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Study of the solid state reaction of $Na_3[Rh(C_2O_4)_3]$ synthesis

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Abstract

The interaction reaction between $Na_3Rh(NO_2)_6$ and $H_2C_2O_4$ was investigated by quasi-isothermal and quasi-isobaric thermogravimetry. The most probable rate-controlling process is the nucleation growth reaction (ratio 1 : 3) and the phase boundary reaction (ratio 1 : 1)

The processes of ligand substitution in crystalline coordination compounds are studied in depth in thermal decomposition reactions. The solid state reactions of the synthesis are less extensively investigated.

To study the interaction between $Na_3[Rh(NO_2)_6]$ and $H_2C_2O_4 \cdot 2H_2O$, derivatograms of oxalic acid, of the rhodium complex and of their mixture in the ratio complex : acid = 1 : 3.1 were obtained using a MOM (Hungary) derivatograph, a ceramic sample holder and Al_2O_3 reference material. The heating rate was 5°C min^{-1}, the helium flow was 4 l h^{-1}, and the sensitivities were 1/5 for DTA, 1/10 for DTG and 100 mg for TG.

The thermal curves show that $H_2C_2O_4 \cdot 2H_2O$ decomposes (after dehydration) in the interval 130–240°C ($t^0_{max} = 205$°C). The rhodium complex is stable up to 300°C. The reaction in the mixture is observed in the range 120–260°C ($t^0_{max} = 150$°C). The solid state reaction and decomposition of the $H_2C_2O_4$ residue seemed to overlap in the range 150–260°C.

The stoichiometry of the formation of the oxalate complex could not be determined, and the temperature interval of its stability under the conditions of traditional thermoanalytical experiment with linear heating could not be fixed precisely.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

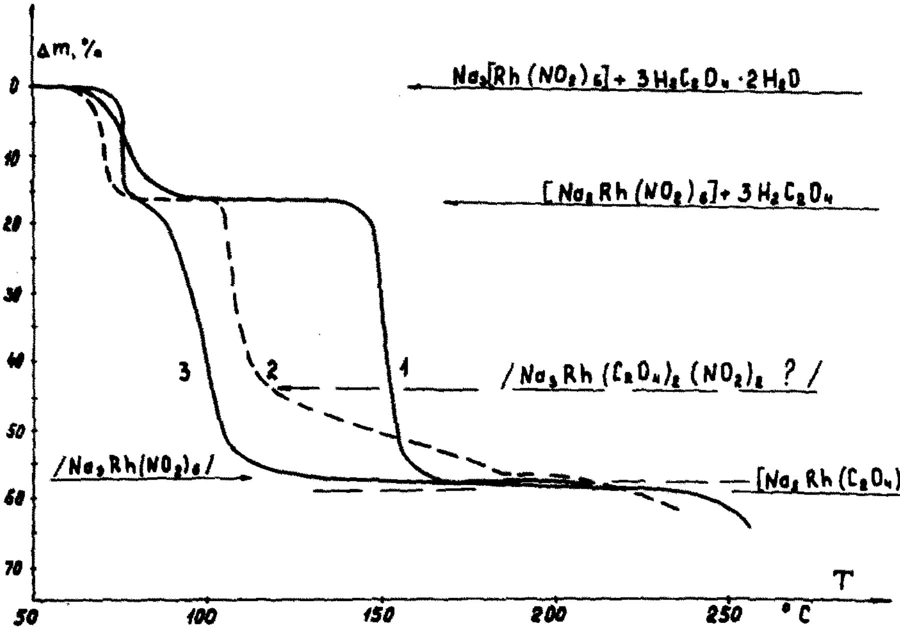

Fig. 1. The interaction of $Na_3[Rh(NO_2)_6]$ and $H_2C_2O_4 \cdot 2H_2O$ on heating: quasi-isothermal heating, 0.4 mg min^{-1}; sample mass, 89.6 mg rhodium complex + 75.6 mg $H_2C_2O_4 \cdot 2H_2O$: curve 1, the complex and the acid are decomposed in two different open crucibles; curve 2, the mixture of the complex and the acid is decomposed in an open crucible; curve 3, the mixture of the complex and the acid is decomposed in a labyrinth sample holder.

The interaction between $Na_3[Rh(NO_2)_6]$ and $H_2C_2O_4$ was investigated by quasi-isothermal and quasi-isobaric thermogravimetry [1] (Derivatograph Q-1500-D, MOM (Hungary)); $q = 0.4$ mg min^{-1}, in a self-generated atmosphere (Fig. 1).

After dehydration of the acid, the reaction in the mixture is clearly seen to occur before the decomposition of $H_2C_2O_4$ (90–110°C and 140°C respectively). In the open sample holder (where the pressure of the evolving gas is low, approx. 0.05 atm) the substitution reaction has no time to proceed to completion but is interrupted by the decomposition reaction of $H_2C_2O_4$.

However, the formation of the oxalate complex reaches practically 100% in a labyrinth sample holder. The exchange reaction is probably promoted under the high pressure of the evolving gas (approx. 1.0 atm), because it proceeds 20°C lower and is over before the start of the decomposition of $H_2C_2O_4$.

The kinetics of the substitution process were studied using a gas-flow reactor with a conductometric detector [2]; the sample had a mass of 10 mg, the helium flow rate was 100 cm^3 min^{-1} and the heating rate was 4°C min^{-1}. The integral method was used for calculation of the kinetic parame-

TABLE 1

Values of the kinetic parameters at different values of m in the equation of nucleation

m	E (kJ mol^{-1})	log A
3/4	60.7	5.2
1/2	127.7	14.0
2/3	82.9	8.1
1/4	194.7	22.7
1/3	172.1	19.8

ters. The selection of the kinetic equation was carried out by the linear function 1 g $G(\alpha)$ versus $1/T$ (computer program TA IB) [3,4].

Two variations of the experiment were done:

1. We investigated the chemical interaction in a mixture of the two fine grained substances, with $Na_3[Rh(NO_2)_6]:H_2C_2O_4 \cdot 2H_2O = 1:3.1$. In this case the best description of the reaction kinetics is the equation of nucleation [6]:

$$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^m$$

where $m = 1/4$, $1/3$, $1/2$ or $3/4$. The results are shown in Table 1.

The integral method does not make it possible to select a kinetic equation with a definite nucleation law, i.e. a definite value of m. Ozawa's method [5] was also used; here the linear function log ϕ_i versus $1/T$ is analysed, where ϕ_i is the heating rate and T_i is the temperature of reaching the definite transformation degree α_i. We chose heating rates of 3.0, 3.8, 4.2 and 7.2°C min^{-1} and $\phi_i = 10\%$, 30% and 50%. A value of $E = 216$ kJ mol^{-1} was calculated according to this approximate method. The closest value of E obtained from the equation of nucleation has $m = 1/4$.

Thus, $E = 185 \pm 17$ kJ mol^{-1} and log $A = 21.7 \pm 0.8$, as determined from five experiments with a confidence coefficient of 0.95.

2. The interaction in a mixture of $Na_3[Rh(NO_2)_6]$ and $H_2C_2O_4 \cdot 2H_2O$ with a large excess of $Na_3[Rh(NO_2)_6]$ (ratio 1:1.1 instead of 1:3) was investigated. In principle while studying solid–solid reactions, it is recommended that the relatively large grains of one substance be covered with a thin coating of a fine-grained second substance. It is impossible to use an excess of $H_2C_2O_4 \cdot 2H_2O$ because decomposition of the surplus acid will begin before the substitution reaction finishes: the gas evolution peaks are not separated. Therefore, we performed an experiment with an excess of $Na_3[Rh(NO_2)_6]$, the residue of which merely decomposes above 300°C at an appreciable rate.

The completely fine-grained complex was mixed with large grains of acid. In this case the reaction kinetics (of gas evolution) are best described by the equation of a shrinking sphere: $f(\alpha) = (1-\alpha)^{2/3}$, from which

$E = 178 \pm 12$ kJ mol^{-1} and log $A = 20.5 \pm 1.5$, the root-mean-square deviation being presented.

The kinetic parameters obtained in both variations of the experiment are in good agreement (within the limits of error). The probable kinetic equations describing the processes have a physical meaning: in the first case, it is the random nucleation on the contacts of small grains (of equal sizes) of the complex and the acid; in the second case, it is the reaction on the surface of the acid grains with adjoining layers of fine-grained complex, with the reaction penetrating deep into the grain.

Therefore it is reasonable to suggest that the synthesis reaction is the rate-limiting step.

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