In Situ Monitoring of Solid-State Polymerization Reactions in Sodium Chloroacetate and Sodium Bromoacetate by ^{23}Na and ^{13}C Solid-State NMR Spectroscopy

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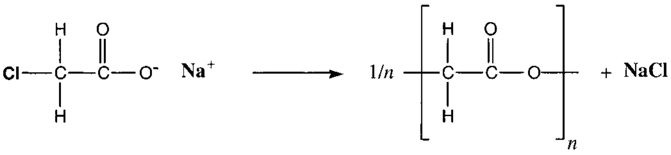
Abstract: The thermally induced solid-state polymerization reactions in sodium chloroacetate and sodium bromoacetate, leading to poly(hydroxyacetic acid) (polyglycolide) and NaCl and NaBr, respectively, were studied by isothermal in situ solid-state NMR spectroscopy at 120, 130 and 140 °C with a time resolution of the order of 5 to 25 min. The nuclei probed were ^{23}Na and ^{13}C, allowing the parent compounds (sodium halogenoacetates) and both reaction products (polymer and alkali halide) to be monitored. For sodium chloroacetate, there is no evidence for the involvement of intermediate phases during the reaction whereas this cannot be excluded for sodium bromoacetate. The crystal structure of sodium bromoacetate was determined directly from powder diffraction data by the Monte Carlo method, and was found to be isostructural with sodium chloroacetate. The topochemical reaction mechanism proposed previously for sodium chloroacetate is thus also applicable for the polymerization reaction in sodium bromoacetate. The mechanistic and kinetic information obtained from our in situ solid-state NMR investigations is compared and contrasted with information obtained from other in situ probes of the polymerization reactions in these materials.

Keywords: NMR spectroscopy • polymerizations • solid-state chemistry • solid-state reactions

Introduction

It has been known since the middle of the 19th century that alkali halogenoacetates undergo a reaction in the solid state upon heating above about 100 °C.[1] At the end of the last century,[2] it was realized that the reaction involves a polymerization to produce the simplest polyester, poly(hydroxyacetic acid) (also called polyglycolide). In the case of sodium chloroacetate, the reaction is:



$$\mathrm{Cl{-}CH_2{-}C({=}O){-}O^-\ Na^+} \longrightarrow 1/n\left[\mathrm{{-}CH_2{-}C({=}O){-}O{-}}\right]_n + \mathrm{NaCl}$$

The reaction leads to micrometer-sized NaCl crystals dispersed in a matrix of polyglycolide.[3] In principle, the halogen and the metal can be varied for this reaction type. In a systematic study of most combinations of halogen (Cl, Br, I) and metal (Li, Na, K, Rb, Cs, Ag, NH_4) we have shown that the polymerization reaction does occur in most cases, with the exception of three lithium salts and sodium iodoacetate.[3] A number of crystal structure determinations on halogenoacetates, mostly carried out using powder diffraction data (for discussions of this method see for example[4–8]) due to the lack of crystals suitable for single crystal X-ray diffraction, have now provided a structural basis for interpretation of these results.[9–11] A number of in situ experiments involving X-ray spectroscopy (EXAFS),[12] X-ray diffraction (XRD),[12, 13] infrared (IR) spectroscopy[14] and small-angle X-ray scattering (SAXS)[15] have shown that the reaction occurs in the solid state with no detectable intermediate phases involved. However, we emphasize that these methods are mostly sensitive to the structural arrangement of the reactants and products (for

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example EXAFS, XRD or SAXS), and are not necessarily sensitive to details of the chemical nature of reactants, products and possible intermediates. In general, in situ studies are preferred over ex situ experiments on quenched aliquots as, in the latter, it is often not clear whether chemical and/or structural changes occur upon quenching and storage of an aliquot before the analysis.[16, 17]

Solid-state NMR spectroscopy represents a powerful tool for identification and quantification of different chemical species. Techniques such as magic angle spinning (MAS), high-power proton decoupling and cross polarization (CP) have made it possible within the last few decades to routinely measure high-resolution NMR spectra of solid samples.[18–21] Temperature-resolved experiments have been carried out previously on solid-state phase transformations[22, 23] and solid-state reactions,[24–26] demonstrating that detailed information can be derived from such experiments. High-resolution solid-state NMR studies are particularly sensitive to the chemical and local structural changes associated with solid-state reactions, and thus represent a vital addition to the range of in situ probes that have been used hitherto to characterize the solid-state reactions in alkali halogenoacetates.

In the work reported here, sodium chloroacetate and sodium bromoacetate were chosen as they are the most extensively characterized examples of the "halogenoacetate family". Our solid-state NMR study has focused on ^{23}Na-NMR spectroscopy to probe the sodium halogenoacetate parent phase and the sodium halide (NaCl, NaBr) formed in the reaction, and ^{13}C-NMR spectroscopy to probe the sodium halogenoacetate parent phase and the polyglycolide formed in the reaction (Table 1). For a given temperature, the reaction is faster in the case of sodium bromoacetate.[3] In order to relate the NMR spectroscopic observations to structural features, we have also determined the crystal structure of sodium bromoacetate from powder X-ray diffraction data using the Monte Carlo method for structure solution.[6, 27, 28] The crystal structure of sodium chloroacetate has been determined previously.[10]

Abstract in German: *Die thermisch induzierte Festkörper-Polymerisationsreaktion in Natriumchloracetat und Natriumbromacetat, die quantitativ zu poly-Hydroxyessigsäure (Polyglycolid) und NaCl bzw. NaBr führt, wurde mittels in situ Festkörper-NMR-Spektroskopie untersucht. Die Reaktion wurde isotherm bei 120, 130 und 140 °C mit einer Zeitauflösung von ca. 5–25 Minuten durchgeführt. Sowohl ^{23}Na- als auch ^{13}C-NMR Spektroskopie wurden eingesetzt, so daß Edukte (Halogenacetate) als auch Produkte (Polymer und Alkalihalogenide) detektiert werden konnten. Im Fall von Natriumchloracetate konnten keine strukturell definierten Zwischenprodukte nachgewiesen werden, während diese für Natriumbromacetat nicht ausgeschlossen werden können. Weiterhin wurde die Kristallstruktur von Natriumbromacetat aus Röntgenpulverdaten mittels Monte-Carlo Methoden bestimmt. Natriumbromacetat kristallisiert isostrukturell mit Natriumchloracetat, so daß der früher vorgeschlagene topochemische Polymerisationsmechanismus für Natriumchloracetat auch in diesem Fall gelten sollte. Die mechanistischen und kinetischen Ergebnisse dieser in situ NMR-Studie werden mit den Resultaten anderer in situ Experimente für diesen Reaktionstyp verglichen.*

Table 1. Experimental conditions for in situ solid-state NMR spectroscopy experiments.

Sample	sodium chloroacetate	sodium bromoacetate	sodium bromoacetate, ^{13}C enriched
observed nucleus	^{23}Na	^{23}Na	^{13}C
temperature/°C	140	130	120
total time/h	47	23	46
time per spectrum/s	1536	300	900
number of spectra	110	276	184
MAS frequency/Hz	7060	6200	4600
conversion	final reaction ca. 92 %	final reaction ca. 96 %	final reaction ca. 42 %

Results and Discussion

Sodium chloroacetate: ^{23}Na-NMR spectroscopy

An in situ ^{23}Na-NMR experiment was carried out for sodium chloroacetate at 140 °C over a period of 47 h. Figure 1 shows ^{23}Na-NMR spectra of sodium chloroacetate and sodium bromoacetate and the final reaction products. Figure 2 shows the course of the reaction in sodium chloroacetate in a pseudo-three-dimensional representation of ^{23}Na-NMR spectra. A broad multiplet in the region of $\delta = -30$ to -5 corresponds to the sodium cation in sodium chloroacetate,

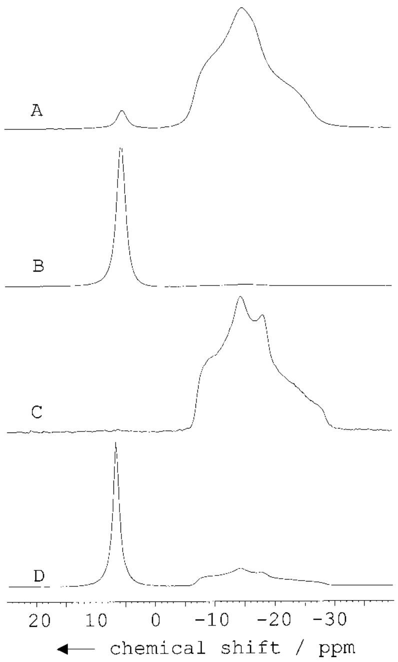

Figure 1. Solid-state ^{23}Na-NMR spectra of (A) sodium bromoacetate (containing a small impurity amount of NaBr), (B) the final product obtained from the in situ study of sodium bromoacetate, containing NaBr/polyglycolide/sodium bromoacetate, (C) sodium chloroacetate, and (D) the final product obtained from the in situ study of sodium chloroacetate containing NaCl/polyglycolide/sodium chloroacetate. The spectra were recorded at 130 (sodium bromoacetate) and 140 °C (sodium chloroacetate).

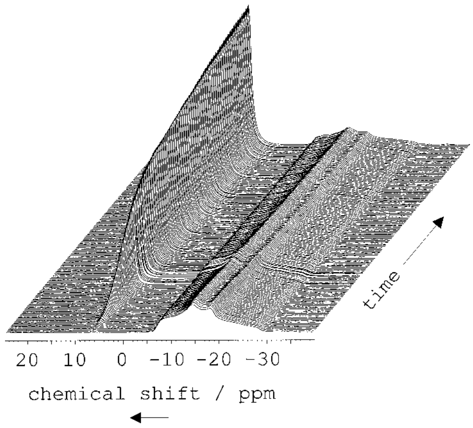

Figure 2. Solid-state ^{23}Na-NMR spectra recorded as a function of time at 140 °C for sodium chloroacetate over a period of 47 h. The solid-state polymerization reaction to produce NaCl is clearly observed. The multiplet ranging from $\delta = -30$ to -5 corresponds to sodium chloroacetate, and the sharp single line at $\delta = 7$ corresponds to NaCl.

indicating an unsymmetrical environment. The central transition ^{23}Na MAS NMR lineshape of sodium chloroacetate could be simulated using $\chi = 1.53$ MHz, $\eta = 0.63$ and $\delta = -5.3$. Consistent with this observation, in the crystal structure of sodium chloroacetate,[10] there is an unsymmetrical coordination (neither octahedral nor trigonal-prismatic) of the sodium cation by six oxygen atoms with Na ··· O distances in the range of 2.4–2.7 Å. The Na^+ and four oxygens (from different anions) lie close to the same plane, with two oxygens (from the same anion) lying above this plane. On the other hand, the highly symmetrical octahedral environment of sodium in NaCl leads to a sharp single line at $\delta = 7$ in the ^{23}Na-NMR spectrum.

Although these signals change in relative intensity during the reaction, they do not change in position or shape, and no other signals are detected; this suggests that the reaction occurs in a single-step without involving any intermediate phases. This conclusion is in agreement with previous in situ X-ray diffraction experiments[29] and in situ EXAFS experiments.[12, 29] However, it must be emphasized that diffraction techniques are sensitive only to the crystalline phases present, and that the ability of EXAFS to detect small amounts of additional phases is limited. In contrast, solid-state NMR represents a highly sensitive technique that can probe both crystalline and amorphous phases with high sensitivity (provided the signals from the different phases are sufficiently well resolved).

The final conversion of the reaction after 47 h is about 42 % (assessed from the sodium chloroacetate peak). A preliminary experiment at 130 °C gave about 32 % conversion after 88 h. These reaction rates compare well with earlier kinetic data on this reaction,[30, 31] and represent a significantly slower reaction than for sodium bromoacetate (see below).

Suitably normalized intensities for both sodium chloroacetate and sodium chloride are shown in Figure 3. Both curves have a very similar shape, consistent with a situation in which the rates of decay of the parent phase and production of the product phase are equal, and consistent with a situation in which no intermediate phases are involved.

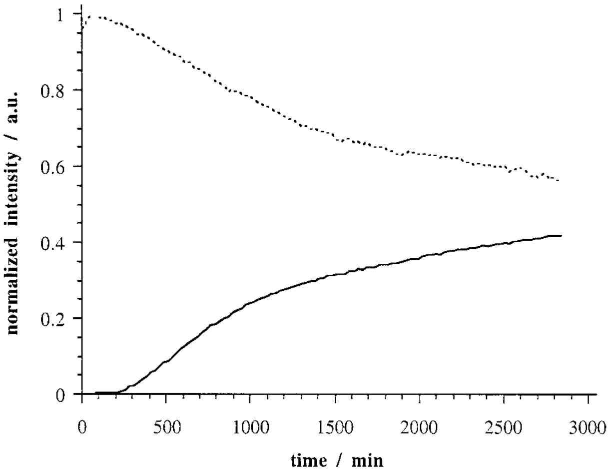

Figure 3. Variation of signal intensities as a function of time in solid-state ^{23}Na-NMR spectra recorded for sodium chloroacetate at 140 °C for 47 h. The dotted line shows normalized intensity values computed for the parent compound sodium chloroacetate, whereas the solid line refers to the product NaCl (same data as in Figure 2).

Sodium bromoacetate: ^{23}Na-NMR spectroscopy

The ^{23}Na-NMR spectrum of sodium bromoacetate is shown in Figure 1. The spectrum closely resembles that of sodium chloroacetate: A broad multiplet covers the range $\delta = -30$ to -5. This lineshape was simulated using $\chi = 1.52$ MHz, $\eta = 0.7$ and $\delta = -5.7$. The similarity with sodium chloroacetate underlines the fact (evident from the structure determination discussed below) that both compounds are isostructural. In the reaction product, a sharp single line at $\delta = 5$ corresponds to NaBr (Figure 1). Note that a small amount of NaBr is already present at the beginning of the experiment. We ascribe this fact to a partial thermal reaction that has occurred between preparation of the sample and the NMR experiment, probably arising mainly during the heating from room temperature to 130 °C (ca. 30 min) at the start of the NMR experiment.

An in situ solid-state ^{23}Na-NMR experiment was carried out for 23 h at 130 °C with a time resolution of 300 s (Figure 4). Qualitatively, the results are similar to those

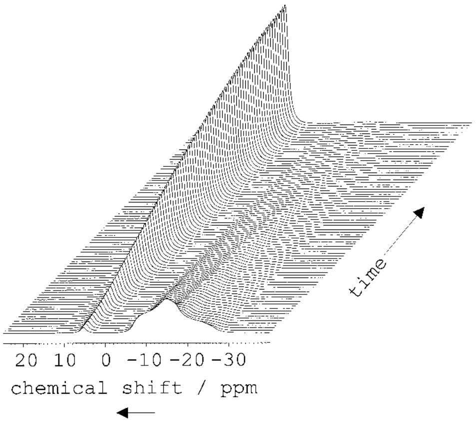

Figure 4. Solid-state ^{23}Na-NMR spectra recorded as a function of time at 130 °C for sodium bromoacetate over a period of 23 h. The solid-state polymerization reaction to produce NaBr is clearly observed. The multiplet ranging from $\delta = -30$ to -5 corresponds to sodium bromoacetate, and the sharp single line at $\delta = 5$ corresponds to NaBr.

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obtained for sodium chloroacetate. No intermediates phases containing ^{23}Na are detectable at any stage during the reaction. The two signals in the ^{23}Na-NMR spectrum are well separated, and integration is readily carried out. Figure 5 shows normalized intensity data for this reaction. The final reaction extent is about 96%, determined from the integrals of the sodium bromoacetate peak. At the start of the reaction, about 5% of NaBr are already present (determined by comparing the integrals of the NaBr peak at the start and at the end of the experiment).

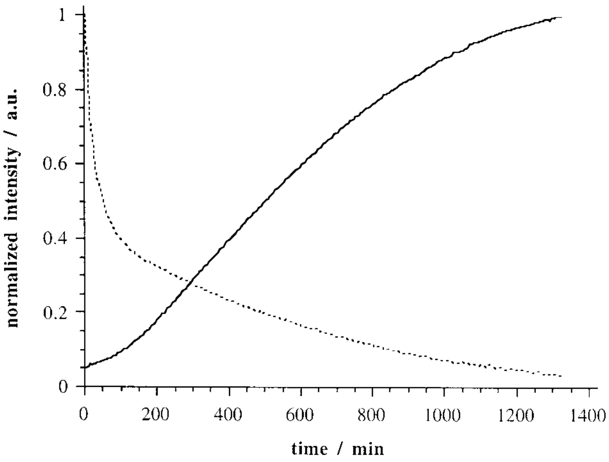

Figure 5. Variation of signal intensities as a function of time in solid-state ^{23}Na-NMR spectra recorded for sodium bromoacetate at 130°C for 23 h (same data as in Figure 4). The dotted line shows normalized intensity values computed for the parent compound sodium bromoacetate, and the solid line refers to the product NaBr.

In a reaction without intermediates, the halogenoacetate should be consumed at the same rate as the products (NaX and polyglycolide) are formed. From Figure 5 it is clear that the lines showing the decay of the parent phase and the formation of the product phase have different curvature, with the amount of sodium bromoacetate appearing to decrease at a significantly faster rate than the rate of formation of NaBr. This is different from the situation found for sodium chloroacetate. Clearly, this observation could point to the formation of an intermediate phase. However, no NMR signals from another phase containing ^{23}Na was observed. A similar observation was made in our in situ ^{13}C-NMR experiment on sodium bromoacetate (see below for a discussion).

Sodium bromoacetate: ^{13}C-NMR spectroscopy

The experiments with ^{23}Na-NMR spectroscopy discussed above probe the sodium ions as they change their local environment from halogenoacetate anions to halide anions. To assess the polymerization reaction more directly, it is more informative to study the organic part of the molecule as it undergoes the solid-state polymerization reaction. Consequently, we have carried out in situ ^{13}C-NMR studies of the reaction in sodium bromoacetate to produce polyglycolide and NaBr. The results are shown in Figures 6 and 7.

The ^{13}C-NMR spectrum of sodium bromoacetate contains a doublet for the methylene carbon at $\delta = 30.3$ and 59.2 due to coupling (residual dipolar interaction) of this ^{13}C nucleus with the adjacent $^{79/81}$Br nucleus. This behaviour is well documented for similar systems (and also for ^{13}C nuclei bonded to $^{35/37}$Cl).[32–35] Remote second-order quadrupolar effects are also observed for the carboxylate carbon at about $\delta = 176$ (Figure 6). Polyglycolide shows two signals at $\delta = 63.8$ (methylene) and 168.8 (carboxylate), in good agreement with literature data on polyglycolide[13, 30] and its copolyesters with polylactide.[36]

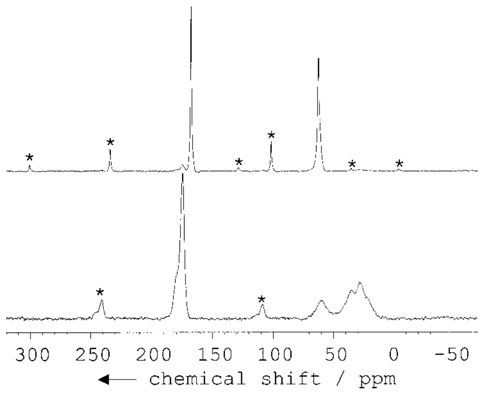

Figure 6. ^{13}C CPMAS NMR spectra of sodium bromoacetate (bottom) and the product obtained from the solid-state polymerization reaction (top: after 46 h at 120°C). The multiplet at $\delta = 30.3/59.2$ in sodium bromoacetate results from residual dipolar interaction between the methylene ^{13}C and the $^{79/81}$Br nucleus directly bonded to it. Spinning side bands are marked as (*). The spectra were recorded at 120°C.

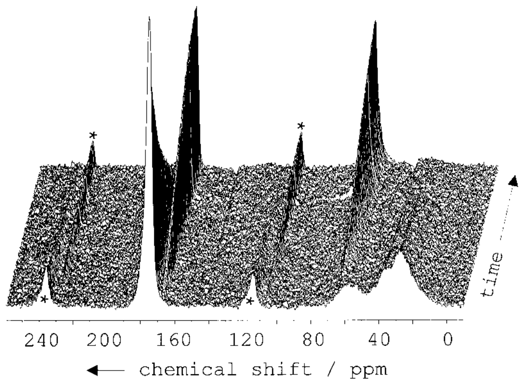

Figure 7. Reaction of sodium bromoacetate to produce polyglycolide and NaBr at 120°C, followed over a period of 46 h by high-resolution ^{13}C CPMAS-NMR for ^{13}C enriched samples ($NaOO^{13}C\text{-}CH_2Br/NaOOC\text{-}^{13}CH_2Br$, 1:1 ratio). Spinning side bands are marked as (*).

Again, there is no direct evidence for intermediates, suggesting a single-step reaction. However, as with the ^{23}Na-NMR data on this compound, there is a mismatch between the rate of loss of sodium bromoacetate and the rate of gain of polyglycolide (Figure 8), with a significant delay in the formation of polyglycolide relative to the loss of sodium bromoacetate.

Crystal structure determination: The crystal structure of sodium bromoacetate was solved from X-ray powder diffraction data (Figure 9) as no crystals of suitable size and quality for single-crystal X-ray diffraction studies could be obtained. Details of the crystal structure solution and refinement are described in the Experimental Section. Sodium bromoacetate

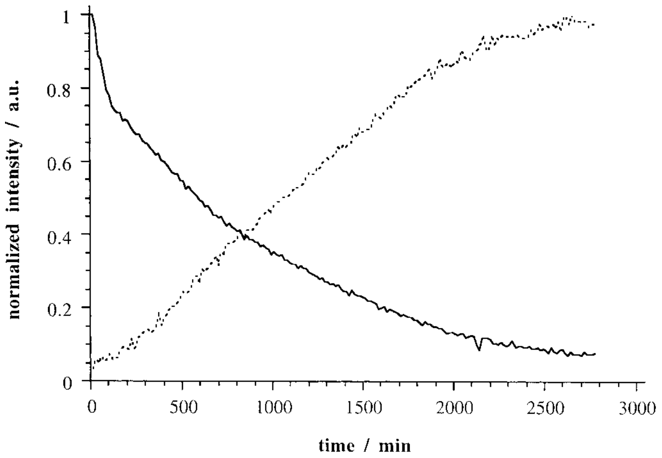

Figure 8. Variation of signal intensities as a function of time in high-resolution solid-state ^{13}C NMR spectra recorded for ^{13}C-enriched sodium bromoacetate at 120 °C. The dotted line refers to the parent compound sodium bromoacetate and the solid line refers to the product polyglycolide. The data were determined by integration of the peaks of the carboxylate carbon in each phase.

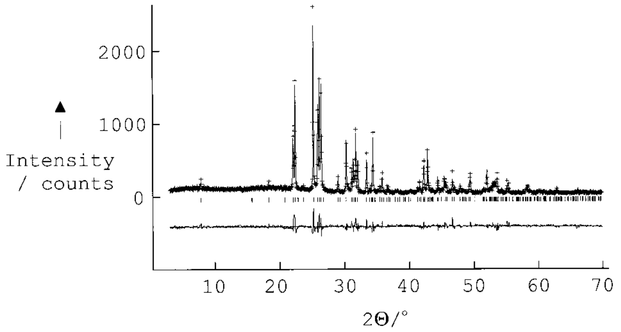

Figure 9. Final Rietveld refinement plot for sodium bromoacetate, showing experimental and calculated diffraction patterns (top) and the difference diffraction pattern (bottom).

is isostructural with sodium chloroacetate.[10] The structural parameters are shown in Tables 2 and 3, and the crystal packing arrangement is shown in Figure 10.

As with sodium chloroacetate,[10] a polymerization within the chains of chloroacetate anions along the crystallographic *b*-axis appears to be the most likely reaction mechanism (see ref.[10] for a detailed discussion). This mechanism is consistent with all previous results obtained using in situ methods, including this work, that support a topochemical[37–40] polymerization. However, as it is well known that solid-state reactions are often initiated near defects in the crystal,[39, 41] this proposed mechanism is at best considered as highly probable, rather than strictly proven.

Table 2. Crystallographic data for sodium bromoacetate and sodium chloroacetate. The structural similarity is obvious.

	sodium bromoacetate (this work)	sodium chloroacetate[10]
crystal system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$
a/ pm	708.11(8)	711.77(3)
b/ pm	537.27(6)	536.09(3)
c/ pm	1130.06(11)	1081.27(5)
β/°	91.95(1)	92.434(4)
V/10^6 pm^3	429.68	412.21
Z	4	4
ρ_{calc}/ g cm^{-3}	2.49	1.88

Table 3. Fractional atomic coordinates in the final refined crystal structure of sodium bromoacetate. No refinement of hydrogen atoms was performed. The final profile R factors were $R_{wp} = 14.9\,\%$ and $R_p = 11.9\,\%$.

Atom	x/a	y/b	z/c
Br	0.7337(5)	0.4678(5)	0.6176(4)
Na	0.8925(13)	0.2488(16)	0.9121(12)
C1	0.664(4)	0.7565(20)	0.8266(9)
C2	0.696(4)	0.7813(12)	0.6998(9)
O1	0.6349(16)	0.5512(20)	0.8730(12)
O2	0.6434(19)	0.9536(20)	0.8853(10)

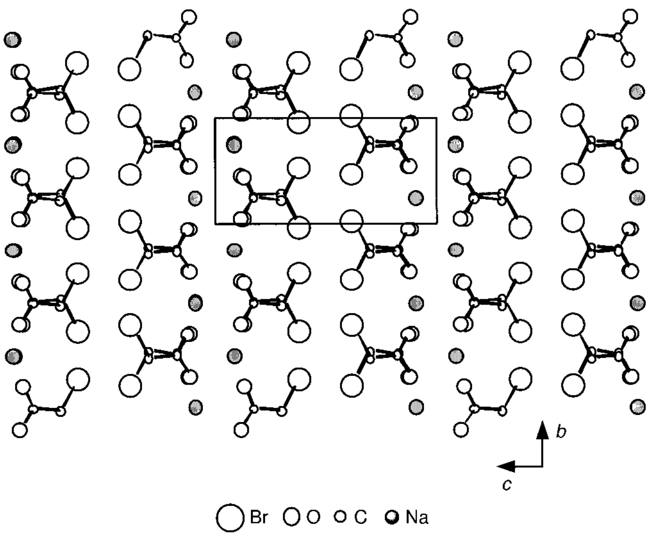

Figure 10. Final refined crystal structure of sodium bromoacetate (hydrogen atoms not shown) viewed along the crystallographic *a* axis.

Conclusion

The solid-state polymerization reactions in sodium chloroacetate and sodium bromoacetate were monitored in situ using ^{23}Na-NMR and ^{13}C-NMR spectroscopy. No well defined intermediate species were detectable in any of the NMR spectra recorded. It may therefore be concluded that the reaction occurs in a single step or involves intermediates that are either present in sufficiently small amounts or in a sufficiently broad range of local environments over a sufficiently short period of time relative to the time resolution of the experiment that they give no detectable signals in the NMR spectra. As now discussed, this question can be addressed when the NMR spectra are evaluated quantitatively by peak integration to give the relative amounts of phases present.

In both experiments (^{13}C and ^{23}Na NMR) on sodium bromoacetate, a mismatch between the rate of decay of the parent compound (sodium bromoacetate) and the rate of formation of the products (NaBr and polyglycolide) is observed. This suggests that some NMR intensity may indeed be related to an intermediate phase, although no peaks are detected in addition to those of the parent compound and products. The reaction could occur via a number of poorly defined intermediates that result in low intensity and perhaps broad (particularly for ^{23}Na) signals in the NMR spectra. Therefore, NMR intensity could be "lost" due to the existence of such species without distinct signals representing these species being detected.

For ^{13}C-NMR spectroscopy, these species could be related to a number of temporarily-present glycolide-oligomers and perhaps to a variety of different chain-end configurations. In fact, we have shown by viscosimetry that the average polymer chain length increases as a function of reaction,[31] indicative of a stepwise growth of the polymer chains during the reaction. The same type of situation could pertain to the environment of Na^+ as detected by ^{23}Na solid-state NMR spectroscopy. Sodium has to change its environment from a six-fold oxygen coordination to a six-fold bromine coordination during the reaction, and it is conceivable that this process occurs via a range of intermediate species representing a broad distribution of local structural situations, such as sodium in interstitial positions or within disordered parts of the crystal, and representing different combinations of near-neighbouring bromine and oxygen atoms. Thus, although intermediates were not detected, their presence cannot be excluded for sodium bromoacetate.

At present, we cannot explain the different behaviour of sodium chloroacetate (with no evidence for intermediates) and sodium bromoacetate (with possible intermediates). However, in both cases our NMR experiments have shown that no significant amounts of well defined intermediates are produced during the reaction. For such complex systems undergoing solid-state reactions, the occurrence of intermediate species that are difficult or impossible to detect appears likely, and the different rates of reaction for sodium chloroacetate and sodium bromoacetate could lead to different amounts of temporarily present intermediates.

In conclusion, we emphasize that solid-state NMR spectroscopy was essential to obtain these new insights concerning the solid-state transformations in sodium halogenoacetates, as other methods (e.g., diffraction or EXAFS) are not sensitive to such subtle changes in the local environments. The complementary nature of these techniques, and their ability when applied under in situ conditions to probe chemical and structural changes directly as they occur, represents a powerful strategy with which to investigate chemical transformations in solids. It is reasonable to generalize that a comprehensive understanding of the nature of such solid-state reactions may be derived only from the application of a multi-disciplinary experimental strategy of this type.

Experimental Section

Synthesis: Sodium chloroacetate and sodium bromoacetate were prepared by neutralization of chloroacetic acid and bromoacetic acid, respectively, with NaOH in ethanol, followed by recrystallization from ethanol.[13] The materials were characterized thoroughly using IR spectroscopy, ^{1}H-NMR spectroscopy in solution, X-ray powder diffraction, elemental analysis (C, H) and differential scanning calorimetry (DSC). ^{13}C-enriched sodium bromoacetate was prepared by neutralizing a mixture of 5 *wt*% HOO^{13}C-CH$_2$-Br, 5 *wt*% HOOC-^{13}CH$_2$-Br and 90 *wt*% HOOC-CH$_2$-Br (natural abundance of ^{13}C) with NaOH in ethanol, followed by precipitation and solvent removal.[13]

Solid-state NMR spectroscopy: High-resolution ^{23}Na- and ^{13}C-NMR spectra were recorded at 79.4 MHz and 75.5 MHz (7.05 T), respectively, on a Bruker MSL300 spectrometer. The samples were studied as polycrystalline powders in zirconia rotors (4 mm and 7 mm external diameters) using MAS frequencies ($\tilde{\nu}_r$) in the range of 4 to 8 kHz. ^{23}Na MAS NMR spectra were obtained using single-pulse excitation with 0.8 μs pulse duration and 2.3 s recycle time. The standard ^{1}H,^{13}C cross-polarization (CP) ^{13}C-NMR technique was used (with high-power proton decoupling applied during acquisition). Typical parameters were: ^{1}H 90° pulse, duration 5.2 μs, CP contact time 10 ms, recycle delay 14 s. ^{13}C chemical shifts are given relative to tetramethylsilane (TMS), established with the use of adamantane (methine carbon signal at $\delta = 29.47$) as an external standard, whereas ^{23}Na chemical shifts are given relative to 0.1M aqueous NaCl solution used as an external standard.

The quadrupolar interaction parameters and ^{23}Na isotropic chemical shifts for the parent compounds were obtained from simulations of the central transition MAS NMR lineshapes using the POWDER program (Bruker Aspect 3000 software package).

For in situ experiments, the samples were put into rotors and heated to the reaction temperature as fast as practically possible. For each experiment, the starting time ($t = 0$) was assigned as the time at which the sample temperature had reached the preset value. The time to heat from room temperature to the reaction temperature was about 30 min in each case.

Powder diffraction and structure determination: An X-ray powder diffractogram was recorded for sodium bromoacetate at ambient temperature on a Siemens D5000 instrument operated in transmission mode (Cu$_{K\alpha1}$ radiation, $\lambda = 154.06$ pm, germanium monochromator, position-sensitive detector covering 8° in 2Θ). The total 2Θ range was 3 to 70° (step size 0.02°, total count time 60 min). The powder diffraction pattern was indexed using the program ITO[42] (resulting in $a = 7.09$ Å, $b = 5.38$ Å, $c = 11.32$ Å, $\beta = 91.92°$). The space group $P2_1/a$ was assigned on the basis of systematic absences. The unit cell parameters suggested a close similarity to the previously known structure of sodium chloroacetate.[10]

The structure of sodium bromoacetate was solved by the Monte Carlo method,[6, 27, 28] using the program OCTOPUS.[43] Two independent structural fragments were used: the organic fragment Br-C-COO$^-$ (representing the non-hydrogen atoms of the bromoacetate anion with geometry taken in analogy to sodium chloroacetate), and the sodium cation Na$^+$. The bromoacetate unit was subjected to translational and rotational displacements, with 20 rotations per translation. The sodium cation was subjected to translational displacements only. A total of 5000 Monte Carlo moves was carried out. For both units, the maximum allowed translational displacement in each Monte Carlo move was 0.2 Å along each of the three crystallographic axes, and the maximum allowed rotational displacement of the bromoacetate unit was constrained to ±45° about each of three orthogonal axes passing through the carboxylate carbon atom (C1). The parameter S[6, 27, 28] (which behaves in a manner analogous to temperature in Monte Carlo based energy simulations) was chosen such that about 40–50% of the trial structures were accepted in the Monte Carlo calculation. The trial structure with the lowest R_{wp} in the Monte Carlo calculations was taken as the structure solution and used as the initial structural model for Rietveld refinement. Subsequent Rietveld refinement using the GSAS program package[44] gave the final structure reported in Tables 2 and 3 and shown in Figure 9. All isotropic displacement parameters U_{iso} were fixed at 0.025 Å^2, and standard restraints were applied to bond lengths and angles.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (M.E.), the Fonds der Chemischen Industrie (M.E.), the Deutscher Akademischer Austauschdienst/British Council (M.E. and K.D.M.H.), the EPSRC (K.D.M.H. and J.M.T.), and the University of Birmingham (L.E.) for financial support. University of London Intercollegiate Research Services are thanked for the providing the facilities for the solid-state NMR spectroscopy (to A.E.A.). Experimental assistance from Bernd Hasse (Hamburg) is gratefully acknowledged.

[1] R. Hoffmann, *Liebigs Ann. Chem.* **1857**, *102*, 1–20.
[2] R. Anschütz, *Chem. Ber.* **1892**, *25*, 3506–3512.
[3] M. Epple, O. Herzberg, *J. Mater. Chem.* **1997**, *7*, 1037–1042.
[4] L. B. McCusker, *Acta Crystallogr. Sect. A* **1991**, *47*, 297–313.
[5] A. K. Cheetham, A. P. Wilkinson, *Angew. Chem.* **1992**, *104*, 1594–1608; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1557–1570.
[6] K. D. M. Harris, M. Tremayne, *Chem. Mater.* **1996**, *8*, 2554–2570.
[7] D. M. Poojary, A. Clearfield, *Acc. Chem. Res.* **1997**, *30*, 414–422.
[8] K. D. M. Harris, *J. Chin. Chem. Soc.* **1999**, *46*, 23–34.
[9] M. Epple, H. Kirschnick, *Chem. Ber.* **1997**, *130*, 291–294.
[10] L. Elizabé, B. M. Kariuki, K. D. M. Harris, M. Tremayne, M. Epple, J. M. Thomas, *J. Phys. Chem. B* **1997**, *101*, 8827–8831.
[11] H. Ehrenberg, B. Hasse, K. Schwarz, M. Epple, *Acta Crystallogr. Sect. B* **1999**, *55*, 517–524.
[12] M. Epple, U. Sazama, A. Reller, N. Hilbrandt, M. Martin, L. Tröger, *J. Chem. Soc. Chem. Commun.* **1996**, 1755–1756.
[13] M. Epple, H. Kirschnick, *Chem. Ber.* **1996**, *129*, 1123–1129.
[14] M. Epple, H. Kirschnick, J. M. Thomas, *J. Therm. Anal.* **1996**, *47*, 331–338.
[15] O. Herzberg, R. Gehrke, M. Epple, *Polymer* **1999**, *40*, 507–511.
[16] H. Schmalzried, *Chemical Kinetics of Solids*, VCH, Weinheim, **1995**.
[17] J. M. Thomas, *Chem. Eur. J.* **1997**, *3*, 1557–1562.
[18] C. A. Fyfe, *Solid State NMR for Chemists*, CRC Press, **1984**.
[19] G. Engelhardt, D. Michel, *High-resolution solid-state NMR of silicates and zeolites*, Wiley, Chichester, **1987**.
[20] B. Blümich, *Adv. Mater.* **1991**, *3*, 237–245.
[21] L. v. Wüllen, B. Gee, L. Züchner, M. Bertmer, H. Eckert, *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 1539–1549.
[22] R. K. Harris, M. M. Sünnetcioglu, R. D. Fischer, *Spectrochim. Acta* **1994**, *50A*, 2069–2078.
[23] A. E. Aliev, S. P. Smart, I. J. Shannon, K. D. M. Harris, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2179–2185.
[24] T. Xu, J. F. Haw, *J. Am. Chem. Soc.* **1994**, *116*, 7753–7759.
[25] A. R. Brough, C. M. Dobson, I. G. Richardson, G. W. Groves, *J. Mat. Sci.* **1994**, *29*, 3926–3940.
[26] D. B. Ferguson, J. F. Haw, *Anal. Chem.* **1995**, *67*, 3342–3348.
[27] K. D. M. Harris, M. Tremayne, P. Lightfoot, P. G. Bruce, *J. Am. Chem. Soc.* **1994**, *116*, 3543–3547.
[28] K. D. M. Harris, B. M. Kariuki, M. Tremayne, *Mater. Sci. Forum* **1998**, *278–281*, 32–37.
[29] M. Epple, G. Sankar, J. M. Thomas, *Chem. Mater.* **1997**, *9*, 3127–3131.
[30] M. Epple, L. Tröger, *J. Chem. Soc. Dalton Trans.* **1996**, 11–16.
[31] K. Schwarz, M. Epple, *Macromol. Chem. Phys.* **1999**, *200*, 2221– 2229.
[32] B. Nagasaka, S. Takeda, N. Nakamura, *Chem. Phys. Lett.* **1994**, *222*, 486.
[33] S. H. Alarcon, A. C. Olivieri, S. A. Carss, R. K. Harris, *Angew. Chem.* **1994**, *106*, 1708–1709; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1624–1625.
[34] A. E. Aliev, K. D. M. Harris, P. J. Barrie, S. Camus, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3729–3730.
[35] A. E. Aliev, K. D. M. Harris, R. K. Harris, S. A. Carss, A. C. Olivieri, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3167–3176.
[36] G. Kister, G. Cassanas, M. Vert, *Polymer* **1998**, *39*, 3335–3340.
[37] H. W. Kohlschütter, L. Sprenger, *Z. Phys. Chem.* **1932**, *B16*, 284–302.
[38] G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678.
[39] J. M. Thomas, *Phil. Trans. Roy. Soc.* **1974**, *A277*, 251.
[40] G. Wegner, *Pure Appl. Chem.* **1977**, *49*, 443–454.
[41] J. M. Thomas, *Pure Appl. Chem.* **1979**, *51*, 1065–1082.
[42] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89.
[43] Program OCTOPUS96 (Monte Carlo Technique for Powder Structure Solution), M. Tremayne, B. M. Kariuki, K. D. M. Harris, **1996**.
[44] Program GSAS, Los Alamos Lab. Report No. LA-UR-86–748, Los Alamos National Laboratory: Los Alamos, NM, A. C. Larson, R. B. von Dreele, **1987**.

Received: May 26, 1999 [F 1807]