J. Chem. Thermodynamics **1999**, 31, 1551–1559
Article No. jcht.1999.0554
Available online at http://www.idealibrary.com on IDEAL®

JCT

Enthalpies of combustion of 2-iodosobenzoic acid and 4-nitrosophenol: the dissociation enthalpy of the I–O bond

Maria D. M. C. Ribeiro da Silva,[a] M. Agostinha R. Matos, Maria Luísa C. C. H. Ferrão, Luísa M. P. F. Amaral, Margarida S. Miranda,

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

W. E. Acree Jr,

Department of Chemistry, University of North Texas, Denton TX 76203-0068, U.S.A.

and G. Pilcher

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

The standard (p° = 0.1 MPa) molar enthalpies of combustion in oxygen, at T = 298.15 K, for crystalline 2-iodosobenzoic acid, (OI)C_6H_4COOH, and 4-nitrosophenol, (ON)C_6H_4OH, were measured by rotating-bomb calorimetry and static-bomb calorimetry, respectively. These values were used to derive the standard molar enthalpies of formation of the crystalline compounds.

		$\Delta_f H_m^{\circ}$(cr)/(kJ · mol^{-1})
2-iodosobenzoic acid	2-(OI)C_6H_4COOH	−336.9 ± 2.5
4-nitrosophenol	4-(ON)C_6H_4OH	−70.2 ± 2.1

An indirect method was used for assessing the dissociation enthalpy of the (I–O) bond in the iodoso derivative, D_m°(I–O)/(kJ · mol^{-1}) = (264.5 ± 8.1), which is the first value reported for an iodine–oxygen bond in an organic molecule.

KEYWORDS: 2-iodosobenzoic acid; 4-nitrosophenol; dissociation enthalpy of the (I–O) bond; enthalpy of combustion

[a]To whom correspondence should be addressed (E-mail: mdsilva@fc.up.pt).

0021–9614/99/121551 + 09 $30.00/0

1. Introduction

To provide a predictive basis for the outcome of primary oxo transfer reactions, Holm *et al.*[1,2] introduced a simple reactivity scale, compiling the values of the enthalpies of reaction for a series of reactions in a decreasing order. The utility of this scale is analogous to that of a table of standard reduction potentials, in view of a prediction of the direction of a large number of oxo transfer reactions. Holm's compilation includes values for enthalpies of reactions for strong donors and acceptors, but the thermodynamic data required to calculate values for couples involving certain other strong oxo donors, such as the iodosoarenes, have not been reported.

The enthalpy changes of the following reactions involving generalized acceptor/donor couples oxygen atom, X/XO or Y/YO,

$$X + 1/2\ O_2(g) = XO \quad (1)$$

$$Y + 1/2\ O_2(g) = YO \quad (2)$$

may be obtained as the difference in standard molar enthalpies of formation of products and reactants. If $|T \cdot \Delta_r S_m| \ll |\Delta_r H_m|$ and $\Delta_r H_m$ (1) $> \Delta_r H_m$ (2), the reaction:

$$XO + Y = X + YO \quad (3)$$

is thermodynamically favourable. For an oxidized molecule such as XO, the bond dissociation enthalpy D(X–O) can be calculated as the enthalpy of the reaction:

$$XO(g) = X(g) + O(g). \quad (4)$$

A systematic investigation of the influence of the molecular environment in the immediate vicinity of the (N–O) bond has received special attention in our research groups for the last decade. The molar dissociation enthalpies of (N–O) bonds, D_m^o (N–O), have been reported for different classes of compounds, including some nitrocompounds.[3–5] The determination of D_m^o (N–O) in a nitrocompound, being the enthalpy of the dissociation reaction $RNO_2(g) = RNO(g) + O(g)$, requires the knowledge of the standard molar enthalpies of formation, in the gaseous state of both the nitro and nitroso compounds. In this work, we aimed to calculate D_m^o (N–O) for 4-nitrophenol, from the standard molar enthalpies of formation of the gaseous 4-nitrophenol, $\Delta_f H_m^o$ {4-$(O_2N)C_6H_4OH$, g}[6,7] and 4-nitrosophenol, $\Delta_f H_m^o$ {4-$(ON)C_6H_4OH$, g}. For the latter, the energy of combustion of the crystalline compound has been measured and the standard molar enthalpy of formation in the condensed state was derived. Measurement of the enthalpy of sublimation of this compound was found to be not possible due to thermal decomposition of 4-nitrosophenol on heating.

The dissociation enthalpy of the iodine–oxygen bond in iodoso compounds D_m^o (I–O) may also be calculated as the enthalpy of the reaction $RIO(g) = RI(g) + O(g)$, if the standard molar enthalpies of formation of all the species involved are known. The literature does not give any value for D_m^o (I–O) in an organic molecule, and that is derived in this paper by considering the couple 2-iodobenzoic acid and 2-iodosobenzoic acid.

The standard molar enthalpy of formation in the gaseous state for 2-iodobenzoic acid can be obtained from the literature values for its standard molar enthalpy of formation in

the crystalline state,[8] and standard molar enthalpy of sublimation.[9] This paper reports the standard molar enthalpy of formation of 2-iodosobenzoic acid in the crystalline phase, being the first measurement of an iodosocompound. It has not been possible to measure its enthalpy of sublimation because of thermal decomposition, which led us to use an indirect method of assessing D°_{m} (I–O).

For the general reaction, in which all the reactants and products are in the solid state,

$$RNO + 2\text{-}IC_6H_4CO_2H = RN + 2\text{-}(OI)C_6H_4CO_2H, \quad (5)$$

if the enthalpies of sublimation of the species on the left hand side and right hand side balance, then $\Delta_r H^{\circ}_{m} = D^{\circ}_{m}(N–O) - D^{\circ}_{m}(I–O)$. We have tested this hypothesis with twelve examples where $D^{\circ}_{m}(N–O)$[3,5,10–15] has been determined, and a mean value with its standard deviation for $D^{\circ}_{m}(I–O)$ was derived as (264.3 ± 2.8) kJ · mol^{-1} showing the above hypothesis to be reasonably well obeyed.

2. Experimental

The 2-iodosobenzoic acid was prepared by oxidation of 2-iodobenzoic acid with potassium permanganate according to the method of Verma and co-workers.[16] The sample was further purified by three recrystallizations from hot water. Elemental analyses were in agreement with expected values and the compositions in mass fractions were: found $10^2 \cdot w(C) = 31.73$, $10^2 \cdot w(H) = 1.96$, $10^2 \cdot w(I) = 48.10$; calculated $10^2 \cdot w(C) = 31.85$, $10^2 \cdot w(H) = 1.91$, and $10^2 \cdot w(I) = 48.07$.

The 4-nitrosophenol was prepared according to a published literature method.[17] Phenol was slowly dissolved in an ice-cooled aqueous solution of sodium hydroxide and potassium nitrite. Sulfuric acid (3.5 mol · dm^{-3}) was then slowly added to the resulting solution by stirring. The reaction mixture was stirred for an additional 2 hours, and the temperature of the mixture was maintained at 273 K. The crystalline product of 4-nitrosophenol was collected by low-pressure filtration, washed several times with cold water, and then further purified four times by vacuum sublimation. As the compound decomposes, it was kept under nitrogen during purification and only freshly sublimed material was used in the combustion experiments. Purity was checked by i.r. spectroscopy as well as the carbon dioxide recovery ratio. The average ratio $\langle r \rangle$ of the mass of carbon dioxide observed in the combustion experiments to that calculated from the mass of sample, together with an estimated density of the sample, was ρ(g · cm^{-3}) = 1.2, $\langle r \rangle = (0.9990 \pm 0.0009)$, with uncertainty of twice the standard deviation of the $\langle r \rangle$ mean.

The enthalpy of combustion of 2-iodosobenzoic acid was determined with an isoperibol rotating bomb calorimeter[18,19] with a twin-valve stainless-steel bomb lined with platinum. The rotation mechanism allowed simultaneous axial and end-over-end rotation of the bomb. This rotation was started when the temperature rise of the main period reached about 0.63 of its total value, and was continued throughout the rest of the experiment. With this procedure, the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the thermostated jacket.[20] The calorimeter was calibrated using benzoic acid (Bureau of Analysed Samples CRM 190-r) having a massic energy of combustion under standard

bomb conditions of $-(26432.3 \pm 3.8)$ J · g^{-1}. The calibration results were corrected to give the energy equivalent ε(calor) corresponding to an average mass of water added to the calorimeter of 5222.5 g. One set of six calibration experiments was made in oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of water added to the bomb, leading to an energy equivalent of the calorimeter ε(calor) = (25172.2 ± 1.5) J · K^{-1}, where the uncertainty quoted is the standard deviation of the mean. A series of six comparison experiments was also performed by burning benzoic acid in the presence of a mass 1.0 g of solid iodine sealed in Melinex polyester bags (0.025 mm thickness), and a volume 10.00 cm^3 of KI (aq, 0.9 mol · dm^{-3}). These experimental conditions are similar to those observed after combustion of the iodine derivative, and the value obtained for ε(calor) = (25191.2 ± 1.2) J · K^{-1} is 0.075 per cent different from that previously obtained under certificate conditions. We decided to use this value as ε(calor) for the combustion experiments of the iodine derivative to obviate any systematic error in the calculation of the corrections for the standard state ΔU_Σ.

The procedure for determining the energies of combustion of 2-iodosobenzoic by rotating bomb calorimetry is similar to the one already described for other iodine compounds.[21] Samples in pellet form were ignited in oxygen at a pressure of 3.04 MPa with a volume of 10.00 cm^3 of KI of concentration 0.9 mol · dm^{-3} added to the bomb. Ignition temperatures were chosen so that the final temperatures were close to 298.15 K. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For all the combustion experiments with iodo-compounds, the final solution was titrated against $Na_2S_2O_3$(aq). The amount of I_2 found was exactly as expected. A value for $\Delta_{sol}U_m(I_2) = (3.7 \pm 0.1)$ kJ · mol^{-1}[22] was used for the molar energy of solution of I_2(cr) in KI(aq).

For dry Melinex, $\Delta_c u^\circ = -(22902 \pm 5)$ J · g^{-1}.[23] This value has been previously confirmed by combustion in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported.[23] Hexadecane (Aldrich Gold Label, mass fraction $w > 0.99$) stored under nitrogen was used as an auxiliary combustion aid in measurements. The standard massic energy of combustion of the hexadecane was measured, $-\Delta_c u^\circ(l) = (47145.8 \pm 1.3)$ J · g^{-1}, and it is in good agreement with the value of Fraser and Prosen[24] for a sample with $w = 0.9996$, $-\Delta_c u^\circ(l) = (47155.0 \pm 3.8)$ J · g^{-1}.

For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^\circ = 16250$ J · g^{-1};[25] this value has been previously confirmed in our laboratory. Corrections for carbon formation were based on -33 kJ · g^{-1} for the massic energy of combustion of carbon.[25] The nitric acid formed was determined using Devarda's alloy method[26] and corrections were based on -59.7 kJ · mol^{-1} for the molar energy of formation of 0.1 mol · dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).[27] At $T = 298.15$ K, $(\partial u/\partial p)_T$ for these solids was assumed to be -0.2 J · g^{-1} · MPa^{-1}, a typical value for organic solids. For the iodoso compound, $-\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.*[28]

The enthalpy of combustion of 4-nitrosophenol was measured by using a static bomb calorimeter[29,30] with a Parr 1105 model bomb. The energy equivalent of the

calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples CRM 190-r) having a massic energy of combustion under standard bomb conditions of $-(26432.3 \pm 3.8)$ J · g^{-1}. From nine calibration experiments ε(calor) = (15908.3 ± 1.0) J · K^{-1} for an average mass of water added to the calorimeter of 3119.6 g, where the uncertainty quoted is the standard deviation of the mean. Hexadecane (Aldrich Gold Label, $w > 0.99$) stored under nitrogen was used as an auxiliary combustion aid in measurements, to reproduce a convenient temperature rise in the calorimeter, since difficulties in purifying the compound led to very small amounts of purified samples. Samples in pellet form were ignited at $T = (298.150 \pm 0.001)$ K in oxygen at a pressure of 3.04 MPa with a volume of 1.00 cm^3 of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. The corrections for the cotton thread fuse, carbon formation, and nitric acid formation were made as previously described for the rotating bomb combustion calorimetry. At $T = 298.15$ K, $(\partial u/\partial p)_T$ for these solids was assumed to be -0.2 J · g^{-1} · MPa^{-1}, a typical value for organic solids. For the nitroso compound, $-\Delta_c u^o$ was calculated by the procedure given by Hubbard *et al.*[28] The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 1995.[31] The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse and that lost due to carbon formation.

3. Results

Detailed results for a typical combustion experiment on each compound, as results for a typical comparison experiment, are given in table 1; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the mass assigned for ε(calor) (5222.5 g for the rotating bomb calorimeter and 3119.6 g for the static bomb calorimeter); ΔU_Σ is the correction to the standard state; the remaining terms are as previously described.[27] For rotating bomb measurements, the final calorimeter temperature was close to $T = 298.15$ K, whereas for the static bomb measurements samples were ignited at $T = 298.15$ K. The ΔU(IBP) was calculated according to:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O, l) \cdot \Delta m(H_2O)\}\Delta T_{ad} + \varepsilon_i(T_i - 298.15)/\text{K} + \varepsilon_f(298.15 - T_i - \Delta T_{ad})/\text{K} + \Delta U(\text{ign}), \quad (6)$$

where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. The individual values of $-\Delta_c u^o$ together with the mean and its standard deviation are given in table 2. Table 3 lists the derived standard molar enthalpies of combustion and of formation in the crystalline state at $T = 298.15$ K. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_f H_m^o$ from $\Delta_c H_m^o$, the standard molar enthalpies of formation at $T = 298.15$ K for H_2O(l) : $-(285.83 \pm 0.04)$ kJ · mol^{-1}[32] and for CO_2(g) : $-(393.51 \pm 0.13)$ kJ · mol^{-1},[32] were used.

TABLE 1. Typical combustion experimental results for a comparison experiment, and for 2-iodosobenzoic acid and 4-nitrosophenol, at T = 298.15 K

	Comparison experiment	2-iodosobenzoic acid	4-nitrosophenol
$m(CO_2, \text{total})/g$			1.69578
$m(BA)/g$	0.60767		
$m(I_2)/g$	1.04538		
$m(cpd)/g$		0.85443	0.48157
$m(Melinex)/g$	0.05770		
$m(n\text{-}C_{16}H_{34})/g$		0.24844	0.21178
$m(fuse)/g$	0.00265	0.00291	0.00275
$\varepsilon_i/(J \cdot K^{-1})$	51.64	51.73	15.46
$\varepsilon_f/(J \cdot K^{-1})$	60.84	58.94	16.24
$\Delta m(H_2O)/g$	1.9	−2.6	0.0
$(T_i/K) - 273.15$	24.3842	24.1047	25.0001
$(T_f/K) - 273.15$	25.0871	24.9914	26.4431
$\Delta T_{ad}/K$	0.69022	0.86936	1.37136
$-\Delta U(IBP)/J$	17429.16	21933.62	21837.09
$\Delta U(HNO_3)/J$	1.43	3.46	37.85
$-\Delta U(C)/J$			1.32
$\Delta U(ign)/J$	1.29	1.93	1.19
$\Delta_{sol}U(I_2)/J$	15.24	5.99	
$\Delta U_\Sigma/J$	27.65	25.51	12.04
$\varepsilon(calor)/(J \cdot K^{-1})$	25191.0	25180.3	15908.3
$-m\Delta_c u^o(Melinex)/J$	1321.34		
$-m\Delta_c u^o(n\text{-}C_{16}H_{34})/J$		11712.79	9984.65
$-m\Delta_c u^o(fuse)/J$	43.04	47.26	44.66
$-\Delta_c u^o(cpd)/(J \cdot g^{-1})$		11879.96	24418.49

4. Discussion

Considering a hypothetical solid reaction (7), involving the pairs 2-iodobenzoic acid/2-iodosobenzoic acid, (2-IC_6H_4COOH/2-$(OI)C_6H_4COOH$), and 4-aminonitrosobenzene/4-aminonitrobenzene, {4-$(CH_3)_2NC_6H_5NO$/4-$(CH_3)_2NC_6H_5NO_2$}:

$$4\text{-}(CH_3)_2NC_6H_5NO_2(cr) + 2\text{-}IC_6H_4COOH(cr) = 4\text{-}(CH_3)_2NC_6H_5NO(cr) + 2\text{-}(IO)C_6H_4COOH(cr), \quad (7)$$

and using the values for the standard molar enthalpies of formation $\Delta_f H_m^o$[4-$(CH_3)_2NC_6H_5NO_2$, cr] = −(38.5 ± 1.6) kJ · mol^{-1},[5] $\Delta_f H_m^o$ [(4-$CH_3)_2NC_6H_5NO$, cr] = (103.0 ± 1.6) kJ · mol^{-1},[5] $\Delta_f H_m^o$(2-IC_6H_4COOH, cr) = −(302.3 ± 4.1) kJ · mol^{-1},[8] and $\Delta_f H_m^o$[2-$(IO)C_6H_4COOH$, cr] = −(336.9 ± 2.5) kJ · mol^{-1}, measured in the present

TABLE 2. Individual values of the massic energy of combustion $-\Delta_c u^o$ of 2-iodosobenzoic acid and 4-nitrosophenol at $T = 298.15$ K ($p^o = 0.1$ MPa). The mean values are represented by $\langle \Delta_c u^o \rangle$

2-iodosobenzoic acid	4-nitrosophenol
$-\Delta_c u^o/(J \cdot g^{-1})$	
11853.52	24401.29
11867.46	24414.14
11854.39	24418.49
11876.63	24442.82
11858.55	24407.72
11879.96	
11873.17	
$-\langle \Delta_c u^o \rangle/(J \cdot g^{-1})^a$	
11866.2 ± 4.1	24416.9 ± 7.1

[a] Mean value and standard deviation of the mean.

TABLE 3. Derived standard ($p^o = 0.1$ MPa) molar energies of combustion $\Delta_c U^o_m$, standard molar enthalpies of combustion $\Delta_c H^o_m$, for standard molar enthalpies of formation $\Delta_f H^o_m$ for 2-iodosobenzoic acid and 4-nitrosophenol at $T = 298.15$ K. Uncertainties are given as twice the standard deviation of the mean

	$\frac{-\Delta_c U^o_m(cr)}{kJ \cdot mol^{-1}}$	$\frac{-\Delta_c H^o_m(cr)}{kJ \cdot mol^{-1}}$	$\frac{\Delta_f H^o_m(cr)}{kJ \cdot mol^{-1}}$
2-iodosobenzoic acid	3132.9 ± 2.3	3132.3 ± 2.3	−336.9 ± 2.5
4-nitrosophenol	3006.0 ± 1.9	3005.4 ± 1.9	−70.2 ± 2.1

work, the enthalpy of the reaction (7) is calculated as $\Delta_r H^o_m = (106.9 \pm 5.3)$ kJ · mol^{-1}. Because of the structural similarities, it is reasonable to assume that the enthalpies of sublimation of the products will be nearly equal to those of the reactants so that $\Delta_r H^o_m = D^o_m(N–O) - D^o_m(I–O)$.

The value of $D^o_m(N–O)$ in 4-dimethylaminonitrobenzene has been determined as (371.4 ± 3.5) kJ · mol^{-1},[5] hence $D^o_m(I–O)$ in 2-iodosobenzoic acid is assessed as (264.5 ± 8.1) kJ · mol^{-1}, where an additional uncertainty of ±5 kJ · mol^{-1} has been included because of the assumption made about enthalpies of sublimation. Then, for the reaction:

$$4\text{-}(O_2N)C_6H_4OH(cr) + 2\text{-}IC_6H_4COOH(cr) = 4\text{-}(ON)C_6H_4OH(cr) + 2\text{-}(IO)C_6H_4COOH(cr), \quad (8)$$

and using the values for the standard molar enthalpies of formation $\Delta_f H_m^o$ {4-$(O_2N)C_6H_4$OH, cr} = $-(207.1 \pm 1.1)$ kJ · mol^{-1},[7] and the two values measured in the present work, $\Delta_f H_m^o$ {2-$(IO)C_6H_4COOH$, cr} = $-(336.9 \pm 2.5)$ kJ · mol^{-1} and $\Delta_f H_m^o$ {4-$(ON)C_6H_4OH$, cr} = $-(70.2 \pm 2.1)$ kJ · mol^{-1}, the enthalpy of the reaction (8) is calculated as $\Delta_r H_m^o = (102.3 \pm 5.3)$ kJ · mol^{-1}, showing that within the limits of experimental uncertainty, D_m^o (N–O) in 4-nitrophenol is equal to that in 4-dimethylaminonitrobenzene.

From the dissociation reaction:

$$4\text{-}(O_2N)C_6H_4OH(g) = 4\text{-}(ON)C_6H_4OH(g) + O(g), \quad (9)$$

and assuming the value for D_m^o (N–O) (371.4 ± 3.5) kJ · mol^{-1}[5] in 4-nitrophenol, as well as $\Delta_f H_m^o$ (4-nitrophenol, g) = $-(114.7 \pm 1.2)$ kJ · mol^{-1}[7] and $\Delta_f H_m^o$(O, g) = (249.17 ±0.10) kJ · mol^{-1},[32] then $\Delta_f H_m^o$ (4-nitrosophenol, g) = (7.5 ± 3.7) kJ · mol^{-1}. It has been shown previously[4] that the increment in $\Delta_f H_m^o$(g) for substitution of NO on the benzene ring is (122.4 ± 2.2) kJ · mol^{-1}. With $\Delta_f H_m^o$(phenol, g) = $-(96.4 \pm 0.9)$ kJ · mol^{-1},[8] the estimated value for $\Delta_f H_m^o$ (4-nitrosophenol, g) is (26.0 ± 2.4) kJ · mol^{-1} and, by comparison with the above experimental value, it is apparent that 4-nitrosophenol is exceptionally stabilized by (18.5 ± 4.4) kJ · mol^{-1}. A similar magnitude of additional stabilization of 20 kJ · mol^{-1} was reported for 4-dimethylaminonitrosobenzene.[5] The consequence of these exceptional stabilization energies is that dimerization in the solid state would be endothermic. Actually this particular nitroso compound is monomeric and green, not dimeric and white.

In terms of Holm's scale,[2] we have $\Delta_r H_m^o = -(136.1 \pm 4.2)$ kJ · mol^{-1} for reaction (10) and $\Delta_r H_m^o = -(35.6 \pm 4.8)$ kJ · mol^{-1} for reaction (11):

$$4\text{-nitrosophenol(cr)} + 1/2O_2(g) = 4\text{-nitrophenol(cr)}, \quad (10)$$

$$2\text{-iodobenzoicacid(cr)} + 1/2O_2(g) = 2\text{-iodosobenzoicacid(cr)}, \quad (11)$$

which would place the oxidizing potential of 4-nitrophenol at about the same level as manganese dioxide, but kinetic considerations would almost certainly render 4-nitrophenol useless as an oxidizing reagent. For 2-iodosobenzoic acid, the oxidizing potential would be at a level similar to perchlorate, and this may find a use in oxidations.

Thanks are due to Fundação para a Ciência e Tecnologia, FCT-Lisboa, for financial support given through Centro de Investigação em Química da Universidade do Porto (research unit number 81) and for the research project PRAXIS XXI (project PCEX / QUI / 0062 / 96). One of us (LMPFA) thanks Fundação para a Ciência e Tecnologia for the award of a postdoctoral fellowship (PRAXIS XXI/BPD/16319/98).

REFERENCES

1. Holm, R. H. *Chem. Rev.* **1987**, 87, 1401–1449.
2. Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, 12, 571–589.
3. Acree Jr., W. E.; Tucker, S. A.; Pilcher, G.; Chowdhary, A.; Ribeiro da Silva, M. D. M. C.; Monte, M. J. S. *J. Chem. Thermodynamics* **1993**, 25, 1253–1261.
4. Acree Jr., W. E.; Bott, S. G.; Tucker, S. A.; Ribeiro da Silva, M. D. M. C.; Matos, M. A. R.; Pilcher, G. *J. Chem. Thermodynamics* **1995**, 27, 1433–1440.
5. Acree Jr., W. E.; Tucker, S. A.; Pilcher, G.; Toole, G. *J. Chem. Thermodynamics* **1994**, 26, 85–90.

6. Finch, A.; Gardner, P G.; Wu, D. *Thermochim. Acta* **1983**, 66, 333–342.
7. Sabbah, R.; Gouali, M. *Aust. J. Chem.* **1994**, 47, 1651–1660.
8. Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*, Vol. 1. Thermodynamics Research Center: College Station, TX: **1994**.
9. Tan, Z.; Sabbah, R. *Thermochim. Acta* **1994**, 231, 109–120.
10. Ribeiro da Silva, M. D. M. C.; Matos, M. A.; Vaz, M. C.; Santos, L. M. N. B. F.; Pilcher, G.; Acree Jr.; Powell, J. R. *J. Chem. Thermodynamics* **1998**, 30, 869–878.
11. Acree Jr., W. E.; Bott, S. G.; Tucker, S. A.; Ribeiro da Silva, M. D. M. C.; Matos, M. A. R.; Pilcher, G. *J. Chem. Thermodynamics* **1996**, 28, 673–683.
12. Acree Jr., W. E.; Tucker, S. A.; Zvaigzne, A. I.; Meng-Yan, Y.; Pilcher, G.; Ribeiro da Silva, M. D. M. C. *J. Chem. Thermodynamics* **1991**, 23, 31–36.
13. Leitão, M. L. P.; Pilcher, G.; Acree Jr., W. E.; Zvaigzne, A. I.; Tucker, S. A.; Ribeiro da Silva, M. D. M. C. *J. Chem. Thermodynamics* **1990**, 22, 923–928.
14. Acree Jr., W. E.; Tucker, S. A.; Ribeiro da Silva, M. D. M. C.; Matos, A. R.; Conçalves, J. M.; Ribeiro da Silva, M. A.V.; Pilcher, G. *J. Chem. Thermodynamics* **1995**, 27, 391–398.
15. Kirchner, J. J.; Acree Jr., W. E.; Pilcher, G.; Shaofeng, Li. *J. Chem. Thermodynamics* **1986**, 18, 793–799.
16. Verma, K. A.; Sanghi, A. J.; Gupta, D. *J. Chromatography* **1988**, 457, 345–353.
17. Leonard, N. J.; Curry, J. W. *J. Org. Chem.* **1952**, 17, 1071–1076.
18. Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Lopes, A. J. M. *J. Chem. Thermodynamics* **1993**, 25, 229–235.
19. Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Jiye, F. *J. Chem. Thermodynamics* **1994**, 26, 839–846.
20. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1960**, 60, 1080–1089.
21. Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Silva, A. M. O. A. *J. Chem. Thermodynamics* **1995**, 27, 633–641.
22. Carson, A. S.; Laye, P. G.; Pedley, J. B.; Welsby, A. M. *J. Chem. Thermodynamics* **1993**, 25, 261–269.
23. Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, 56, 1776–1783.
24. Fraser, F. M.; Prosen, E. J. *J. Res. Nat. Bur. Stand.* **1955**, 55, 329–333.
25. Coops, J.; Jessup, R. S.; van Nes, K. *Experimental Thermochemistry*, Vol. 1. Rossini, F. D.: editor. Interscience: New York. **1956**, Chap. 3.
26. Vogel, A. I. *Quantitative Inorganic Analysis*. Longmans: London. **1978**.
27. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, II, Suppl. no. 2
28. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*, Vol. 1. Rossini, F. D.: editor. Interscience: New York. **1956**, Chap. 5.
29. Ribeiro da Silva, M. D. M. C.; Ribeiro da Silva, M. A. V.; Pilcher, G. *J. Chem. Thermodynamics* **1984**, 16, 1149–1155.
30. Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Port. Quím.* **1984**, 26, 163–172.
31. Copler, T. B. *J. Phys. Chem. Ref. Data* **1997**, 26, 1239–1253.
32. *CODATA Key Values for Thermodynamics*. Cox, J. D.; Wagman, D. D.; Medvedev, V. A.: editors. Hemisphere: New York. **1989**.

(Received 4 March 1999; in final form 2 June 1999)

O-774