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A kinetic investigation of the tris(4-morpholinecarbodithionato-*S*,*S*′)cobalt(III) complex formation by the intralattice and interlattice reactions

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Abstract

The kinetics of tris-(4-morpholinecarbodithionato-*S*,*S*′)cobalt(III) formation by the intralattice and interlattice reactions of hexaaminecobalt(III) cation with dithiocarbamato anion was investigated under isothermal conditions.

The intralattice reaction, conducted in the solid hexaaminecobalt(III) 4-morpholinecarbodithionate salt, proceeded well at temperatures of 50–80°C, conforming to the phase boundary R_n reaction mechanism ($E_a = 92.6$ kJ mol^{-1}, $A = 5.28 \times 10^9$ s^{-1}).

The interlattice reaction, conducted in the mixture of hexaaminecobalt(III) chloride and potassium 4-morpholinecarbodithionate powders, proceeded well at temperatures of 140–200°C. The effect of the particle size of the powders and of the powder packing pressure on the kinetic parameters were also investigated. In the first half of the reaction, the random nucleation F_1 mechanism seems to operate ($E_a = 200$–265 kJ mol^{-1}, $A = 8.6 \times 10^{18}$–3.6×10^{27} s^{-1}); later the diffusional mechanism prevails.

In addition, a fast initial process in the interlattice reaction has been discovered and investigated at lower temperatures (80–115°C). It conforms to the random nucleation F_1 reaction mechanism ($E_a = 63$ kJ mol^{-1}, $A = 1.6 \times 10^5$ s^{-1}).

INTRODUCTION

The solid-state chemistry of uncharged transition metal chelate complexes may be considered important because of their potential application in the synthesis of specific materials, such as metal films [1] and high-temperature superconductors [2]. For these purposes, the transition metals were mainly chelated with β-diketonates. However, our attention has focussed on the solid-state chemistry of the closely related dithioacidato chelating ligands. The unusually high solid-state reactivity of these ligands towards transition metals had been noted [3] and investigated by us in hexaamminecobalt(III) alkylxanthates [4].

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Investigating the reactivity of the more thermally stable dithiocarbamato chelating ligands towards transition metals, we conducted a variety of heterogeneous solid–solid reactions and we have been surprised to find that at moderately high temperatures, below 200°C, dithiocarbamate salts attacked transition metal complexes, oxides, minerals and alloys, producing chelate dithiocarbamato complexes. Because the obtained neutral complexes are completely extractable by organic solvents, this has provided a direct route for the preparation of the useful precursors for syntheses of specific materials containing these metals. However, for the optimization of the heterogeneous reactions involved, their mechanisms have to be understood.

Therefore, in the present work we investigated the kinetics of the solid-state reaction between a dithiocarbamato anion and hexaamminecobalt(III) cation. This reaction is very convenient because both interlattice and intralattice solid-state reactions can take place. Thus, for the interlattice reaction we selected a reaction system containing potassium 4-morpholinecarbodithionate (mdtc) and hexaamminecobalt-(III) chloride salts. For the intralattice reaction the hexaaminecobalt(III) 4-morpholinecarbodithionate salt ($[Co(NH_3)_6](mdtc)_3$) was selected. Both reactions should yield the same product: tris(4-morpholinecarbodithionato-*S*,*S*′)cobalt(III) complex ($[Co(mdtc)_3]$).

EXPERIMENTAL

Materials

Potassium 4-morpholinecarbodithionate was prepared according to the reported procedure [5], as was hexaamminecobalt(III) chloride [6]. In order to prepare a fine powder of hexaamminecobalt(III) chloride, this complex was dissolved in water and precipitated by a large quantity of ethanol. Both salts were thoroughly dried in an exsiccator over phosphorous pentoxide.

Hexaamminecobalt(III) 4-morpholinecarbodithionate was prepared by the reported procedure [3] and dried overnight at 0°C in an exsiccator over phosphorous pentoxide.

Interlattice reaction

The solid reactants, hexaaminecobalt(III) chloride and potassium 4-morpholinecarbodithionate were each separated (using the corresponding sieves) into the four particle size fractions 63–125 μm, 90–125 μm, 125–250 μm and >250 μm. The fractions were dried at 110°C in an oven. Dry solid reactants of the corresponding particle sizes were thoroughly mixed in the mole ratio 1:12 (20 mg of $[Co(NH_3)_6]Cl_3$ and 180 mg of

Kmdtc). The reaction mixture (≈200 mg) was then transferred into a 10 cm^3 test tube. In the experiments with pelleted samples, a packing pressure of 2×10^4 kPa was applied to the reaction mixture sample in a standard IR pelleting machine and the obtained pellet was placed in a test tube. For each kinetic experiment, 10 identically prepared samples in 10 test tubes were placed in an oil ultrathermostat. After being kept at constant temperature (±0.5°C) for selected times, pairs of test tubes were consecutively removed from the thermostat and then put in ice water to quench the reaction. Afterwards, their contents were treated several times with dry chloroform in order to extract the green $[Co(mdtc)_3]$ obtained. The extracts were poured into a 25 cm^3 volumetric flask and diluted with the necessary volume of chloroform. The concentrations of the obtained solutions were determined spectrophotometrically at 617 nm.

Intralattice reaction

For each kinetic experiment, 10 small, round glass vessels (1 cm^3) containing 25 mg of dry pulverized $[Co(NH_3)_6](mdtc)_3$ salt were placed in an oven at constant temperature (±0.5°C) under a flow of dry nitrogen. The subsequent procedure was as described for the interlattice reaction above.

Spectrophotometric determination

A Beckman DU-2 spectrophotometer was used for the spectrophotometric analysis. Beer–Lambert's law was checked at 617 nm.

RESULTS

Kinetic investigations of solid-state reactions have shown that the processes involved are generally complex [7, 8]. However, they can be interpreted by the following simple kinetic equation

$$g(\alpha) = kt, \tag{1}$$

where α is the degree of reaction completeness (the fraction of a sample reacted in time t) and k is the rate constant. Therefore, all the complexity of the reaction is described by the function $g(\alpha)$. This function is known for some well-understood reaction mechanisms, such as the random nucleation, phase boundary and diffusional mechanisms [7, 8]. Consequently, the first step in the analysis of our kinetic data was to determine which (if any) of the known $g(\alpha)$ functions could be applied to the investigated reactions. For this purpose, the measured α versus t data were subjected to the $g(\alpha)$ versus t linear regression analysis. The general criteria [9] for the selection of the best fitting $g(\alpha)$ function were applied.

Thus if for two, or more, $g(\alpha)$ functions, the linear regression coefficient (r) of the close values were obtained for N points, then Snedecor's test $(F = r^2(N-2)/(1-r^2))$ was applied.

Intralattice reaction

The intralattice reaction of the tris(4-morpholinecarbodithionato-S,S')cobalt(III) synthesis from the solid hexaamminecobalt(III) 4-morpholinecarbodithionate salt was observed to proceed well at slightly elevated temperatures (50–80°C). The reaction has the stoichiometry

$$[Co(NH_3)_6](mdtc)_3 \rightarrow [Co(mdtc)_3] + 6NH_3$$

because a complete conversion was observed (Fig. 1). The reaction is very much accelerated by a trace of water in an insufficiently dried sample. Furthermore, the moisture in the air at the relatively low temperature at which the reaction was conducted, caused similar acceleration. Therefore, the reaction was conducted in a stream of dry nitrogen.

At one temperature (70.5°C) the reaction was followed to completeness. The corresponding plot of the reaction completeness degree versus

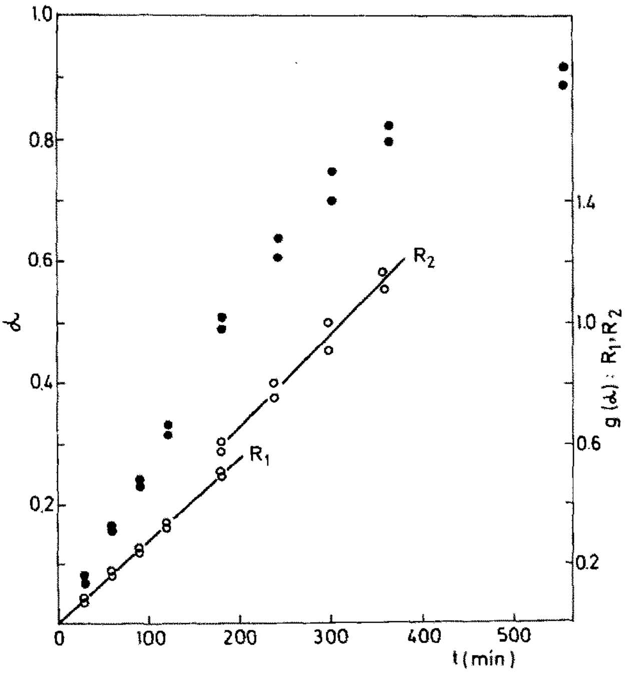


Fig. 1. Isothermal (70.5°C) conversion-time plot (●) of tris(4-morpholinecarbodithionato-S,S')cobalt)(III) in the solid hexaamminecobalt(III) 4-morpholinecarbodithionate salt. The linear plots (○) of the best-fitted $g(\alpha)$ functions, R_1 ($g(\alpha) = \alpha$, $r = 0.9987$, $F = 1150$) and R_2 ($g(\alpha) = [1-(1-\alpha)^{1/2}]$, $r = 0.9890$, $F = 134$), are also presented.

TABLE 1

Kinetic parameters of the intralattice reaction process ($0 < \alpha < 0.5$) of tris(4-morpholinecarbodithionato-*S,S′*)cobalt(III) synthesis in the solid hexaamminecobalt(III) 4-morpholinecarbodithionate, obtained by applying the F_1 phase-boundary model ($g(\alpha) = \alpha$) reaction chemistry

T (°C)	$k \times 10^5$ (s^{-1})	(r)	Activation parameters
50.3	0.59	(0.9972)	
60.5	1.55	(0.9903)	$E_a = 92.6$ kJ mol^{-1}
70.5	4.58	(0.9989)	$A = 5.28 \times 10^9$ s^{-1}
80.0	10.7	(0.9989)	($r = 0.9992$)

time is presented in Fig. 1. The best fitting $g(\alpha)$ functions were found to be those describing the phase boundary reaction mechanisms. The first half of the reaction ($0 < \alpha < 0.5$) proceeded according to the phase boundary reaction model of R_1 type ($g(\alpha) = \alpha$), whereas later ($0.5 < \alpha < 0.8$) the reaction is better described by the R_2 model ($g(\alpha) = 2[1 - (1 - \alpha)^{1/2}]$). The rate constants calculated according to the two models do not differ appreciably. However, the statistical criteria of the $g(\alpha)$ fitting gave high confidence for only the first half of the reaction, where data dissipation is small. Therefore, the temperature dependence of the rate constant was followed for only the first half of the reaction. The obtained rate constants and activation parameters are presented in Table 1.

Interlattice reaction

The interlattice reaction of the tris(4-morpholinecarbodithionato-*S,S′*)cobalt(III) synthesis in the mixture of hexaamminecobalt(III) chloride and potassium 4-morpholinecarbodithionate powders was observed to proceed well at relatively low temperatures (140–200°C). This solid–solid heterogeneous reaction exhibited the stoichiometry

$$[Co(NH_3)_6]Cl_3 + 3Kmdtc \rightarrow [Co(mdtc)_3] + 3KCl + 6NH_3$$

because complete transformation of hexaamminecobalt(III) complex into tris(dithiocarbamato)cobalt(III) complex was observed.

At one temperature (195°C), and for one particle size fraction (125–250 μm) of the reacting powders, the reaction was followed to completeness. The corresponding plot of the reaction completeness degree versus time is presented in Fig. 2. The $g(\alpha)$ function which produced the best fitting of the data in the first half of the reaction is $g(\alpha) = -\ln(1 - \alpha)$, that is one describing the random nucleation reaction model of F_1 type. However, this process seems to take place only after some small part of the reaction is completed ($\alpha_0 \approx 0.1$). In the second half

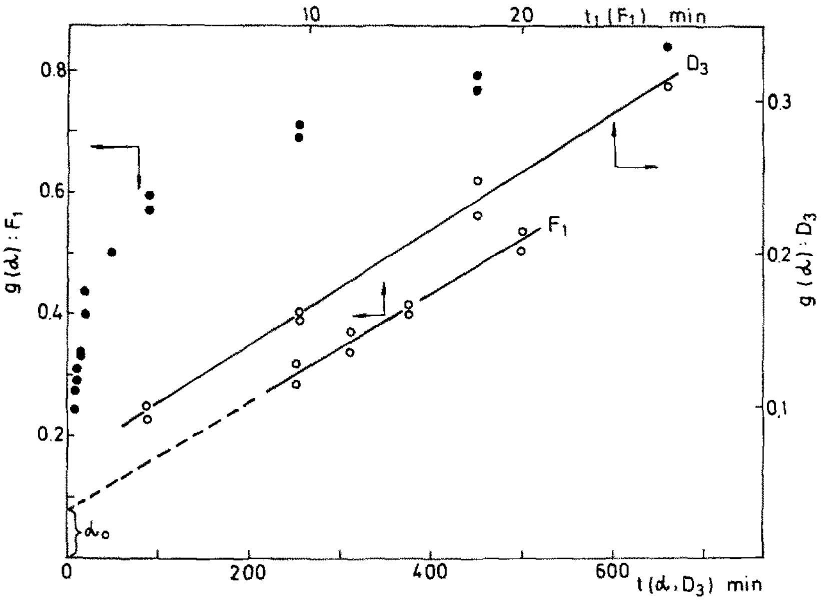


Fig. 2. Isothermal (195°C) conversion-time plot (●) of the interlattice synthesis of tris(4-morphlinecarbodithionato-*S*,*S*′)cobalt(III) in the mixture (1:12 mole ratio) of hexaamminecobalt(III)chloride and potassium 4-morpholinecarbodithionate powders (125–250 μm). The linear plots (○) of the best-fitted $g(\alpha)$ functions F_1 ($g(\alpha) = -\ln(1-\alpha)$, $r = 0.98$, $F = 140$) and D_3 ($g(\alpha) = 1.5[1-(1-\alpha)^{1/3}]^2$, $r = 0.9924$, $F = 325$), are also presented.

of the reaction, a diffusional mechanism prevails, because the best-fitted function is of D_3 type ($g(\alpha) = 1.5[1-(1-\alpha)^{1/3}]$). The temperature dependence of the rate constant was investigated for only the first half of the reaction, applying the F_1 reaction mechanism model. The investigation was carried out for the four fractions of the powder particle sizes. The obtained rate constants and activation parameters are given in Table 2. From these results, it can be seen that the reaction is faster for the mixture of powders having smaller particles. The reaction is accelerated about ten times in going from above 250 μm down to 63–90 μm particle size fractions. In all cases the existence of a fast initial reaction was established (α_0). However, the extent of this fast reaction is rapidly diminished with increasing powder particle size.

In the subsequent investigation, the reacting powders of the one particle size fraction (90–125 μm) were pressed into pellets under pressure of 2×10^4 kPa. The reaction was followed to completeness at one temperature (165°C). The corresponding plot of the reaction completeness degree versus time is presented in Fig. 3A. For the first half of the reaction, two $g(\alpha)$ functions produced equally good fittings of the experimental data. As with the unpressed powders, the random nucleation F_1 mechanism could be well applied. The other possibility is

TABLE 2

Kinetic parameters of the interlattice reaction process ($\alpha_0 < \alpha < 0.5$) of the tris(4-morpholinecarbodithionato-*S*,*S*′)cobalt(III) synthesis in the mixture (1:12 mole ratio) of hexaamminecobalt(III) chloride and potassium 4-morpholinecarbodithionate powders of selected particle size fractions, with or without applied packing pressure (2×10^4 kPa, pellets)

T (°C)	Model	$k \times 10^5$ (s^{-1})	α_0	(r)	Activation parameters
63–90 μm particle size fraction					
165	F_1	1.59	0.10	(0.9981)	$E_a = 203$ kJ mol^{-1}
175		5.45	0.10	(0.9977)	$A = 2.43 \times 10^9\ s^{-1}$
185		18.1	0.12	(0.9900)	($r = 0.9998$)
90–125 μm particle size fraction					
165	F_1	1.31	0.08	(0.9915)	$E_a = 200$ kJ mol^{-1}
175		4.38	0.07	(0.9968)	$A = 8.60 \times 10^{18}\ s^{-1}$
185		14.4	0.10	(0.9900)	($r = 0.9999$)
125–250 μm particle size fraction					
165	F_1	1.01	0.09	(0.9914)	$E_a = 205$ kJ mol^{-1}
176		4.70	0.08	(0.9940)	$A = 3.06 \times 10^{19}\ s^{-1}$
185		11.0	0.08	(0.9900)	($r = 0.9980$)
195		40.0	0.07	(0.990)	
>250 μm particle size fraction					
165	F_1	0.177	0.03	(0.9945)	$E_a = 225$ kJ mol^{-1}
175		0.525	0.03	(0.9932)	$A = 1.02 \times 10^{21}\ s^{-1}$
185		2.67	0.02	(0.9950)	($r = 0.9973$)
195		9.13	0.03	(0.9930)	
Pellets, 90–125 μm particle size fraction					
145	F_1	0.280	0.17	(0.9973)	$E_a = 265$ kJ mol^{-1}
154		1.51	0.19	(0.9967)	$A = 3.65 \times 10^{27}\ s^{-1}$
165		9.1	0.2	(0.990)	($r = 0.9994$)
145	D_4	0.0250	0.17	(0.9970)	$E_a = 243$ kJ mol^{-1}
154		0.140	0.18	(0.9970)	$A = 5.61 \times 10^{23}\ s^{-1}$
165		0.613	0.2	(0.990)	($r = 9961$)

application of the diffusional mechanism of D_4 type. In the second half of the reaction, the diffusional D_4 mechanism ($g(\alpha) = 1.5[1 - 2/3\alpha - (1 - \alpha)^{2/3}]$) prevails (Fig. 4A). The temperature dependence of the rate constant was investigated for only the first half of the reaction.

The rate constants calculated according to the two processes differ greatly (Table 2). A comparison of the rate constants of the unpressed and pressed reaction mixture, assuming the F_1 mechanism, indicates a ten-fold acceleration of the reaction in the pelleted samples. Another interesting observation is that a fast initial reaction is more important in the pellets ($\alpha_0 \approx 0.2$). This makes it possible to investigate this fast initial reaction, although at a much lower temperature so that the reaction is slow enough for our experimental procedure. Accordingly, the reaction

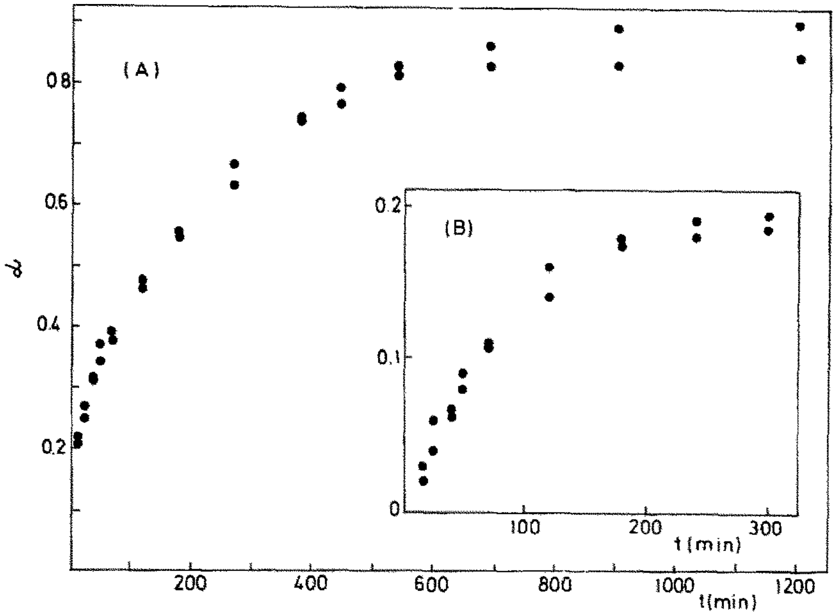


Fig. 3. Isothermal conversion-time plots (●) of the slower (165°C) (A) and faster (90°C) (B) processes of the interlattice synthesis of tris(4-morpholinecarbodithionato-*S,S'*)cobalt(III) in the pelleted mixture (1:12 mole ratio) of hexaamminecobalt(III) chloride and potassium 4-morpholinecarbodithionate powders (90–125 μm).

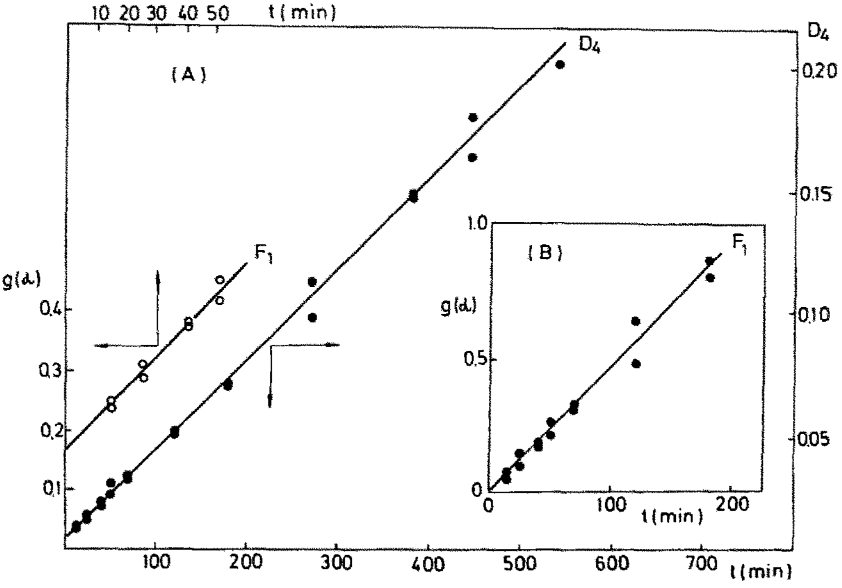


Fig. 4. Linear plot of the best-fitted $g(\alpha)$ functions, F_1 ($g(\alpha) = -\ln(1-\alpha)$), $r = 0.990$, $F = 294$) and D_4 ($g(\alpha) = 1.5[1 - 2\alpha/3 - (1-\alpha)^{2/3}]$), $r = 0.9978$, $F = 4312$, of the isothermal reaction at 165°C (A), and the best-fitted $g(\alpha)$ function F_1 ($g(\alpha) = -\ln(1 - \alpha/\alpha_0)$, $\alpha_0 = 0.21$, $r = 0.992$, $F = 800$) of the isothermal reaction at 90°C (B).

TABLE 3

Kinetic parameters of the interlattice reaction fast initial process ($0 < \alpha < 0.2$) of the tris(4-morpholinecarbodithionato-*S*,*S'*)cobalt(III) synthesis in a pelleted mixture (1:12 mole ratio) of hexaamminecobalt(III) chloride and potassium 4-morpholinecarbodithionate powders (125–250 μm), according to the F_1 reaction mechanism

T (°C)	$k \times 10^4$ (s^{-1})	(r)	Activation parameters
90	1.76	(0.992)	
95	2.46	(0.997)	$E_a = 62.1$ kJ mol^{-1}
105	3.61	(0.995)	$A = 1.55 \times 10^5$ s^{-1}
115	70	(0.990)	($r = 0.993$)

was studied in the temperature range 90–115°C. At one temperature (90°C), the reaction was followed to completeness (Fig. 3B). The $g(\alpha)$ function producing the best fitting of the data was that describing the random nucleation mechanism of the F_1 type (Fig. 4B). The temperature dependence of the calculated rate constant and activation parameters are given in Table 3. A very much lower activation energy and higher rate constants were obtained for this process.

DISCUSSION

The reaction of tris(4-morpholinecarbodithionato-*S*,*S'*)cobalt(III) synthesis that we have investigated in all the studied case is formally the same

$$[Co(NH_3)_6]^{3+} + 3dtc^- = [Co(dtc)_3] + 6NH_3$$

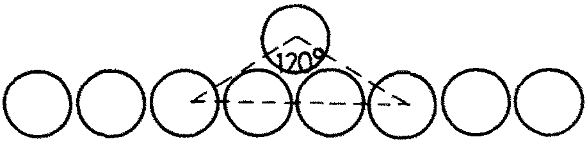
The reacting ions are situated in the same lattice (intralattice reaction) or in separate lattices (interlattice reaction). In the case of interlattice reactions, particles containing the $[Co(NH_3)_6]^{3+}$ ions were most probably completely surrounded by the particles containing dtc^- ions, because the mole ratio of the corresponding reacting salts was 1:12.

The kinetic investigation of the inter- and intralattice synthesis of tris(4-morpholinecarbodithionato-*S*,*S'*)cobalt(III) complex has produced some results that are not unexpected. Thus, the intralattice reaction has been found to proceed well at considerably lower temperatures than the interlattice reaction. At the temperature of interlattice reaction, the intralattice reaction is calculated to have a few thousand times larger a reaction rate. The mechanism of the intralattice reaction, established to be in accordance with the phase boundary R_n mechanism, is the same as that of hexaaminecobalt(III) chloride decomposition [9]. This may be expected if the transition state of NH_3 by dithiocarbamato ligand substitution is of dissociative type, as is known to be the case in the ligand substitution reaction of cobalt(III) complexes in solution [10].

For the interlattice reaction, the considerable acceleration of the reaction when the reacting powders are of smaller particle sizes, as well as when high packing pressure is applied, was to be expected because good contact between the reacting particles is essential for the reaction. The random nucleation mechanism of the early stage of the reaction agrees with the expectation that contacting areas of the particles became reaction nuclei. In the later stage, the diffusional mechanism predominates.

An unexpected result is the discovery of the fast initial process in the interlattice reaction. The extent of this process depends critically on the contact between reacting particles. The process was almost absent when the reaction was conducted between large particles, becoming more important with decreasing particle size. Upon application of the packing pressure, the process reached about 20% of the reaction completeness. Furthermore, this was the process exhibiting the lowest activation energy and the lowest preexponential factor. This indicates very strongly that the fast initial reaction occurs between a loosely bound surface species. An estimation of the residual crystal lattice energy of an isolated ion on a surface (Scheme 1) gives one third of the crystal lattice energy. The activation energy for the ligand substitution reaction between hexaamminecobalt(III) chloride and sodium dithiocarbamate must be connected with the crystal lattice energies, primarily through the activation energy for diffusion [8]; thus the observed activation energy of the reaction between the surface species (≈ 60 kJ mol^{-1}) is found to be one third of the activation energy between the bulk species (≈ 200 kJ mol^{-1}). It is interesting that the intralattice reaction exhibits an activation energy (92.6 kJ mol^{-1}) that is roughly half the activation energy of the main interlattice reaction.

The spread of values for the activation energies of the interlattice reaction processes is large, from 62 to 260 kJ mol^{-1}. Yet the activation parameters of the interlattice processes are found to be in a remarkably good isokinetic relationship (Fig. 4). This could be considered [11] to be a consequence of the fact that one and the same reaction took place in all the interlattice processes. In comparison (Fig. 5), the intralattice reaction activation parameters deviate from the isokinetic relationship in a sense



Scheme 1.

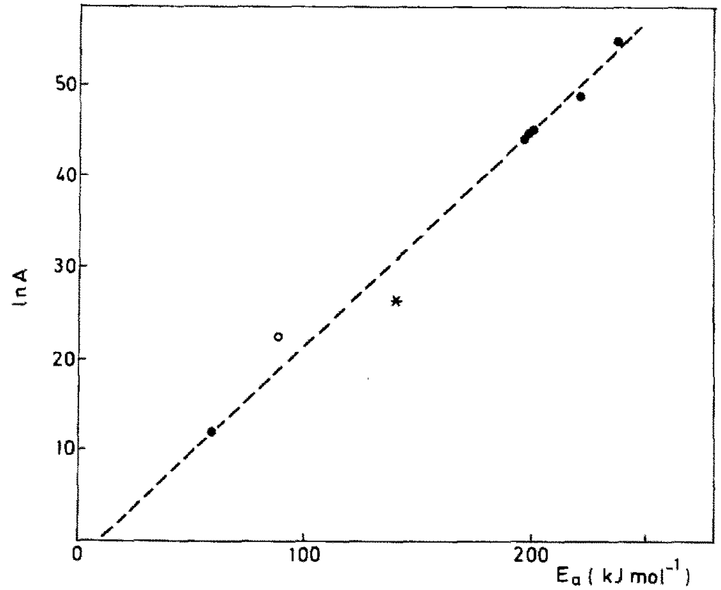


Fig. 5. Isokinetic relationship of the activation parameters of the interlattice reaction processes (●) of tris(4-morpholinecarbodithionate-*S*,*S*′)cobalt(III) synthesis (T_{iso} = 438°C, $\ln A_0 = -2.14$, $r = 0.9995$). Corresponding data of the intralattice reaction process (○) and hexaamminecobalt(III) chloride decomposition reaction (*, ref. 9) are presented for comparison.

that the activation energy versus pre-exponential factor is more favourable. In contrast, the activation energy versus pre-exponential factor is less favourable in the reaction of hexaamminecobalt(III) decomposition. As a consequence, the interlattice reaction proceeds well at considerably lower temperatures than the decomposition of hexaaminecobalt(III) salt, although, overall, it has the higher activation energy.

Therefore, the requirement for the low-temperature interlattice reaction, a seemingly difficult process, is the favourable pre-exponential factor. Obviously, the process that we have studied could only be easily accomplished at a gas–solid boundary (escape of ammonia) and the supply of reacting ions from a surface contact is very convenient in the interlattice reaction. The fast initial interlattice reaction, presumably due to a loosely bound surface species, is even comparable in efficiency to the intralattice reaction. This indicates that a low-temperature tribochemical method of interlattice synthesis of metal dithiocarbamates may be the most convenient one.

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