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THERMAL DECOMPOSITION OF MCl_2[M = Co(II), Ni(II), Cu(II)] IN SODIUM NITRATE–POTASSIUM NITRATE EUTECTIC MELT

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ABSTRACT

Anhydrous Co(II), Ni(II) and Cu(II) chlorides decompose in $NaNO_3$–KNO_3 eutectic melts at a much lower temperature than the corresponding chlorides alone in air. Powder X-ray diffraction studies confirm the presence of Co_3O_4, NaCl, KCl; NiO, NaCl, KCl; CuO, NaCl, KCl phases in the reaction systems. NO_2 and O_2 are liberated during the reaction. It is considered that the decomposition is a heterogeneous solid–liquid reaction between MCl_2 (solid) and the nitrate eutectic melt. The kinetics of decomposition at different temperatures have also been studied and from the results, thermodynamic parameters have been calculated.

INTRODUCTION

Kerridge and co-workers [1–5] studied a number of reactions in nitrate and nitrite eutectic melts. Recently, Rastogi et al. [6] studied the decomposition of MSO_4 [M = Co(II), Ni(II), Cu(II)] in a $NaNO_3$–KNO_3 eutectic melt and found that the decomposition reaction occurs at a much lower temperature. However, the mechanism of decomposition of such reactions has not been completely understood. In order to understand the mechanism of such decomposition reactions, the present study has been undertaken.

The present paper describes the decomposition reactions of $CoCl_2$, $NiCl_2$ and $CuCl_2$ in $NaNO_3$–KNO_3 eutectic melts.

EXPERIMENTAL

Materials

Analar grade $NaNO_3$, KNO_3, $CoCl_2 \cdot 6\ H_2O$, $NiCl_2 \cdot 6\ H_2O$ and $CuCl_2 \cdot 2\ H_2O$ (B.D.H.) were used. The eutectic of $NaNO_3$ and KNO_3 was prepared in 45 : 55 percent ratio as described previously [7]. $CoCl_2 \cdot 6\ H_2O$, $NiCl_2 \cdot 6\ H_2O$ and $CuCl_2 \cdot 2\ H_2O$ were dehydrated at 150°C, above 50°C and 100°C, respectively, till the weights of the samples were constant.

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Procedure

Thermal studies

Thermogravimetric studies of metal chlorides + eutectic, metal chlorides + sodium nitrate, and metal chlorides + potassium nitrate were carried out with a thermogravimetric analyzer (supplied by P&D Division, Sindri, Dhanbad-India) in air using a corning glass crucible. The heating rate was 4°C min^{-1}. The minimum weight losses could be recorded up to 0.0001 g and the uncertainty in temperature was ± 10°C. Each experiment was repeated three times and the reproducibility of the results were within $< \pm 1\%$. DTA and TG studies of metal chlorides in the eutectic were carried out with a recording thermal analyzer (Paulik–Paulik–Erdey MOM derivatograph, Hungary).

The kinetics of thermal decomposition in air of metal chlorides in the eutectic melt have also been studied by a manual thermogravimetric analyzer using a corning glass crucible. The weight losses were noted at different intervals of time at constant temperature. A known weight of the eutectic and anhydrous metal chlorides were taken during the experiment.

Powder X-ray diffraction studies

The powder X-ray diffraction patterns of the residues left in thermogravimetric experiments were obtained with an X-ray diffractograph (XRD-5, General Electric, U.S.A.) using Cu K_α radiation.

Gravimetric estimations

Reaction products obtained after thermogravimetric studies were washed with water in order to separate the insoluble oxides. Cobalt, nickel and copper were estimated gravimetrically in the oxides by standard methods [8].

Qualitative analysis of the evolved gases

The evolved gases were tested in the usual way and found to be NO_2 and O_2.

RESULTS AND DISCUSSION

Reactions of MCl_2[M = Co(II), Ni(II), Cu(II)] in the $NaNO_3$–KNO_3 eutectic melt have been investigated by thermal methods. The reactions of MCl_2 in KNO_3 and MCl_2 in $NaNO_3$ melts have also been studied. Thermogravimetric studies (Table 1, Fig. 1) indicate that MCl_2 in the eutectic melt decomposes at a lower temperature as compared to the decomposition in $NaNO_3$ or KNO_3 melt alone. Table 1 also lists the decomposition temperatures of MCl_2 when heated alone. These decomposition temperatures are comparatively very high. The weight losses obtained from the thermogravimetric studies are in good agreement with the weight losses obtained by

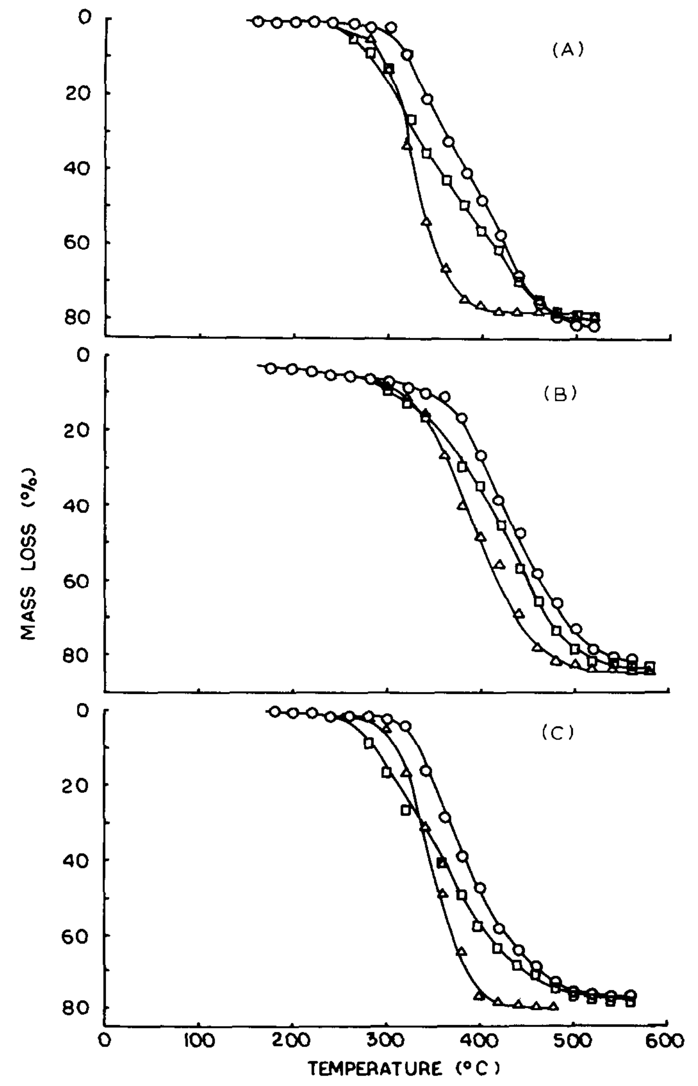

Fig. 1. TG curves for decomposition of the systems: (A) ○, $CoCl_2$ (0.1130 g)+KNO_3 (0.2575 g); △, $CoCl_2$ (0.1380 g)+$NaNO_3$ (0.2500 g); □, $CoCl_2$ (0.1730 g)+ $NaNO_3$–KNO_3 eutectic (0.2860 g): (B) ○, $NiCl_2$ (0.1000 g)+KNO_3 (0.2290 g); △, $NiCl_2$ (0.1445 g)+$NaNO_3$ (0.3665 g); □, $NiCl_2$ (0.1865 g)+$NaNO_3$–KNO_3 eutectic (0.2530 g): (C) ○, $CuCl_2$ (0.1040 g)+KNO_3 (0.2420 g); △, $CuCl_2$ (0.0910 g)+$NaNO_3$ (0.2095 g); □, $CuCl_2$ (0.1370 g)+$NaNO_3$–KNO_3 eutectic (0.1530 g).

calculation using eqns. (1)–(6). DTA studies indicate a number of endotherms below 600°C (Table 2, Fig. 2). The endotherm at around 120°C is due to the phase transformation of KNO_3. The endotherm at around 220°C is due to the melting of the eutectic. There are two endotherms in the region 300–400°C which indicate the decomposition of the metal salts. The two peaks suggest that two closely associated processes occur simultaneously. It

TABLE 1

Decomposition temperatures

System	Decomposition temperature (°C)
$CoCl_2$	Sublimes (1049 B.P.)
$CoCl_2$–KNO_3	320
$CoCl_2$–$NaNO_3$	300
$CoCl_2$–$NaNO_3$/KNO_3 eutectic	280
$NiCl_2$	973
$NiCl_2$–KNO_3	380
$NiCl_2$–$NaNO_3$	340
$NiCl_2$–$NaNO_3$/KNO_3 eutectic	340
$CuCl_2$	993
$CuCl_2$–KNO_3	340
$CuCl_2$–$NaNO_3$	320
$CuCl_2$–$NaNO_3$/KNO_3 eutectic	280

is postulated that the metal halides are first converted into metal nitrates which immediately decompose into metal oxides.

X-Ray diffraction studies of the reaction products obtained at the end of the TG studies indicate the presence of the corresponding oxides (e.g. Co_3O_4, NiO and CuO), NaCl and KCl. The observed and reported *d* values (Table 3) are in good agreement for the oxides, NaCl and KCl. The reaction products were washed with water and the insoluble oxides thus obtained were analysed. The metals were estimated gravimetrically and the observed and calculated percentages of the metals are given in Table 4. These results also indicate the formation of corresponding metal oxides, e.g. Co_3O_4, NiO and CuO. The evolved gases were qualitatively identified as NO_2 and O_2.

From these results the overall reactions are represented as

$$CoCl_2 + NaNO_3 + KNO_3 \rightarrow Co(NO_3)_2 + NaCl + KCl \quad (1)$$

TABLE 2

DTA peak temperatures

System	Peak temperature (°C)
$CoCl_2$–$NaNO_3$/KNO_3 eutectic	120 (Phase transformation)
	220 (Melting of eutectic)
	320, 400 (Decomposition of metal chloride)
$NiCl_2$–$NaNO_3$/KNO_3 eutectic	120 (Phase transformation)
	220 (Melting of eutectic)
	340, 380 (Decomposition of metal chloride)
$CuCl_2$–$NaNO_3$/KNO_3 eutectic	120 (Phase transformation)
	220 (Melting of eutectic)
	300, 360 (Decomposition of metal chloride)

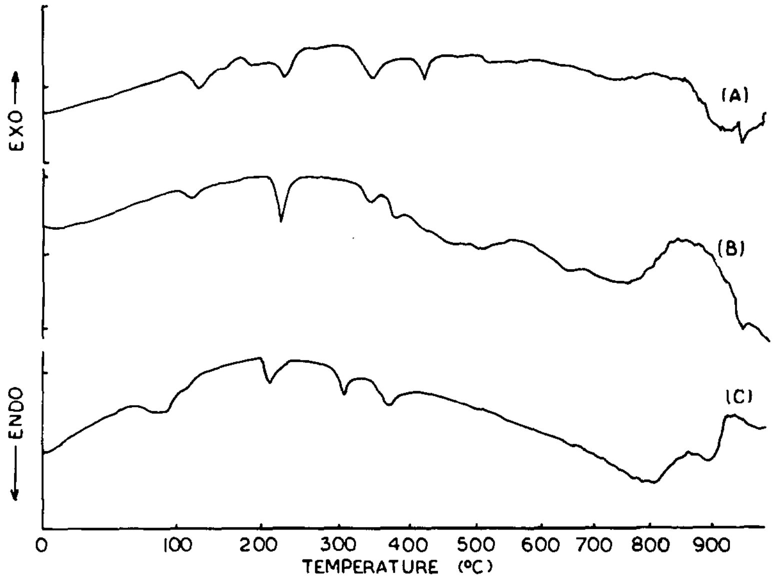

Fig. 2. DTA curves for (A) $CoCl_2 + NaNO_3$–KNO_3 eutectic (eutectic 198 mg, $CoCl_2$ 90 mg); (B) $NiCl_2 + NaNO_3$–KNO_3 eutectic (eutectic 192 mg, $NiCl_2$ 120 mg); (C) $CuCl_2 +$ $NaNO_3$–KNO_3 eutectic (eutectic 100 mg, $CuCl_2$ 50 mg).

$$3\ Co(NO_3)_2 \rightarrow Co_3O_4 + 6\ NO_2 + O_2 \tag{2}$$

$$NiCl_2 + NaNO_3 + KNO_3 \rightarrow Ni(NO_3)_2 + NaCl + KCl \tag{3}$$

$$Ni(NO_3)_2 \rightarrow NiO + 2\ NO_2 + \tfrac{1}{2}\ O_2 \tag{4}$$

$$CuCl_2 + NaNo_3 + KNO_3 \rightarrow Cu(NO_3)_2 + NaCl + KCl \tag{5}$$

$$Cu(NO_3)_2 \rightarrow CuO + 2\ NO_2 + \tfrac{1}{2}\ O_2 \tag{6}$$

The kinetics of isothermal decomposition of the metal chlorides in the eutectic melt have also been studied at different temperatures. It is found that Jander's equation [eqn. (7)] fits the kinetic data.

$$\left\{1 - (1 - \alpha)^{1/3}\right\}^2 = kt \tag{7}$$

where α is the fraction decomposed at any time t, and k is an apparent rate constant for the process. Plots of $\{1 - (1 - \alpha)^{1/3}\}^2$ vs. t gave straight lines (Figs. 3–5) indicating the validity of eqn. (7). The values of k at different temperatures are given in Table 5. When log k was plotted vs. $1/T$ (Fig. 6), straight lines were obtained showing that the Arrhenius equation [eqn. (8)] is obeyed.

$$k = A\ e^{-E/RT} \tag{8}$$

where k is the rate constant, R is the gas constant, T is the temperature in degrees absolute, A is a constant and E is the energy of activation. From the

TABLE 3

X-Ray diffraction lines for the reaction products (Only three lines given, in order of decreasing intensity.)

Reaction system	Compounds	d(Å)	
		Repd.	Obsd.
$CoCl_2$–$NaNO_3$/KNO_3 eutectic	Co_3O_4	2.44	2.43
		1.43	1.43
		1.55	1.55
	NaCl	2.82	2.81
		1.99	1.99
		1.63	1.63
	KCl	3.15	3.13
		2.22	2.22
		1.40	1.42
$NiCl_2$–$NaNO_3$/KNO_3 eutectic	NiO	2.09	2.09
		2.41	2.41
		1.48	1.48
	NaCl	2.82	2.81
		1.99	1.99
		1.63	1.63
	KCl	3.14	3.14
		2.22	2.22
		1.81	1.81
$CuCl_2$–$NaNO_3$/KNO_3 eutectic	CuO	2.52	2.53
		2.32	2.32
		1.86	1.86
	NaCl	2.82	2.82
		1.99	1.99
		1.63	1.63
	KCl	3.15	3.14
		2.22	2.22
		1.82	1.82

slope of the lines, the activation energies have been calculated and are given in Table 6. The thermodynamic parameters such as entropy of activation, ΔS^*, free energy of activation, ΔG^*, and the enthalpy of activation, ΔH^*, have also been calculated and are given in Table 6.

TABLE 4

Gravimetric estimation of metals in different oxides

Metal oxide	Metal	
	Obsd. (%)	Calcd. (%)
Co_3O_4	72.25	73.40
NiO	77.50	78.60
CuO	78.42	79.87

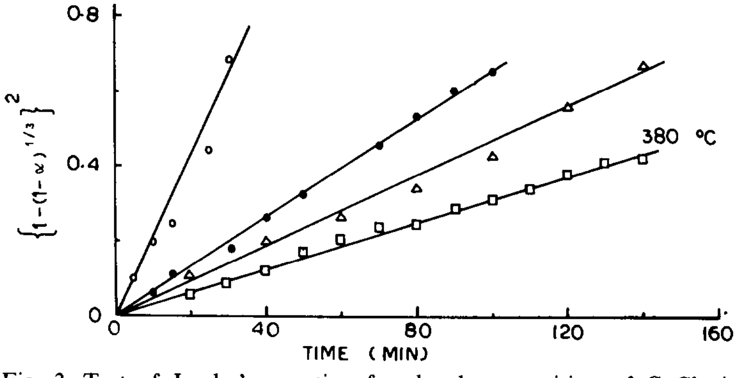

Fig. 3. Test of Jander's equation for the decomposition of $CoCl_2$ in the $NaNO_3$–KNO_3 eutectic melt. ○, 440°C; ●, 420°C, △, 400°C; □, 380°C.

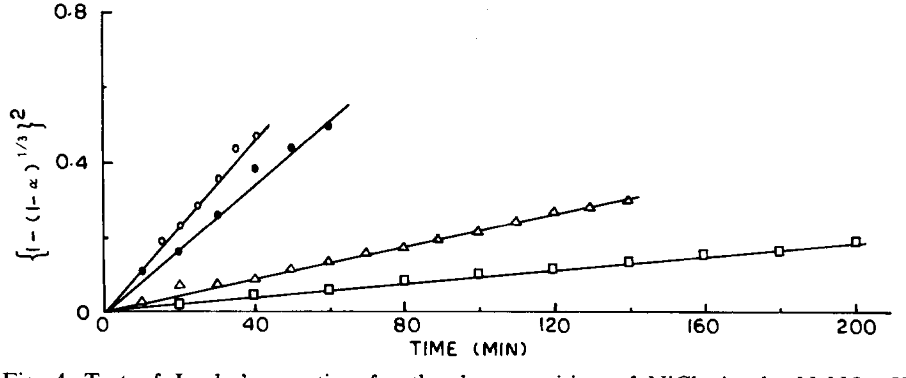

Fig. 4. Test of Jander's equation for the decomposition of $NiCl_2$ in the $NaNO_3$–KNO_3 eutectic melt. ○, 460°C; ●, 440°C; △, 420°C; □, 400°C.

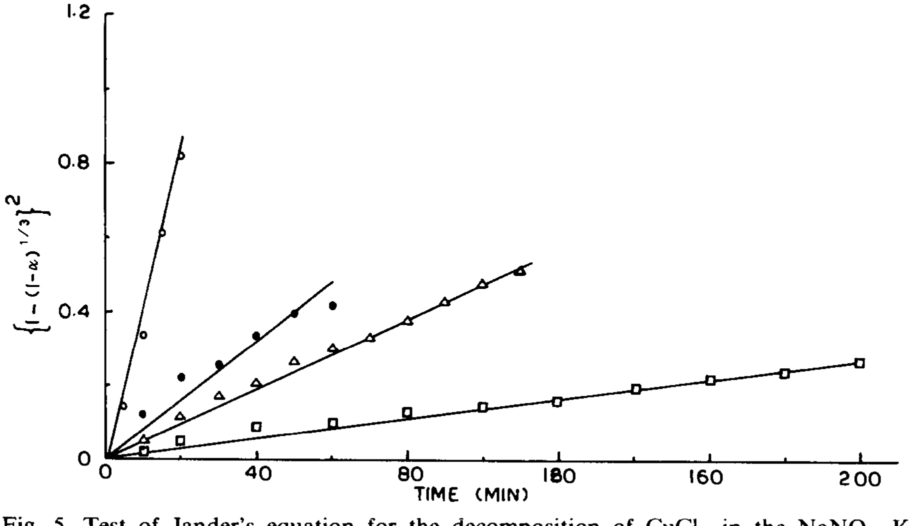

Fig. 5. Test of Jander's equation for the decomposition of $CuCl_2$ in the $NaNO_3$–KNO_3 eutectic melt. ○, 420°C; ●, 400°C; △, 380°C, □, 360°C.

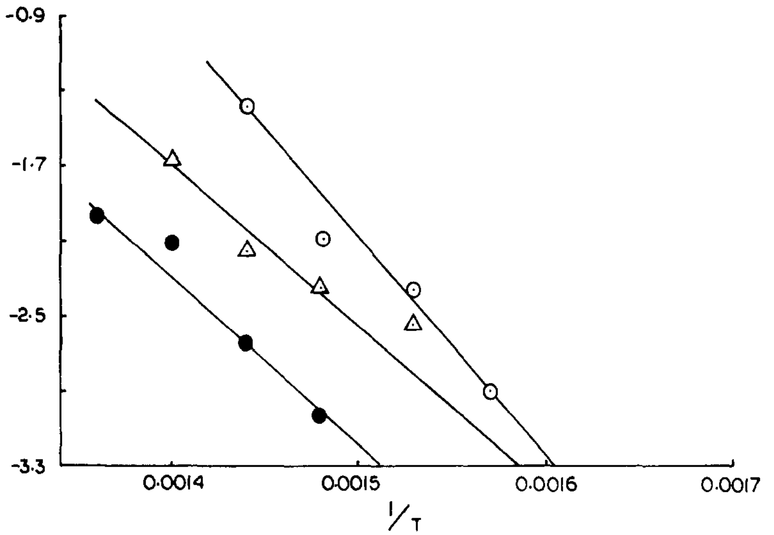

Fig. 6. Arrhenius plots for: △, $CoCl_2 + NaNO_3$–KNO_3 eutectic system; ●, $NiCl_2 +$ $NaNO_3$–KNO_3 eutectic system; ⊙, $CuCl_2 + NaNO_3$ eutectic system.

The solubility of MCl_2 in the nitrate eutectic melt were also tested qualitatively and it was found that the chloride salts are insoluble. Thus, the reaction between metal chlorides and the nitrate eutectic can be considered as a solid–liquid reaction. From the results, it appears that, initially, the nitrate ions are adsorbed at the surface of the metal chlorides forming a loose activated complex. The positive entropy of activation values indicate

TABLE 5

Apparent rate constants for decomposition

System	Temp. (°C)	Weight of eutectic (g)	Weight of metal chlorides (g)	$k \times 10^3$ (min^{-1})
$CoCl_2$–$NaNO_3/KNO_3$ eutectic	380	0.2720	0.1165	3.1
	400	0.5250	0.2505	4.6
	420	0.6440	0.3120	6.2
	440	0.4695	0.2130	21.4
$NiCl_2$–$NaNO_3/KNO_3$ eutectic	400	0.2195	0.1130	0.9
	420	0.2070	0.1050	2.1
	440	0.3160	0.1415	8.3
	460	0.2255	0.1130	10.6
$CuCl_2$–$NaNO_3/KNO_3$ eutectic	360	0.1960	0.1225	1.2
	380	0.2135	0.1205	4.8
	400	0.2040	0.1085	8.3
	420	0.3760	0.1260	43.5

TABLE 6

Thermodynamic parameters

System	E (kcal $mole^{-1}$)	ΔS^* (kcal deg^{-1} $mole^{-1}$)	ΔG^* (kcal)	ΔH^* (kcal)
$CoCl_2$–$NaNO_3$/KNO eutectic	39	0.1349	−53.1622	37.6674
$NiCl_2$–$NaNO_3$/KNO_3 eutectic	41	0.1412	−55.3442	39.6674
$CuCl_2$–$NaNO_3$/KNO_3 eutectic	55	0.1576	−52.4218	53.6674

that the activated states are more disordered and hence have a greater tendency for decomposition. As soon as a critical temperature is reached, the loose activated complex is converted into the corresponding metal nitrates by double decomposition, which ultimately decomposes into the corresponding oxides. The energy of activation values for decomposition varies in the order

$$E_{CoCl_2} < E_{NiCl_2} < E_{CuCl_2}$$

However, this will depend on the lattice energy of the metal chlorides: the higher the lattice energy (U), the higher will be the energy of activation. This is actually the case (Table 7) and the values vary in the order

$$U_{CoCl_2} < U_{NiCl_2} < U_{CuCl_2}$$

Since the decomposition reactions are fast, it is suggested that first of all a small fraction of the metal nitrates is decomposed forming nuclei of the metal oxides at the surface. The oxides thus formed may act as catalysts and autocatalytic decomposition reactions occur. However, when small amounts of the same metal oxides were added to the systems from outside, the rates of decomposition were unaffected. This may suggest that either the oxides obtained during decomposition are not acting as autocatalysts or that the oxides added are inactive catalysts. Further, it is believed that a porous layer of the oxide is formed through which NO_2 and O_2 gases come out and the

TABLE 7

Lattice energy of metal chlorides [a]

Metal chloride	U (kJ $mole^{-1}$)
$CoCl_2$	2709
$NiCl_2$	2753
$CuCl_2$	2774

[a] Ref. 9.

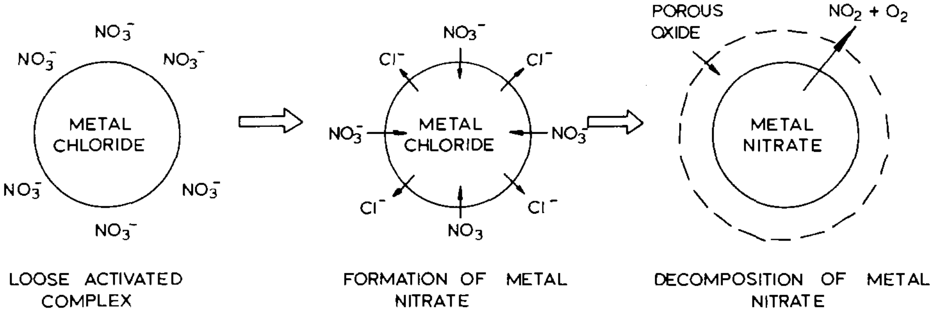

Fig. 7. Schematic representation of the decomposition of MCl_2 [M = Co(II), Ni(II) and Cu(II)].

reaction is completed. The decomposition reaction is represented schematically in Fig. 7.

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REFERENCES

1 D.H. Kerridge, M.T.P. International Review of Science, Inorganic Chemistry Series One, Vol. 2, Butterworths/University Park Press, 1972.
2 D.H. Kerridge and J.D. Buyke, J. Inorg. Nucl. Chem., 38 (1976) 1307.
3 J.D. Burke and D.H. Kerridge, J. Inorg. Nucl. Chem., 37 (1975) 751.
4 D.H. Kerridge, and S.S. Alomer, J. Chem. Soc., Dalton Trans., (1978) 1589.
5 H. Frouzanfar, D.H. Kerridge, J. Inorg. Nucl. Chem., 42 (1980) 1381.
6 R.P. Rastogi, N.B. Singh and S.P. Pandey, Indian J. Chem., 21A (1982) 456.
7 R.P. Rastogi and K.T. Ram Varma, J. Chem. Soc., (1956) 2097.
8 A.I. Vogel, A Text Book of Quantitative Inorganic Chemistry, Longmans, New York, 1961.
9 Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL 61st edn., 1980–1981, p. D-92.