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Mechanochemical Metathesis between $AgNO_3$ and NaX (X = Cl, Br, I) and Ag_2XNO_3 Double-Salt Formation

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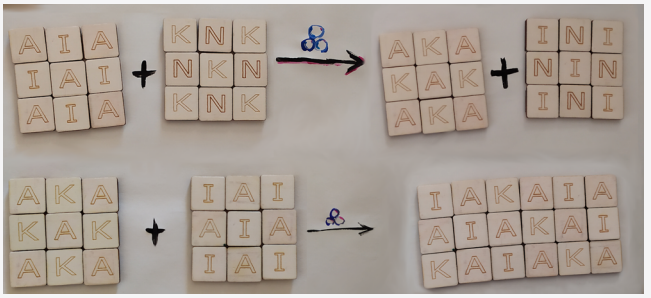
ABSTRACT: Here we describe real-time, *in situ* monitoring of mechanochemical solid-state metathesis between silver nitrate and the entire series of sodium halides, on the basis of tandem powder X-ray diffraction and Raman spectroscopy monitoring. The mechanistic monitoring reveals that reactions of $AgNO_3$ with NaX (X = Cl, Br, I) differ in reaction paths, with only the reaction with NaBr providing the $NaNO_3$ and AgX products directly. The reaction with NaI revealed the presence of a novel, short-lived intermediate phase, while the reaction with NaCl progressed the slowest through the well-defined Ag_2ClNO_3 intermediate double salt. While the corresponding iodide and bromide double salts were not observed as intermediates, all three are readily prepared as pure compounds by milling equimolar mixtures of AgX and $AgNO_3$. The *in situ* observation of reactive intermediates in these simple metathesis reactions reveals a surprising resemblance of reactions involving purely ionic components to those of molecular organic solids and cocrystals. This study demonstrates the potential of *in situ* reaction monitoring for mechanochemical reactions of ionic compounds as well as completes the application of these techniques to all major compound classes.



INTRODUCTION

Mechanochemistry, i.e. chemical reactions performed by exerting mechanical force on solid reactants, has become recognized as a viable synthetic route and an alternative to solution-based protocols.[1−6] In their application to organic,[7−10] inorganic,[11−14] organometallic,[15−19] and coordination and supramolecular chemistry,[20−23] as well as to the preparation of nanoparticles,[14,24] metal−organic frameworks,[25−29] main-group compounds,[30−33] and catalysis,[34−40] mechanochemical reactions are most often performed in closed containers, or vessels, that oscillate, rotate, or swing.[24,25] Under such conditions, obtaining information about the reaction course has been attainable only by periodically interrupting the milling process for sampling of the reaction mixture.[41−48] However, with each opening of the reaction vessel, the conditions inside the milling vessel are disrupted and the reaction mixture experiences hardly reproducible temperature variations,[49] as well as exposure to atmospheric gases and moisture. Also, if the mechanochemically induced reaction continues to proceed after cessation of milling,[50−53] subsequent analysis of such samples will not accurately represent the chemical and physical changes during milling.

It is therefore no surprise that the recent development of *in situ* techniques for uninterrupted reaction monitoring has been a breakthrough in the study and understanding of milling processes and dynamics.[54] These methods, based on powder X-ray diffraction (PXRD),[55−58] Raman spectroscopy,[59−63] temperature[49,64] and pressure monitoring,[65−67] and their simultaneous application,[49,68−71] revealed complex milling reaction mechanisms,[72] involving new polymorphic phases,[68,73] as well as multistep mechanisms[74−77] with crystalline and amorphous intermediates.[54,76,78]

So far, *in situ* monitoring has been applied to reactions of almost all classes of compounds, with the notable exception of reactions of inorganic ionic compounds.[11,12,79−81] Here, we provide the first *in situ* real-time investigation of a purely inorganic mechanochemical transformation, targeting an ion metathesis reaction that is highly familiar to most chemists when it is conducted in solution: immediate formation of an insoluble silver halide upon mixing aqueous solutions of $AgNO_3$ and a sodium halide NaX (X = Cl, Br, I). In aqueous solution, this prototypical reaction is often used as a qualitative test for halide ions since it is dominated by the extremely low solubility of silver halides AgCl, AgBr, and AgI. Solubility, however, should not have a role if this reaction is conducted in

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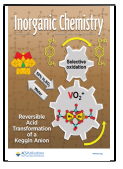

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the absence of water or another solvent, prompting the ball-milling solid-state processes presented herein. On the basis of standard Gibbs energies of formation of reactants and target products, the reactions of $AgNO_3$ and sodium halides, except for NaF, are thermodynamically favorable and as such should be feasible also in the solid state (Figure 1).

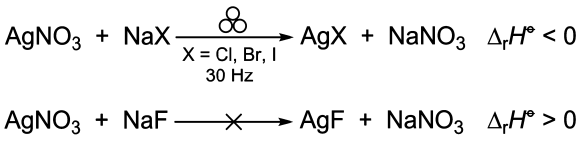

Figure 1. Reactions of silver(I) nitrate and sodium halides.

Mixtures of solid reactants in a 1:1 molar ratio were milled using a vibratory ball mill to yield the expected products, $NaNO_3$ and AgX (X = Cl, Br or I), which was evidenced by PXRD. Reaction paths and rates, however, varied through the series of sodium halides. While the reaction with NaCl was the slowest and that with NaI the fastest overall, only milling with NaBr yielded the products directly from the reactants. We also demonstrate that milling is efficient for the preparation of the mixed salts Ag_2ClNO_3, Ag_2BrNO_3, and Ag_2INO_3. Among these double salts, only Ag_2ClNO_3 was observed to form as an intermediate during the milling of $AgNO_3$ and NaX.

EXPERIMENTAL SECTION

Solution Precipitation of AgCl, AgBr, and AgI. $AgNO_3$ and NaX in 5 mmol amounts were dissolved separately in 20 mL of redistilled water and slowly mixed while ensuring minimal exposure to light. A precipitate formed immediately upon mixing; it was filtered, washed with water, and dried in air for 3 h followed by drying in a desiccator under a reduced pressure of argon for 3 days in the dark.

Laboratory Powder X-ray Diffraction (PXRD) Patterns. These patterns were collected on an Aeris Panalytical diffractometer using Ni-filtered copper radiation in the Bragg–Brentano geometry with the sample prepared as a thin layer on a silicon zero-background holder.

Reaction Monitoring. *In situ* real-time reaction monitoring was achieved by tandem PXRD and Raman spectroscopy *in situ* at the ID15A beamline of the ESRF-The European Synchrotron in Grenoble, France, as previously described,[68] using a remotely controlled IST500 (InSolido Technologies, Croatia) mixer mill operating at 30 Hz. The X-ray beam (E = 70 keV, λ = 0.1771 nm) was set to pass through the bottom of a poly(methyl methacrylate) (PMMA) reaction vessel. The exposure time was set to 4 s, and a waiting time was added to match the 5 s interval between consecutive frames. Diffraction data were collected on a Dectris Pilatus3 X CdTe 2 M detector positioned 730 mm from the sample. We performed radial integration of the raw diffraction images with an ESRF in-house MATLAB script. Raman spectroscopy employed a portable Raman system with a PD-LD (now Necsel) BlueBox laser source having an excitation wavelength of 785 nm and an OceanOptics (now OceanInsight) Maya2000Pro spectrometer coupled with a B&W-Tek fiber optic BAC102 probe. The position of the probe was about 0.8 cm from the bottom of the vessel. Raman spectra were collected every 10 s with an acquisition time of 500 ms and a sum of 20 scans for each spectrum.

As milling vessels, 14 mL PMMA vessels with two 5 mm tungsten carbide (WC) balls (each weighing 1.4 g) were used. The reactants were milled in a 1:1 stoichiometric ratio, and we have kept the total mass of the reaction mixture to 250 mg, adjusting the masses of reactants with different molecular weights. During weighing, vessels were wrapped with aluminum foil to minimize their exposure to light, which was removed after the vessel was mounted onto the ball mill. Light was switched off in the experimental hutch during milling, and the sample may have experienced only minimal exposure to light, except for the Raman laser beam. The ambient temperature in the experimental hutch was 21 °C. Experiments were typically reproduced three times.

Quantitative Rietveld Analysis. This analysis was performed in an automated fashion in the command-line version of the program Topas, usually starting from the same input file for each diffraction pattern. Parameters that were refined included coefficients of the shifted Chebyshev polynomial for background description and parameters describing the peak shape and size: Lorentzian and Gaussian full widths at half-maximum, zero shift, and unit cell parameters. Crystal structure models for reactants and products were checked against the Inorganic Crystal Structure Database (ICSD) or the Crystallography Open Database (COD). Atomic coordinates of the structure models were not refined. For $AgNO_3$ the ICSD entry 1685 was used. ICSD entries 18189 and 26910 were used for NaCl and NaBr, respectively. Crystal structure models of $NaNO_3$ polymorphs were taken from the ICSD entry 2865 for the ordered polymorph and from the ICSD entry 180920 for the disordered polymorph. For AgCl, AgBr, and AgI, ICSD entries 64734, 65061 and 56552, respectively, were used.

Analysis of Raman Spectra. This analysis was performed in MATLAB using in-house scripts. Raman spectra were truncated to the region 1100–765 cm^{-1} and were baseline-corrected using the asymmetric least-squares (ALS) algorithm.[82] Data were normalized by dividing all spectrum data points with the intensity of the peak at 812 cm^{-1}, which belongs to the PMMA reaction vessel. To fit the intensities of Raman peaks at 1046 and 1070 cm^{-1}, we selected the 1085–1025 cm^{-1} spectral range (Figure S2) that was fitted using two Gaussian functions of the general form

$$f(x) = Ae^{-[(x-x_0)/c]^2} + O$$

where A is the band intensity, x_0 is the peak position, c is the bandwidth, and O is the linear offset.

Density Functional Theory Calculations. These calculations were performed with the plane-wave basis set code VASP.[83,84] We used a PBE exchange-correlation functional,[85] with the energy cutoff set to 520 eV. The core–electron interaction was approximated by projector augmented wave (PAW) potentials.[86] The Brillouin zone was sampled with a Monkhorst–Pack mesh[87] with a density of at least 4 Å. The structures were optimized until the change in the energy was smaller than 0.0005 eV.

Residual Gas Analysis (RGA). The composition of gaseous products was determined by a homemade RGA device with an MKS Vac-Check LM78 quadrupole mass spectrometer. We introduced the gaseous products of the mechanochemical reaction in the RGA apparatus by putting the stainless steel capillary (internal diameter of 0.15 mm and length of 1 m) in the milling vessel. The total pressure of the high-vacuum (HV) system was 2.5×10^{-6} mbar during the measurements. An analysis of the atmosphere inside the vessel, by measurement of the partial pressures, was conducted by following the m/z ratios of 28 (for N_2), 30 (NO), 32 (O_2), 46 (NO_2), 70 ($^{35}Cl_2$), 76 (N_2O_3), and 92 (N_2O_4).

RESULTS AND DISCUSSION

A consideration of thermodynamic data (Table S1) indicates that all reactions of $AgNO_3$ and NaX, except that involving NaF, are thermodynamically favorable and should proceed under standard conditions (Table 1). The standard reaction enthalpies and standard Gibbs energies of reaction for NaX (X = Cl, Br, I) are negative, while the standard reaction enthalpy for the reaction with NaF is positive. Since the entropic contribution to the Gibbs energy of ionic solids at room temperature is generally small in comparison to enthalpy, it can be safely assumed that, in the case of NaF, the standard Gibbs energy of the reaction should also be positive. As expected, PXRD analysis of the milled $AgNO_3$ and NaF mixture revealed no new products, even after 2 h of milling (Figure S1). As the

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Table 1. Standard Reaction Enthalpies and Gibbs Energies for the General Reaction NaX + $AgNO_3$ → $NaNO_3$ + AgX (X = Cl, Br, I)[88]

X	$\Delta_r H^\ominus$/kJ mol^{-1}	$\Delta_r G^\ominus$/kJ mol^{-1}
F	28.5	
Cl	−59.3	−59.4
Br	−82.8	−81.5
I	−117.5	−113.7

reaction mixture remained a physical mixture of reactants, it was not considered for an *in situ* study.

$AgNO_3$ + NaCl. In the first set of *in situ* experiments we milled $AgNO_3$ and NaCl. Aside from the formation of AgCl and $NaNO_3$, *in situ* PXRD data revealed the appearance of an intermediate phase (Figure 2a), which was identified as Ag_2ClNO_3, on the basis of PXRD analysis. This phase was previously prepared from an aqueous mixture of $AgNO_3$ and AgCl at 90 °C and from a melt.[89] Attempting a Rietveld analysis of the *in situ* collected PXRD patterns using the crystal structure of $NaNO_3$ in the $R\bar{3}c$ space group did not provide satisfactory refinements of all PXRD patterns. This problem was resolved upon recognizing that $NaNO_3$ had crystallized in a mixture with its other polymorph, having the $R\bar{3}m$ space group.[90] By including both polymorphs, we were able to obtain satisfactory Rietveld refinements for patterns collected through the entire milling experiment. The crystal structure of the polymorph crystallizing in the $R\bar{3}c$ space group (herein designated $NaNO_3$-c), is ordered and stable at room temperature, while the polymorph having the $R\bar{3}m$ space group (designated $NaNO_3$-m) is the high-temperature polymorph exhibiting disorder of the nitrate anion.[90]

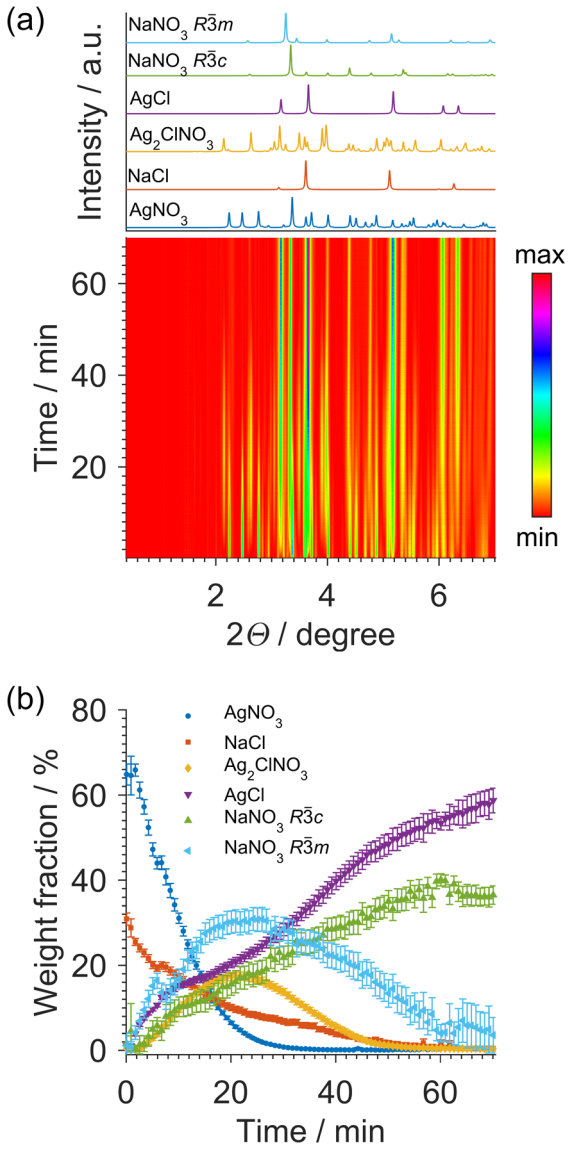

Figure 2. Milling of $AgNO_3$ and NaCl. (a) *In situ* reaction monitoring by synchrotron PXRD. Diffraction patterns of reactants and products are given above the 2D time-resolved spectra. (b) Weight fractions derived from the Rietveld refinement of the above diffraction patterns.

The Inorganic Crystal Structure Database (FIZ Karlsruhe) lists around 40 entries for the two polymorphs of $NaNO_3$, and the phase transition between the two polymorphs has been the subject of numerous studies.[91−93] It is described to be second order with the disorder of the nitrate becoming more and more pronounced as the temperature increases up to 550 K, where the two positions of the nitrate anion become equally populated, the *c* axis is halved, and the space group changes from $R\bar{3}c$ to $R\bar{3}m$. In our case, the *in situ* formation of the $R\bar{3}m$ high-temperature polymorph can be considered as surprising, as these temperatures are never reached in the bulk of the sample during ball milling on a vibratory mill. Its formation may tentatively be attributed to kinetic factors and understood as being in accordance with Ostwald's rule of stages.[94,95]

The formation of the expected products AgCl and $NaNO_3$ commenced almost immediately after the onset of milling (Figure 2b). After about 2 min, we witnessed the appearance of Ag_2ClNO_3, which continued crystallizing simultaneously with $NaNO_3$-c, $NaNO_3$-m, and AgCl for the next 20 min. At that time, Ag_2ClNO_3 and $NaNO_3$-m started to be slowly depleted until, after ∼60 min of milling, only AgCl and $NaNO_3$-c were detectable in the reaction mixture. The reaction profile for the formation of AgCl seems to exhibit two different regimes (Figure 2b). After initial growth in the first 10 min, the formation of AgCl started to follow a sigmoidal trend, indicating a change in the mechanism of the crystal growth of AgCl product. At the early stages of the reaction, $AgNO_3$ was the principal source of Ag^+ ions for the formation of both AgCl and Ag_2ClNO_3. As the reaction proceeded and the amount of $AgNO_3$ was depleted, the formation of Ag_2ClNO_3 slowed down and the latter eventually became the source of Ag^+ ions for the growth of AgCl. Consequently, the formation of AgCl is the result of more than one chemical reaction. This is further evident from the significantly different rates of depletion of NaCl and $AgNO_3$, as Ag_2ClNO_3 is also the source of Cl^- ions in the formation of AgCl.

It is worth noting that a Rietveld analysis yielded an unrealistically high total weight fraction for $NaNO_3$ throughout the middle part of the reaction. We rationalize the higher than expected weight fraction of $NaNO_3$ by recognizing that the nascent AgCl may be partially amorphous. The final weight fractions of 62.7% and 37.3% for AgCl and $NaNO_3$, respectively, are close to the theoretically expected values on the basis of the starting equimolar mixture of $AgNO_3$ and NaCl. A partially amorphous reaction mixture, even for ionic compounds, may not be surprising, as AgCl may form as a partially amorphous material upon fast precipitation from solution[96] and milling is a long-used approach not only for comminution and reduction of particle sizes but also as an

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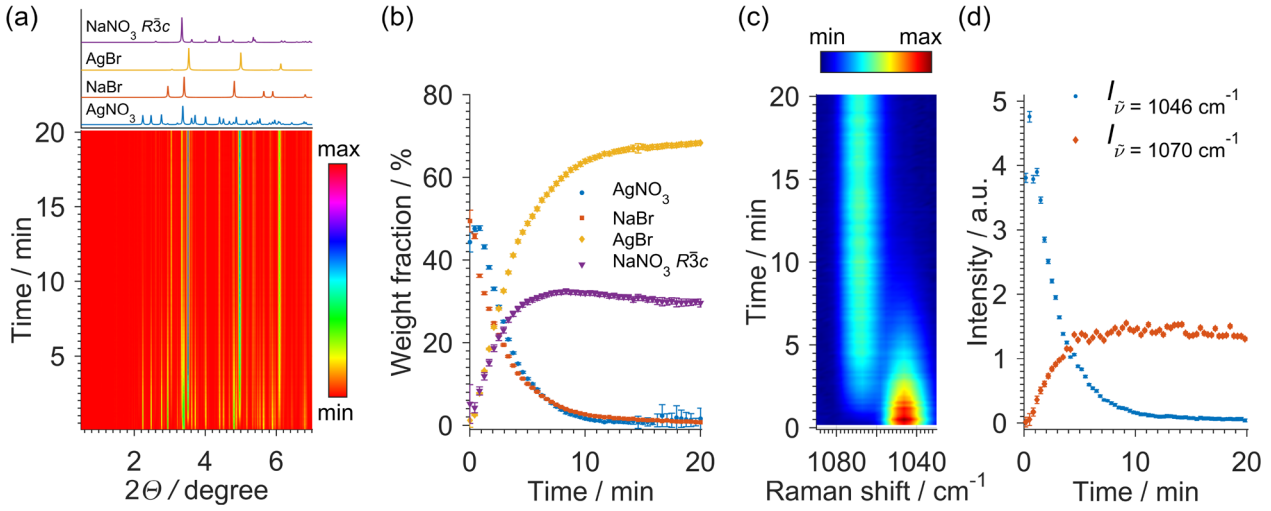

Figure 3. Milling of $AgNO_3$ and NaBr. (a) *In situ* reaction monitoring by synchrotron PXRD. Diffraction patterns of reactants and products are given above the 2D time-resolved spectra. (b) Weight fractions derived from the Rietveld refinement of the *in situ* PXRD patterns. (c) 2D time-resolved Raman spectra for the Raman spectral range 1088−1030 cm^{-1}. (d) Change in the Raman peak intensities at 1046 and 1070 cm^{-1} during milling.

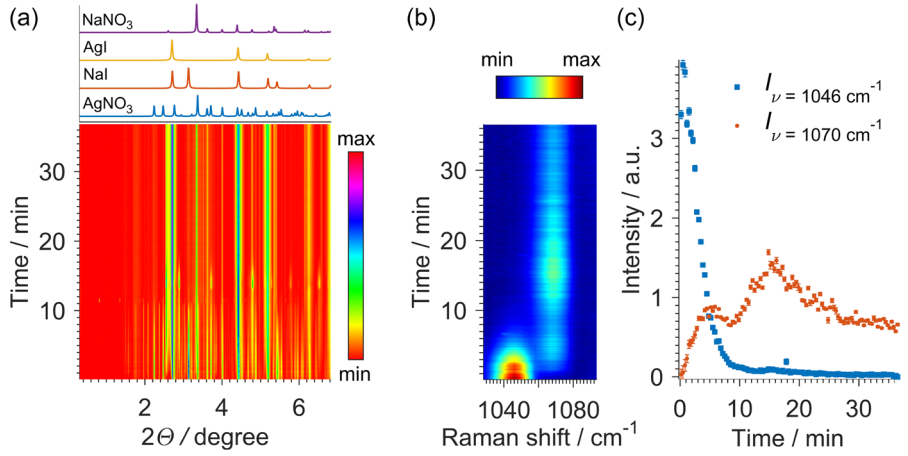

Figure 4. Milling of $AgNO_3$ and NaI. (a) *In situ* reaction monitoring by synchrotron PXRD. Diffraction patterns of reactants and products are given above the 2D time-resolved spectra. (b) 2D time-resolved Raman spectra for the Raman spectral range 1088−1030 cm^{-1}. (c) Change in Raman peak intensities at 1046 and 1070 cm^{-1} during milling. There was an sharp increase in the intensities of Raman band at 1070 cm^{-1} that is more likely due to sticking of the reaction mixture. These changes correlated with the sharp increase in Bragg reflections in PXRD patterns, typically observed in cases of an inhomogeneous distribution of the reaction mixture during milling.[55]

effective way of amorphization of organic, metal−organic, and inorganic materials.[97−101] *In situ* Raman spectroscopy monitoring in this experiment was of no use due to strong fluorescence which completely saturated the detector, even at a very low laser power.

$AgNO_3$ + NaBr. In our second set of *in situ* experiments, we explored the milling reaction of $AgNO_3$ and NaBr. Here, we observed a direct steady transformation from reactants to AgBr and $NaNO_3$ without any intermediate (Figure 3a). According to the Rietveld refinement, the transformation was complete within 10 min of milling (Figure 3b). The formation of AgBr and $NaNO_3$ exhibited an first-order kinetics trend, much the same as was observed for AgCl in the first 10 min. Such similar kinetics could indicate the same reaction mechanism of double ion exchange between $AgNO_3$ and NaCl or NaBr at the onset of milling and before a significant amount of the intermediate Ag_2ClNO_3 has been formed. Here again, after 10 min of milling, there was a steady drop of the weight fraction of $NaNO_3$ from 32 to 30%, which can also be contributed to crystallization of AgBr that may have initially formed in a partially amorphous state. Final weight fractions for $NaNO_3$ and AgBr are in good agreement with their theoretical values of 32% and 68%, respectively (Figure 3b).

Unlike the reaction involving NaCl, the reaction of $AgNO_3$ and NaBr exhibited significantly lower fluorescence in Raman spectra. Nevertheless, we observed a broad fluorescence signal in the spectral region from 1800 to 3250 cm^{-1} (Figure S3). As the reaction proceeded, the fluorescence gradually diminished, correlating with the loss of the intensity of the Raman band at 1046 cm^{-1} and the appearance of a new band at 1070 cm^{-1} (Figure 3c). Both of these bands correspond to symmetric stretching of the NO_3^- ion, the band at 1046 cm^{-1} to NO_3^- stretching in $AgNO_3$ and the band at 1070 cm^{-1} to NO_3^- stretching in $NaNO_3$.[102,103] The intensities of these bands can be used to obtain a reaction profile that displays depletion of $AgNO_3$ and formation of $NaNO_3$ (Figure 3d). Although the intensities of Raman peaks are proportional to the amounts of $AgNO_3$ and $NaNO_3$, careful calibration is still needed for exact

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quantification. Despite this, the curves in both PXRD and Raman monitoring derived reaction profiles exhibit similar trends. While the weight fractions of $NaNO_3$ dropped steadily from 32 to 30% (Figure 3b) after 10 min of milling, the intensities of of the $NaNO_3$ Raman band remained constant (Figure 3d). Again, we find a likely explanation of these observations in the crystallization of partially amorphous nascent AgBr, which would then lower the weight fraction of $NaNO_3$, even if its amount and crystallinity remain steady.

$AgNO_3$ + NaI. Before presenting the results of milling of $AgNO_3$ and NaI, we note that NaI which we had used contained a small amount of one or more unidentified impurities (Figure S5), which could have affected the reactivity of NaI, and these observations should be considered with caution. Milling $AgNO_3$ and NaI resulted in a fast reaction that was complete within 13 min, according to PXRD and Raman spectroscopy (Figure 4). To our surprise, the PXRD data revealed a remarkable transient intermediate phase forming right after depletion of the reactants, the occurrence of which was reproduced in three experiments. This transient phase was short-lived, exhibiting low-intensity Bragg reflections, most notably at d = 12.33 Å (corresponding to 0.82° in 2θ for radiation wavelength λ = 0.177 Å) and 7.51 Å (1.35° in 2θ) (Figure S6). Unfortunately, since its presence in the reaction mixture lasted, on average, less than 60 s, we were not able to isolate it or identify it on the basis of the *in situ* collected patterns. We also could not identify this intermediate in *in situ* Raman spectra. Rietveld analysis was hamstrung here not only by the appearance of a crystallographically unidentified intermediate but also by impurities originating from the starting NaI. While the resulting reaction mixture was predominately composed of AgI and $NaNO_3$, we were unable to assign a phase to the Bragg reflection with d = 3.97 Å (2.55° in 2θ) (Figure 4a and Figures S7 and S8).

We were intrigued by the formation of Ag_2ClNO_3 as an intermediate, since its analogues with bromide and iodide, Ag_2BrNO_3 and Ag_2INO_3, were not observed during mechanochemical metathesis. On consideration that milling reactions have often been found to follow Ostwald's rule of stages,[94,95] where intermediate phases occur starting from a higher-energy content phase which is then transforming into phases of increasingly lower energy content, we have assumed that only Ag_2ClNO_3 would have a lower energy than the mixture of AgX and $AgNO_3$. Since the bromide and iodide analogues are known in the literature, we were interested in preparing Ag_2BrNO_3 and Ag_2INO_3 mechanochemically. Previous reports of their preparation describe a solvent-based synthesis at an elevated temperature.[89,104,105] Here, milling of AgX (X = Cl, Br, I) with $AgNO_3$ at room temperature for 70 min yielded all three Ag_2XNO_3 pure double salts, as evidenced by Rietveld analysis of their PXRD patterns collected *ex situ* (Figures S9−S11).

Since standard enthalpies and Gibbs energies of formation of these double salts are not known in the literature, we have estimated them using solid-state density functional theory (DFT) calculations (Figure 5). Assuming a reaction path with intermediate formation of the Ag_2XNO_3, we find that all three double salts should have formed, according to Ostwald's rule of stages. A likely reason we did not observe formation of Ag_2BrNO_3 and Ag_2INO_3 *in situ* lies in kinetics—$AgNO_3$ potentially reacts more quickly with NaX than with the nascent AgX. While the results of our calculations are in good agreement with the experimental reaction enthalpies (Table 1),

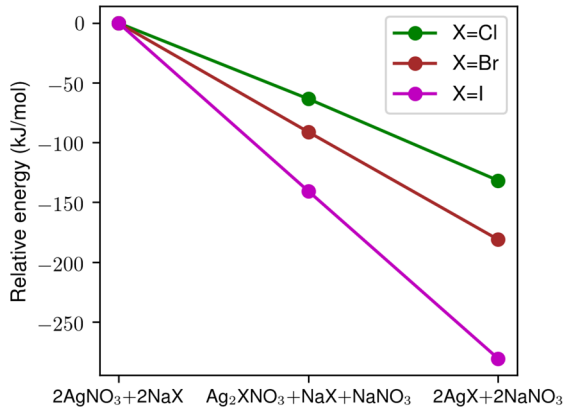

Figure 5. DFT-estimated relative energies of the reaction mixture taking the transformation path via the intermediate double salt Ag_2XNO_3. Energies of the starting and final compositions need to be divided by 2 for comparison with values in Table 1.

one should bear in mind that these calculations assume a temperature of 0 K and yield no entropy contribution and thus cannot calculate Gibbs energies. However, the reaction rates in the NaX series seem to correlate with reaction enthalpies.

Finally, we noticed that some samples had changed color and became slightly purplish or grayish after milling. This was likely due to partial silver reduction, but since we minimized exposure to light during milling, we assumed that high-energy ball impacts may have led to localized high temperatures, causing a disproportionation reaction of AgCl with the formation of elementary Ag(0) and Cl_2. To test this assumption, in a repeated experiment, the atmosphere inside the milling vessel was analyzed by mass spectrometry after 60 min of milling to reveal a slight increase in the partial pressure of Cl_2 (Figure S12). Our mass spectrometer was limited to the detection of ions with a relative mass below 100, and so only the experiment with NaCl was feasible to be analyzed in this way by mass spectrometry. It is worth noting that we did not observe an increase in the amount of any N_xO_y species after milling that could have resulted from decomposition of the nitrate ion, indicating that the potential hot spots during milling did not generate conditions that could lead to nitrate decomposition. We are currently developing a setup which would allow for an *in situ* measurement of gaseous products during milling, in a manner similar to that recently described.[106]

CONCLUSION

In situ monitoring was applied to a ball-milling metathesis reaction between $AgNO_3$ and NaX (X = Cl, Br, I). Reactions, conducted by neat grinding of solids, resulted in the formation of the expected products, AgX and $NaNO_3$. The reaction rates for milling of $AgNO_3$ with NaI and NaBr were similar and were significantly faster then the reaction rate with NaCl. A slower reaction for NaCl was possibly a consequence of the formation of the intermediate Ag_2ClNO_3, while the corresponding intermediates did not form with NaBr and NaI. All three double salts could have been expected as intermediates on the basis of Ostwald's rule of stages and, moreover, can be efficiently prepared by milling of AgX and $AgNO_3$. In addition, we find it interesting that the nascent $NaNO_3$ has crystallized as the unstable disordered polymorph before it transformed into the room-temperature-stable ordered polymorph, and we

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intend to investigate this further. We have thus demonstrated that a metathesis reaction between ionic compounds can be performed efficiently under ambient conditions by ball milling of solids and that such a reaction may exhibit reactive intermediates, much as reactions of organic or metal−organic systems. We also present an efficient and elegant means for the preparation of double salts without any postsynthetic workup required. Having successfully applied *in situ* reaction monitoring to mechanochemical reactions between inorganic ionic compounds, we have completed application of these techniques to mechanochemical reactions of all major classes of compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01196.

Standard reaction enthalpies, entropies, and Gibbs energies, *ex situ* laboratory PXRD patterns, *in situ* Raman spectra, and Rietveld refinement plots (PDF)

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Notes

The authors declare no competing financial interest.

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