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Thermal analysis using X-ray diffractometry for the investigation of the solid state reaction of ammonium nitrate and copper oxide ☆

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Abstract

The crystallographic and kinetic aspects of the solid state reaction of ammonium nitrate and copper oxide were studied by in situ time- and temperature-resolved X-ray diffractometry. The reaction proceeds through an intermediate stage in the form of a solid solution of diamminecopper(II) complex in the ammonium nitrate lattice, subsequently resulting in the formation of diamminecopper(II) dinitrate. The kinetic profiles of the reaction were fitted by a nucleation and growth model. The rate of the reaction was found to increase as the dopant concentration decreased. The reaction takes place with an expansion of the tetragonal lattice of the ammonium nitrate along the base, resulting in a plausible pseudo tetragonal-like structure.

Keywords: Ammonium nitrate; Copper oxide; DSC; Kinetics; Solid state reaction; Temperature-resolved X-ray diffractometry; TGA; Thermal analysis; Time-resolved X-ray diffractometry

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1. Introduction

Conventional thermal analysis techniques like DSC and TGA allow the determination of the enthalpy and weight change of a sample during a reaction as a function of time and temperature. However, these techniques alone cannot identify the reaction products that result from each thermal event, and thus cannot fully characterize the

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reaction. The identification of these products requires analytical techniques such as X-ray diffraction (XRD), infrared and Raman spectroscopy, mass spectroscopy and gas chromatography [1].

Of these techniques, in situ time- and temperature-resolved X-ray diffractometry is often the most appropriate for characterizing reactions when crystalline materials are involved either as reactants or as products. This method enables the recording of series of diffraction patterns, while the samples are heated continuously, stepwise or isothermally during the reaction. These series contain information on the lattice of solids and on the structural changes as a function of time and temperature. Besides, since peak intensities of a phase correlate with its concentration, by in situ measurements it is possible to probe the kinetics of solid state reactions. Recent automation in diffraction measurements and the improvement in X-ray sources and detectors allow convenient acquisition of shorter measurements resulting in higher time and temperature resolution between individual diffraction patterns for isothermal and non-isothermal measurements.

Ammonium nitrate, one of the reactants in the present investigation, crystallizes in at least five different polymorphic forms in the temperature range between − 50 and 170°C [2–6]. The transitions between these forms lead to serious difficulties for the utilization of ammonium nitrate in certain practical applications. In particular, the phase transition between phase IV (− 18–32°C) and phase III (32–84°C) is accompanied by a large change in volume, which causes irreversible growth, break up and caking of pelletized ammonium nitrate. Many approaches have been made to solve this problem. [7–11]

Earlier studies in our laboratory showed that doping of ammonium nitrate with small amounts of copper oxide significantly influences the phase transitions of ammonium nitrate, and detected some clues of possible intermediate formation during the solid state reaction [12]. However, it was not a conclusive study in terms of kinetic and mechanistic paths of the reaction. It was considered worthwhile to reinvestigate the reaction closely. The major objectives of the present investigation involve the crystallographic and kinetic aspects of the solid state reaction between ammonium nitrate and copper oxide.

2. Experimental

Spherical ammonium nitrate, purity 99.5%, atomized from the melt, average particle size < 50 μm was mixed with copper oxide (Analar, Merck) in a mortar, resulting in ammonium nitrate particles of approximately 20 μm. Copper oxide consisted of agglomerates, of which the particle size could not be determined. Beside the stoichiometric ratio of 2:1 mixtures 4:1 and 8:1 with an excess of ammonium nitrate were investigated in an attempt to ease the solid state reaction and to enhance the process of formation of the solid solution of the diammine complex formed in the ammonium nitrate lattice.

Preliminary measurements were made using TGA and DSC with the reaction mixture with different molar ratios. The TGA and DSC traces were recorded in an inert atmosphere with a heating rate of 2 and 0.2°C per min by a Mettler and PL system, respectively.

X-ray diffraction series were measured with a Siemens D 5000 Bragg–Brentano diffractometer equipped with a sealed Cr tube (45 KV, 35 mA) using a mBraun OED-50M position-sensitive proportional counter (PSPC) for fast recording. The measurements were performed by placing the sample on a flat sample holder, area 10 × 14 mm, while the samples were heated by a temperature device (TTK of Paar, Austria) together with a programmable temperature controller using a platinum resistance gauge as temperature sensor. The accuracy of the system was ± 0.3°C, the temperature difference measured between the center and the edge of the sample amounted to 1.5°C.

In the nonisothermal series, samples were heated in steps of 2.5°C at a rate of $2°\mathrm{C\,min}^{-1}$. When the temperature of the next step had been reached, the measurement was started immediately. In the isothermal series the samples were heated at a rate of $60°\mathrm{C\,min}^{-1}$ to temperatures of 100, 105, 110, 115 and 120°C, before the diffraction patterns were recorded quasi continuously in the angular range of 25–65° 2θ. A step size of 0.05° 2θ per channel and a scan time of 20–40 s per pattern were used for the measurements. Some isothermal and nonisothermal experiments were carried out with reduced angular range for obtaining shorter measuring times with higher temperature resolution.

2.1. Data evaluation

The measured diffraction data were evaluated by two procedures. The crystallographic evaluation was performed by peak profile fitting and the kinetic studies by a difference procedure.

The peak position, peak intensity, and peak width of selected reflections of ammonium nitrate, copper oxide, and the product were determined by a least squares fit with a Lorentz function using programs developed in our group. The cell constants were fitted using the *d*-spacings computed from the peak positions. The peak positions, peak intensities, $d(hkl)$ values, lattice constants, and the volume of the unit cell were plotted as a function of time or temperature.

The kinetic evaluation was carried out by means of a difference procedure, which delivers the relative changes in the measured patterns during the reaction [13]. The measured patterns are subtracted from the first pattern already measured. The sum $Y(t_j)$ gives the absolute differences between the corresponding channel contents representing the changes in the diffraction patterns.

$$Y(t_j) = \sum_{i=1}^{n} |Y_i(t_i) - Y_i(t_j)|$$

j = number of the current diagram; i = number of the current channel; n = total number of channels; t = time (temperature for nonisothermal runs).

This data evaluation is particularly useful for probing the initial or final stage of solid state reactions and especially useful for following very small peaks. The procedure can be applied to the whole pattern or to selected angular ranges. For the kinetic evaluation separate difference curves were calculated from the reflections of ammonium nitrate, copper oxide, and the resulting product. The plots of the difference curves normalized to unity representing the progress of the reaction with time were used for kinetic analysis. The rate constants were computed by fitting the difference curves with the most suitable kinetic model.

3. Results and discussion

The solid state reaction between ammonium nitrate and copper oxide proceeds as described by the equation

$$2NH_4NO_3 + CuO \rightarrow [Cu(NH_3)_2](NO_3)_2 + H_2O$$

For investigating this solid state reaction, preliminary experiments were performed with DSC, TG, and nonisothermal XRD in order to obtain the temperature range, in which the reaction takes place. It was then decided to focus the evaluation on molar ratios of 4:1 with an excess of ammonium nitrate to reach a complete reaction of CuO.

The thermogram (4:1) showed a slow weight loss (approx 6.8%) in the temperature region 80–135°C; this is due to the evolution of water formed during the solid state reaction. The DSC curve corroborates the slow weight loss in the TG trace as shown in Fig. 1. A shallow endothermic region was observed in the temperature region 98–118°C, just before the sharp endotherm corresponding to the II → I phase transition of

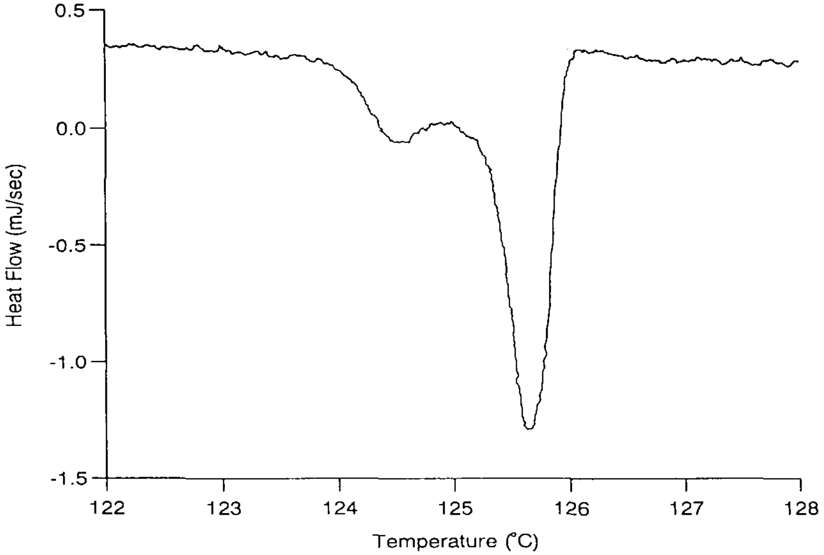


Fig. 1. DSC curve of a mixture of ammonium nitrate and copper oxide, molar ratio 4:1, measured with a heating rate of 0.2°C min^{-1}.

ammonium nitrate. This feeble endotherm depicts the slowness and the low energy change associated with the solid state reaction.

A typical nonisothermal diffraction series (25–65° 2θ) recorded during the stepwise heating (2.5°C per pattern) of a mixture of ammonium nitrate (AN) and copper oxide (CuO) from 20–165°C is shown in Fig. 2. The X-ray diffraction patterns recorded at 20°C contain the peaks of CuO and AN (Phase IV). On heating, the ammonium nitrate IV → II transition takes place at 55°C. An overall observation of the diffraction patterns shows the slow disappearance of the CuO peaks (− 111) and (111) along with the simultaneous vanishing of some ammonium nitrate peaks and the gradual appearance of the product peaks. Irrespective of the molar composition the first product phase appears in the temperature range 124–128°C. For precise observation a series was recorded with a scan time of 10 s per pattern in the angular region 25–46°C 2θ with stepwise heating 4°C per pattern. This series confirms the appearance of the first product peak at 128°C.

After the preliminary measurements temperatures of 100–120°C were selected for the isothermal measurements. The selected temperatures are lower than the temperature observed for the appearance of the product peaks. A qualitative evaluation of the progress of the solid state reaction between ammonium nitrate and copper oxide can be obtained from the isothermal series as shown in Fig. 3. The diffraction patterns contain at the beginning the peaks of phase II of ammonium nitrate and the peaks of copper oxide. With progressing time the CuO peaks (− 111) and (111) vanish almost completely, before the first product peak appears in the range 28.2–30.4° 2θ. With the ammonium nitrate, the most intense (110) and (111) peaks remain throughout the

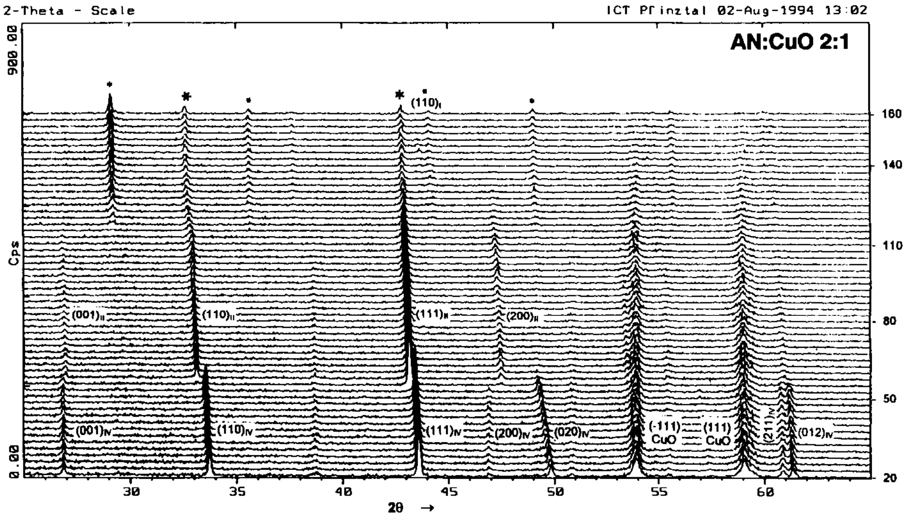


Fig. 2. Temperature-resolved XRD patterns, measured with a mixture of ammonium nitrate and copper oxide, molar ratio 2:1, in temperature intervals of 2.5°C. Large asterisks: former AN peaks, later product peaks; small asterisks: new product peaks.

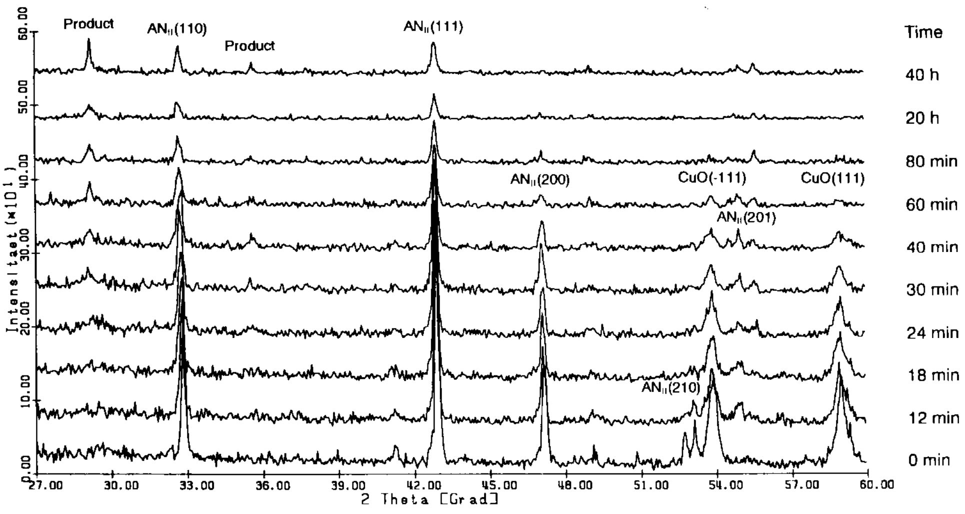


Fig. 3. Time-resolved XRD patterns selected from an isothermal series measured at 120°C with a mixture of ammonium nitrate and copper oxide, molar ratio 4:1.

reaction with a gradual intensity decrease, while the peaks of the (001), (200), (210), and (201) planes disappear with time, the latter two splitting with the progressing reaction.

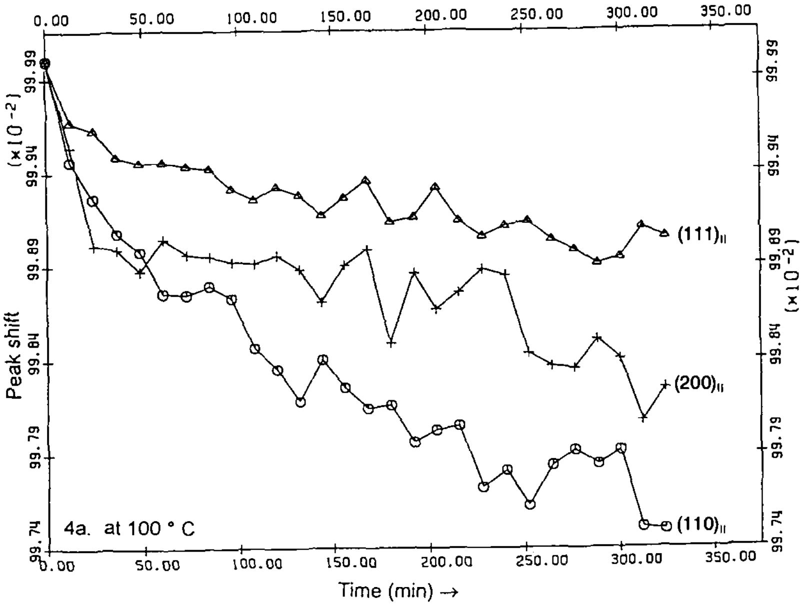
3.1. *Crystallographic evaluation*

The crystallographic evaluation with fitting of the peak positions shows a shift of the (110), (111), and (200) peaks to lower angles, as shown in Figs. 4a and 4b. With the other AN peaks no shift is observed. It is interesting to note that the (110) and (111) peaks have more or less the same tendency in peak shift with time, whereas the (200) peak exhibits an almost abrupt shift towards the lower angle side and then remains constant.

The shift of the AN peaks together with the observation that CuO peaks disappear almost completely before the product peaks appear is interpreted as the formation of a solid solution of the diammine complex in the ammonium nitrate lattice. The different time trend of the (200) peak shift compared to the (110) and (111) peak shifts depicts the more pronounced expansion of the AN lattice along the *a*-axis. This anisotropic expansion along the *a*-axis could be due to the preferential diffusion of the Cu^{2+} ions along this axis, resulting in the solid solution. The time required for the shift of these peaks decreases from 100 to 120°C, revealing the time-dependency of the diffusion process during the solid state reaction.

The peak width determination shows that there is a slight broadening of the (110) and (111) reflections in the initial stage of the solid state reaction as the reaction proceeds, which may be due to the presence of concentration gradients of the dopant inside the reacting ammonium nitrate particles.

The peak intensity determination shows that all the AN peaks except the (110) and (111) peaks vanish to zero intensity with time, which is unexpected, as an excess of AN is



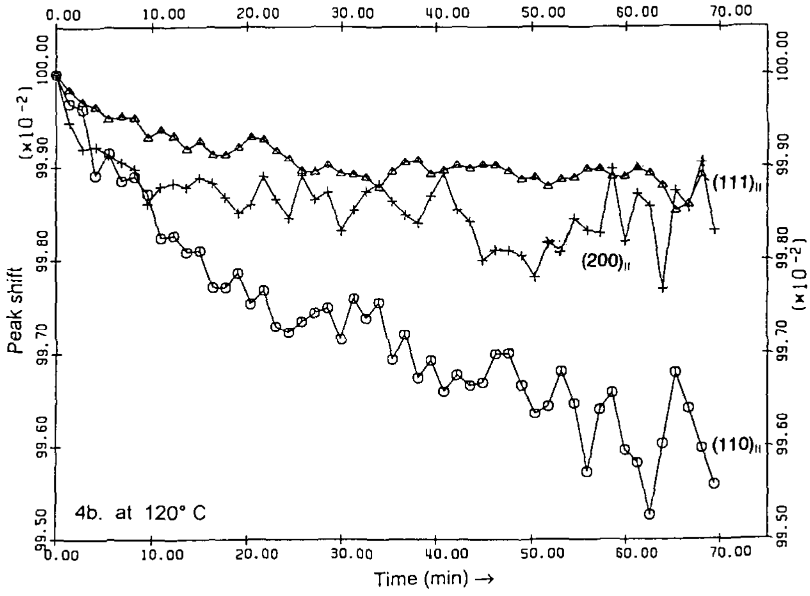


Fig. 4. Peak shifts of ammonium nitrate, phase II, measured in isothermal series at 100 and 120°C with a mixture of ammonium nitrate and copper oxide, molar ratio 4:1, plotted versus time.

used. A typical peak intensity versus time plot for AN peaks is shown in Fig. 5. The last patterns of each isothermal series recorded are almost identical with the typical pattern of diamminecopper(II) nitrate, as is also obtained with diamminecopper dinitrate prepared by decomposition of the tetrammine complex. It is pertinent to note that there are no other peaks of ammonium nitrate except the (110) and (111) peaks. It is assumed that the (110) and (111) planes of the AN lattice gradually become the lattice planes of the formed diamminecopper(II) nitrate as a result of the solid state reaction.

The lattice parameters of phase II of ammonium nitrate fitted by the least-squares method are shown as a function of time in Figs. 6a and 6b. Assuming linear dependence of the lattice parameters according to Vegard's law the nonlinear change of the lattice constants with time represents the nonhomogeneous compositional change of the solid solution in the ammonium nitrate lattice [14]. A typical plot showing the cell volume change with time (100°C) is shown in Figs. 6c. The solute incorporation causes a corresponding expansion of the host lattice, which consequently results in an increase of the unit cell volume.

As a result of the findings discussed above the reaction between ammonium nitrate and copper oxide takes place by the interdiffusion of the Cu^{2+} and H^+ ions into and out of the ammonium nitrate lattice, resulting in a solid solution of diamminecopper(II) nitate inside the ammonium nitrate lattice. With increasing concentration the solubility of the diammine complex in ammonium nitrate is surpassed with time. This results in the gradual formation of the independent diammine complex lattice described by the model, which is discussed with the kinetic evaluation below.

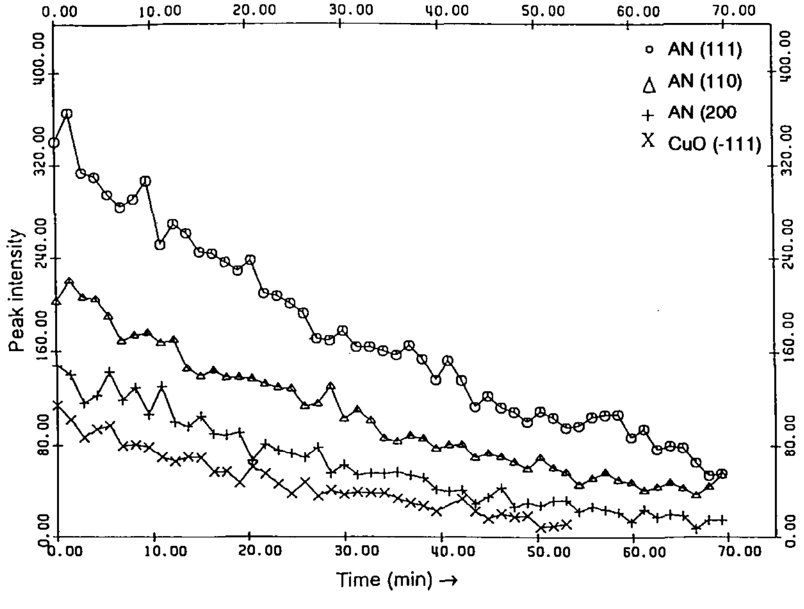
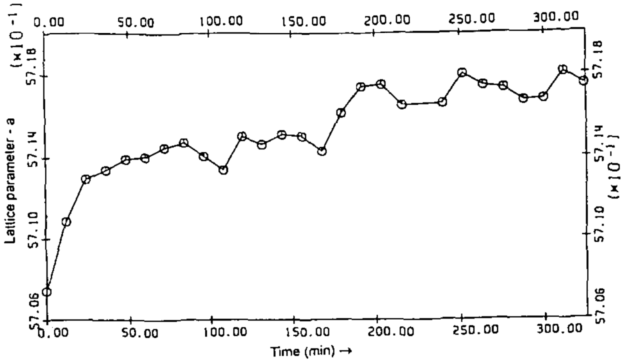
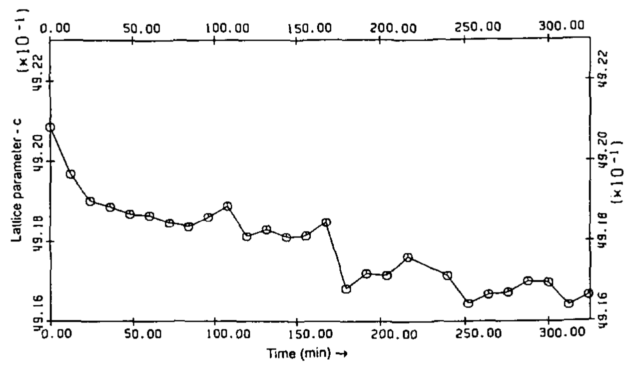


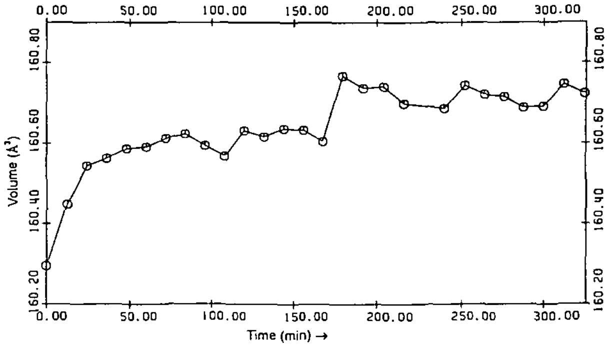
Fig. 5. Peak intensities of ammonium nitrate, phase II, measured in an isothermal series at 120°C with a mixture of ammonium nitrate and copper oxide, molar ratio 4:1, plotted versus time.



6a. Change of lattice parameter - a with time



6b. Change of lattice parameter - c with time



6c. Change of cell volume with time

Fig. 6. Lattice parameters and elemental cell volumes of ammonium nitrate, phase II, measured in an isothermal series at 100°C with a mixture of ammonium nitrate and copper oxide, molar ratio 4:1, plotted versus time.

The lattice parameter determination shows that, as a result of the formatioin of diamminecopper(II) nitrate inside the AN lattice, there is an expansion of the tetragonal lattice along the base and an inconsistent change along the *c* axis. No peak splitting was observed during the latter stage of the solid state reaction especially for the (200) peak (see Fig. 3). So it could be assumed that the formed diamminecopper(II) nitrate has a pseudo tetragonal-like structure. However, literature search revealed that no attempts have been made to elucidate the crystal structure of diamminecopper(II) nitrate except that some correlations were used to support the local copper(II) ion stereochemistry in a series of diamminecopper(II) complexes of unknown structure [15].

3.2. Kinetics and choice of reaction mechanism

Isothermally measured diffraction patterns were recorded at comparatively lower temperatures (100–120°C), so that it was possible to monitor both the reactant and the product peaks during the course of the solid state reaction. The difference method was applied to the individual reactant and product peaks. Typical normalized difference plots of copper oxide (−111), ammonium nitrate (110) and product (28.2–30.4° 2θ) peaks are shown in Fig. 7. The kinetic studies were accomplished by fitting the difference curve of the product peak with the most suitable rate equation. The

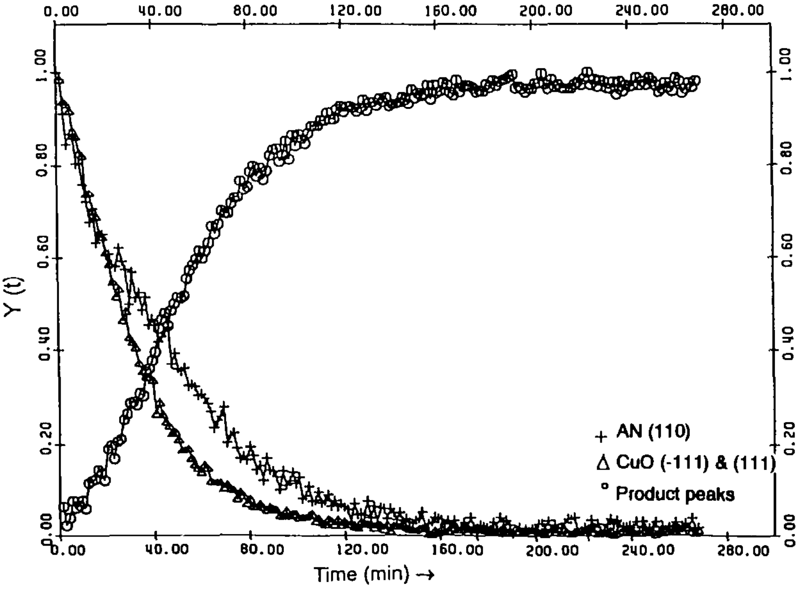


Fig. 7. Normalized difference curves, calculated from an isothermal series at 120°C including separate angular ranges with the peaks of ammonium nitrate, copper oxide, and the reaction product.

experimental difference profile of the product peak at different temperatures over the entire reaction can be well fitted by a phenomenological rate equation of type [16, 17]

$$y = 1 - \exp[-K(T)t^n]$$

where y is the extent of transformation at a given time t, and k is a temperature-dependent effective rate constant independent of time. The experimental and the fitted curves of the product peak at different temperatures are shown in Fig. 8. The rate constants k at different temperatures along with the computed kinetic parameters and the Arrhenius plot are shown in Table 1 and Fig. 9, respectively.

The observed behavior in kinetic profiles is commonly associated with the nucleation and growth type of solid-state transformations, where the interfacial area between the transformed and untransformed regions largely determines the rate. If good contact is maintained at the phase boundaries between the powdered reactants, the reaction takes place by the counter diffusion of cations [18]. According to this mechanism, the reaction rate is controlled by the formation and growth of nuclei on the surface of the reactant. The value of n depends on the shape of the nuclei, the number of nuclei present at the beginning of the reaction and their distribution in the particles. The product curves exhibit, especially at 120°C, typical induction, acceleratory, and decay periods. The value of n at different temperatures is a decimal number. Examples abound in literature which show that n does not necessarily have to be an integer, but can be a decimal [19–21].

The difference curve of the product peak (Fig. 8) shows that the sigmoidal nature of the profiles increases with temperature and visibly forms a good sigmoidal profile at 120°C. This observation is consistent with the literature [22]. The higher the temperature, the more the difference in ionic mobility between the interdiffusing ions and hence the increasing asymmetry of the reaction profile. The initial asymmetric nature of the kinetic profile is due to the difference in ionic mobility between the diffusing H^+ ions and Cu^{2+} ions. This change in ionic mobility of the diffusing ions arises because of the difference in charge and size associated with the interdiffusing cations [22]. Here, the two cation fluxes in the reaction product are coupled through the condition of electroneutrality, resulting in the solid solution of the diammine complex in the AN lattice. In addition, this initial asymmetry in the kinetic profile can also be due to the different jump frequency associated with the different ions coupled with the variation of the defect concentration with composition [22].

Table 1
The rate constants and the kinetic parameters of the reaction

Temperature/°C	k/min^{-1}	E_a/(kJ mol^{-1})	A/min^{-1}
100	0.00284		
105	0.00487		
110	0.00764	101.9	5.57×10^{11}
115	0.01001		
120	0.00190		

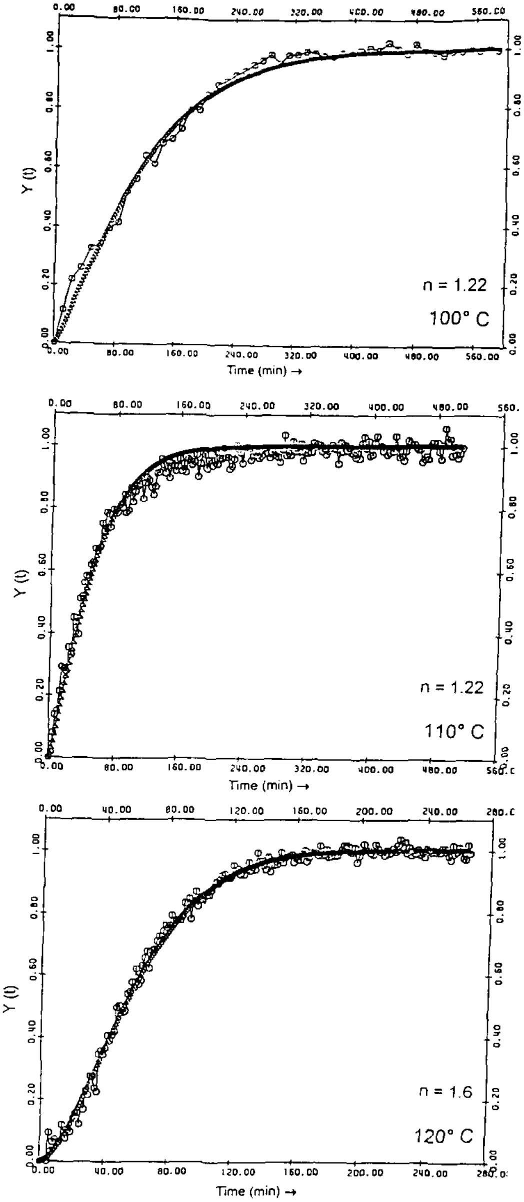


Fig. 8. Difference and fitted curves of the product peaks, calculated from isothermal series measured at 100, 110, and 120°C with a mixture of ammonium nitrate and copper oxide, molar ratio 4:1.

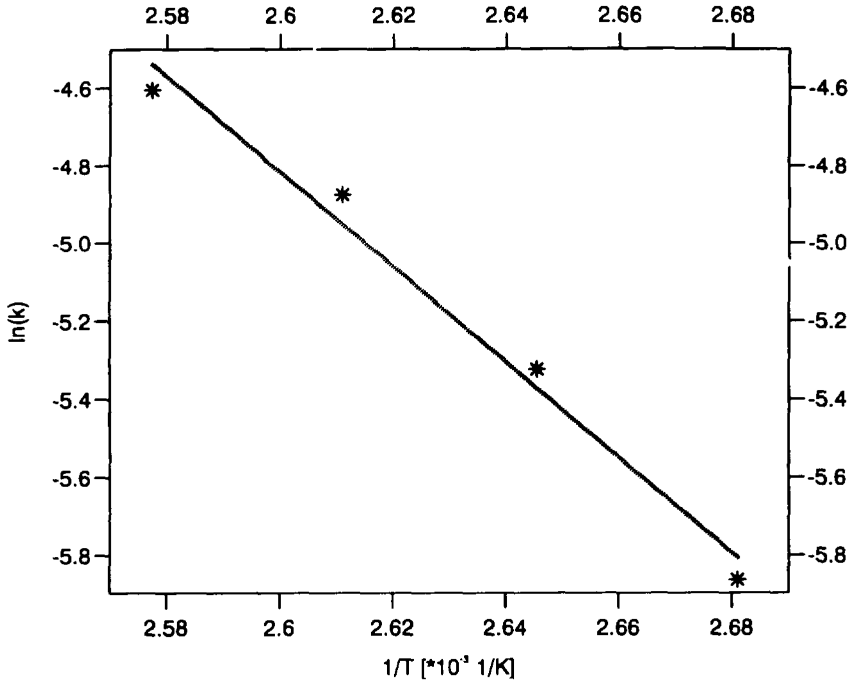


Fig. 9. Arrhenius plot of the reaction of ammonium nitrate with copper oxide, molar ratio 4:1, calculated from isothermal measurements measured at 100, 105, 110, and 115°C.

The experimental kinetic profiles were also analyzed using other mechanistic models, especially the Jander diffusion model for powdered reactants [23]. However, this model gives no good fit of the experimental profile especially at the initial stage of the reaction. This could be due to the inapplicability of the assumption employed in the derivation of the Jander model for this reaction [24]. In a previous study [12] this reaction was assumed as a simple first order consecutive reaction. A close perusal of the fits revealed that the reactant and product profiles are not following a true exponential fit. However, it is not uncommon that some reactions are described almost equally well by first order kinetics [25], the equation for nucleation and growth model [17, 18] and the Jander, Ginstling and Brounshtein, and Carter equations for diffusion models [26, 27].

The activation energy and the frequency factor were calculated with the reaction constants 100–115°C on the basis of the model discussed above, see Table 1 and Fig. 9. The value at 120°C was not included, because it deviates considerably from the tendency observed with the other constants, which may be due to the close neighborhood of the phase transition II/I. The calculated parameters are comparable with the earlier reported values [12].

It was observed that the rate of the solid state reaction between ammonium nitrate and copper oxide is slow for 2:1 molar ratio. The rate increases as the CuO concentration decreases (i.e., 2:1 → 8:1). Obviously, an excess of ammonium nitrate increases the probability of copper oxide making close contact with an ammonium nitrate surface. Besides, the solid solution formation enhanced both effects influencing the rate of the solid state reaction.

4. Conclusions

The kinetic and structural behavior of the solid state reaction between ammonium nitrate and copper oxide has been studied by means of in situ time- and temperature-resolved X-ray diffractometry. The reaction occurs by intermediate solid solution formation ultimately resulting in the formation of the diamminecopper(II) nitrate complex. The kinetic profiles can be well fitted by a nucleation and growth model. The rate of the reaction is increased by use of excess ammonium nitrate. The reaction occurs with an expansion of the tetragonal lattice along the base, resulting in a pseudo tetragonal-like structure of the formed diammine complex.

Acknowledegments

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