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SOME ASPECTS OF HETEROGENEOUS REACTIONS OF INORGANIC SOLIDS

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ABSTRACT

Seven papers on the kinetic and mechanistic aspects of inorganic reactions in the solid state (solid–gas heterogeneous reactions and thermal decomposition of solids) are reviewed. The chlorination kinetics of Cr_2O_3 were investigated by thermogravimetry. The kinetic and mechanistic aspects concerning with the interconversion process $CrO_2 \rightleftarrows CrOOH$ were studied. The kinetic deuterium isotope effect in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ is reviewed. An "intramolecular" solid-state linkage isomerization, $[Co(NH_3)_5NO_2]X_2 \rightleftarrows [Co(NH_3)_5ONO]X_2$, was simulated by a Monte Carlo method. The thermal decomposition of $Fe_2Mn_{0.5}Zn_{0.5}(C_2O_4)_4$ and the crystallization of cubic ferrite from oxides were studied. The thermal dehydration mechanism of single crystalline oxalic acid dehydrate was examined by thermogravimetry. Kinetic parameters of the thermal decomposition of citric acid and complex salts of the metals with citric acid were investigated.

INTRODUCTION

Many papers on the kinetics relating to solid-state inorganic complex reactions and thermal decompositions of solids were presented in Session B1 (Theory, Kinetics Calorimetry) and Session C (Inorganic Chemistry) at the 8th ICTA Conference. Seven interesting papers were chosen for this review of the kinetic and mechanistic aspects of solid-state reactions.

SOLID–GAS HETEROGENEOUS REACTIONS AND THERMAL DECOMPOSITION OF SOLIDS

The paper by Kuffa et al. (Czechoslovakia) was entitled "The chlorination kinetics of chromic oxide" [1]. These investigators are interested in the fundamental kinetic data of the chlorination of Cr_2O_3 and the possibility of decreasing Cr losses. They determined gravimetrically the degree of chlo-

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rination conversion from the amount of evaporated oxychloride in the following reaction:

$$Cr_2O_3 + 2Cl_2 + 0.5O_2 = 2CrO_2Cl_{2(g)}$$

They used a silica spring-type thermobalance provided with purified Cl_2, O_2 and N_2 gas lines. In most instances, cylindrical sample pellets were used for chlorination in the range 900–1100°C. The dependence of temperature, pellet radius and time on the degree of conversion (R) were investigated. A kinetic equation for cylindrical pellets, where height is equal to diameter, was presented. The plots of $1-(1-R)^{1/3}$ vs. time fit straight lines at 1000°C and chlorine concentrations ranging from 5 to 75% for r_0 (original sample radius) = 0.5 cm. The dependences of k (the rate constant) on chlorine and oxygen contents were obtained at 900 and 1000°C. They also found a kinetic equation for the dependence of Cr_2O_3 conversion in an atmosphere consisting of chlorine and oxygen.

Saez-Puche et al. (Spain) reported on the "Kinetic and mechanistic aspects of the interconversion process $CrO_2 \rightleftarrows CrOOH$. Isotopic effects" [2]. They performed reduction and oxidation experiments by using a thermogravimetric (TG) technique and showed that the results of the oxidation of CrOOH to CrO_2 in air can be fitted to at least four different gas–solid kinetic models by representing the TG data according to the Coats and Redfern method. On the other hand, the reduced time plot analysis of the oxidation isotherms obtained in air at 579–608 K indicates that the process corresponds to a two-dimensional Avrami model. The isotherms for the reduction of CrO_2 with deuterium at different temperatures show features different to those obtained in previous work with hydrogen. The reduction obeys a one-dimensional diffusion kinetic model in which the hydrogen diffuses along the empty tunnels parallel to the C-axis that are present in a rutile type structure. They showed that the plot of $\log(D_H/D_D)$ vs. $1/T$ (1.89×10^{-3}–2.05×10^{-3}) fits a straight line that could correspond to the equation according to Ebisuzaki et al. [8]. The increase in the D_H/D_D ratio at low temperatures can be attributed to a tunnel effect, which at these low temperatures become important and promotes the diffusion of hydrogen as compared with deuterium.

A review on "Deuteration effects on the thermal decomposition process of inorganic solids" [3] was presented by Tanaka (Japan) on the basis of his and co-worker's ten papers. He tabulated deuteration effects on the kinetics and thermodynamics of the thermal dehydration of twelve kinds of hydrated salts by means of TG and DSC. He suggested that in the decomposition of solids E is usually slightly larger than ΔH, and both E and ΔH should be examined in explaining deuterium isotope effects on thermal stability for solid decompositions, as the decomposition temperature T derived from dynamic thermal analysis depends not only on the thermodynamics but also on the kinetics. The temperatures where the fraction dehydrated is 0.5

according to TG ($T_{1/2}$) were defined as a measure of the thermal stability of solids. It is reasonable to determine the deuteration effect on ΔH by means of DSC. The isotopic differences of $\Delta H (= \delta \Delta H)$ were summarized. He showed that there is a trend of positive values of ΔH. The kinetic deuterium isotope effect in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ was discussed. The rate of dehydration for $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$, K_H/K_D, was found to be 1.025 ± 0.012 (by a isothermal method). No significant isotope effect on the activation energy, E, was recognized at the same α value between the monohydrate and its deutrium analogue (by a non-isothermal method). This result is reasonable, in that a normal kinetic isotope effect on E of greater than 1 kcal mol^{-1} is well within the experimental error for such a dynamic thermal analysis. He suggested that the enormous kinetic isotope effects reported earlier are dubious. It was pointed out that kinetic isotope effects are detectable through statistics that require a comparable amount of experimental to the isothermal or heating rate method and are fairly insensitive to the kinetic function adopted.

The paper "Kinetics of nitro–nitrito linkage isomerization, $[Co(NH_3)_5NO_2]X_2 \rightleftharpoons [Co(NH_3)_5ONO]X_2$ ($X = Cl^-$, Br^-, NO_3^-), in the solid state. Computer simulation and experimental results" [4] was presented by Boldyreva et al. (U.S.S.R.). It is necessary to correlate structure, morphology, isothermal kinetic data and macroscopic reaction mechanisms with thermoanalytical data. Such a correlation is necessary especially when the "intermolecular" isomerization of solid coordination compounds is studied. The authors suggested that the isomerization of a complex ion at a lattice site can create local stress in the crystal, changing the steric conditions for the transformation of neighbouring ions. Both autocatalysis and autoinhibition complicate the kinetics and the spatial picture of the reaction. They chose the solid-state nitro–nitrito linkage isomerization

$$[Co(NH_3)_5NO_2]Cl_2 \underset{kT}{\overset{h\nu}{\rightleftharpoons}} [Co(NH_3)_5ONO]Cl_2$$

as an example of a solid-state "intramolecular" reaction. In the course of the photoisomerization high internal strains are created, and this causes deformation, bending and destruction of the crystals. They reported that the kinetics of the photoisomerization cannot be described by a first-order law. They 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 kinetics can be described as $\alpha = 1 - \exp(-kt)$. However, here k is not constant, but varies as a function of either time or the degree of conversion. It is interesting that k starts to decrease at very low degrees of conversion (at $\alpha = 1\%$ when the autoinhibition is strong and at $\alpha = 5$–10% when the autoinhibition is weak).

"Kinetic aspects of the Mn–Zn–Fe mixed oxide formation by thermal decomposition of polynuclear coordination compounds" [5] was presented by T. Coseac et al. (Romania). Their paper dealt with the thermal decomposition of $Fe_2Mn_{0.5}(C_2O_4)_4$ and with the crystallization of the cubic ferrite from the mixture of oxides generated by thermolysis of the parent polynuclear coordination compounds (PCC). The TG curves showed three decomposition steps generating CO_2 gas:

$$Fe_2Mn_{0.5}Zn_{0.5}(C_2O_4)_4 \xrightarrow[(I)]{190°C} Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_4 \xrightarrow[(II)]{235°C}$$

$$Fe_2Mn_{0.5}Zn_{0.5}(CO_3)_3O \xrightarrow[(III)]{270°C} Fe_2Mn_{0.5}Zn_{0.5}O_4$$

The temperatures above the arrows correspond to the maxima of the decomposition rates. The kinetic parameters of step I, II and III were discussed on the basis of the Coats–Redfern method. They reported that the satisfactory agreement between the values of the kinetic parameters for the three different heating rates (2.5, 5 and 10 K min^{-1}) shows no heat transfer limitations. X-ray analysis showed that a compound with a cubic ferrite structure and a mixture of cubic ferrite and Fe_2O_3 were formed between 550 and 700°C. The DTA exothermic peak at 470°C was assigned to the crystallization of the mixed Fe–Mn–Zn oxide, the stability range of which is 550–700°C.

Tanaka and Kawabata (Japan) presented the "Thermal dehydration mechanism of oxalic acid dihydrate. II. Single crystal materials" [6]. Using thermogravimetry at both constant and linearly increasing temperature and polarized microscopy, the experimental results obtained were analysed to clarify the dehydration mechanism of single crystalline $(COOH)_2 \cdot 2H_2O$. $F_1(\alpha) = [-\ln(1-\alpha)1/2.4]$ showing random nucleation and its subsequent growth, and $F_2(\alpha) = 1 - (1-\alpha)1/1.3$, showing a phase boundary reaction, were selected as appropriate over the range 55.6 – 64.5°C. They tabulated typical correlation coefficients (r) of the regression analysis of $F(\alpha)$ vs. time plots and rate constant (k) at various temperatures obtained by isothermal gravimetric analysis in terms of the $F(\alpha)$ functions mentioned above. The activation energies were 85.0 ± 12.0 and 86.0 ± 13 kJ mol^{-1} for the functions $F_1(\alpha)$ and $F_2(\alpha)$, respectively. Using the modified Coats and Redfern equation they adapted $R_{1.3}$ to the appropriate $F(\alpha)$ for dehydration, assuming that the kinetic parameters from isothermal analysis are nearly equal to those from dynamic analysis of a run at very low heating rates. The microscopic observation of a partially dehydrated sample showed that the dehydration proceeds mainly by a phase boundary reaction mechanism. On the other hand, random nucleation seems to occur mainly at a spiral growth front arising from screw dislocations during the crystal growth from solution.

J. Masłowska et al. (Poland) presented a paper entitled "Thermoanalytical investigation of citric acid and complex salts of transition metals with citric acid" [7]. They used thermogravimetry, DTA with a static atmosphere of air and a thermofractochromatograph. The thermoanalytical curves of ten metal citrates [Mg(II), Al(III), Ca(II), Cr(III), Mn(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)] showed four or five decomposition stages, with the first stage being associated with the dehydration. For example, the following reaction stages were confirmed:

$$Mg_3(C_6H_5O_7)_2 \cdot 4H_2O \xrightarrow[\text{(I)}]{373-423\ \text{K}} Mg_3(C_6H_5O_7)_2 \cdot 2H_2O \xrightarrow[\text{(II)}]{423-493\ \text{K}}$$

$$Mg_3(C_6H_5O_7)_2 \xrightarrow[\text{(III)}]{495-613\ \text{K}} Mg(C_6H_3O_6)_2 \xrightarrow[+O_2\text{(IV)}]{613-974\ \text{K}} MgO$$

Based on the obtained TG, DTG and DTA curves, the activation energy, frequency factor, reaction order and velocity constant of the dehydration process were tabulated. The thermofractochromatograms of the metal citrates showed that the thermal decomposition of metal citrates is a complicated process composed of several overlapping reactions. They concluded that, assuming T_n, i.e., the temperature at which a spot appears on the TLC plate as a volatility of citration one can state that the volatility of the citrates under investigation decreases in order Zn > Al > Ni > Co > Fe > Mg > Cu > Mn > Ca > Cr. Also, the kinetic parameters indicate that when citrates are heated in the presence of oxygen at very low heating rates then first oxidation occurs and new substances are formed in the crucible.

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