compounds and calculated $DH°(N-O)$ values

	Nitrile N-oxide derivative			Nitrile derivative	
	$\Delta_f H_m°(cr)$	$\Delta_{cr}^g H_m°$	$\Delta_f H_m°(g)$	$\Delta_f H_m°(g)$	$DH_m°(N-O)$
	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$
$2,4,6-(CH_3)_3C_6H_2CNO$	55.9 ± 1.5[44]	77.5 ± 3.7[44]	133.4 ± 4.0	106.4 ± 2.3[44]	222.2 ± 4.6
$2,4,6-(CH_3O)_3C_6H_2CNO$	-320.1 ± 2.1[44]	91.9 ± 1.9[44]	-228.2 ± 2.8	-244.6 ± 2.6[44]	232.8 ± 3.8
$4-ONCC_6H_4CNO$	337.5 ± 1.8[45]	73.0 ± 2.0[45]	410.5 ± 2.7	358.3 ± 2.2[45]	223.1 ± 1.7[a]

[a]Calculated value corresponds to $\langle DH°(N-O) \rangle$ for removal of both oxygen atoms.

lated using the Cox scheme.[19] The $DH°(N-O)$ values in p-azoxyanisole and p-azoxyphenetole are larger than $DH°(N-O)$ in azoxybenzene presumably because the alkoxy groups donate electrons to the π-electron system resulting in slightly increased electron density in the (N–O) bonds. The inductive effects of alkyl groups are greater than that of the phenyl group resulting in increased electron density in the (N–O) bonds in the alkyl derivatives compared with the aryl derivatives causing an increase in the dissociation enthalpy of the (N–O) bond. $DH°(N-O)$ is about 10 $kJ \cdot mol^{-1}$ less in di-$tert$-butyldiazene N-oxide than in di-n-propyldiazene N-oxide consistent with strain energy in the former molecule as shown by a molecular mechanics study by Byström.[56]

Sheremetev $et~al.$[57] reported the standard molar enthalpies of formation of crystalline 4,4′-dinitroazofurazan, $\Delta_f H_m°(cr)/(kJ \cdot mol^{-1}) = 704.6 \pm 4.8$, and 4,4′-dinitroazoxyfurazan, $\Delta_f H_m°(cr)/(kJ \cdot mol^{-1}) = 647.3 \pm 6.7$, determined from enthalpy of combustion measurements. The authors did not perform the sublimation measurements; however, to a first approximation the sublimation enthalpies of both compounds should be about the same. This leads to a (N–O) bond dissociation of $DH°(N-O) = 306.5 \pm [13.0]~kJ \cdot mol^{-1}$ for 4,4′-dinitroazoxyfurazan, which is in agreement with bond dissociation enthalpies of the other azoxycompounds listed in Table 7. The (N–O) bond dissociation enthalpy of 4,4′-diaminoazoxyfurazan is similarly calculated from the published thermochemical data of Chavez $et~al.$[58] The uncertainty in both calculated $DH°(N-O)$ values have been increased to account for the enthalpy of sublimation approximation.

$DH°(N-O)$ in azoxybenzene is approximately 45 $kJ \cdot mol^{-1}$ greater than in diphenylnitrone. If however, we compare the contribution of the (N–O) double bond character in diphenylnitrone [Figs. 4(a), (b)] with that in azoxybenzene [Figs. 4(c), (d)], in the latter, the negative charge is transferred to the more electronegative atom of nitrogen whereas in the former it is transferred to the less electronegative atom of carbon.

Hence, it is expected that the double bond character of the (N–O) bond will be greater in azoxybenzene leading to a greater bond dissociation enthalpy. Hiberty $et~al.$[59,60] reported valence-bond treatments of some 1,3-dipoles including the structures,

and

but as the main purpose of their calculations was to derive weights of structural formulas including both ionic and diradical structures, the results give only a qualitative explanation. The calculations showed that the structural weight
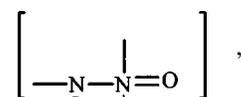
0.134 was almost double that of
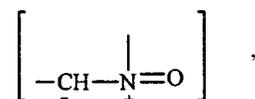
0.074 showing the strengthening of the (N–O) bond in azoxy compounds relative to nitrones.

TABLE 6. Standard molar enthalpies of formation of gaseous nitrone and benzylidene compounds and calculated $DH°(N-O)$ values

	Nitrone derivative			Benzylidene	
	$\Delta_f H_m°(cr)$	$\Delta_{cr}^g H_m°$	$\Delta_f H_m°(g)$	$\Delta_f H_m°(g)$	$DH_m°(N-O)$
	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$
$C_6H_5CH=N(O)C_6H_5$	148.0 ± 2.0[47]	115.0 ± 0.8[47]	263.0 ± 2.1	278.7 ± 2.2[47]	264.9 ± 3.0
$4-CH_3O-C_6H_4CH=N(O)C_6H_5$	-20.9 ± 2.2[47]	130.6 ± 1.2[47]	109.7 ± 2.5	$[127.8 \pm 5.6]$	267.3 ± 6.1
$4-(CH_3)_2CHC_6H_4CH=N(O)C_6H_5$	54.3 ± 2.6[47]	127.2 ± 1.7[47]	181.5 ± 3.1	$[199.8 \pm 5.6]$	267.5 ± 6.4
$2-HO-C_6H_4CH=N(O)C_6H_5$	-62.6 ± 2.0[47]	116.5 ± 1.4[47]	53.9 ± 2.4	$[99.5 \pm 5.6]$	294.8 ± 6.0
$4-O_2NC_6H_4CH=N(O)C(CH_3)_3$	-105.4 ± 1.2[48]	116.5 ± 3.1[48]	11.1 ± 3.6	49.4 ± 3.6[48]	287.5 ± 5.1
$C_6H_5CH=N(O)C(CH_3)_3$	-55.9 ± 1.8[48]	86.8 ± 0.9[48]	30.9 ± 2.0	$[64.7 \pm 6.2]$	283.0 ± 6.5
$4-(CH_3)_2CHC_6H_4CH=N(O)C(CH_3)_3$	-152.7 ± 2.6[48]	101.8 ± 4.1[48]	-50.9 ± 4.9	$[-14.2 \pm 6.2]$	285.9 ± 7.9

TABLE 7. Standard molar enthalpies of formation of gaseous azoxy compounds and azo compounds and calculated $DH°$(N–O) values

	Azoxy compound			Azo compound	
	$\Delta_f H°_m$(cr)	$\Delta_{cr}^g H°_m$	$\Delta_f H°_m$(g)	$\Delta_f H°_m$(g)	$DH°_m$(N–O)
	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})
$C_6H_5N=N(O)C_6H_5$	243.4±2.2[47]	98.6±0.9[47]	342.0±2.4	402.2±2.7[51]	309.4±3.6
4-$CH_3O–C_6H_5N=N(O)C_6H_5$–4-OCH_3	−101.4±2.6[52]	134.8±3.7[52]	33.4±4.5	[100.6±6.1]	316.4±7.6
4-$C_2H_5O–C_6H_5N=N(O)C_6H_5$–4-$OC_2H_5$	−163.6±2.6[52]	126.2±2.7[52]	−37.4±3.7	[33.2±6.1]	319.8±7.1
n-$C_3H_7N=N(O)nC_3H_7$	−82.7±1.4[53]	51.7±0.2[53]	−31.0±1.4	55.3±3.5[54]	331.5±3.8
$(CH_3)_3CN=N(O)C(CH_3)_3$[a]	−153.5±2.1[53]	45.9±0.3[53]	−107.6±2.1	−35.6±3.6[55]	321.2±4.2
2,3-Diazabicyclo[2.2.1]-hept-2-ene N-oxide			127.8±1.4[56]	207.3±0.9[24]	328.7±1.7
4,4′-Dinitroazoxyfurazan	647.3±6.7[57]			704.6±4.8[b57]	306.6± [13.0]
4,4′-Diaminoazoxyfurazan	444[58]			536[38b]	341.2± [13.0]

[a]$(CH_3)_3CN=N(O)C(CH_3)_3$ is a liquid at 298.15 K.
[b]Tabulated enthalpy of formation is for the crystalline state.

7. Furoxans

Table 8 lists the thermochemical results for furoxans and furazans with estimated values indicated by brackets [ ]. The Cox scheme[19] was shown to be satisfactory for the 5-substituted benzofurazans because the calculated value for $\Delta_f H°_m$ (5-methoxybenzofurazan, g) was (149.7±2.4) kJ·mol^{-1} in agreement with the experiment value of (147.1 ±1.8) kJ·mol^{-1}. It was not possible to use the Cox scheme to estimate $\Delta_f H°_m$(g) for 4-nitrobenzofurazan because of steric hindrance between the nitro group and the nearest nitrogen atom in the furazan ring as shown by $\Delta_f H°_m$(benzene, g) − $\Delta_f H°_m$(nitrobenzene, g) =(15.1±0.9) kJ·mol^{-1}, whereas $\Delta_f H°_m$(benzofuroxan, g) −$\Delta_f H°_m$(4-nitrobenzofuroxan, g)=−(1.3±3.4) kJ·mol^{-1}. This estimation was made by using molecules that show a similar interaction between a nitro group and an adjacent nitrogen by

$\Delta_f H°_m$(4-nitrobenzofurazan, g)

$\quad = \Delta_f H°_m$(benzofurazan, g) + $\Delta_f H°_m$(8-nitroquinoline, g)

$\quad - \Delta_f H°_m$(quinoline, g).

Remarkably, $DH°$(N–O) in the benzofuroxan derivatives seems to be unaffected by substitution into the aromatic ring and the weighted mean value of $DH°$(N–O) in these compounds is (245.9±1.2) kJ·mol^{-1} and these values are close to those for dimethyfuroxan, dimethylfuroxan dinitrate, and dicyanofuroxan for which $DH°$(N–O) was derived assuming the enthalpies of sublimation of the furoxan and furazan were equal. An experimental enthalpy of formation of $\Delta_f H°_m$/(kJ·mol^{-1})=93.3 is quoted in the literature[69] for tetramethylenefuroxan, but without the corresponding enthalpy for tetramethylenefurazan we are unable to calculate the $DH°$(N–O) value for this compound.
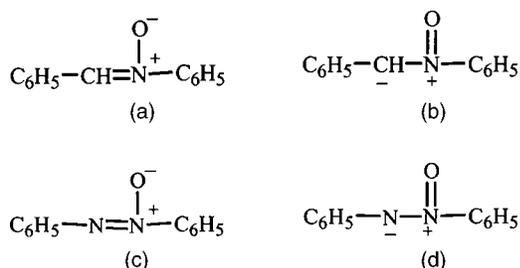
The tautomerism of substituted benzofuroxans has been studied by ^{1}H nuclear magnetic resonance (NMR)[70,71] and can occur thermally or photochemically[72] and is believed to proceed via a di-orthonitrosobenzene derivative, as it is shown in the scheme represented in Fig. 5.

Ab initio calculations show that the energy of the anti-dinitrosobenzene structure was 50.2 kJ·mol^{-1} above that for benzofuroxan, which provides a value for the activation energy in the gaseous state.[73] From thermochemical studies on nitrosobenzene derivatives,[74] the increment in $\Delta_f H°_m$(g) for substitution of (NO) into benzene was derived as (122.4 ±2.2) kJ·mol^{-1}, hence $\Delta_f H°_m$(g) for o-dinitrosobenzene is calculated according to the Cox scheme as (331.4±4.5) kJ·mol^{-1} giving a value of (32.9±5.0) kJ·mol^{-1} for the activation energy of the tautomerism and this is in reasonable agreement with the *ab initio* calculation. Similar considerations for 4-nitrobenzofuroxan show that the anti-dinitrosobenzene structure would not be permitted due to steric hindrance in the proposed transition state and this compound does not exhibit tautomerism.

8. Quinoxaline Di-*N,N*-Oxides and Pyrazine Di-*N,N*-Oxide

Table 9 lists the available thermochemical results for some quinoxaline di-*N,N*-oxides and for pyrazine di-*N,N*-oxide

FIG. 4. Structural valence formula for diphenylnitrone and azoxybenzene compounds.
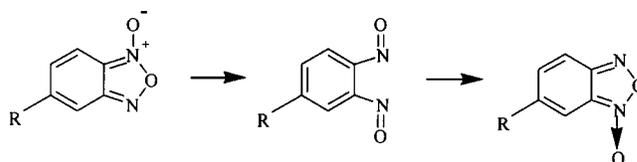
FIG. 5. Tautomerism of substituted benzofurazan *N*-oxides.

TABLE 8. Standard molar enthalpies of formation of gaseous benzofuraxan and benzofurazan derivatives and calculated DH°(N–O) values

Compound	Furoxan derivative			Furazan	DH^{o}_{m}(N-O)
	$\Delta_f H^o_m$ (cr)	$\Delta^g_{cr} H^o_m$	$\Delta_f H^o_m$ (g)	$\Delta_f H^o_m$ (g)	
	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})
	218.9 ± 1.4 [42]	79.6 ± 1.7 [42]	298.5 ± 2.2	300.2 ± 2.2 [42]	250.9 ± 3.0
	52.3 ± 3.3 [61]	96.0 ± 1.6 [61]	148.3 ± 3.7	147.1 ± 1.8 [61]	248.0 ± 3.7
	175.2 ± 1.8 [61]	92.2 ± 1.2 [61]	267.4 ± 2.2	$[268.0 \pm 2.3]$	249.8 ± 3.2
	193.5 ± 1.8 [61]	81.2 ± 1.8 [61]	274.7 ± 2.5	$[269.6 \pm 2.5]$	244.1 ± 3.5
	202.6 ± 2.1 [61]	97.3 ± 1.6 [61]	299.9 ± 2.6	$[306.6 \pm 6.2]$	255.9 ± 6.7
	184.1 ± 0.8 [62]	$96.2 \pm [3.8]$ [62]	280.3 ± 4 [62]	$[285.1 \pm 4]$	254 ± 6[a]
	45.45 ± 0.9 (l) [63]	56.95 ± 0.8 [63]	102.3 ± 1.2	107.3 ± 3.8 [63]	254.2 ± 4.1
	-43.25 ± 0.5 (l) [64]	64.45 ± 0.8 [64]	21.2 ± 1.0	10.8 ± 1.9 [64]	238.8 ± 2.1
	465.75 ± 0.8 [65]			456.1 ± 5.4(cr)	240 ± 10
	633.8 ± 4.6 [66,67]	$[102.1 \pm 4.0]$ [66]	735.9 ± 6.2	733.9 ± 4.5 [66]	247.2 ± 7.7
	625.5 ± 0.8 [66,67]	$[118.0 \pm 4.0]$	743.5 ± 4.1 [66]	735.9 ± 6.2	241.6 ± 7.4
	583.6 ± 3.7 [66,67]	172.0 ± 2.6 [66]	755.6 ± 4.5	743.5 ± 4.1	237.12 ± 6.1
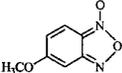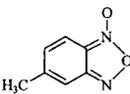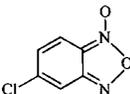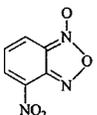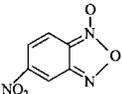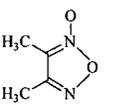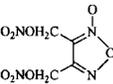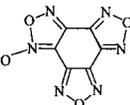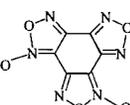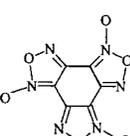
[a]A larger value of $\langle DH^o_m$(N–O)$\rangle = (297.3 \pm 2.3)$ kJ·mol^{-1} is calculated for the bond dissociation enthalpy in the crystalline phase based on published enthalpy of formation data of crystalline 5-nitrobenzofurazan, $\Delta_f H^o_m$(cr)$=(214.2 \pm 2.1)$ kJ·mol^{-1}, and 5-nitrobenzofuroxan, $\Delta_f H^o_m$(cr)$=184.1 \pm 0.8)$ kJ·mol^{-1} (see Ref. 68). The value of DH^o_m(N–O)$=(254 \pm 6$ kJ·mol^{-1} is based on using group additivity methods for estimating the standard enthalpy of formation of gaseous 5-nitrobenzofurazan.

TABLE 9. Standard molar enthalpies of formation of gaseous pyrazine di-N-oxide and quinoxaline di-N-oxide derivatives and calculated $DH°$(N–O) values

| Compound | Quinoxaline di-N-oxides Pyrazine-di-N-oxide | | | Quinoxalines Pyrazine | $\langle DH^o_m(N\text{-}O)\rangle$ |
| | $\Delta_f H^o_m$ (cr) | $\Delta^g_{cr} H^o_m$ | $\Delta_f H^o_m$ (g) | $\Delta_f H^o_m$ (g) | |
	(kJ·mol⁻¹)	(kJ·mol⁻¹)	(kJ·mol⁻¹)	(kJ·mol⁻¹)	(kJ·mol⁻¹)
(structure)	115.1 ±1.4 [75]	112.0 ±1.9 [75]	227.1 ± 2.4	240.3 ± 4.0 [76]	255.8 ± 2.0
(structure)	62.9 ± 3.6 [75]	107.0 ±6.2 [75]	169.9 ± 7.2	[208.1 ± 6.5]	268.3 ± 4.9
(structure)	−83.9 ± 4.4 [75]	117.0 ±2.4 [75]	33.1 ± 5.0	[37.9 ± 6.8]	251.6 ± 4.2
(structure)	−267.0 ± 1.9 [75]	118.3 ±2.6 [75]	−148.7 ± 3.2	[−162.4 ± 7.1]	242.3 ± 3.9
(structure)	187.8 ± 5.9 [75]	167.4 ±4.0 [75]	355.2 ± 7.1	[311.4 ± 8.1]	227.3 ± 5.4
(structure)	25.0 ± 3.6 [77]	124.4 ± 2.7 [77]	149.4 ± 4.5 [77]	172.9 ± 3.0 [78]	260.9 ± 2.7
(structure)	−311.4 ± 3.7 [77]	133.4 ± 2.1 [77]	−178.0 ± 4.3	−159.2[± 5.0] [77]	258.6 ± 3.3
(structure)	102.6± 5.8 [77]	146.6 ± 3.2 [77]	249.2 ± 6.6	−289.4[± 5.0] [77]	269.3 ± 4.1
(structure)	244.1 ± 4.0 [79]	139.7 ± 3.7 [79]	383.8 ± 5.4 [79]	382.0[± 6.3] [79]	248.3 ± 8.3
(structure)	69.6 ± 1.7 [75]	116.9 ± 0.8 [75]	186.5 ± 1.9	196.1 ± 1.3 [80]	254.0 ± 1.2
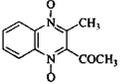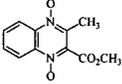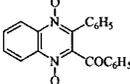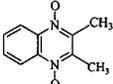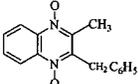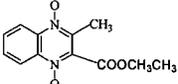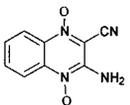
[Fig. 1(i)]. To derive values for $\langle DH°(\text{N–O})\rangle$, values of $\Delta_f H°_m$(g) for the corresponding quinoxaline derivatives were estimated. In the same study, Acree *et al.*[75] measured $\Delta_f H°_m$(g) for 2-methyl-5-pyrazinecarboxylic acid and obtained $-(213.6\pm1.5)$ kJ·mol⁻¹. The value estimated by assuming the enthalpy increments in $\Delta_f H°_m$(g) for substitution into pyrazine to be the same as for benzene was $-(212.8 \pm3.0)$ kJ·mol⁻¹ thus providing a basis for the estimated values in Table 9; however, no allowances were made for steric hindrance.

As expected, the $\langle DH°(\text{N–O})\rangle$ values in quinoxaline di-N,N-oxide [Fig. 1(h)] and in pyrazine di-N,N-oxide are equal, but there are large reductions 2-methyl-3-carboxymethoxy quinoxaline di-N,N-oxide and in 2-phenyl-3-benzoylquinoxaline di-N,N-oxide. *Ab initio* calculations of the optimized geometries of these molecules showed steric hindrance to be present. The quinoxaline moiety is planar but steric hindrance forces the attached groups out of this plane, thus reducing the delocalization energy. This steric hindrance is attenuated in the molecules with the oxygen atoms removed thus providing a qualitative explanation for the reductions in the $\langle DH°(\text{N–O})\rangle$ values.

Numerical values in Table 9 represent the average bond dissociation enthalpy for removal of both oxygen atoms from

TABLE 10. Standard molar enthalpies of formation of gaseous azo N,N-dioxide derivatives and azo-derivatives and calculated $DH°(N–O)$ values

Compound	Azo-N,N-dioxide derivative			Azo-derivative	$\langle DH_m°(N\text{-}O)\rangle$
	$\Delta_f H_m°(cr)$	$\Delta_{cr}^g H_m°$	$\Delta_f H_m°(g)$	$\Delta_f H_m°(g)$	
	$(kJ\cdot mol^{-1})$	$(kJ\cdot mol^{-1})$	$(kJ\cdot mol^{-1})$	$(kJ\cdot mol^{-1})$	$(kJ\cdot mol^{-1})$
$H_3C-N=N-CH_3$ (N,N-dioxide)	0.8 ± 1.6[81]	69.9 ± 3.9[81]	70.7 ± 4.2	$[144.7 \pm 4.1]$	286.2 ± 2.9
$(H_3C)_3C-N=N-C(CH_3)_3$ (N,N-dioxide)	-209.6 ± 2.8[82]	76.1 ± 0.8[82]	-133.5 ± 2.9	-35.6 ± 3.6[55]	298.2 ± 2.3
diphenyl azo-N,N-dioxide	241.4 ± 2.8[82]	87.0 ± 0.8[82]	328.4 ± 2.9	402.2 ± 2.7[51]	286.1 ± 2.0
bis(nitrophenyl) azo-N,N-dioxide	217.1 ± 2.5[82]	95.4 ± 1.3[82]	312.5 ± 2.8	$[372.0 \pm 3.2]$	279.0 ± 5.0
tetramethyl azo-N,N-dioxide	100.3 ± 2.9[83]	107 ± 12[83]	207.3 ± 12.3	$[284.4 \pm 4.6]$	287.8 ± 6.6
hexamethyl azo-N,N-dioxide	33.5 ± 3.3[83]	107 ± 12[83]	140.6 ± 12.5	$[213.6 \pm 5.3]$	285.7 ± 6.8
tetraethyl azo-N,N-dioxide	-0.5 ± 3.8[84]	$[120 \pm 12]$[84]	119.5 ± 12.7	$[191.4 \pm 5.8]$	285 ± 7

pyrazine di-N,N-oxide and the quinoxaline di-N,N-oxide under consideration. In the case of 2,3-dimethylquinoxaline-1,4-dioxide, 2-methyl-3-ethoxycarbonylquinoxaline-1,4-dioxide, and 2-methyl-3-benzylquinoxaline-1,4-dioxide theoretical computations[77] have also been used to obtain the first and second $DH°(N–O)$ values, as well as the average $DH°(N–O)$ value. Calculated values were in excellent agreement with the experimental results listed in Table 9. For the three compounds studied, computations showed that the first $DH°(N–O)$ values increased in the order ethoxycarbonyl<benzyl<methyl. The second $DH°(N–O)$ values were nearly identical due to similar neighboring, i.e., a methyl group in an adjacent position.

9. Azo-N,N-Dioxides

Azo-N,N-dioxides are in fact dimers of nitroso compounds as it is shown in the following equation:

$$2\ R\text{-}NO \rightarrow R\text{-}N=N\text{-}R \quad (\text{with } O \uparrow \ O \uparrow) \quad (10)$$
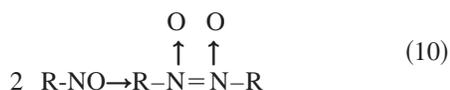
From $\Delta_f H_m°(g)$ of the azo-N,N-dioxide with that of the corresponding azoderivative, the mean (N–O) bond dissociation enthalpy can be derived. If $\Delta_f H_m°(g)$ of the corresponding azoxy compound is available, then the successive (N–O) bond dissociation enthalpies can be derived. Also, if

$\Delta_f H_m°(g)$ of the nitroso compound is known, then the dissociation enthalpy of the (N=N) bond can be derived. Variation in $DH°(N=N)$ can provide a basis for an understanding of why some nitroso compounds dimerize and some do not.

Table 10 lists the thermochemical quantities that are available for deriving $\langle DH°(N–O)\rangle$ in azo-N,N-dioxides. It is apparent that $\langle DH°(N–O)\rangle$ for the azobenzene-N,N-dioxide derivatives is roughly constant and is unaffected by substitution in the ortho position in the benzene rings. The crystal structure of azobenzene-N,N-dioxide was studied by Dieterich et al.[85,86] who found the molecule to be in the cis configuration, the central C(NO)–C(NO) moiety was nonplanar and the benzene rings make angles of 112.0° with the best plane of the C(NO)–C(NO) group. Consequently, the ortho groups on the benzene rings are well removed from the (N–O) bonds and so have little effect on them.

Table 11 lists, as far as possible, the successive (N–O) bond dissociation enthalpies in azo-N,N-dioxides, but unfortunately, many of the quantities in Table 11 are estimates. $DH°(N–O)_1$ is $\Delta_f H_m°(g)$ for reaction (11) and $DH°(N–O)_2$ is $\Delta_f H_m°(g)$ for reaction (12)

$$R\text{-}N(O)=N(O)(g) = R\text{-}N=N(O)\text{-}R(g) + O(g), \quad (11)$$

$$R\text{-}N=N(O)\text{-}R(g) = R\text{-}N=N\text{-}R(g) + O(g). \quad (12)$$
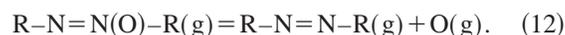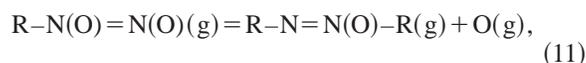
As can be expected $DH°(N–O)_1 \langle DH°(N–O)_2$, presumably because of the relief of the repulsion between the two (N–O) bonds in the azo-N,N-dioxides. The constancy of

TABLE 11. Enthalpies of dissociation of the (N–O) bonds for azo N,N-dioxide derivatives

Compound	$\Delta_f H^o_m(g)$ Derivatives azo N,N-dioxide $(kJ\cdot mol^{-1})$	$\Delta_f H^o_m(g)$ Derivatives azoxy $(kJ\cdot mol^{-1})$	$DH^o_1(N\text{-}O)$ $(kJ\cdot mol^{-1})$	$\Delta_f H^o_m(g)$ Derivatives "azo" $(kJ\cdot mol^{-1})$	$DH^o_2(N\text{-}O)$ $(kJ\cdot mol^{-1})$
$H_3C-N=N-CH_3$ (N,N-dioxide)	70.7 ± 4.2 [81]	$[62.4 \pm 4.2]$	245.7 ± 5.9	$[144.7 \pm 4.1]$	331.5 ± 6.0
$(H_3C)_3C-N=N-C(CH_3)_3$ (N,N-dioxide)	-133.5 ± 2.9 [82]	-107.6 ± 2.1 [53]	275.1 ± 3.6	-35.6 ± 3.6 [55]	321.2 ± 4.2
diphenyl azo N,N-dioxide	328.4 ± 2.9 [82]	342.0 ± 2.4 [47]	262.8 ± 3.8	402.2 ± 2.7 [51]	309.4 ± 3.6
bis(2-nitrophenyl) azo N,N-dioxide	312.5 ± 2.8 [82]	$[311.8 \pm 5.0]$	248.5 ± 7.0	$[372.0 \pm 3.2]$	309.4 ± 6.0
tetramethyl (2,6-dimethylphenyl) azo N,N-dioxide	207.3 ± 12.3 [83]	$[224.2 \pm 5.0]$	266.1 ± 13.0	$[284.4 \pm 4.6]$	309.5 ± 13.5
trimethyl-substituted azo N,N-dioxide	140.6 ± 12.5 [83]	$[153.4 \pm 5.0]$	262.0 ± 13.5	$[213.6 \pm 5.3]$	309.4 ± 13.6
tetraethyl-substituted azo N,N-dioxide	119.5 ± 12.7 [84]	$[131.2 \pm 9.0]$	261.0 ± 15.5	$[191.4 \pm 5.8]$	309.4 ± 10.7

$DH°(N–O)_2$ for the azoxybenzene derivatives is a consequence of the estimation procedure, that the enthalpy increment in $\Delta_f H^o_m(g)$ for substitution into the azobenzene derivative is the same as for the azoxybenzene derivative, and so this is without great significance.

Table 12 lists $DH°(N=N)$ values in the azo-di-N,N-oxides derived from the enthalpy of the following reaction:

$$\underset{R-N=N-R(g)}{\overset{O\quad O}{\overset{\uparrow\quad\uparrow}{}}} = 2\ RNO(g). \tag{13}$$
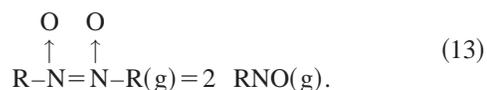
An explanation of the derivation of $\Delta_f H^o_m(g)$ for the nitroso compounds is required. $\Delta_f H^o_m(g)$ for dimethylazo-di-N-oxide was derived by Batt and Milne[81] from static-bomb combustion measurements and vapor pressure as a function of temperature. Christie *et al.*[87] studied the gaseous equilibrium Eq. (14) as a function of temperature to derive $\Delta_r H^o_m$ so that $\Delta_f H^o_m(CH_3NO,g)$ was obtained

$$\underset{CH_3-N=N-CH_3}{\overset{O\quad O}{\overset{\uparrow\quad\uparrow}{}}} = 2\ CH_3NO. \tag{14}$$
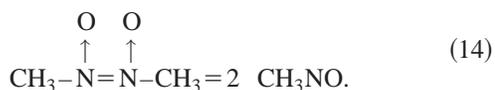
$\Delta_f H^o_m((CH_3)_3CNO,g)$ was estimated by taking the difference in the $\Delta_f H^o_m(g)$ between nitrosomethyl and nitroso-*tert*-butyl to equal that between methylamine and *tert*-butylamine. Choo *et al.*[88] from very low pressure pyrolysis

derived the activation energy for the dissociation presented in Eq. (15) and by assuming zero activation energy for the reverse reaction, the enthalpy of this dissociation is $(215.5 \pm 4.2)\ kJ\cdot mol^{-1}$

$$C_6H_5NO(g) = C_6H_5(g) + NO(g). \tag{15}$$
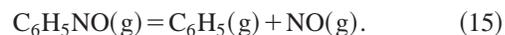
With $\Delta_f H^o_m(NO,g)/(kJ\cdot mol^{-1}) = (90.3 \pm 0.2)$,[21] and $\Delta_f H^o_m(C_6H_5,g)/(kJ\cdot mol^{-1}) = (335 \pm 8)$,[89] $\Delta_f H^o_m(C_6H_5NO,g)$ was derived. $\Delta_f H^o_m(g)$ for 2-nitronitrosobenzene was estimated by application of the Cox scheme.[19] $\Delta_f H^o_m(g)$ for the alkyl-substituted nitrosobenzenes were determined from the enthalpies of decomposition of the solid azo-di-N,N-oxide to be gaseous nitroso compound as measured by microcalorimetry.[83]

In the azobenzene di-N,N-oxide derivatives $DH°(N=N)$ is reduced in the presence of *ortho* alkyl groups in contrast with $DH°(N–O)$ values which are unaffected by the presence of ortho groups.

Enthalpies of dissociation of some dimeric nitroso compounds in solution have been determined using spectroscopic,[90,91] NMR,[92–94] and pulse voltammetry,[95] by measuring equilibrium constants as functions of temperature and the results are shown in Table 13. For the dimers of nitrosobenzene and of 2-methylnitrosobenzene, both *cis* and *trans* forms were present with the *cis* form being energetically more stable by about 13 kJ·mol^{-1}. For the dimer of 2,6-dimethylnitrosobenzene, Azoulay *et al.*[96,97] found only the *trans* form so it is probable that all derivatives with two

TABLE 12. Standard molar enthalpies of formation of gaseous azo di-*N,N*-oxide and nitroso compounds and calculated $DH°(N=N)$ values

Compound	Di-*N,N*-oxide $(\Delta_f H_m^O (g)/kJ\cdot mol^{-1})$	Nitroso compound $(\Delta_f H_m^O (g)/kJ\cdot mol^{-1})$	$DH_m^o (N = N)$ $(kJ\cdot mol^{-1})$
	70.7 ± 4.2 [81]	69.9 ± 3.3 [87]	69.1 ± 7.8
	-133.5 ± 2.9 [82]	$[-27.6 \pm 3.5]$	78.3 ± 7.5
	328.4 ± 2.9 [82]	209.8 ± 8.0 [83]	91.2 ± 8.5
	312.5 ± 2.8 [82]	$[193.9 \pm 2.3]$	75.3 ± 5.4
	207.3 ± 12.3 [83]	139.8 ± 1.6 [83]	72.3 ± 12.7
	140.6 ± 12.5 [83]	107.4 ± 1.9 [83]	74.2 ± 13.1
	119.5 ± 12.7 [84]	100.1 ± 3.4 [84]	80.7 ± 13.1

ortho alkyl groups exist solely in *trans* forms. Solvation of these polar molecules is expected to be exothermic and will be greater for the dissociated products than for the dimer, hence the apparent dissociation enthalpies in solution will be less than the corresponding values in the gaseous state.

10. Nitroso Compounds

Nitrosobenzene, and its methyl, bromo, and nitro derivatives form white crystalline solids, which on melting yield green liquids. Crystal structure determinations of nitrosobenzene,[85,86] 2-nitrosobenzoic acid,[85] 4-bromonitrosobenzene,[101] and 2,4,6-tribromonitrosbenzene[102] show these compounds to be dimeric in the crystalline state. Crystal structure determination of the green solids, 4-iodonitro-

TABLE 13. (N=N) bond dissociation enthalpies in select azobenzene di-*N,N*-oxides derived from solution phase measurements

Compound	Solvent		$DH_m^o(N=N)$ $(kJ\cdot mol^{-1})$	Ref.
$(C_6H_5NO)_2$	$CDCl_3$	*trans*	42.5 ± 1.2	93
	$CDCl_3$	*cis*	55.4 ± 1.7	93
$(2\text{-}CH_3C_6H_4NO)_2$	CH_3CN	*trans*	45.6 ± 2.1	92
	CH_3CN	*cis*	58.5 ± 2.5	92
$(2\text{-}CH_3OC_6H_4NO)_2$	CD_2Cl_2	*cis*	44.8 ± 2.8	94
$(2,6\text{-}(CH_3)_2C_6H_3NO)_2$	CH_3CN	*trans*	54.0 ± 2.7	96
$(2,4,6\text{-}(CH_3)_3C_6H_2NO)_2$	C_6H_6		50.6 ± 4.2	91
	CH_3CN		55.9 ± 2.6	95
$(2,3,5,6\text{-}(CH_3)_4C_6HNO)_2$	C_6H_6		61.1 ± 5.0	90
$(2,3,4,5,6\text{-}(CH_3)_5C_6NO)_2$	C_6H_6		50.2 ± 5.0	90
$(2,6\text{-}(CH_3)_2\text{-}4\text{-}CH_3OC_6H_2NO)_2$	CD_2Cl_2	*trans*	36.9 ± 1.4	94
	CD_2Cl_2	*cis*	49.5 ± 1.4	94

sobenzene,[103] and 4-dimethylaminonitrosobenzene[104] show these compounds to be monomeric in the crystalline state.

There are two extreme causes as to why some nitroso compounds do not dimerize in the solid state: (i) exceptional stabilization of the monomer with some consequent destabilization of the hypothetical dimer; and (ii) bulky groups substituted ortho to the nitroso goup may prevent dimerization due to steric hindrance. There are examples showing each of these effects. Mijs *et al.*[105] proposed that an electron donating group substituted para to the nitroso group causes additional stabilization of the monomer (a) due to increased contributions of quinonoid forms (b) associated with a consequent reduction in the (N–N) bond order in the hypothetical dimer (c) due to contributions from (d) (see Fig. 6).

Table 14 lists observed and calculated values of $\Delta_f H_m^°(g)$ for some nitroso compounds. For the calculated values an average increment in $\Delta_f H_m^°(g)$ for substitution of NO into the benzene ring of (122.4 ± 2.2) kJ·mol^{-1} was used. $\Delta_f H_m^°(g)$ for the benzene derivatives were taken from Ref. 24 except that $\Delta_f H_m^°(g)$ for $(CH_3)_3CC_6H_5$, $-(22.6\pm1.2)$ kJ·mol^{-1} was used to estimate $\Delta_f H_m^°(g)$ of $1,3,5\text{-}((CH_3)_3C)_3C_6H_3$.

It is clear from the values in Table 14, that the alkyl substituted nitrosobenzenes have expected $\Delta_f H_m^°(g)$ values but 4-dimethylaminonitrosobenzene, 4-diethylaminonitrosobenzene, and 4-hydroxynitrosobenzene all show considerable stabilization.

Table 15 lists several $DH°(N-O)$ values in nitrobenzene derivatives and for the alkyl-substituted nitrobenzenes, the observed and calculated $\Delta_f H_m^°(g)$ values are compared, not so for $4\text{-}(CH_3)_2NC_6H_4NO_2$ because of interaction between the *N,N*-dimethylamino and the nitro group.

$DH°(N-O)$ for $4\text{-}(CH_3)_2NC_6H_4NO_2$ is 20 kJ·mol^{-1} less

FIG. 6. Structural valence formulas for 4-substituted nitrosobenzenes and 4,4'-disubstituted azobenzene N,N-dioxides.

than that for nitrobenzene and this represents the additional stabilization in $4\text{-}(CH_3)_2NC_6H_4NO$ over that in the nitro derivative; for the latter has an expected $\Delta_fH^\circ_m(g)$ value because the following reaction has $\Delta_rH^\circ_m/kJ\cdot mol^{-1}=(9.9\pm5.7)$:

$$C_6H_5NH_2(g)+4\text{-}(CH_3)_2NC_6H_4NO_2(g)$$

$$=C_6H_5N(CH_3)_2(g)+4\text{-}NH_2C_6H_4NO_2(g). \quad (16)$$
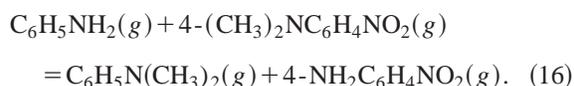
If $DH^\circ(N{=}N)$ in nitrosobenzene dimer was assigned as (91.2 ± 8.5) kJ·mol^{-1} (Table 12), the stabilization energy in $4\text{-}(CH_3)_2NC_6H_4NO$ would reduce the $DH^\circ(N{=}N)$ value in the hypothetical dimer to about 51 kJ·mol^{-1}. It is a reasonable assumption that the enthalpy of sublimation of the hypothetical dimer would not be larger than 107 kJ·mol^{-1} and would probably be less. Consider the following cycle:

$$2\text{ monomer (g)} \xrightarrow{-51\text{ kJ·mol}^{-1}} \text{dimer (g)}$$

$$\uparrow 164\text{ kJ·mol}^{-1} \qquad \uparrow 107\text{ kJ·mol}^{-1}$$

$$2\text{ monomer(cr)} \xrightarrow{6\text{ kJ·mol}^{-1}} \text{dimer (cr)}$$
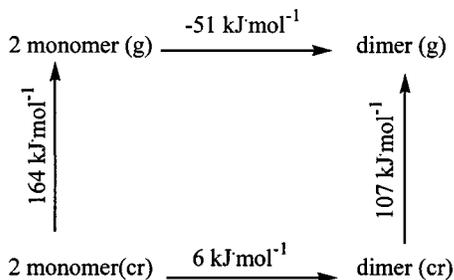
Dimerization in the solid state would be endothermic so it does not occur.

For nitrosobenzene, a similar analysis requires the enthalpy of sublimation of the monomer and it can be assumed that this would not be larger than 82 kJ·mol^{-1} (i.e., that for $4\text{-}(CH_3)_2NC_6H_4NO$), so that it can be established as the following cycle:

TABLE 14. Comparison of observed and calculated standard molar enthalpies of formation of gaseous nitroso compounds

Compound	$\Delta_fH^\circ_m(g)/(kJ\cdot mol^{-1})$		
	Observed	Calculated	$\Delta\Delta_fH^\circ_m(g)$
C_6H_5NO	209.8 ± 8.0[83]	205.0 ± 2.3	4.8 ± 8.3
$2,6\text{-}(CH_3)_2C_6H_3NO$	139.8 ± 1.6[83]	139.7 ± 2.3	0.1 ± 2.8
$2,4,6\text{-}(CH_3)_3C_6H_2NO$	107.4 ± 1.9[83]	106.5 ± 2.6	0.9 ± 3.2
$2,6\text{-}(C_2H_5)_2C_6H_3NO$	100.1 ± 3.4[84]	$100.6\pm[3.3]$	$-0.5\pm[4.7]$
$2,4,6\text{-}((CH_3)_3C)_3C_6H_2NO$	-117.4 ± 5.4[84]	-110.6 ± 4.3	-6.8 ± 6.9
$4\text{-}(CH_3)_2N\text{-}C_6H_4NO$	185.0 ± 2.3[98]	222.9 ± 5.2	-37.9 ± 5.7
$4\text{-}(C_2H_5)_2N\text{-}C_6H_4NO$	151.8 ± 5.3[99]	184.5 ± 7.9	-32.7 ± 5.7
$4\text{-}HO\text{-}C_6H_4NO$	7.5 ± 3.7[100]	26.0 ± 2.4	-18.5 ± 4.4

$$2\text{ monomer (g)} \xrightarrow{-91\text{ kJ·mol}^{-1}} \text{dimer (g)}$$

$$\uparrow 164\text{ kJ·mol}^{-1} \qquad \uparrow 87\text{ kJ·mol}^{-1}$$

$$2\text{ monomer(cr)} \xrightarrow{-14\text{ kJ·mol}^{-1}} \text{dimer (cr)}$$
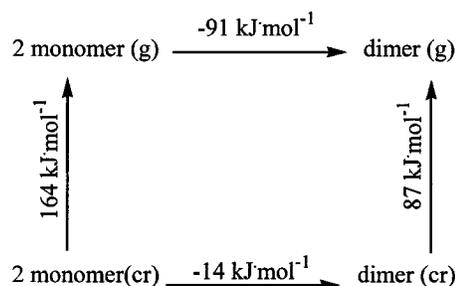
In this case, dimerization in the solid state would be exothermic.

$4\text{-}(C_2H_5)_2NC_6H_4NO$ is stabilized by about the same amount as in $4\text{-}(CH_3)_2NC_6H_4NO$ because the following gaseous reaction is thermoneutral. $\Delta_rH^\circ_m/kJ\cdot mol^{-1}=(5.2\pm10.6)$ so a similar analysis would show that dimerization in the solid state would be endothermic. For $4\text{-}HOC_6H_4NO$, the stabilization shown in Table 14 is 18.5 kJ·mol^{-1}, which is consistent with this compound not dimerizing in the solid state

$$4\text{-}(CH_3)_2NC_6H_4NO(g)+4\text{-}(C_2H_5)_2NC_6H_5(g)$$

$$=4\text{-}(C_2H_5)_2NC_6H_4NO(g)+4\text{-}(CH_3)_2NC_6H_5(g). \quad (17)$$
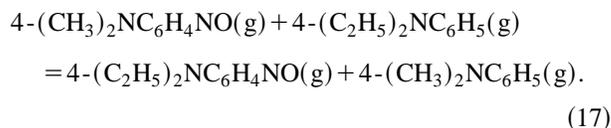
It should be noted that an electron-donating group in the para-ring position does not necessarily guarantee that the nitrosobenzene will not exist as a monomeric solid. Take for example the substituted 4-methoxynitrosobenzenes. The parent compound is bluish-green indicative of the momomeric

TABLE 15. Comparison between observed and calculated standard enthalpies of formation of substituted nitrobenzene derivatives and calculated $DH^\circ(N{-}O)$ values.

Compound	$\Delta_fH^\circ_m(g)/(kJ\cdot mol^{-1})$			
	Observed	Calculated	$\Delta\Delta_fH^\circ_m(g)$	$DH^\circ_m(N{-}O)/(kJ\,mol^{-1})$
$C_6H_5NO_2$	67.5 ± 0.6[24]	—	—	391.5 ± 8.1
$4\text{-}CH_3\text{-}C_6H_4NO_2$	31.0 ± 3.8[24]	35.3 ± 1.1	-4.3 ± 4.0	
$2,6\text{-}(CH_3)_2\text{-}C_6H_3NO_2$	8.6 ± 1.6[83]	2.2 ± 1.2	6.4 ± 2.0	380.4 ± 2.3
$2\text{-}C_2H_5\text{-}C_6H_4NO_2$	11.2 ± 6.6[24]	14.8 ± 1.4	-3.6 ± 6.7	
$4\text{-}C_2H_5\text{-}C_6H_4NO_2$	7.4 ± 6.6[24]	14.8 ± 1.4	-7.4 ± 6.7	
$2,4,6\text{-}((CH_3)_3C)_3\text{-}C_6H_2NO_2$	-189.9 ± 4.4[84]	-248.1 ± 3.8	58.2 ± 5.8	321.7 ± 7.0
$4\text{-}(CH_3)_2N\text{-}C_6H_4NO_2$	62.8 ± 2.6[98]	—	—	371.4 ± 3.5

TABLE 16. Standard molar enthalpies of formation of gaseous nitro and nitroso compounds and calculated $DH°$(N–O) values

	Nitro compound $\Delta_f H_m°(g)/kJ \cdot mol^{-1}$	Nitroso compound $\Delta_f H_m°(g)/kJ \cdot mol^{-1}$	$DH_m°$(N–O)/kJ·mol^{-1}
CH_3NO_2	-74.3 ± 0.5[106,107]	69.9 ± 3.3[81]	393.4 ± 3.5
$(CH_3)_3CNO_2$	-177.1 ± 3.3[108]	-29 ± 4[109]	397 ± 5
$C_6H_5CH_2NO_2$	30.7 ± 2.8[110]	-174 ± 7[109]	393 ± 7
$C_6H_5NO_2$	67.5 ± 0.6[24]	209.8 ± 8.0[83]	392 ± 8
$2,6\text{-}(CH_3)_2C_6H_3NO_2$	8.6 ± 1.6[83]	139.8 ± 1.6[83]	380.4 ± 2.3
$2,4,6\text{-}(CH_3)_3C_6H_2NO_2$	-26.8 ± 2.2[83]	107.4 ± 1.9[83]	383.4 ± 2.9
$2,4,6\text{-}((CH_3)_3C)_3C_6H_2NO_2$	-189.9 ± 4.4[84]	-117.4 ± 5.4[84]	321.7 ± 7.0
$1\text{-}O_2N\text{-Adamantane}$	175.4 ± 1.7[111]	-24.6 ± 5.0[111]	400 ± 5
$2\text{-}(O_2N)C_6H_4NO_2$	116.7 ± 1.2[24,112]	$[193.9 \pm 2.3]$	326.4 ± 2.6
$4\text{-}(CH_3)_2N\text{–}C_6H_4NO_2$	62.8 ± 2.6[98]	185.0 ± 2.3[98]	371.4 ± 3.5

form. Crystalline 2-methyl-4-methoxynitrosobenzene, 3,5-dimethyl-4-methoxynitrosobenzene, and 3-methyl-4-methoxynitrosobenzene are also green or bluish–green in color. 2,6-Dimethyl-4-methoxynitrosobenzene, on the other hand, is an off-white crystal at ambient room temperature.[94] Placement of methyl substituents in both the 2- and 6-ring positions does have a significant effect on the stabilizing ability of the methoxy group. Calorimetric measurements on the various methyl-substituted 4-methoxynitrosobenzenes would shed additional light on this matter.

Table 15 shows destabilization of (58.2 ± 5.8) kJ·mol^{-1} in $2,4,6\text{-}((CH_3)_3C)_3C_6H_2NO_2$, whereas the corresponding nitroso compound has an expected $\Delta_f H_m°(g)$ value (Table 14). If $2,4,6\text{-}((CH_3)_3C)_3C_6H_2NO$ were to dimerize it would be reasonable to assume that the steric strain energy would be at least twice that shown in the corresponding nitro derivative, i.e., ≈ 116 kJ·mol^{-1}. As $DH°$(N=N) in nitrosobenzene dimer is (91.5 ± 8.5) kJ·mol^{-1}, it is clear that steric hindrance would prevent formation of the dimer.

11. Nitro Compounds

The dissociation enthalpy for the terminal (N–O) bond in nitro compounds is $\Delta_f H_m°(g)$ for reaction (18), thus $\Delta_f H_m°(g)$ values are required for R–NO$_2$ and R–NO and the values available at present are listed in Table 16

$$R\text{–}NO_2(g) = R\text{–}NO(g) + O(g). \quad (18)$$
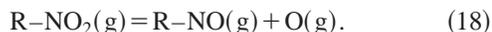
The $DH°$(N–O) values for the aliphatic nitro compounds and nitrobenzene are the same (394 ± 4) kJ·mol^{-1}. The effect of ortho groups in nitrobenzene is to reduce $DH°$(N–O) due to steric hindrance and as expected, this effect is larger for *tert*-butyl groups than for methyl groups. As explained previously, the reduction $DH°$(N–O) in 4-dimethylaminonitrobenzene is due to greater stabilization in the nitroso compound relative to the nitro derivative.

To derive a value for $DH°$(N–O) in 1-nitroadamantane, two quantities must be estimated. 1-nitrosoadamantane is a dimer, dimerization in the solid state must be exothermic (greater than -1.7 kJ·mol^{-1} to overcome the entropy term, taking the entropy of dimerization to be simply $R \ln 2$). For nitrosobenzene we estimated that dimerization in the solid state was -12 kJ·mol^{-1}; in this case it will be smaller and a

reasonable estimate seems to be $-(5 \pm 2)$ kJ·mol^{-1}. The enthalpy of sublimation of the hypothetical monomeric 1-nitrosoadamantane can be assumed to be the same as that for adamantanone, i.e., 76.1 ± 1.5 kJ·mol^{-1}, but the uncertainty should be increased, say threefold to ± 4.5. The relevant thermodynamic cycle is given below:
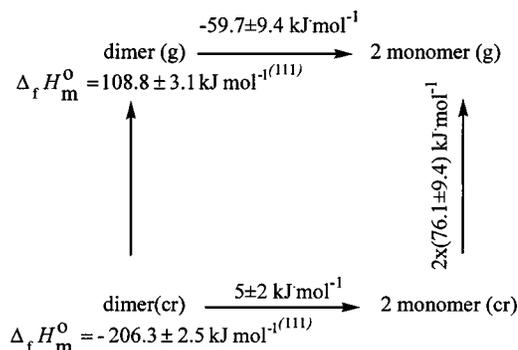
$DH°$(N=N) in the dimer can be calculated by Eq. (19), assuming $\Delta_f H_m°(\text{monomer}, g) = -(24.6 \pm 5.0)$ kJ·mol^{-1}

$$DH°(N=N) = 2\Delta_f H_m°(\text{monomer}, g) + (108.8 \pm 3.1). \quad (19)$$

The value $DH°(N=N) = (59.7 \pm 9.4)$ kJ·mol^{-1} does not seem unreasonable. The bond dissociation enthalpy in 1-nitroadamantane is then calculated as the enthalpy for Reaction (20), given by Eq. (21), which is in good agreement with $DH°$(N–O) values for other aliphatic nitro compounds

$$1\text{-nitroadamantane}(g) \rightarrow 1\text{-nitrosoadamantane}(g) + O(g), \quad (20)$$
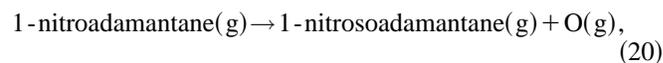
$$DH°(N\text{–}O) = -(24.6 \pm 5.0) + 249.2 + (175.4 \pm 1.7)$$

$$= (400 \pm 5). \quad (21)$$

There is also sufficient thermodynamic data for calculating a bond dissociation enthalpy for the removal of an oxygen atom from 1,2-dinitrobenzene to form 2-nitro-1-nitrosobenzene. The estimated value of the enthalpy of formation of 2-nitro-1-nitrosobenzene, $\Delta_f H_m°(g) = 193.9 \pm 2.3$ kJ·mol^{-1}, is given in Table 12. The tabulated value is then combined with $\Delta_f H_m°(cr) = 21.2 \pm 0.8$ kJ·mol^{-1},[24] and the enthalpy of sublimation of 95.5 ± 0.9 kJ·mol^{-1},[112] to give $DH°$(N–O) $= 326.4 \pm 2.6$ kJ·mol^{-1}. The calculated bond

TABLE 17. Standard molar enthalpies of formation of gaseous R–N–NO$_2$ and R–N–NO and calculated $DH°$(N–O) values

	R–N–NO$_2$ $\Delta_f H_m°(g)/(kJ \cdot mol^{-1})$	R–N–NO $\Delta_f H_m°(g)/(kJ \cdot mol^{-1})$	$DH_m°$(N–O)/(kJ·mol^{-1})
1-nitropiperidine	-44.5 ± 1.9[24]	16.6 ± 1.5[24]	310.3 ± 2.4
N-nitromorpholine	-131.0[113]	-87.9[113]	292.3
1,4-dinitropiperazine	58.3 ± 2.2[24]	194.3 ± 2.2[24]	317.2 ± 3.1[a]
hexahydro-1,3,5-trinitro-1,3,5-triazine	66.5 ± 2.0(cr)[24]	285.9 ± 2.3(cr)[24]	$322.3 \pm [7]$[b]

[a]Calculated value corresponds to $\langle DH°(N-O) \rangle$ for removal of an oxygen atom from both nitro groups.
[b]Calculated value corresponds to $\langle DH°(N-O) \rangle$ for removal of an oxygen atom from all three nitro groups.

dissociation for 1,2-dinitrobenzene is very close to the value for the *tert*-butyl nitrobenzene derivative, suggesting that at least one of the two nitro groups is not in the plane of the phenyl ring because of steric hindrance. Hence it is much easier to remove an oxygen atom in 1,2-dinitrobenzene than in nitrobenzene.

12. Nitramines

Nitramines and nitrosamines are considered separately from the nitro and nitroso compounds just discussed because the NO$_2$ and NO groups are attached to a nitrogen atom (i.e., R–NNO$_2$ and R–NNO), rather than a carbon atom. Secondary nitramines are highly energetic compounds and are currently used as explosive and powder propellant components. There is very limited enthalpy of formation data[24,113–115] for nitramines at the present time. The values at present are given in Table 17. The dissociation enthalpy of the terminal (N–O) bond in nitramines is given by $\Delta_r H_m°(g)$ for Reaction (19)

$$R-N-NO_2(g) \rightarrow R-N-NO(g) + O(g). \quad (22)$$

Enthalpy of sublimation data is not available in the case of hexahydro-1,3,5-trinitro-1,3,5-triazine and hexahydro-1,3,5-trinitroso-1,3,5-triazine so we have based the $DH°$(N–O) computation on the formation enthalpies of the two crystalline compounds. This is equivalent to assuming that $\Delta_{cr}^g H_m°$ is the same for both compounds. Examination of the numerical entries in Tables 16 and 17 reveals that the bond dissociation enthalpies of nitramines are generally less than those of nitroalkanes and nitrobenzenes.

13. Alkyl Nitrates

The dissociation enthalpy of the terminal (N–O) bond in alkyl nitrates is given by $\Delta_r H_m°(g)$ for Reaction (23)

$$R-O-NO_2(g) \rightarrow R-O-NO(g) + O(g). \quad (23)$$

The values available at present are given in Table 18, and although the thermochemical data of alkyl nitrites are not as firmly established as those for the nitrates, nevertheless $DH°$(N–O) appears to be constant in alkyl nitrates.

14. Oxygen Atom Transfer Reactions in the Gaseous State

The generalized oxygen atom transfer reaction in the gaseous phase can be written as follows:

$$XO(g) + Y(g) = X(g) + YO(g). \quad (24)$$
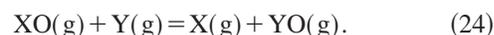
The standard entropy change of this reaction will be small so that if such reactions are ordered in terms of decreasing standard Gibbs energy changes, the same order is to be expected in terms of decreasing standard enthalpies of reaction. Holm[13] devised a thermodynamic reactivity scale by considering the generalized oxygen atom transfer reaction as the combination of two reactions, (25) and (26), so that $\Delta_r H_m°$ for reaction (24) will be given by $\Delta_r H_m°$ [Eqs. (26)–(25)]

$$X(g) + \tfrac{1}{2}O_2(g) = XO(g), \quad (25)$$

$$Y(g) + \tfrac{1}{2}O_2(g) = YO(g). \quad (26)$$

As the standard entropy for Reaction (24) is small, the standard entropy changes for Eqs. (25) or (26) will be approximately equal so that ordering reactions (25) or (26) in terms of decreasing $\Delta_r H_m°$ will give the same order as for $\Delta_r G_m°$.

Table 19 lists $\Delta_r H_m°$ values for reaction (25) in decreasing order and where possible giving realistic experimental uncertainties. This list extends that given by Holm and Donahue;[14] they also listed values for the solid state and for solution but the work discussed in this review is solely for the gaseous state.

TABLE 18. Standard molar enthalpies of formation of gaseous alkylnitrates and alkylnitrites and calculated $DH°$(N–O) values

	Nitrate $\Delta_f H_m°(g)/(kJ \cdot mol^{-1})$	Nitrite $\Delta_f H_m°(g)/(kJ \cdot mol^{-1})$	$DH_m°$(N–O)/(kJ·mol^{-1})
CH$_3$ONO$_2$	-122.2 ± 4.3[116,117]	-66.1 ± 1.0[118,119]	305.3 ± 4.4
C$_2$H$_5$ONO$_2$	-154.1 ± 1.0[116,120]	-101.3 ± 4.5[121]	302.0 ± 4.6
n-C$_3$H$_7$ONO$_2$	-173.9 ± 1.3[120]	-118.8 ± 4.1[122]	304.3 ± 4.3
i-C$_3$H$_7$ONO$_2$	-191.0 ± 1.3[120,123]	-133.5 ± 4.1[122]	306.7 ± 4.3

TABLE 19. Transfer thermodynamic reactivity scale for gas phase reaction: $X + \frac{1}{2} O_2 = XO$

X	XO	$\Delta_r H_m^\circ/(\text{kJ·mol}^{-1})$	Reference
O_2	O_3	$+144.2 \pm 2.1$	124
H_2O	H_2O_2	$+105.5 \pm 2.5$	21
N_2	N_2O	$+82.1 \pm 5.0$	21
Cl_2	Cl_2O	$+80.3 \pm 1.3$	21
$tert$-BuOH	$tert$-BuOOH	$+66.1 \pm 2.6$	24
MeOMe	MeOOMe	$+58.4 \pm 1.4$	24
ClO_2	ClO_3	$+52.5 \pm 9.5$	21
$1\text{-}O_2NC_{10}H_{15}$	$1\text{-}O_2NOC_{10}H_{15}$	$+49.7 \pm 3.0$	111
$2,4,6\text{-}Me_3C_6H_2CN$	$2,4,6\text{-}Me_3C_6H_2CNO$	$+27.0 \pm 4.6$	44
$2,4,6\text{-}(MeO)_3C_6H_2CN$	$2,4,6\text{-}(MeO)_3C_6H_2CNO$	$+16.4 \pm 3.8$	44
$tert$-Bu_2O	$tert$-BuOO$tert$Bu	$+12.9 \pm 3.3$	24
$SeCl_2$	$SeOCl_2$	$+6.8 \pm 8.0$	21
ClO	ClO_2	$+0.7 \pm 2.0$	21
Furazan	Furoxan	-1.7 ± 3.1	42
Me_3N	Me_3NO	-6.3 ± 5.0	23
PhN=N(O)Ph	PhN(O)=N(O)Ph	-13.6 ± 3.8	47, 82
$c\text{-}C_5H_5N$	$c\text{-}C_5H_5NO$	-15.7 ± 2.0	23, 24
PhCH=NPh	PhCH=N(O)Ph	-15.7 ± 3.0	47
$tert$BuN=N(O)$tert$Bu	$tert$-BuN(O)=N(O)$tert$BU	-25.9 ± 3.6	53, 82
PhCH=N$tert$Bu	PhCH=N(O)$tert$Bu	-33.8 ± 6.5	48
$2\text{-}IC_6H_4CO_2H$	$2\text{-}OIC_6H_4CO_2H$	-35.6 ± 4.8	100
EtONO	$EtONO_2$	-49.9 ± 6.5	21
OsO_3	OsO_4	-53.5 ± 3.0	21
MeONO	$MeONO_2$	-56.1 ± 4.5	24
NO	NO_2	-57.1 ± 0.2	21
PhN=NPh	PhN=N(O)Ph	-60.2 ± 3.6	47, 51
$tert$-BuN=N$tert$Bu	$tert$-BuN=N(O)$tert$Bu	-72.0 ± 4.2	53, 55
N_2O_3	N_2O_4	-74.6 ± 2.5	21
nPrN=NnPr	nPrN=N(O)nPr	-82.3 ± 3.8	53, 54
SO_2	SO_3	-98.9 ± 1.5	21
$H_2C=CH_2$	C_2H_4O	-105.1 ± 0.7	24
RuO_3	RuO_4	-105.9 ± 13.9	125
Me_2S	Me_2SO	-113.8 ± 1.0	24
$MeCH=CH_2$	$MeCHCH_2O$	-114.7 ± 1.0	24
PhS_2	PhS_2O	-124.4 ± 4.1	24
CH_4	CH_4O	-127.1 ± 0.5	24
$4\text{-}NO\text{-}C_6H_4OH$	$4\text{-}NO_2\text{-}C_6H_4OH$	-136.1 ± 4.2	100
C_6H_5NO	$C_6H_5NO_2$	-142.3 ± 8.0	24, 83
CH_3NO	CH_3NO_2	-144.2 ± 0.6	81, 106, 107
$SOCl_2$	SO_2Cl_2	-148.3 ± 1.2	125
$MoCl_4$	$MoOCl_4$	-171 ± 15	14
Ph_3As	Ph_3AsO	-180 ± 15	14
SCl_2	$SOCl_2$	-189.7 ± 3.8	125
$(MeO)_2SO$	$(MeO)_2SO_2$	-204.0 ± 2.8	24
SOF_2	SO_2F_2	-210.5 ± 5.2	126
Sn_2Et_6	$(Et_3Sn)_2O$	-220.1 ± 6.7	127
Me_2SO	Me_2SO_2	-221.8 ± 3.1	24
Ge_2Et_6	$(Et_3Ge)_2O$	-242.7 ± 4.5	127
O	O_2	-249.17 ± 0.10	22
CH_3CHO	CH_3CO_2H	-266.7 ± 1.7	24
HCHO	HCO_2H	-270.1 ± 0.8	24
PCl_3	$POCl_3$	-270.3 ± 2.6	125
WCl_4	$WOCl_4$	-281 ± 12	21
CO	CO_2	-283.0 ± 0.2	22
SO	SO_2	-301.8 ± 0.3	125
PPh_3	PPh_3O	-308.8 ± 15	128
Me_3P	Me_3PO	-333.3 ± 9.3	128
$(EtO)_3P$	$(EtO)_3PO$	-370.7 ± 2.0	129
$NbCl_3$	$NbOCl_3$	-392.3 ± 5.4	21
Si_2Me_6	$(Me_3Si)_2O$	-473.7 ± 7.7	129, 130

A couple with a more positive $\Delta_r H_m^\circ$ has the thermodynamic feasibility of transferring the oxygen atom of XO to Y for a couple of lower $\Delta_r H_m^\circ$. Although a negative $\Delta_r G_m^\circ$ is essential for a reaction to proceed, another essential requirement is for an acceptable kinetic pathway of sufficiently low activation energy. Holm and Donahue discuss oxygen atom transfers at various metal centers and also the importance of oxygen atom transfer in enzyme reactions.

15. Conclusions and Recommendations

Published thermochemical data enabled calculation of bond dissociation enthalpies for several important classes of organic compounds that contain a terminal (N–O) bond. Calculated DH°(N–O) values for most of the substituted pyridine-*N*-oxides considered were found to be between 253 and 266 kJ·mol^{-1}, unless the compound possessed special stabilizing effects or steric hindrance. This observation provides a method for estimating $\Delta_f H_m^\circ$(g) for other pyridine *N*-oxides from $\Delta_f H_m^\circ$(g) of the corresponding pyridine derivative. This approximate constancy of DH°(N–O) in pyridine *N*-oxides arises because the effect on $\Delta_f H_m^\circ$(g) of substitution into pyridine *N*-oxide is fairly closely matched by the corresponding effect of substitution into pyridine. To within experimental uncertainty, the (N–O) bond dissociation enthalpy for 6-methoxyquinoline-*N*-oxide also falls within this range, as do the average (N–O) bond dissociation enthalpies of pyrazine-1,4-dioxide and several substituted quinoxaline-1,4-dioxides.

Calculated (N–O) bond dissociation enthalpies of nitrones, DH°(N–O) = (275 ± 10) kJ·mol^{-1}, and substituted azoxybenzenes, DH°(N–O) = (320 ± 10) kJ·mol^{-1}, were both larger, and the calculated values were found to depend only slightly on whether the –CH=N(O)– and –N=N(O)– moieties were attached to an alkyl- or aromatic-carbon atom. Oxygen removal from an alkyl nitrate to form an alkylnitrite was found to require approximately 305 kJ·mol^{-1} based on published enthalpy of formation data for four compounds. Bond dissociation enthalpies of substituted furoxans and benzofuroxans fell between 237 and 256 kJ·mol^{-1}. For other classes of compounds containing the terminal (N–O) bond, there is not sufficient experimental data available at the present time to permit generalized observations regarding the (N–O) bond strength.

16. Acknowledgments

17. References

[1] H. Kaur and M. J. Perkins, Can. J. Chem. **60**, 1587–1592 (1982).

[2] C. Lagercrantz, Acta Chem. Scand. **43**, 78–81 (1989).

[3] C. Lagercrantz, Acta Chem. Scand. **43**, 503–505 (1989).

[4] L. Mathew, E. Y. Osei-Twum, and J. Warkentin, Can. J. Chem. **69**, 1398–1402 (1991).

[5] A. Albini and M. Alpegiani, Chem. Rev. **84**, 43–71 (1984).

[6] M. Sato, K. Shimada, K. Hirota, and Y. Maki, J. Am. Chem. Soc. **108**, 6039–6041 (1986).

[7] L. Skálová, M. Nobilis, B. Szotáková, V. Wsól, V. Kubicek, V. Baliharová, and E. J. Kvasnicková, Chemico-Biological Interactions **126**, 185–200 (2000).

[8] M. L. Greer, J. R. Duncan, J. L. Duff, and S. C. Blackstock, Tetrahedron Lett. **38**, 7665–7668 (1997).

[9] M. A. Ortega, M. J. Morancho, F. J. Martínez-Crespo, Y. Sainz, M. E. Montoya, A. Ceráin, and A. Monge, Eur. J. Med. Chem. **35**, 21–30 (2000).

[10] B. Ganley, G. Chowdhury, J. Bhansali, J. D. Daniels, and K. S. Gates, Bioorg. Med. Chem. **9**, 2395–2401 (2001).

[11] M. Bioani, H. Cerecelto, M. Gonçález, M. Risso, C. Olea-Azar, O. E. Piro, E. Castellano, A. L. Ceráin, O. Ezpeleta, and A. Monge-Vega, Eur. J. Med. Chem. **36**, 771–782 (2001).

[12] H. Nagasawa, M. Yamashita, N. Mikamo, M. Shimamura, S. Oka, Y. Uto, and H. Hori, Biochem. Physiol. Part A **132**, 33–40 (2002).

[13] R. H. Holm, Chem. Rev. **87**, 1401–1449 (1987).

[14] R. H. Holm and J. P. Donahue, Polyhedron **12**, 571–589 (1993).

[15] L. Batt and G. N. Robinson, in *Chemistry of Amines, Nitrosocompounds and Nitrocompounds and Their Derivatives*, edited by S. Patai (Wiley, Chichester, 1982), Vol. 2, Chap. 24.

[16] J. F. Liebeman, M. S. Campbell, and S. W. Slayden, in *The Chemistry of Amino, Nitroso, Nitro and Related Groups, Supplement F2*, edited by S. Patai (Wiley, New York, 1996), Chap. 8.

[17] J. F. Liebman, H. Y. Afeefy, and S. W. Slayden, in *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, edited by S. Patai (Wiley, New York, 1997), Vol. 2.

[18] S. W. Benson and J. H. Buss, J. Chem. Phys. **29**, 546–572 (1958).

[19] J. D. Cox, "A method of estimating the enthalpies of formation of benzene derivatives in the gas state," NPL Report CHEM83, June 1978.

[20] T. L. Cottrell, *The Strengths of Chemical Bonds*, 2nd ed. (Butterworths Scientific Publications, London, 1958).

[21] The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data 11, Supplement No. 2 (1982).

[22] J. D. Cox, D. D. Wagman and V. A. Medvedev, *CODATA, Key Values for Thermodynamics* (Hemisphere, New York, 1989).

[23] W. V. Steele, R. D. Chirico, W. B. Collier, J. A. Hossenlopp, A. Nguyen, and M. M. Strube, *Thermochemical and Thermophysical Properties of Organic Nitrogen Compounds Found in Fossil Fuels*, NIPER-188 (DOE Fossil Energy, Bartlesville Project Office, 1986). Available from NTIS Order No. DE-87001204.

[24] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, Texas, 1994), Vol 1.

[25] A. Haaland, H. Thomassen, and Y. Sterstrøm, J. Mol. Struct. **263**, 299–310 (1991).

[26] C. Airoldi and L. J. Gonçalves, Thermochim. Acta **194**, 259–263 (1992).

[27] Li Shaofeng and G. Pilcher, J. Chem. Thermodyn. **20**, 463–465 (1988).

[28] P. O. Dunstan, Thermochim. Acta **181**, 143–154 (1991).

[29] P. O. Dunstan, Thermochim. Acta **240**, 91–100 (1994).

[30] M. D. M. C. Ribeiro da Silva, M. A. R. Matos, M. C. Vaz, L. M. N. B. Santos, G. Pilcher, W. E. Acree, Jr., and J. R. Powell, J. Chem. Thermodyn. **30**, 869–878 (1998).

[31] J. Bickerton, G. Pilcher, and G. Al-Takhin, J. Chem. Thermodyn. **16**, 373–378 (1984).

[32] M. D. M. C. Ribeiro da Silva, M. A. R. Matos, M. S. Miranda, V. M. F. Morais, and W. E. Acree, Jr., J. Chem. Thermodyn. **36**, 107–113 (2004).

[33] S. Suradi, N. El Saiad, G. Pilcher, and H. A. Skinner, J. Chem. Thermodyn. **14**, 45–50 (1982).

[34] W. E. Acree, Jr., S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, J. M. Gonçalves, M. A. V. Ribeiro da Silva, and G. Pilcher, J. Chem. Thermodyn. **27**, 391–398 (1995).

[35] W. H. Johnson, J. Res. Natl. Bur. Stand. **79A**, 425–429 (1975).

[36] V. P. Lebedev, V. V. Chironov, A. N. Kizin, I. F. Falyakkov, I. Sh. Saifullin, O. R. Klyuchnikov, Yu. D. Orlov, and Yu. A. Lebedev, Izvest. Akad. Nauk. Ser. Khim. 660–662 (1995).

[37] M. D. M. C. Ribeiro da Silva, J. M. Gonçalves, S. C. C. Ferreira, L. C. M.

da Silva, M. J. Sottomayor, G. Pilcher, W. E. Acree, Jr., and L. E. Roy, J. Chem. Thermodyn. **33**, 1263–1275 (2001).

[38] M. D. M. C. Ribeiro da Silva, L. M. N. B. F. Santos, A. L. R. Silva, O. Fernandes, and W. E. Acree, Jr., J. Chem. Thermodyn. **35**, 1093–1100 (2003).

[39] M. Laing and C. Nicholson, J. South African Chem. Inst. **24**, 186–195 (1971).

[40] D. Ülkü, B. P. Huddle, and J. C. Morrow, Acta Cryst. **B27**, 432–436 (1971).

[41] A. S. Shahawry, M. M. Seleim, and M. S. Saleh, J. Proc. Pakistan Acad. Sci. **25**, 81–89 (1988).

[42] M. L. P. Leitão, G. Pilcher, W. E. Acree, Jr., A. I. Zvaigzne, S. A. Tucker, and M. D. M. C. Ribeiro da Silva, J. Chem. Thermodyn. **22**, 923–928 (1990).

[43] R. Curti, V. Riganti, and S. Locchi, Acta Cryst. **14**, 133–138 (1961).

[44] W. E. Acree, Jr., S. A. Tucker, A. I. Zvaigzne, M.-Y. Yang, G. Pilcher, and M. D. M. C. Ribeiro da Silva, J. Chem. Thermodyn. **23**, 31–36 (1991).

[45] W. E. Acree, Jr., S. A. Tucker, and G. Pilcher, J. Chem. Thermodyn. **24**, 213–216 (1992).

[46] M. Shiro, M. Yamakawa, and T. Kubota, Acta Cryst. **B35**, 712–716 (1979).

[47] J. J. Kirchner, W. E. Acree, Jr., G. Pilcher, and Li Shaofeng, J. Chem. Thermodyn. **18**, 793–799 (1986).

[48] W. E. Acree, Jr., J. J. Kirchner, S. A. Tucker, G. Pilcher, and M. D. M. C. Ribeiro da Silva, J. Chem. Thermodyn. **21**, 443–448 (1989).

[49] V. P. Lebedev, V. V. Chironov, Yu. N. Matyushin, and V. I. Pepekin, Khim. Fiz. **21**, 28–32 (2002).

[50] O. H. Wheeler and P. H. Gore, J. Am. Chem. Soc. **78**, 3363–3366 (1956).

[51] A. R. Dias, M. E. Minas da Piedade, J. A. Martinho Simões, J. A. Simoni, C. Teixeira, M.-Y. Yang, and G. Pilcher, J. Chem. Thermodyn. **24**, 439–447 (1992).

[52] W. E. Acree, Jr., S. A. Tucker, G. Pilcher, M. I. Paz-Andrade, and M. D. C. M. Ribeiro da Silva, J. Chem. Thermodyn. **25**, 653–659 (1993).

[53] K. Byström, J. Chem. Thermodyn. **13**, 139–145 (1981).

[54] P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, J. Am. Chem. Soc. **96**, 2381–2387 (1974).

[55] P. S. Engel, R. A. Melaugh, M. Månsson, J. W. Timberlake, A. W. Garner, and F. D. R. Rossini, J. Chem. Thermodyn. **8**, 607–621 (1976).

[56] K. Byström, J. Computational Chem. **4**, 308–312 (1983).

[57] A. B. Sheremetev, V. O. Kulagina, N. S. Aleksandrova, D. E. Dmitriev, Y. A. Strelenko, V. P. Lebedev, and Y. N. Matyushin, Propellants, Explosives, Pyrotechnics **23**, 142–149 (1998).

[58] D. Chavez, L. Hill, M. Hiskey, and S. Kinkead, J. Energ. Mater. **18**, 219–236 (2000).

[59] P. C. Hiberty and C. Leforestier, J. Am. Chem. Soc. **100**, 2012–2017 (1978).

[60] P. C. Hiberty and G. Ohanessian, J. Am. Chem. Soc. **104**, 66–70 (1982).

[61] W. E. Acree, Jr., S. G. Bott, S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, and G. Pilcher, J. Chem. Thermodyn. **28**, 673–683 (1996).

[62] L. M. Kostikova, Yu N. Matyushin, V. I. Pepekin, and T. S. Pivina, Int. Annu. Conf. ICT **34**, 120/1–120/7 (2003).

[63] Yu N. Matyushin, V. I. Pepekin, S. P. Golova, and T. I. Godovikova, Khmel'nitskii, L. I. Izvest. Akad. Nauk.SSSR Ser.Khim. 181–183 (1971).

[64] V. I. Pepekin, Yu N. Matyushin, A. D. Nikolaev, A. P. Kirsand, L. Platanova, and Yu A. Lebedev, Izvest. Akad. Nauk. SSSR Ser.Khim **8**, 1870–1871 (1975).

[65] E. C. Lupton and G. Hess, J. Chem. Eng. Data **20**, 135–137 (1975).

[66] Yu N. Matyushin, V. I. Pepekin, V. P. Lebedev, V. V. Chironov, L. M. Kostikova, and Y. O. Inozemteev, Int. Ann. Conf. ICT **30**, 77/1–77/9 (1999).

[67] Yu N. Matyushin, V. P. Lebedev, V. V. Chironov, and V. I. Pepekin, Khim. Fiz. **21**, 58–61 (2002).

[68] Y. N. Matushin and V. P. Lebedev, Int. Ann. Conf. ICT **28**, 98/1–98/10 (1997).

[69] V. G. Prokudin, Int. Ann. Conf. ICT **29**, 142/1–142/6 (1998).

[70] A. H. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, J. Chem. Soc. (B) 914–919 (1967).

[71] A. J. Boulton, P. J. Hall, and A. R. Katritzky, J. Chem. Soc. (B) 636–640 (1970).

[72] G. Calzaferri, R. Gleiter, K. H. Knauer, H.-D. Martin, and E. Schmidt, Angew. Chem. **13**, 86–88 (1974).

[73] M. Ponder, J. E. Fowler, and H. F. Schaefer III, J. Org. Chem. **59**, 6431–6436 (1994).

[74] W. E. Acree, Jr., S. G. Bott, S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, and G. Pilcher, J. Chem. Thermodyn. **27**, 1433–1440 (1995).

[75] W. E. Acree, Jr., J. R. Powell, S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, J. M. Gonçalves, L. M. N. B. F. Santos, V. M. F. Morais, and G. Pilcher, J. Org. Chem. **62**, 3722–3726 (1997).

[76] M. A. V. Ribeiro da Silva, M. A. R. Matos, and V. M. F. Morais, J. Chem. Soc. Faraday Trans. **91**, 1907–1910 (1995).

[77] M. D. M. C. Ribeiro da Silva, J. R. B. Gomes, J. M. Gonçalves, E. A. Sousa, S. Pandey, and W. E. Acree, Jr., J. Org. Chem. **69**, 2785–2792 (2004).

[78] M. A. V. Ribeiro da Silva, V. M. F. Morais, M. A. R. Matos, C. M. A. Rio, and C. M. G. Piedade, S. Struct. Chem. **7**, 329–336 (1996).

[79] M. D. M. C. Ribeiro da Silva, J. R. B. Gomes, J. M. Gonçalves, E. A. Sousa, S. Pandey, and W. E. Acree, Jr., Org. Biomol. Chem. **2**, 2507–2512 (2004).

[80] J. Tjebbes, Acta Chem. Scand. **16**, 916–921 (1962).

[81] L. Batt and R. T. Milne, Int. J. Chem. Kinet. **5**, 1067–1069 (1973).

[82] V. I. Pepekin, V. P. Lebedev, A. R. Balepin, and Yu A. Lebedev, Dokl. Akad. Nauk SSSR **221**, 1118–1121 (1975).

[83] W. E. Acree, Jr., S. A. Tucker, G. Pilcher, A. Chowdhary, M. D. M. C. Ribeiro da Silva, and M. J. S. Monte, J. Chem. Thermodyn. **25**, 1253–1261 (1993).

[84] W. E. Acree, Jr., S. G. Bott, S. A. Tucker, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, and G. Pilcher, J. Chem. Thermodyn. **27**, 1433–1440 (1995).

[85] D. A. Dieterich, I. C. Paul, and D. Y. Curtin, J. Am. Chem. Soc. **96**, 6372–6380 (1974).

[86] D. A. Dieterich, I. C. Paul, and D. Y. Curtin, J. Chem. Soc., Chem. Commun. 1710–1711 (1970).

[87] M. I. Christie, J. S. Frost, and M. A. Voisey, Trans. Faraday Soc. **61**, 674–680 (1965).

[88] K. Y. Choo, D. M. Godden, and S. W. Benson, Int. J. Chem. Kinetics **7**, 713–724 (1975).

[89] J. H. Kiefer, L. J. Mizerka, M. R. Patel, and H. C. Wei, J. Phys. Chem. **89**, 2013–2019 (1985).

[90] R. Okazaki and N. Inamoto, J. Chem. Soc. B 1583–1586 (1970).

[91] V. von Keussler and W. Luttke, Z. Elektrochem. **63**, 614–623 (1959).

[92] M. Azoulay and G. Wettermark, Tetrahedron **34**, 2591–2596 (1978).

[93] K. G. Orrell, V. Sik, and D. Stephenson, Magn. Reson. Chem. **25**, 1007–1011 (1987).

[94] B. G. Gowenlock, M. J. Maidment, K. G. Orrell, I. Prokes, and J. R. Roberts, J. Chem. Soc., Perkin Trans. 2, 1904–1911 (2001).

[95] M. Culcasi, P. Tordo, and G. Gronchi, J. Phys. Chem. **90**, 1403–1407 (1986).

[96] M. Azoulay, R. Lippman, and G. Wettermark, J. Chem. Soc., Perkin Trans. II **1981**, 256–259 (1981).

[97] M. Azoulay and E. Fischer, J. Chem. Soc., Perkin Trans. II 637–642 (1982).

[98] W. E. Acree, Jr., S. A. Tucker, G. Pilcher, and G. Toole, J. Chem. Thermodyn. **26**, 85–90 (1994).

[99] M. D. M. C. Ribeiro da Silva, M. A. R. Matos, G. Pilcher, and W. E. Acree, Jr., J. Chem. Thermodyn. **30**, 271–274 (1998).

[100] M. D. M. C. Ribeiro da Silva, M. A. R. Matos, M. L. C. C. H. Ferrão, L. M. P. F. Amaral, M. S. Miranda, W. E. Acree, Jr., and G. Pilcher, J. Chem. Thermodyn. **31**, 1551–1559 (1999).

[101] S. Darwin and D. C. Hodgkin, Nature (London) **166**, 827–828 (1950).

[102] C. P. Fenimore, J. Am. Chem. Soc. **72**, 3226–3231 (1950).

[103] M. S. Webster, J. Chem. Soc., 2841–2845 (1956).

[104] Ch. R. Rømming and H. J. Talberg, Acta Chem. Scand. **27**, 2246–2248 (1973).

[105] W. J. Mijs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga, Rec. Trav. Chem. **77**, 746–752 (1958).

[106] N. D. Lebedeva and V. L. Ryadnenko, Russ. J. Phys. Chem. **47**, 1382 (1973).

[107] J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp, and

G. Waddington, J. Am. Chem. Soc. **76**, 4791–4796 (1954).

[108] Yu K. Knobel, E. A. Miroshnichenko, and Yu A. Lebedev, Dokl. Akad. Nauk. SSSR **190**, 348–350 (1970).

[109] A. A. Boyd, B. Noziere, and R. Desclau, J. Phys. Chem. **99**, 10815–10823 (1995).

[110] V. I. Pepekin, Yu A. Lebedev, A. A. Fainzil'berg, G. G. Rozantsev, and A. Y. Apin, Russ. J. Phys. Chem. **43**, 1454–1455 (1969).

[111] Y. N. Matyushin, Y. P. Lebedev, E. A. Miroshnichenko, L. M. Kostikova, and Y. O. Inosemzev, Int. Annu. Conf. ICT **32**, 102/1–102/12 (2001).

[112] S. P. Verevkin, Thermochim. Acta **307**, 17–25 (1997).

[113] O. F. Golovanova, G. V. Sitonina, V. I. Pepekin, B. L. Korsunskii, and F. I. Dubovikskii, Izvest. Akad. Nauk SSSR, Ser. Khim. 1012–1016 (1988).

[114] E. A. Miroshnichenko, T. S. Kon'kova, and Yu N. Matyushin, Dokl. Phys. Chem. **392**, 253–255 (2003).

[115] M. F. Zimmer, E. E. Baroody, M. Graff, G. A. Carpenter, and R. A. Robb, J. Chem. Eng. Data **11**, 579–581 (1966).

[116] P. Gray and M. W. T. Pratt, J. Chem. Soc. 2163–2168 (1957).

[117] J. D. Ray and R. A. Ogg, Jr., J. Phys. Chem. **63**, 1522–1523 (1959).

[118] G. Geisler and W. Thierfelder, Z. Phys. Chem. (Frankfurt) **29**, 248–257 (1961).

[119] J. D. Ray and A. A. Gershon, J. Phys. Chem. **66**, 1750–1752 (1962).

[120] D. M. Fairbrother, H. A. Skinner, and F. W. Evans, Trans. Faraday Soc. **53**, 779–783 (1957).

[121] P. Gray and A. Williams, Chem. Rev. **59**, 239–328 (1959).

[122] L. Batt, K. Christie, R. T. Milne, and A. J. Sumners, Int. J. Chem. Kinet. **6**, 877–885 (1974).

[123] P. Tavernier and M. Lamouroux, Mem. Poudres **39**, 335–356 (1957).

[124] L. V. Gurvich, G. A. Khachkurzov, V. A. Medvedev, I. V. Veyts, G. A. Bergman, V. S. Yungman, N. P. Rtishcheva, and L. F. Kuratova, *Thermodynamic Properties of Individual Substances* (Izv. AN SSSR, Moscow, 1982).

[125] O. Kubacheroski and C. B. Alcock, *Metalurgical Thermochemistry*, 5th ed. (Pergamon, Oxford, 1979).

[126] M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, J. Phys. Chem. Ref. Data **3**, 311–480 (1974).

[127] J. B. Pedley and J. Rylance, Sussex *NPL Computer-Analyzed Thermochemical Data, Organic and Organometallic Compounds* (University of Sussex Press, 1977).

[128] G. Pilcher and H. A. Skinner, *The Chemistry of the Metal-Carbon Bond*, edited by F. R. Hartley and S. Patai (Wiley, New York, 1982).

[129] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).

[130] G. Pilcher, M. L. P. Leitão, M.-Y. Yang, and R. Walsh, J. Chem. Soc., Faraday Trans. **87**, 841–846 (1991).