PCCP

Time-resolved photoacoustic calorimetry of aqueous peroxodisulfate photolysis in the presence of nitrite anions

María S. Churio,*†[a] Marta A. Brusa,†[a] María A. Grela,*†[a] Sonia G. Bertolotti†[b] and Carlos M. Previtali†[b]

[a] Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, CC 624, (7600) Mar del Plata, Argentina. E-mail: schurio@mdp.edu.ar; magrela@mdp.edu.ar; Fax: 54 223 4753150

[b] Departamento de Química y Física, Facultad de Ciencias Exactas, Fisicoquímicas y Naturales, Universidad Nacional de Río Cuarto, (5800) Río Cuarto, Argentina

The photodissociation of aqueous peroxodisulfate in the presence of nitrite anions was studied between 282 and 292 K by time-resolved photoacoustic calorimetry at 266 nm. Aqueous peroxodisulfate was chosen as the calorimetric reference, thus enabling the measurement of the enthalpy and volume changes associated with the reaction of the photoproduced sulfate radicals with nitrite anions to form SO_4^{-2} and NO_2 in the submicrosecond time range. The enthalpy change obtained (-192 ± 19 kJ mol^{-1}) is consistent with available thermochemical data for related species. The interpretation of the measured reaction volume (-13.8 ± 0.7 mL mol^{-1}) points to the ionic charge accumulation on the sulfate anion as the dominating change causing the contraction of the solvent. The comparative analysis of our experimental result and data for partial molar volumes and electrostriction volumes of electrolytes, reinforces the concept that particularly in the case of water, more realistic models for the solvent are needed involving structure rather than continuous features.

Introduction

As a photothermal method, photoacoustic calorimetry (PAC) deals with the heat delivered by the radiationless deactivation processes taking place during phototransformations. Through this method, the enthalpy change ΔH and volume change ΔV that accompany light induced reactions can be determined measuring, by means of a piezoelectric element, the pressure change arising upon illumination of a sample in a condensed medium.[1]

We have recently applied PAC to the study of peroxodisulfate anion photodissociation in aqueous solutions at 266 nm.[2]

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^{\cdot-} \qquad (1)$$
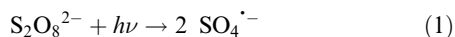
Our work yielded $\Delta \bar{V}_1 = 8.9 \pm 0.5$ mL mol^{-1} and $\Delta H_1 = 120 \pm 11$ kJ mol^{-1}, respectively. The observed enthalpy change afforded the first direct determination of the bond dissociation energy of the species in aqueous media, thus allowing the comparison with already available data in the gas phase. The measured volume change could be ascribed to the perturbation of water structure around peroxodisulfate and sulfate radicals.[2]

Here we propose that the above mentioned study can provide a useful benchmark to further explore the structural interactions of charged species with water molecules, owing to the high reactivity of sulfate radicals. In fact, rate constants for the oxidation of inorganic anions by sulfate span the range between 1×10^7 and 3×10^9 M^{-1} s^{-1}.[3] The upper limit corresponds to strongly reducing agents such as sulfite, azide or iodide, whereas the lower bound corresponds to hydrogen abstraction reactions, e.g., from P–H bonds.

† Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina (CONICET).

To illustrate our proposal, we performed a time-resolved study of reaction (1) in the presence of nitrite.[3]

Sulfate radicals, which are relative long-lived species in the absence of added substrates, are quantitatively reduced to SO_4^{2-} within ca. 2 μs under the presence of 1 mM NO_2^- at room temperature,[3,4] according to reaction (2):

$$SO_4^{\cdot-} + NO_2^- \rightarrow SO_4^{2-} + NO_2 \qquad (2)$$
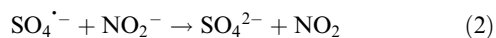
By applying deconvolution techniques to the photoacoustic signal, the time resolution of the method can be extended from the nanosecond to microseconds time range, allowing the determination of the enthalpy and volume changes taking place in reactions (1) and (2).[5,6]

Experimental

Materials

Sodium nitrite ($NaNO_2$, Mallinckrodt) and potassium peroxodisulfate ($K_2S_2O_8$, Merck) were used as received. Solutions were freshly prepared using Millipore Milli-Q purified water. Stock solutions of $NaNO_2$ and $K_2S_2O_8$ were mixed to obtain the final desired concentrations ([$NaNO_2$] = 1 mM, [$K_2S_2O_8$] = 30 mM). A few drops of concentrated aqueous KOH were added to adjust the pH at 5.5 ± 0.1 [pK_a (HNO_2) = 3.37],[7] thus ensuring [NO_2^-] $\gg$ [HNO_2].

The temperature of the solutions was varied between 282 and 292 K, and measured with an accuracy of ± 0.1 K. Absorption spectra of the mixed solutions were recorded on a Shimadzu UV-2001-PC. Unless indicated, the absorbance of solutions at $\lambda = 266$ nm was 0.30 ± 0.01.

Time-resolved photoacoustic calorimetry (TR-PAC)

The PAC set-up was already described by Brusa *et al.*[2] In this case, the laser beam width, coming from a Nd : YAG Spectron Laser SL400 operating at 266 nm, was shaped with a rectangular slit (0.5 mm width × 5 mm height), allowing a time resolution of the TR-PAC experiments from *ca.* 20 ns up to 3 μs using deconvolution techniques.[5,8,9] Incident laser fluence was attenuated with a dichromate aqueous solution. The laser beam went through a beam splitter so that a known fraction of the pulse was checked for constant energy in every measurement using a pyroelectric energy meter, Melles–Griot model 13PEM001. The total laser energy beyond the slit was <150 μJ per pulse. In all cases, the plots of the photoacoustic signal amplitude *vs.* the laser energy were linear with zero intercepts, indicating that bi-photonic processes or signal saturation do not take place.

Photoacoustic signals were obtained as the average of *ca.* 20 laser shots. The deconvolution procedures were performed using a multi-exponential sequential kinetic model supplied by the Sound Analysis 3000 1.50 D software (Quantum Northwest Inc., Spokane, WA).

In TR-PAC the sample signal is deconvoluted from that obtained upon irradiation of a reference solution. Usually, the reference solution contains an absorbing compound that converts the photon energy entirely into heat and undergoes no net conformational changes within the time-window of the measurement. Instead, we chose aqueous potassium peroxodisulfate as the calibration compound. For this reference, the fraction α of the absorbed energy which is delivered as heat, is less than one.[1,2] However, by working at the same peroxodisulfate concentration, the matching of the thermoelastic parameters of both sample and reference solutions is warranted.

According to the deconvolution treatment, the measured signal is a numerical convolution of the time derivative of the photoinduced time-dependent overall volume change (of both structural and enthalpic origins) and the instrumental response, obtained with the reference solution. On this basis, the measured signal is described as a sum of single-exponential decay functions for the time evolution of the pressure.[5,6] For the investigated system, just two single-exponential functions probed to give good quality fittings of the signals:

$$H(t) = \left(\frac{\varphi_a}{\tau_a}\right) exp\left(-\frac{t}{\tau_a}\right) + \left(\frac{\varphi_b}{\tau_b}\right) exp\left(-\frac{t}{\tau_b}\right) \qquad (3)$$

where $H(t)$ is the signal due to the volume (pressure) change on the detector (transducer), τ_a is related to the prompt process releasing heat during the time response of the transducer, τ_b is the lifetime of the transient occurring within the pressure integration time, and φ_a, φ_b are the respective relative contributions to the measured volume change.

Each relative amplitude φ contains the heat released q and the structural volume change ΔV of the step involving that transient. A simple energy balance relates the relative contribution of a particular step i to the total absorbed energy:

$$E_\lambda \varphi_i = q_i + \frac{\Delta V_i}{\chi} \qquad (4)$$

Here E_λ denotes the energy of one mol of photons at the irradiation wavelength, and χ is the thermal expansivity of the solution given by $\chi = (\beta/C_p\rho)$, where β is the cubic expansion coefficient, C_p the specific heat capacity and ρ the density of the solution. Notice that ΔV_i represents the total volume change produced by step i and not the molar volume change, $\Delta \bar{V}_i$. If Φ_i is the quantum yield for reaction i, then $\Delta V_i = \Phi_i \Delta \bar{V}_i$.

It should be stressed that, in this particular case, the signal obtained from the selected reference solution contains contributions coming from the fraction α of the absorbed energy E_λ which is released as heat, and also from the structural
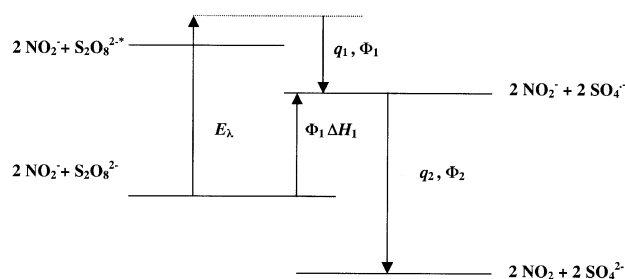
Scheme 1 Energy profile for the photodissociation of peroxodisulfate in the presence of nitrite in aqueous solution.

volume change ($\Phi_1 \Delta \bar{V}_1/\chi$), amounting to a total quantity E', such as:

$$E' = \alpha E_\lambda + \frac{\Phi_1 \Delta \bar{V}_1}{\chi} \qquad (5)$$

Considering that the enthalpy change per quantum absorbed by the reference is $\Phi_1 \Delta H_1$, we get:

$$\alpha = 1 - \frac{\Phi_1 \Delta H_1}{E_\lambda} \qquad (6)$$

and by replacing eqn. (6) in eqn. (5) and rearranging, eqn. (7) is obtained:

$$E' = E_\lambda - \Phi_1 \Delta H_1 + \frac{\Phi_1 \Delta \bar{V}_1}{\chi} \qquad (7)$$

Thus, applying eqn. (4) for a total quantity E', the relative amplitude φ_1 can be expressed as:

$$\varphi_i = \frac{q_i}{E'} + \frac{\Delta \bar{V}_i}{\chi E'} \qquad (8)$$

Scheme 1 shows an energy level diagram for the species involved in the photolysis of peroxodisulfate and nitrite at 266 nm [*i.e.* reactions (1) and (2)]. To apply the previous analysis to this system, we assign each step i to the reactions (1) and (2), respectively [*i.e.* $a = 1$ and $b = 2$ in eqn. (3)]. Notice from Scheme 1 that $q_1 = E_\lambda - \Phi_1 \Delta H_1$ and $q_2 = -2\Phi_1 \Phi_2 \Delta H_2$. In the last equation, ΔH_2 is the molar enthalpy change of reaction (2) and the factor ($2\Phi_1 \Phi_2$) accounts for the number of moles of sulfate radicals involved in this reaction per mol of absorbed photons.

By replacing in eqn. (8) we obtain:

$$\varphi_1 = 1 \qquad (9)$$

$$\varphi_2 = \frac{q_2}{\left(E_\lambda - \Phi_1 \Delta H_1 + \frac{\Phi_1 \Delta \bar{V}_1}{\chi}\right)} + \frac{\Delta V_2}{\left[\chi\left(E_\lambda - \Phi_1 \Delta H_1 + \frac{\Phi_1 \Delta \bar{V}_1}{\chi}\right)\right]} \qquad (10)$$

Using the following substitutions $\Delta V_2 = 2 \Phi_1 \Phi_2 \Delta \bar{V}_2$, and $D = (E_\lambda \chi - \Phi_1 \Delta H_1 \chi + \Phi_1 \Delta \bar{V}_1)$ and rearranging we arrive at:

$$\varphi_2 = -\frac{2\Phi_1 \Phi_2 \Delta H_2 \chi}{D} + \frac{2\Phi_1 \Phi_2 \Delta \bar{V}_2}{D} \qquad (11)$$

The above equation is used to derive the values of ΔH_2, $\Delta \bar{V}_2$ as discussed in the next section.

Results and discussion

Under 266 nm excitation, absorption of the sample is mostly due to the peroxodisulfate species. Although NO_2^- absorption spectrum extends into the UV range, the fraction of radiation
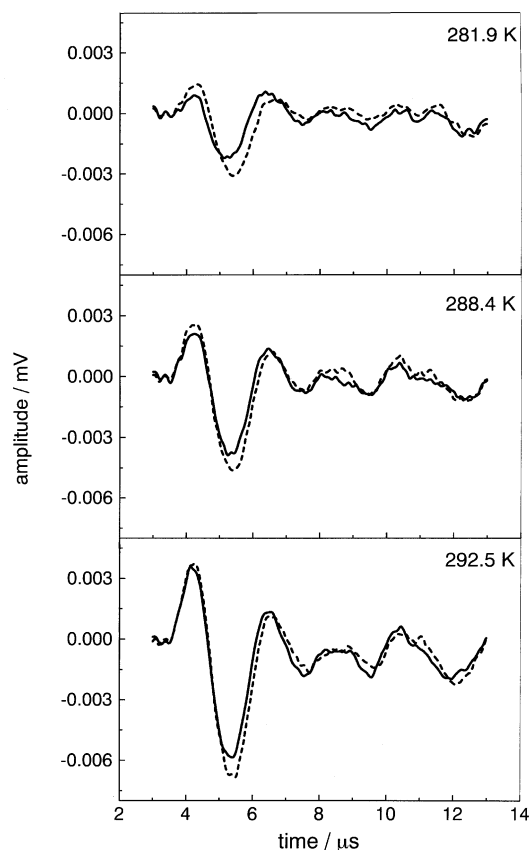
Fig. 1 Comparison of PAC signals obtained at 281.9 K (top), 288.4 K, and 292.5 K (bottom). Solid lines correspond to the signals obtained for the sample (1 mM $NaNO_2$ + 30 mM $K_2S_2O_8$ in water), and dotted lines for the reference (30 mM $K_2S_2O_8$ in water).
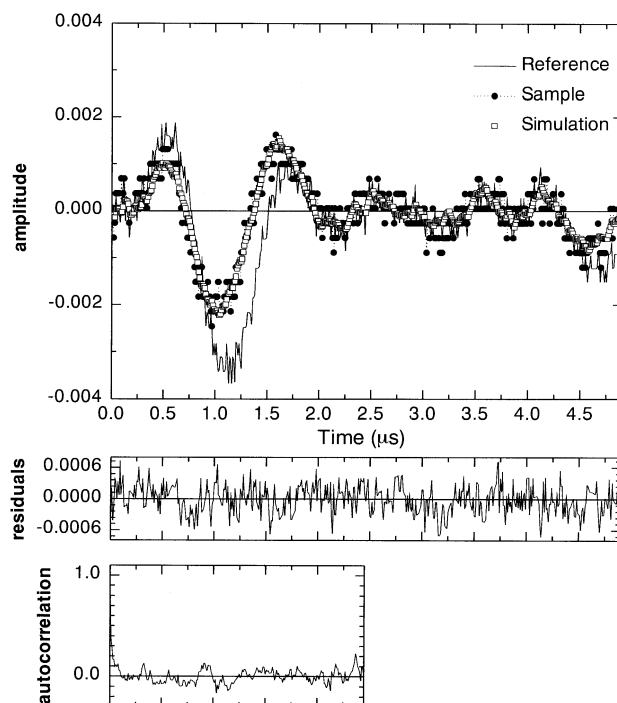

Fig. 2 PAC signals for sample (circles) and reference (line) registered at 281.9 K and the corresponding simulated signal for the sample (squares) according to the parameters extracted by deconvolution. In the deconvolution procedure, φ_1 was fixed at a value of 1 and a sequential model was assumed (see eqn. (3)). The parameters for this fitting with two exponential components yield: $\tau_1 = 35$ ns; $\tau_2 = 211$ ns, $\varphi_2 = -0.8793$, and the sum of the squares of the residuals, $\Sigma^2 = 7.247 \times 10^{-8}$. Bottom insets show, respectively, the residuals and the autocorrelation function.

intensity absorbed by NO_2^- in the sample solutions amounts to less than 3% of the total.[10]

Fig. 1 shows the optoacoustic signals obtained for the sample solution (30 mM $S_2O_8^{2-}$ and 1 mM NO_2^-) and the reference solution (30 mM $S_2O_8^{2-}$) at three different temperatures. It is clear from the comparison of sample and reference signals at any particular temperature that they are temporally shifted one from each other, specially at low temperatures, and that their amplitudes are also unbalanced. This behaviour can be explained by the occurrence of some chemical process involving NO_2^- and taking place on a time scale different from that of the photoinduced reaction in the reference system, but still within the resolution time range of technique. In order to resolve the input of that process, which was ascribed to reaction (2), the signals were deconvoluted consistently with eqn. (3). A sequential mechanism was assumed.[8]

During the deconvolution procedure the amplitude φ_1 was fixed at a value of 1, given that this contribution is assigned to the same reaction occurring in the absence of nitrite, whereas φ_2 and the two lifetimes were first allowed to vary without restrictions. The goodness of the fit was judged by the value of the sum of the squares of the residuals, Σ^2, and by visual inspection of the residuals and autocorrelation (see Fig. 2). The results, showed on Table 1, yielded two quite different decay times τ_1 and τ_2 averaging 21 ± 5 ns and 263 ± 80 ns. The values for τ_1 are attached to the transducer response and they are ascribed to reaction (1), whereas the values for τ_2, are in line with the expected shortening of $SO_4^{\bullet-}$ lifetime in the presence of NO_2^-, as already mentioned in the Introduction. The dispersion in τ_1 values may be related to the fact that process 1 develops promptly below the transducer response and it cannot be resolved; however, the somewhat erratic temperature dependence in τ_2 merits further analysis. First, using

the reported value of k_2,[3,4] we verified that the mean lifetime, τ_2, estimated as $\tau_2 = \ln 2/k_2 [NO_2^-]_0$ is 350 ns in reasonable agreement with the mean value obtained in our experimental conditions (see Table 1). Thus, we repeated the deconvolution procedure assuming a constant (temperature independent) value of τ_2, close to our mean value, $\tau_2 \cong 300$ ns. We found that the results for Σ^2 as well as for the residuals were almost indistinguishable from those obtained previously, although the values φ_2 and τ_1 were slightly modified. Thus, we considered that the temperature dependence observed for τ_2 may not be real, but actually the result of the algorithm forcing the variation in this parameter beyond the experimental uncertainties.

Table 1 Parameters obtained[a] from the deconvolution[b] of PAC signals at different temperatures[c]

T/K	φ_2	τ_1/ns	τ_2/ns
281.9	-0.856 ± 0.010	28 ± 5	238 ± 30
283.2	-0.691 ± 0.048	21 ± 4	316 ± 23
285.4	-0.600 ± 0.010	20 ± 2	415 ± 60
288.2	-0.412 ± 0.030	25 ± 5	231 ± 41
290.6	-0.289 ± 0.032	16 ± 3	191 ± 36
292.5	-0.290 ± 0.026	15 ± 4	187 ± 16

[a] Experimental conditions: $[NaNO_2] = 1$ mM, $[K_2S_2O_8] = 30$ mM in water at pH $= 5.5 \pm 0.1$, $\lambda = 266$ nm. [b] The reaction model for the deconvolution was a two-steps sequential mechanism. φ_1 was fixed at a value of 1, and φ_2 and the lifetimes τ_1, τ_2 were allowed to vary without restrictions. Residuals, autocorrelation functions and fitted curves were checked in each run. [c] Data obtained from the average of the parameters recovered from two to four signals measured at each temperature.
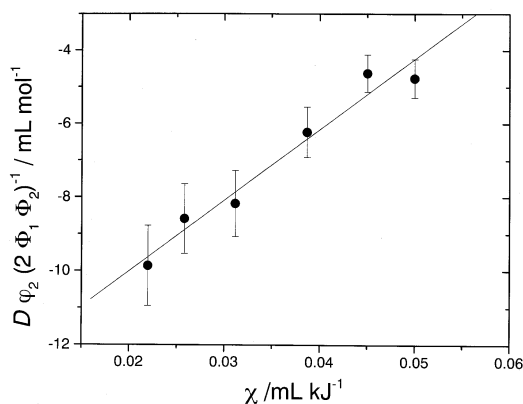
Fig. 3 Linear correlation (solid line) of the experimental data (●) to eqn. (12). Error bars were calculated from the combination of the maximal uncertainties in experimental quantities estimated in 11%. The slope and the intercept obtained by linear regression (192 ± 19 kJ mol^{-1} and -13.8 ± 0.7 mL mol^{-1}) yield $-\Delta H_2$ and $\Delta \bar{V}_2$, respectively.

The set of φ_2 values shown in Table 1 were used in the linearized form of eqn. (11):

$$\frac{\varphi_2 D}{2\Phi_1 \Phi_2} = -\Delta H_2 \chi + \Delta \bar{V}_2 \qquad (12)$$

to derive the enthalpy and volume changes of reaction (2). Notice that term D depends on temperature through the values of χ and also of Φ_1, the quantum yield of peroxodisulfate dissociation, which was already shown to vary with temperature.[2] The values of χ were taken as well from our previous work. We have considered $\Phi_2 \sim 1$ provided that the depletion of sulfate radicals by reaction (2) is much faster than their self-reaction under present experimental conditions.

In accordance with eqn. (12), we found that $(\varphi_2 D/2\Phi_1 \Phi_2)$ shows a good linear correlation with χ when using either the set of values in Table 1 or the values obtained by fixing $\tau_2 = 300$ ns (not shown for simplicity). From the intercept and the slope obtained by linear regression analysis with the data on Table 1 (see Fig. 3), we get $\Delta \bar{V}_2 = -13.8 \pm 0.7$ mL mol^{-1} and $\Delta H_2 = -192 \pm 19$ kJ mol^{-1}; whereas using the values of φ_2 recovered from the deconvolution with a constant value of $\tau_2 = 300$ ns, the results for the volume and enthalpy changes of reaction (2) are the same within the estimated uncertainties. This proves that the differences observed in φ_2 values at fixed or variable τ_2 are not propagated in the derived parameters beyond the reported errors.

Reaction enthalpy change

The enthalpy of formation of the aqueous species comprised in reaction (2) can be correlated on the basis of this experimental result and that from Brusa *et al.* for the dissociation of aqueous peroxodisulfate $\Delta H_1 = 120 \pm 11$ kJ mol^{-1}:[2]

$$\Delta H_2 = \Delta H_f(NO_2)_{aq} + \Delta H_f(SO_4^{2-})_{aq} - \Delta H_f(NO_2^-)_{aq}$$
$$- \tfrac{1}{2}\Delta H_f(S_2O_8^{2-})_{aq} - \tfrac{1}{2}\Delta H_1 \qquad (13)$$

Using literature values for $\Delta H_f(S_2O_8^{2-})_{aq} = -1344.9$ kJ mol^{-1},[11] $\Delta H_f(SO_4^{2-})_{aq} = -909.34 \pm 0.40$ kJ mol^{-1},[12] $\Delta H_f(NO_2^-)_{aq} = -104.6$ kJ mol^{-1}[11] and ΔH_2 from this work, we obtained $\Delta H_f(NO_2)_{aq} = 0 \pm 20$ kJ mol^{-1}. The uncertainty is an estimation assuming a typical error (± 4 kJ mol^{-1}) in the enthalpies of $(S_2O_8^{2-})_{aq}$ and $(NO_2^-)_{aq}$.

This result can be compared with the following estimation based on Henry's constant for NO_2, $H(T) = 1.2 \times 10^{-2}$ M atm^{-1}.[13] Assuming $S(NO_2)_{aq} - S(NO_2)_g \approx S(CO_2)_{aq} - S(CO_2)_g \approx -94.5$ J mol^{-1} K^{-1},[14,15] it is possible to calculate $\Delta H_f(NO_2)_{aq} - \Delta H_f(NO_2)_g = -17.2$ kJ mol^{-1} K^{-1}. By taking

the corresponding parameter in gas phase as reference: $\Delta H_f(NO_2)_g = 33$ kJ mol^{-1},[16] the estimation yields $\Delta H_f(NO_2)_{aq} = 15.8$ kJ mol^{-1}. This value agrees with above determined one within the mutual errors, lending support to our procedures.

Further evaluation of the results can be carried out using redox data for the species transformed by reaction (2), such as $E^0(NO_2/NO_2^-) = 1.04$ V and $E^0(SO_4^{\bullet-}/SO_4^{2-}) = 2.43$ V.[17,18] This data allows the derivation of the reaction Gibbs energy $\Delta G_2 = -134.1$ kJ mol^{-1}. On the other hand, combination of this value with our experimental enthalpy ΔH_2, affords $\Delta S_2 = -97.3$ J mol^{-1} K^{-1}. By combining this figure with the previous determined value of ΔS_1, we get $S(NO_2)_{aq} - S(NO_2^-)_{aq} = \Delta S_2 - S(SO_4^{2-})_{aq} + \tfrac{1}{2}(\Delta S_1 + S(S_2O_8^{2-})_{aq}) = 84.7$ J mol^{-1} K^{-1}. This value compares well with the difference $S(OH)_{aq} - S(OH^-)_{aq} = 100$ J mol^{-1} K^{-1}, as expected, provided that also one negative charge has been attached on going from OH to OH$^-$.[15]

Reaction volume change

The molar volume change accompanying reaction (2) is $\Delta \bar{V}_2 = -13.8 \pm 0.7$ mL mol^{-1}. The negative sign indicates a volume contraction on going from reactants to products which can be expressed by:

$$\Delta \bar{V}_2 = [\bar{V}(NO_2)_{aq} - \bar{V}(NO_2^-)_{aq}] + [\bar{V}(SO_4^{2-})_{aq} - \bar{V}(SO_4^{\bullet-})_{aq}] \qquad (14)$$

The main change driven by the reaction seems to be charge redistribution because no appreciable changes in molecular geometry are expected to take place on going from NO_2^- to NO_2 or from $SO_4^{\bullet-}$ to SO_4^{2-}.[19,20] In fact, the N–O bond lengths and O–N–O angles are 1.20 Å and 134°, respectively, in NO_2, and 1.24 Å and 115.5° in NO_2^-.[21] In order to examine this topic with more detail let us express eqn. (14) as follows:

$$[\bar{V}(NO_2)_{aq} - \bar{V}(NO_2^-)_{aq}] = \Delta \bar{V}_2 - [\bar{V}(SO_4^{2-})_{aq}$$
$$- \tfrac{1}{2}\bar{V}(S_2O_8^{2-})_{aq} - \tfrac{1}{2}\Delta \bar{V}_1] \qquad (15)$$

Taking the volume change for aqueous peroxodisulfate dissociation (8.9 ± 0.5) mL mol^{-1} from our earlier work[2] and literature values for $\bar{V}(S_2O_8^{2-})_{aq} = 79.6 \pm 0.5$ mL mol^{-1},[22] and for $\bar{V}(SO_4^{2-})_{aq} = 13.98$ mL mol^{-1},[20,23] we deduced that the difference between the molar volumes of NO_2^- and NO_2 is $[\bar{V}(NO_2)_{aq} - \bar{V}(NO_2^-)_{aq}] = 16.5 \pm 1.5$ mL mol^{-1}. It should be stressed that this difference, which is obtained here from experimental data exclusively, is commonly referred to in the literature as arising from the electrostriction phenomena.[20,24] The assignment $\bar{V}_{el}(NO_2^-)_{aq} \approx \bar{V}(NO_2^-)_{aq} - \bar{V}(NO_2)_{aq}$ is based on the fact that the volume of NO_2—an uncharged species, consequently free from electronic effects—may be considered equivalent to the intrinsic volume V^0 of the corresponding ion, neglecting any geometrical difference between them, *i.e.* $V(NO_2)_{aq} \equiv V^0(NO_2^-)_{aq}$.

The available data for the related species nitrate, with the same convention for partial molar volumes of ions in water at 25 °C, $\bar{V}(NO_3^-)_{aq} = 29$ mL mol^{-1},[20] and the calculated intrinsic volume $\bar{V}^0(NO_3^-)_{aq} = 43$ mL mol^{-1},[25] differ in *ca.* -14 mL mol^{-1} which is consistent with our report.

Besides, it should be noticed that the measured volume contraction for reaction (2) can be explained by the concentration of the anionic charges on SO_4^{2-}, which seems to be the dominant feature in determining the total volume change. In fact, our data support: $\bar{V}(SO_4^{2-})_{aq} - \bar{V}(SO_4^{\bullet-})_{aq} = \bar{V}(SO_4^{2-})_{aq} - \tfrac{1}{2}[\bar{V}(S_2O_8^{2-})_{aq} + \Delta \bar{V}_1] = -30.3$ mL mol^{-1}.[2]

For comparison purposes we reproduce—from the review of Millero[20]—the following differences between the experimental volume of some ions: $\bar{V}(SO_4^{2-})_{aq} - \bar{V}(HSO_4^-)_{aq} = -21.7$ mL

mol^{-1}, $\bar{V}(HPO_4^{2-})_{aq} - \bar{V}(H_2PO_4^{-})_{aq} = -21.4$ mL mol^{-1}, $\bar{V}(CO_3^{2-})_{aq} - \bar{V}(HCO_3^{-})_{aq} = -27.7$ mL mol^{-1}.

We adhere to the idea that the above differences are mainly due to the increase in the electric field of the ion causing a contraction of the solvent around it, however this can hardly be explained *via* continuum concepts for visualizing the system.[26,27]

The simple exercise of calculating the electrostriction contribution to the volume difference $\bar{V}_{el}(SO_4^{2-})_{aq} - \bar{V}_{el}(SO_4^{\bullet-})_{aq}$, or $\bar{V}_{el}(NO_2^{-})_{aq} - \bar{V}_{el}(NO_2)_{aq}$, provided we consider a spherical ion of constant radius r, leads to $\bar{V}_{el}(SO_4^{2-})_{aq} - \bar{V}_{el}(SO_4^{\bullet-})_{aq}, = -3B/r$ and $\bar{V}_{el}(NO_2^{-})_{aq} - \bar{V}_{el}(NO_2)_{aq} = -B/r$ (where B is a constant, in accordance to the model used by Drude–Nernst).[28] Even after the replacement of the theoretical value in water $B = 4.175$ Å mL mol^{-1}, with higher semiempirical values of 8.0 or 13.4 Å mL mol^{-1}, the calculated contributions are much lower than the experimental values, for any reasonable value of r.[26,27] For instance, considering $B = 13.4$ Å mL mol^{-1} and an estimation of $r = 2.95$ Å for sulfate species and $r = 2.76$ Å for nitrite, we get -13.6 mL mol^{-1} and -4.8 mL mol^{-1}, respectively.[2]

Instead, a more realistic model considers the electrostriction limited to the region close to the ion, where dielectric saturation occurs such that the volume varies approximately linearly with the charge Z.[29,30] Under this approach, Akitt estimates electrostriction volumes in water for monocharged and dicharged polyatomic ions of 19.8 and 53 mL mol^{-1}, respectively,[30] which are more consistent with the reported experimental differences from above and with our results for electrostriction volumes of sulfate, sulfate radical and nitrite anions.

Conclusions

By applying the TR-PAC technique to the photolysis of aqueous peroxodisulfate in the presence of nitrite anions we were able to determine the enthalpy and volume changes associated with the electron transfer reaction between the sulfate radical and nitrite anion. The measured enthalpy change is consistent with previous estimations of the heat of formation of aqueous NO_2 and with recent reports on the peroxide bond dissociation energy in $S_2O_8^{-2}$, ΔH_1.[2,15] In addition, we conclude that the observed volume change, $(-13.8 \pm 0.7$ mL mol$^{-1})$, is mainly determined by charge redistribution between species. Analysis of the results reinforces the idea that continuous models for the solvent are completely inadequate to describe solute–solvent interactions in the case of structured solvents like water.

Acknowledgements

References

1 S. E. Braslavsky and G. E. Heibel, *Chem. Rev.*, 1992, **92**, 1381.
2 M. A. Brusa, M. S. Churio, M. A. Grela, S. G. Bertolotti and C. M. Previtali, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2383.
3 P. H. Wine, Y. Tang, R. P. Thorn, J. R. Wells and D. D. Davis, *J. Geophys. Res., D: Atmos.*, 1989, **94**, 1085.
4 The value of the rate constant for reaction (2), k_2, depends on the ionic strength, I. The estimation was made at $T = 298$ K, pH = 5.5, and $I = 0$ using $k_2 = 9.8 \times 10^8$ M^{-1} s^{-1}, as reported in ref. 3. Under the present experimental conditions ($I = 0.091$ M), k_2 rises to 2.0×10^9 M^{-1} s^{-1}.
5 J. E. Rudzki, J. L. Goodman and K. S. Peters, *J. Am. Chem. Soc.*, 1985, **107**, 7849.
6 K. S. Peters and G. J. Snyder, *Science*, 1988, **241**, 1053.
7 *CRC Handbook of Chemistry and Physics*, D. R. Lide Ed., CRC Press, Boca Raton, Fl., 73rd edn., 1992–1993, p. 8–41.
8 T. Gensch, C. Viappiani and S. E. Braslavsky, in *Encyclopedia of Spectroscopy and Spectrometry*, ed. J. C. Lindon, Academic Press, London, 1999, 1124.
9 The acoustic transit time for the experiment is estimated from the width of the laser beam passing through the aqueous samples (0.5 mm), thus establishing a heat integration time of *ca.* 340 ns.
10 From our experimental determinations, the molar absorption coefficient for both species at 266 nm is $\varepsilon_{266}(NO_2^-) \cong \varepsilon_{266}(S_2O_8^{2-}) \cong 10$ M^{-1} cm^{-1}.
11 Data derived from the heat of formation of the corresponding sodium or potassium salts, J. A. Dean, *Lange's Handbook of Chemistry*, XIV edn., McGraw–Hill, New York, 1992, p. 6.93.
12 *CRC Handbook of Chemistry and Physics*, D. R. Lide Ed., CRC Press, Boca Raton, Fl., 73rd edn., 1992–1993, p. 5–2.
13 S. Mertes and A. Wahner, *J. Phys. Chem.*, 1995, **99**, 14 000.
14 *CRC Handbook of Chemistry and Physics*, D. R. Lide Ed., CRC Press, Boca Raton, Fl., 73rd edn., 1992–1993, p. 5–3.
15 G. Merényi, J. Lind, S. Goldstein and G. Czapski, *J. Phys. Chem. A*, 1999, **103**, 5685.
16 *NIST Standard Reference Database*, Version 2.02, National Bureau of Standards and Technology, Gaithersburg, MD, 1994.
17 D. M. Stanbury, in *Advances in Inorganic Chemistry*, ed. A. G. Sykes, Academic Press, San Diego, 1989, p. 69.
18 G. V. Buxton, M. Bydder and G. A. Salmon, *Phys. Chem. Chem. Phys.*, 1999, **1**, 269.
19 F. Ayrancy and B. E. Conway, *J. Chem. Soc., Faraday Trans.*, 1983, **79**, 1357.
20 F. J. Millero, *Chem. Rev.*, 1971, **71**, 147.
21 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry. A Comprehensive Text*, J. Wiley and Sons, USA, 1972, p. 354.
22 I. V. Olofsson, J. Spitzer and L. G. Hepler, *Can. J. Chem.*, 1978, **56**, 1871.
23 Several methods to obtain absolute ionic volumes have been reviewed (G. Hefter, Y. Marcus, *J. Sol. Chem.* 1997, **26**, 249). In any case, adoption of extra thermodynamic assumptions is unavoidable, and the existing data from the various methods show little agreement for the whole set of electrolytes. In general, it appears that ionic volumes cannot be estimated to better than ± 2 to 4 ml mol^{-1}. For the analysis followed in this work, we have considered the data compiled by Millero on the assumption $V(H^+) = 0$ (ref. 20).
24 E. Whalley, *J. Chem. Phys.*, 1963, **38**, 1400.
25 D. M. P. Mingos, A. L. Rol and J. Burgess, *J. Chem. Soc., Dalton Trans.*, 1993, 423.
26 C. D. Borsarelli and S. E. Braslavsky, *J. Phys. Chem. A*, 1999, **103**, 1719.
27 C. D. Borsarelli and S. E. Braslavsky, *J. Photochem. Photobiol., B*, 1998, **43**, 222.
28 P. Drude and W. Z. Nernst, *Z. Phys. Chem. (Leipzig)*, 79, **15**, 1894.
29 J. Feitelson and D. Mauzerall, *J. Phys. Chem. B*, 2002, **106**, 9674.
30 J. W. Akitt, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2259.