Simultaneous X-ray absorption fine-structure spectroscopy (XAFS) and differential scanning calorimetry (DSC)

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Combination of *in situ* X-ray absorption fine-structure spectroscopy and differential scanning calorimetry enables following of structural as well as energetic changes during a solid-state reaction.

Solid-state reactions are usually very complex processes. A good understanding of the underlying mechanisms is only possible by applying different complementary techniques probing different sample properties. Of high importance is the tracing of structural and energetic properties during the reaction. In order to avoid undesired artifacts, it is generally of advantage to apply *in situ* techniques that yield direct information while the sample is reacting.

We combined two important methods to give a new *in situ* technique. The first is X-ray absorption fine-structure spectroscopy (XAFS) which yields structural and compositional information about different chemical elements in a sample.[1,2] The quick-XAFS mode ('QEXAFS') allows one to record spectra with a good signal-to-noise ratio in a few minutes or less.[3,4] One advantage of XAFS is its applicability to liquid, glassy or amorphous systems where diffractometry is difficult to employ. A number of successful couplings of XAFS and X-ray diffractometry[5–7] have been reported.

The second technique is differential scanning calorimetry (DSC). Energetic parameters obtained from this method can be used to extract compositional or kinetic data.[8] The time resolution of this method is of the order of seconds. Coupling of DSC with X-ray diffractometry has been accomplished by a number of workers.[9–14]

The combination of XAFS and DSC allows a thorough insight into the mechanism and kinetics of reacting sample systems. This is demonstrated for the solid-state elimination reaction of sodium bromoacetate [eqn. (1)].

$$NaO_2CCH_2Br(s) \rightarrow NaBr(s) + 1/n[O_2CCH_2]_n(s) \qquad (1)$$

This type of exothermic elimination reaction occurs in many halogenoacetates of the general formula MO_2CCH_2X.[15] A detailed study on the solid-state polymerization reaction in sodium chloroacetate (*inter alia* with *ex situ* XAFS) was recently published.[16] The organic part of the molecule polymerizes quantitatively to polyglycolide, the simplest polyester. By other techniques (thermal analysis, SEM, X-ray diffractometry) it was established that the reaction occurs in the solid state without intermediates. The enthalpy of reaction (1) is −23.4(20) kJ mol^{-1}.[15]

The reaction was followed *in situ*† by recording X-ray absorption spectra at the bromine K-edge and the thermal signal from DSC. Sodium bromoacetate was thoroughly mixed with boron nitride (BN) to achieve an optimum absorption of the X-rays in the DSC crucible (edge jump of $\Delta\mu d \approx 1$). The calorimeter was heated at a rate of +1 K min^{-1} from 120 to 200 °C. X-Ray absorption spectra were recorded in the QEXAFS mode every 2.25 min.

The baseline corrected DSC curve is shown in Fig. 1. The reaction is clearly visible as an exothermic peak between 140 and 180 °C. Fig. 2 displays the Fourier transforms calculated from the recorded absorption spectra. Major changes occur in the immediate vicinity of the bromine atom. The major peak in sodium bromoacetate represents the carbon neighbour at 1.96(3) Å (lit.:[17] 1.937 Å). This peak diminishes during the reaction. In the reaction product, NaBr, six sodium neighbours surround each bromine atom. The experimental Br–Na distance is 2.94(3) Å (lit.:[17] 2.981 Å, at room temperature).

Quantitative evaluation of the Fourier transforms with respect to the coordination numbers of the Br–C shell in sodium bromoacetate as well as the Br–Na shell in sodium bromide

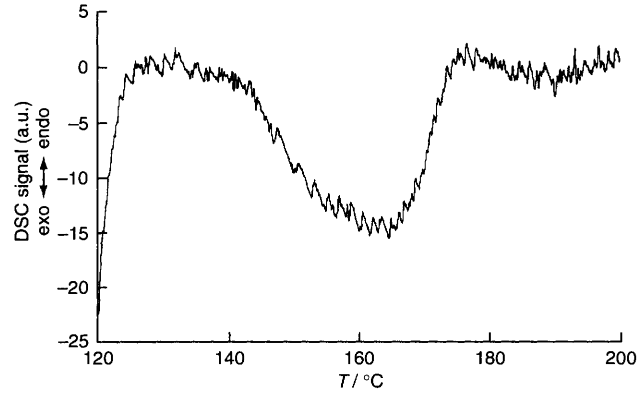

Fig. 1 Baseline-corrected DSC measurement of the elimination reaction of sodium bromoacetate (120–200 °C, heating rate +1 K min^{-1}). The small oscillations most likely arise from changing energy absorption (below/above the edge) during the XAFS scans.

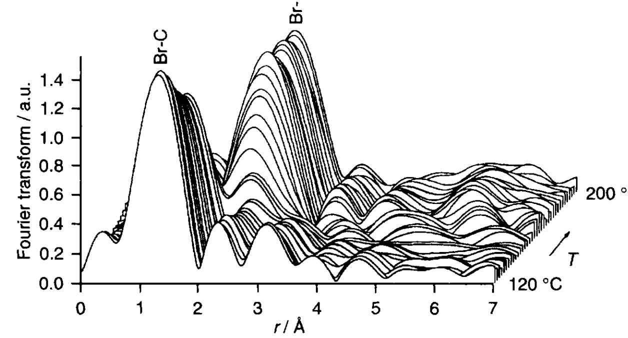

Fig. 2 Pseudo-three-dimensional representation of the Fourier transform magnitudes calculated from the XAFS data taken during the DSC scan (not phase-shift corrected)

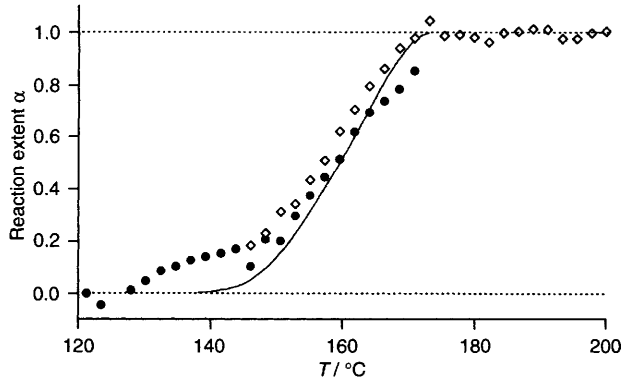

Fig. 3 Reaction extent α determined from DSC and from quantitative evaluation of XAFS spectra; (●) reaction extent derived from normalized coordination number of the carbon neighbour in sodium bromoacetate (Br–C); (◇) reaction extent derived from normalized coordination number of the six sodium neighbours in sodium bromide (Br–Na); (—) reaction extent by DSC

yields the reaction extent α.[16] If no intermediates occur, this should give the same results for parent and product bromine coordination shells, respectively. This information can also be derived by integration of the DSC curve of the calorimeter, assuming that the differential enthalpy of reaction $d(\Delta_r H)/dt$ is proportional to the differential reaction extent $d\alpha/dt$.[8]

The extent of reaction computed from XAFS and DSC is displayed in Fig. 3. The values derived from the coordination numbers for parent phase and product are in good agreement. This observation confirms that no intermediates are formed. Good agreement is also noted with the DSC signal, showing that indeed different features (structual changes by XAFS and enthalpic changes by DSC) of the same process [reaction (1)] are recorded. The changes determined by XAFS occur somewhat earlier than the change in DSC signal. This may be attributed to the fact that the information from XAFS comes from the small part of the sample that is transmitted by the X-ray beam (about one-tenth of the sample volume) whereas the the DSC signal arises from the whole sample volume. Possibly, the constant high-energy irradiation leads to some acceleration of the reaction, and therefore some deviation between the irradiated and non-irradiated sample. A similar result was obtained in another experiment studying the same compound.

This work reports, to the best of our knowledge, the first successful coupling of XAFS and DSC.

Full details of the experimental setup and the evaluation procedure will be reported in a forthcoming publication.

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Footnote

† *Experimental details*: A Mettler FP 80/84 differential scanning calorimeter was placed vertically into the synchrotron X-ray beam. This calorimeter was originally developed for simultaneous DSC and microscopy. The hole of *ca.* 1 mm diameter in the sample holder where the sample crucible is placed for microscopy was used for the synchrotron X-ray beam to pass through. Standard aluminium crucibles were used to contain the samples and were completely filled with an intimate mixture of sodium bromoacetate and inert boron nitride. The reference crucible was completely filled with boron nitride. The crucibles were fixed in a vertical arrangement by small poly(tetrafluoroethylene) (PTFE) rings between the crucible and sample holder. Experiments with temperatures up to 300 °C were possible with this arrangement.

The calorimeter was mounted to an *y–z* translation device enabling a correct positioning of the sample. The monochromatic X-ray beam was of dimensions *ca.* 0.8×0.8 mm^2. The position of the calorimeter was adjusted into the centre of the beam, so that small beam displacements did not affect the experiment. By calibrating the calorimetric set-up with pure indium dispersed in boron nitride a melting point of 157.0 °C was registered (lit.:[18] 156.6 °C).

X-Ray absorption fine-structure spectroscopy (XAFS) was carried out at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY), Germany, at beamline X (ROEMO II). This line is equipped with a Si(311) double crystal monochromator, yielding approximately 10^8 photons s^{-1} mm^{-2} at the sample. Experiments were performed at the bromine K-edge (*ca.* 13470 eV) in transmission mode. Evaluation of the XAFS data was performed with the programs FEFF, AUTOBK and FEFFIT from the University of Washington package.[19–21]

Quantitative evaluation of the X-ray spectra was performed by fitting the first shells of parent (Br–C) and product phase (Br–Na), respectively. To minimize the number of fitting parameters, Debye–Waller factors (σ^2) were determined previously by analysing the spectra of the pure substances at different temperatures and employing a linear approximation for their temperature dependence. The distances were allowed to vary freely, except at low concentrations of sodium bromoacetate or sodium bromide where they were fixed; otherwise, fitting to completely unreasonable values occurred. Therefore, the maximum number of fit parameters was four ($r_{\text{Br–C}}$, $r_{\text{Br–Na}}$, N_{C} and N_{Na}).

Sodium bromoacetate was prepared according to ref. 15. Its purity was checked by elemental analysis (C, H), ^{1}H and ^{13}C NMR spectroscopy in D_2O, X-ray powder diffraction and DSC.

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