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The effect of anions on the thermal decomposition of the hexaamminecobalt(III) cation

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Abstract

Thermal decomposition reactions of hexaamminecobalt(III) chloride in the presence of anion salts KY ($Y = Cl^-$, Br^-, I^-, CN^-, SCN^-, OH^-) are investigated, mainly by gas chromatographic, infrared spectroscopic and X-ray diffraction methods. Kinetic parameters are calculated. The deammine activation energy is found to vary with the different anions (Y), increasing in the order $OH^- < SCN^- < I^- < CN^-$, $Br^- < Cl^-$. Possible mechanisms and factors affecting the results are discussed.

INTRODUCTION

Early in 1963, Wendlandt [1] reported the thermal decomposition of $[Co(NH_3)_6]Cl_3$ in a helium atmosphere by DTA. The dissociation stoichiometry was given as

$$6[Co(NH_3)_6]Cl_3 \rightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 28NH_3 \qquad (1)$$

The identical result was obtained by using techniques of thermogravimetry, evolved gas analysis (EGA) and mass spectrometric analysis [2–7] although the types of intermediate compounds formed were different [2,4,7]. A calorimetric study was reported by Tsuchiya et al. [8]. An electrical conductivity (EC) study was carried out by Wendlandt [9] and a high-frequency method was used by Ust-Kachkintsev et al. [10]. An electron microscopy study of $[Co(NH_3)_6]Cl_3$ crystals at 170–220°C showed that the initial decomposition stages are topotactic [11]. Ingier-Stocka [12] further calculated the activation energy of the dissociation process of the complex.

A few papers have reported the solid state reaction of $[Co(NH_3)_6]Cl_3$ with other compounds. Flora [13] studied mixtures of $[Co(NH_3)_6]Cl_3$ with nitrates of all the alkali metals and NH_4^+ by a derivatographic method.

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Lazarenko et al. [14] reported the thermal decomposition of $[Co(NH_3)_6]Cl_3$ in the presence of powdered Zn or Sn.

In recent years, the solid state reactions of multi-component systems have been investigated in this laboratory [15a]. The effects of anions (Cl^-, Br^-, I^-) on the decomposition of $[M(NH_3)_5(H_2O)]X_3$ (M = Co(III), Cr(III)) have been studied previously [15b].

The present work will describe gas chromatographic studies of the solid state reactions between $[Co(NH_3)_6]Cl_3$ and potassium salts KY ($Y = Cl^-$, Br^-, I^-, CN^-, SCN^-, OH^-) in a hydrogen atmosphere. Kinetic parameters of deammination reactions are calculated. The properties of added anions are found to affect the stability of $[Co(NH_3)_6]Cl_3$ appreciably.

EXPERIMENTAL

Materials

Hexaamminecobalt(III) chloride[16] and cobalt(II) thiocyanate [17] were prepared according to the literature. Potassium salts KY ($Y = Cl^-$, Br^-, I^-, CN^-, SCN^-, OH^-) were all AnalaR grade and were dried by P_2O_5.

Samples were obtained by mixing $[Co(NH_3)_6]Cl_3$ with KY at 1:6 mole ratio and grinding in a mortar in a dry glove bag.

Apparatus

The apparatus used was constructed in this laboratory [18]. The conditions were similar to those described previously [19]. A furnace heating rate of 4.5°C min^{-1} was employed. The gaseous products evolved during the pyrolysis procedure were quickly swept into the chromatographic separation column at intervals of 20°C by turning a stopcock. The various gas chromatographic patterns for the evolved gases could be obtained as a function of temperature.

Infrared spectra

Infrared spectra were recorded using a Nicolet-FT-IR 170 sx instrument.

X-ray diffraction

X-ray diffractograms were obtained using a Shimadzu Model XD-3A X-ray diffractometer with a copper target.

RESULTS AND DISCUSSION

Figure 1 gives the evolved gas analysis (EGA) curves of hexaamminecobalt(III) chloride in the range 40–400°C in a hydrogen atmosphere,

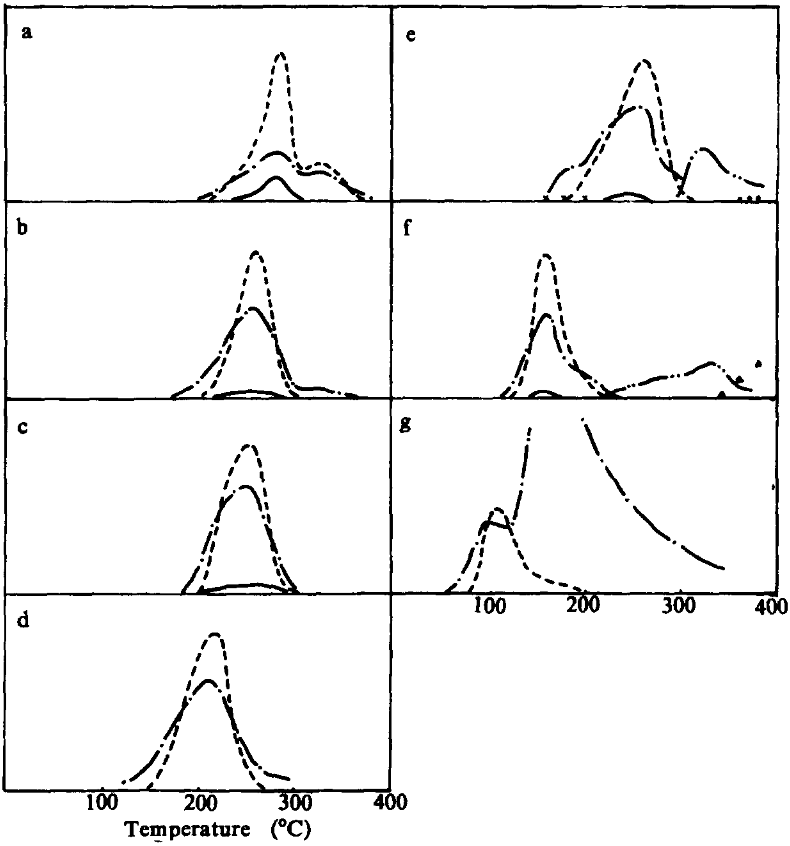

Fig. 1. EGA curves of $[Co(NH_3)_6]Cl_3 + KY$ systems in a hydrogen atmosphere. (a) $[Co(NH_3)_6]Cl_3$; (b) $[Co(NH_3)_6]Cl_3 + KCl$; (c) $[Co(NH_3)_6]Cl_3 + KBr$; (d) $[Co(NH_3)_6]Cl_3 + KI$; (e) $[Co(NH_3)_6]Cl_3 + KCN$; (f) $[Co(NH_3)_6]Cl_3 + KSCN$; (g) $[Co(NH_3)_6]Cl_3 + KOH$. --- NH_3; —— N_2; × × × × × $(CN)_2$; ······ CH_4; -▲- H_2S; -··- HCN; -·- HCl (a, b, e, f), HCl+HBr (c), HI (d), H_2O (g).

both for the pure salt and with an anion added. This shows that the evolution of ammonia from the pure complex $[Co(NH_3)_6]Cl_3$ begins at about 200°C, the maximum intensity for gas evolution being obtained at 280°C, followed by a second broad peak in the 300–360°C temperature range. The results are in agreement with those reported by Wendlandt [1] and by Watt [2], but the first and second peaks are somewhat higher than those reported by Onodera [6], which may result from the faster heating rate here compared with the 1°C min^{-1} used by Onodera.

The stoichiometry of the thermal decomposition of this compound agrees with that previously proposed by Wendlandt and Watt as given in eqn. (1).

$[Co(NH_3)_6]Cl_3 + KY (Y = Cl^-, Br^-, I^-)$

With the addition of KCl or KBr, the EGA curves (Fig. 1b, 1c) show that the evolution of ammonia begins at a about 200°C; the corresponding maximum intensities, which are found at 260°C, are somewhat lower than that of the pure compound. The amount of HX (X = Cl, Br) increases compared with that for the pure compound. This indicates that the existence of KCl or KBr does not affect the initial reaction of the complex. With the continuing evolution of ammonia, more and more crystal defects are produced. The excess anions in the system could then substitute into the crystal lattice, and this would have an effect on the further decomposition reaction, decreasing the peak maxima.

If $[Co(NH_3)_6]Cl_3$ was mixed with KI, the evolution of ammonia began at about 140°C (Fig. 1d); the corresponding peak temperature was 220°C, which is 60°C lower than that of the pure complex and with no N_2 appearing in the EGA curve. This could be interpreted as resulting from the redox property of the reactants.

As has been reported [20], $[Co(NH_3)_6]Cl_3$ in the $^1A_{1g}(Oh)$ ground state experiences a one electron reduction to the corresponding Co(II) complex in the $^4T_{1g}(Oh)$ state with a standard redox potential, $E°_{III/II} = 0.11$ [19]. The complex could be excited to the $^1T_{1g}(Oh)$ state. Hence, a standard redox potential could be obtained or the couple of the cobalt(III) complex in the $^1T_{1g}(Oh)$ state/the cobalt(II) complex in the $^4T_{1g}(Oh)$ state, $E°_{III/II} = 2.71$ [19].

As we know, I^- is a good reducing agent with a standard redox potential, $E^\circ_{I_2/I^-} = 0.53$. When $[Co(NH_3)_6]Cl_3$ is heated to a certain temperature, some molecules should acquire enough energy to transfer to the excited state, increasing the redox potential of Co(III). The electrons transferring from I^- to Co(III) make the complex decompose at a lower temperature.

Simmons and Wendlandt [7] proposed that, for cobalt(III) complexes containing iodide, a reduction of the cobalt ion obviously had taken place during the thermal decomposition process. The reducing agent could be co-ordinated ammonia, co-ordinated iodide ion or ionic iodide ion.

In the present work, with excess KI present, Co(III) would be reduced to Co(II) by iodide ion only. The green product was probably CoI_2. This reaction could be described as

$$2[Co(NH_3)_6]Cl_3 + 6KI \rightarrow 2CoI_2 + 12NH_3 + 6KCl + I_2$$

$$I_2 + H_2 \rightarrow 2HI$$

If the reducing agent was powdered Zn or Sn, Lazarenko et al. [14] found that the decomposition rate of $[Co(NH_3)_6]Cl_3$ increased and the decomposition temperature decreased, which further indicates that the reducing agents play an important role in the decomposition process of the complex.

[Co(NH$_3$)$_6$]Cl$_3$ + KCN

The EGA curve for the [Co(NH$_3$)$_6$]Cl$_3$ and KCN system (Fig. 1e) shows that the evolution of ammonia began at about 180°C, the maximum intensity for gas evolution appearing at 260°C, which is slightly lower than that for the pure complex. Above 300°C the deammine reaction is complete and HCN and CH$_4$ are produced. This would appear to indicate that the solid reaction takes place in two steps. Firstly, the complex decomposes to give the intermediate by CN$^-$ entering into the inner coordination sphere. Then this intermediate decomposes in the second step.

Figure 2(b) is the IR spectrum of [Co(NH$_3$)$_6$]Cl$_3$ and KCN on heating to 300°C. It can be clearly observed that the characteristic vibration bands of co-ordinated NH$_3$ disappear. The sharp peaks at 2175 and 453 cm^{-1} show the existence of Co(CN)$_2$·xH$_2$O [21], and bands at 2129 and 417 cm^{-1} indicate a small quantity of K$_3$[Co(CN)$_6$] [19] appearing in the solid product. The absorption band at 2084 cm^{-1} shows the presence of unre-

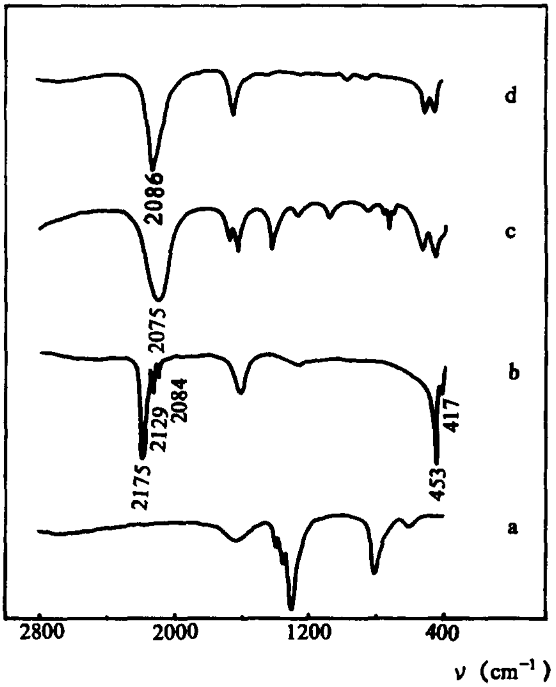

Fig. 2. Infrared spectra: (a) [Co(NH$_3$)$_6$]Cl$_3$; (b) 300°C, [Co(NH$_3$)$_6$]Cl$_3$ + KCN; (c) 200°C, [Co(NH$_3$)$_6$]Cl$_3$ + KSCN; (d) Co(NCS)$_2$.

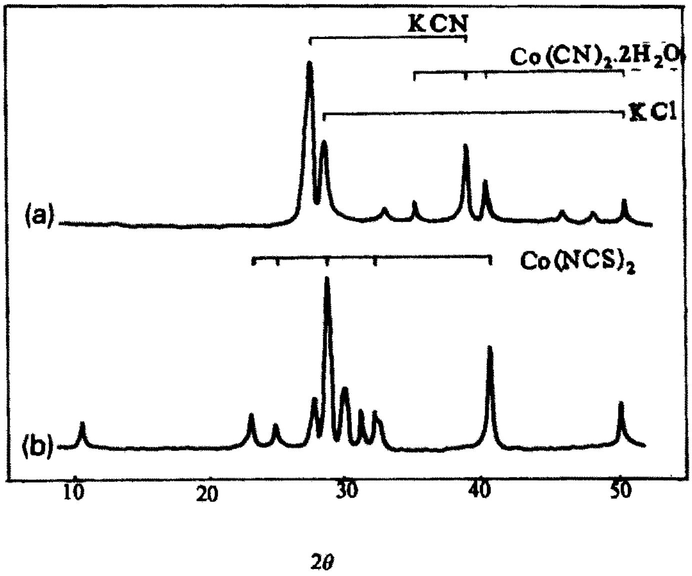

Fig. 3. XRD results for solid products in a hydrogen atmosphere: (a) 300°C, $[Co(NH_3)_6]Cl_3 + KCN$; (b) 200°C, $[Co(NH_3)_6]Cl_3 + KSCN$.

acted KCN [19]. This is further proved by XRD (as shown in Fig. 3a), which indicates the existence of $Co(CN)_2 \cdot 2H_2O$, KCN and KCl. The reaction is

$$6[Co(NH_3)_6]Cl_3 + 12KCN \rightarrow$$

$$6Co(CN)_2 + 28NH_3 + 6NH_4Cl + N_2 + 12KCl$$

$$[Co(NH_3)_6]Cl_3 + 6KCN \rightarrow K_3[Co(CN)_6] + 3KCl + 6NH_3$$

The $Co(CN)_2$ can easily absorb water vapor to form $Co(CN)_2 \cdot xH_2O$.

$[Co(NH_3)_6]Cl_3 + KSCN$

When $[Co(NH_3)_6]Cl_3$ was mixed with KSCN, the EGA curve (see Fig. 1f) indicates that the evolution of ammonia began at about 120°C, and the corresponding maximum was 160°C, which is 120°C lower than that of the pure complex. This noticeable effect may be concerned with the thermal phase transition of KSCN occurring at 140°C. When the temperature approaches 140°C, the out-of-plane torsional oscillation and the flipping motion of thiocyanate ions will disappear completely [22]. During this process, a large number of lattice vacancies may be formed, and any short range ordering interactions are likely to be weakened [23], which might accelerate the decomposition reaction at a lower temperature. We have studied the solid reactions between KSCN and several other Co(III)–ammine complexes. The corresponding peak temperatures of ammonia are all at about 140°C. This further indicates the important role of the phase transition of KSCN.

Figure 1f also shows that the $[Co(NH_3)_6]Cl_3$ had decomposed almost completely at about 220°C. Above that temperature, HCN and H_2S are produced, indicating the decomposition of the intermediate.

The IR spectrum of the solid product formed by heating the mixture at 200°C is shown in Fig. 2c. The broad absorption band appearing at about 2075 cm^{-1} belongs to the antisymmetric stretching vibration of NCS, indicating the existence of $Co(NCS)_2$ (2086 cm^{-1}) and $[Co(NCS)_4]^{2-}$ (2075 cm^{-1}) [24]. The corresponding XRD result shows the presence of $Co(NCS)_2$. The reaction is

$$6[Co(NH_3)_6]Cl_3 + 12KSCN \rightarrow$$
$$6Co(NCS)_2 + 6NH_4Cl + 28NH_3 + N_2 + 12KCl$$
$$Co(NCS)_2 + 2KSCN \rightarrow K_2[Co(NCS)_4]$$

$[Co(NH_3)_6]Cl_3$ + KOH

The pronounced effect of OH^- on the decomposition of the complex can be seen in Fig. 1g. The evolution of ammonia began at 80°C; the corresponding maximum was at 110°C, 170°C lower than that of pure complex. The effect is probably due to the strong hydrogen-bond interaction between OH^- and NH_3, which weakens the Co–NH_3 bond, so that it breaks easily on heating. Another reason is that OH^- is a stronger Lewis base than NH_3. In this base environment, hydroxide can take the place of ammonia and expel it from the system, thus facilitating the solid reaction. The reaction can be described as

$$6[Co(NH_3)_6]Cl_3 + 18KOH \rightarrow 6CoO + 34NH_3 + N_2 + 18KCl + 12H_2O$$
$$2[Co(NH_3)_6]Cl_3 + 6KOH \rightarrow Co_2O_3 + 12NH_3 + 6KCl + 3H_2O$$
$$Co_2O_3 + H_2 \rightarrow 2CoO + H_2O$$

Kinetic parameters

The kinetic parameters are determined on the basis of the kinetic relation

$$g(\alpha) = \int_{T_1}^{T_2} k_0 \exp(-E_a/RT)\,dT$$

Solutions of the equation are resolved by the widely employed approximation of Coats and Redfern (see ref. 25) to give the expression as

$$\ln(g(\alpha)/T^2) = \ln(AR\beta^{-1}E^{-1}) - E/RT$$

TABLE 1

Kinetic parameters calculated for the solid state deammine reactions

Sample	Physical mechanism	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS J mol^{-1} K^{-1})	Correlation coefficient
$[Co(NH_3)_6]Cl_3$	F1	129	124	16	0.993560
$[Co(NH_3)_6]Cl_3 + KCl$	F1	127	118	10	0.990364
$[Co(NH_3)_6]Cl_3 + KBr$	F1	105	96	−26	0.991319
$[Co(NH_3)_6]Cl_3 + KCN$	F1	107	98	−23	0.991988
$[Co(NH_3)_6]Cl_3 + KI$	F1	90	87	−37	0.964540
$[Co(NH_3)_6]Cl_3 + KSCN$	F1	78	71	−49	0.948095
$[Co(NH_3)_6]Cl_3 + KOH$	F1	44	42	−105	0.922509

where α is the fraction decomposed, with A being the frequency factor, β the heating rate and E the activation energy. The expression $g(\alpha)$ depends on the physical mechanism of the solid state reaction reported in the literature [25]. The kinetic parameters obtained are given in Table 1 with the functions which give the best fits for the above systems.

It is interesting to note that the function F1 based on nucleation and one-dimensional growth gives the best fits. The deammine activation energy values increase with different added anions in the order OH^- (44 kJ mol^{-1}) < SCN^- (78 kJ mol^{-1}) < I^- (90 kJ mol^{-1}) < CN^- (107 kJ mol^{-1}), Br^- (105 kJ mol^{-1}) < Cl^- (127 kJ mol^{-1}).

According to Laidler [26], when a discontinuous product phase occurs, the rate-determining step may be chemical process occurring at the phase boundary: that is, the breaking and reforming of bonds at the interface. When material transport is the rate-controlling process, the reaction is diffusion controlled.

For the phase boundary controlled nuclei growth (F1), the anion effects include contributions from the donacity of the added anions, for halides in the order $I^- > Br^- > Cl^-$, which shows the same order of anion effects on activation energies.

Factors affecting the solid reactions

To summarize all the above results, the effects of added ions on the decomposition of $[Co(NH_3)_6]Cl_3$ could be deduced as below.

Co-ordination ability

For a reagent such as CN^-, the solid product would be changed by its strong co-ordination ability, with slight effect on the mechanism of the decomposition.

Redox property

By the existence of reducing agents (KI, Zn and Sn, for example), the Co(III) ion in $[Co(NH_3)_6]Cl_3$ is reduced to cobalt(II) by means of an electron transfer from them to form the thermally unstable $[Co(NH_3)_6]Cl_2$, which immediately dissociates, decreasing the decomposition activation energy.

Phase transition

KSCN has a lower transition temperature (140°C) than the true halides. Near this temperature, the solid state reaction takes place easily because numerous defects are produced and short range ordering interactions are weakened. Reactions of KSCN with other cobalt–ammine complexes lead to the same conclusion.

Role of OH^-

The strong H-bond interaction of OH^- with ligand NH_3 greatly decreases the stability of $[Co(NH_3)_6]Cl_3$. On the other hand, as a strong Lewis base, OH^- makes NH_3 evolve more easily from the inner co-ordination sphere. Further research on the effects of KSCN and KOH on the reactions of co-ordination compounds is in progress.

REFERENCES

1 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 545.
2 G.W. Watt, Inorg. Chem., 3 (1964) 325.
3 N. Tanaka and M. Nanjo, Bull. Chem. Soc. Jpn., 37 (1964) 1330.
4 L.W. Collins, W.W. Wendlandt and E.K. Gibson, Thermochim. Acta, 8 (1974) 123.
5 E.V. Boldyreva and N.Z. Lyakhov, Mater. Sci. Monogr., 28B (1985) 649.
6 S. Onodera, Bull. Chem. Soc. Jpn., 50 (1977) 123.
7 E.L. Simmons and W.W. Wendlandt, J. Inorg. Nucl. Chem., 28 (1966) 2187.
8 R. Tsuchiya, A. Uehara and T. Nakayama, Bull. Chem. Soc. Jpn., 56 (1983) 3294.
9 W.W. Wendlandt, Thermochim. Acta, 37 (1980) 89.
10 V.F. Ust-Kachkintsev, F.R. Verzhbitskii and T.M. Donskikh, Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk., 4 (1974) 42; Chem. Abstr., 66:7985c.
11 E.V. Boldyreva and N.Z. Lyakhov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 2 (1984) 24; Chem. Abstr., 101:46493v.
12 E. Ingier-Stocka, J. Therm. Anal., 33 (1987) 487; Chem. Abstr., 109:216884h.
13 T. Flora, Mikrochim. Acta, (1966) 915; Chem. Abstr., 66:7985c.
14 G.A. Lazarenko, L.N. Neokladnova, L.A. Skoblikova and M.V. Zaretskii, Koord. Khim., 6 (1980) 275; Chem. Abstr., 92:136032u.
15 a. X.P. Wang, H.Z. Zhu, X.Q. Xin, A.B. Dai and H.H. Zhang, Acta Chimica Sinica, 49 (1991) 371; H.Z. Zhu, R.J. Chong, X.Q. Xin and A.B. Dai, Inorg. Chem. Chin., 5 (1989) 54; L.M. Zheng, X.Q. Xin and Y.H. Mei, Acta Chimica Sinica, in press (1991).
b. X.P. Wang, L.M. Zheng and X.Q. Xin, Inorg. Chem. Chin., in press.
16 J. Bjerrum and J.P. McReynolds, Inorg. Synth., 2 (1946) 216.
17 A. Rosenhein and R. Cohn, Z. Anorg. Chem., 27 (1901) 289.
18 J.N. Niu, X.Q. Xin and A.B. Dai, Acta Chimica Sinica, 4 (1986) 335.
19 J.H. Yuan, X.Q. Xin and A.B. Dai, Thermochim. Acta, 130 (1988) 77.

20 Y. Hiramatsu, K.-I. Okamoto and J. Hidaka, Inorg. Chim. Acta, 82 (1984) L13.
21 P.S. Poskozim, R. Shute, R. Taylor and J. Wysocki, J. Inorg. Nucl. Chem., 35 (1973) 687.
22 M. Sakiyama, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 36 (1963) 1025.
23 Z. Iqbal, L.H. Sarma and K.D. Moller, J. Chem. Phys., 57 (1972) 4728.
24 C. Pecile, Inorg. Chem., 5 (1966) 210.
25 C.H. Bamford and C.F.H. Tipper, Chemical Kinetics, Vol. 22, Reactions in the Solid State, Elsevier, Amsterdam, 1980.
26 K.J. Laidler, Chemical Kinetics, McGraw-Hill, New York, 1965, p. 316.