

KINETICS OF NITRO-NITRITO LINKAGE ISOMERIZATION

$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2 \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^- , NO_3^-) IN THE SOLID STATE. COMPUTER SIMULATION AND EXPERIMENTAL RESULTS

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ABSTRACT

An "intramolecular" solid-state linkage isomerization $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2 \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$ was simulated by a Monte Carlo method. Both the kinetics and the spatial picture of the reaction were studied. An anomalous retardation of the reaction and a sort of the ordering of the product were observed. The results of the simulation were compared with the experimental data.

Kinetics and mechanism of solid state reactions cannot be interpreted by sole evaluation of thermoanalytical measurements. It is rather necessary to correlate structure, morphology, isothermal kinetics data and macroscopic reaction mechanism with thermoanalytical data[1]. Such a correlation is necessary even when the so called "intramolecular" solid state reactions, e.g. "intramolecular" isomerization of solid coordination compounds, are studied. An "intramolecular" solid state reaction involves only the complex ions at the lattice sites, the lattice itself remaining unchanged. Still the reactions of this type can be autocatalytic or autoinhibitory[2]. The isomerization of a complex ion at a lattice site can create local stress in the crystal, change the steric conditions for the transformation of the neighbouring ions, etc. Thus, the isomerization of a complex ion can affect the rate of further isomerization of the neighbouring ions. Both autocatalysis and autoinhibition complicate the kinetics (essential deviations from the first-order-law are observed) and the spatial picture of the reactions. Therefore, when the kinetics, the morphology of the product and the mechanism of a solid state "intramolecular" isomerization are studied, it is necessary, that the possibility of either autocatalysis or autoinhibition should be taken into account.

The solid state nitro-nitrito linkage isomerization

$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 \xrightleftharpoons[\text{RT}]{h\nu} [\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ is an example of a solid state "intramolecular" reaction. The isomerization is known to proceed via the formation of a solid solution of one isomeric form in another[3]. The reaction was shown to be "intramolecular"[3]. The photoisomerization involves only the complex ions, while crystal structure remains otherwise intact[3]. During the thermal isomerization chemical reaction and structural transformation are separated in time[3]. In the course of the photoisomerization high internal strains are created, and this results in the deformation (bending) and destruction of the crystals[4]. The kinetics of the photoisomerization cannot be described by the first-order law ($\alpha = 1 - \exp(-kt)$, $k = \text{const}$); it was shown both on powder samples[5] and on single crystals (our data). An early retardation of the reaction is observed. In the course of the photoisomerization the colour of the crystals changes uniformly all over the surface[4].

The effective size of $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ -ion was estimated to be approximately 1,2 times as great as that of the $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ -ion [6]. Hence, one may expect the larger $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ -ions, formed in the course of the solid state photoisomerization, to serve as local sources of strains in the crystal, and this is as if equivalent to local "rises of pressure" near the product. Since the photoisomerization is retarded when pressure increases [6], the reaction may be expected to show autoinhibitory effects. We have simulated the kinetics and the spatial picture of an autoinhibitory solid state reaction, assuming that the reaction is not accompanied by a structural transformation. A Monte Carlo simulation technique was used. The intensity of the autoinhibition was characterized by a variable parameter A. The value of A ran from zero to unity, big values corresponding to weak inhibition and small ones - to strong inhibition. The algorithm of the simulation is discussed in details in the poster.

The kinetics of the simulated autoinhibitory reaction does not follow the first-order law ($\alpha = 1 - \exp(-kt)$, $k = \text{const}$), whatever the intensity of the autoinhibition is. A retardation of the reaction is observed beginning from very low degrees of conversion. The time, at which the degree of conversion is equal to unity ($\alpha = 1$), greatly increases. The curves $\alpha(t)$ tend to acquire gradually quasi-stationary values $\alpha^* < 1$. The value of α^* depends on the intensity

of the autoinhibition, characterized by the parameter A . The kinetics can be described as $\alpha = 1 - \exp(-kt)$ (by analogy with the first-order law). However, here k is not constant, but varies as a function of either time or the degree of conversion. Physically, k characterises the mean probability of the reaction at a given moment, averaged over the lattice. As it should be expected, the value of k decreases with increasing α . It is interesting to note that k starts to decrease at very low degrees of conversion (at $\alpha \approx 1\%$ when the autoinhibition is strong and at $\alpha \sim 5-10\%$ when the autoinhibition is weak). At first k (α) decreases linearly and then, at a definite degree of conversion (determined by the intensity of autoinhibition), acquires gradually a quasi-stationary value (but for $A=0$, corresponding to the strongest possible autoinhibition).

We have also investigated the spatial picture of the simulated reaction. We plotted the charts of product distribution and calculated corresponding radial distribution functions. The distribution of the product was shown to get somehow ordered with increasing the intensity of autoinhibition.

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