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Mechanistic considerations for anation reactions in the solid state*

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CONTENTS

ABSTRACT

The controversy regarding the mechanisms of anation reactions in the solid state is examined. Historically, these reactions have been considered as S_N2 since the nature of the anion affects the reaction. However, principles of reaction kinetics for solid state processes lead to as many as 17 possible rate laws. The role of free space, which increases as the difference between the sizes of the cation and anion increases, appears to be rate-determining in some cases. In most instances, the observed anion effect is readily explained in terms of free space (a defect-diffusion model) rather than S_N1 or S_N2. Consequently, rate laws based on nucleation or diffusion control appear to be more applicable to anation reactions. The review of a large number of anation reactions is presented to show the applicability of the defect-diffusion model.

1. INTRODUCTION

Solid-state reactions of coordination compounds have been studied for many years. For example, the reaction

$$[Cr(NH_3)_5H_2O]X_3(s) \rightarrow [Cr(NH_3)_5X]X_2(s) + H_2O(g) \qquad (1)$$

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(where $X = Cl$, Br, I, or NO_3) was first studied over 100 years ago [1]. The loss of ethylenediamine from $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$ to yield *cis*-$[Cr(en)_2Cl_2]Cl$ and *trans*-$[Cr(en)_2(NCS)_2]NCS$, respectively, was studied long ago by Pfeiffer and co-workers [2,3]. The Bailar school, consisting of Rollinson [4,5], O'Brien [6], LeMay [7,8], House [9,10] Hertzenberg [11,12], Kutal [13], Fujiwara [14–16], and others continued the study of solid-state reactions of coordination compounds. These studies include anation and racemization as well as geometrical and linkage isomerizations. The influence of Professor Bailar was particularly strong in this area for almost 50 years.

It has been stated that the substitution of one ligand in the coordination sphere of a complex is the most fundamental reaction in coordination chemistry. Undoubtedly, the loss of a neutral volatile ligand and its replacement by an anion,

$$[ML_5Y]X_n(s) \rightarrow [ML_5X]X_{n-1}(s) + Y(g) \qquad (2)$$

is the most fundamental reaction of solid complexes. While many reactions of this type are known, their mechanisms are not well understood and have been the subject of controversy for many years. Part of this stems from attempts to use concepts applicable to gas- or solution-phase processes to explain reactions in solids. Other difficulties are those which are attendant to the study of reactions in solids. In this review, some of these problems will be discussed for anation reactions in an attempt to provide a framework for interpreting the mechanisms of reactions of this type. However, only a few of the thousands of known anation reactions will be discussed.

2. REACTIONS IN THE SOLID STATE

2.1 General considerations

The rate of a reaction in the solid state cannot be expressed in terms of concentration since any particle of a solid material has the same concentration. Generally, the fraction of the reaction complete, α, is chosen as the reaction variable. It is readily apparent that if α is the fraction of the sample reacted, $(1-\alpha)$ is the fraction of the material remaining unreacted. Many of the rate laws are expressed as functions of $(1-\alpha)$. The reaction rate can be expressed as $d\alpha/dt = k(T)\,f(\alpha)$, and a reaction is complete when $\alpha = 1$. If we examine the behavior of α as a function of time for many reactions in the solid state, the general relationship is as shown in Fig. 1.

Reactions in which a volatile ligand is evolved are conveniently followed by thermogravimetric analysis (TGA) by comparing the observed mass loss with that expected for a complete reaction. Several regions may be present in the α vs. time curve. For example, region A represents the rapid evolution of adsorbed gases, resulting in a small initial mass loss. Region B represents an induction period where

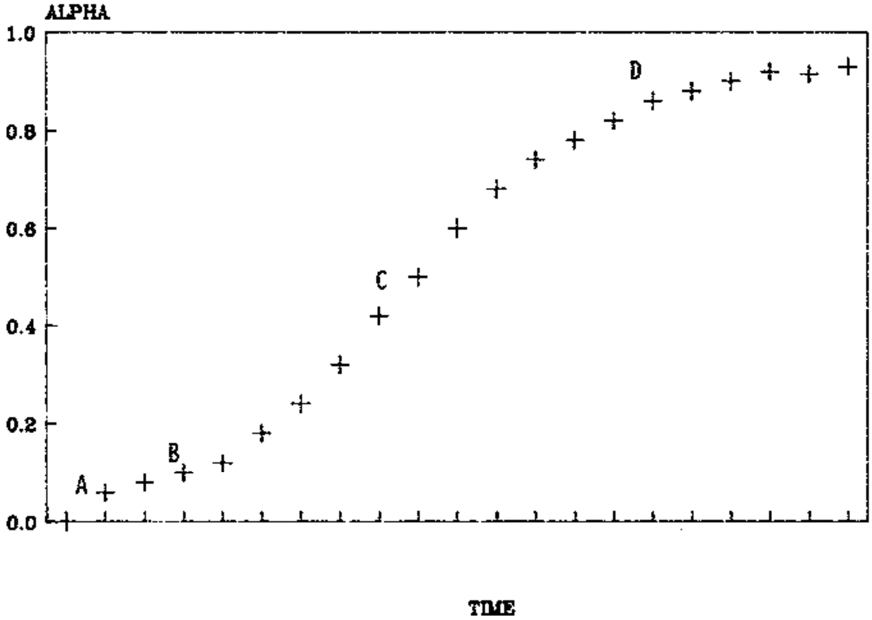

Fig. 1. A typical plot of α vs. time for a solid state reaction.

the rate is beginning to increase. In the region labeled C, the reaction is taking place at its maximum rate. Region D is called the decay region, and it represents a state where the reaction is slowing down as it approaches completion. In this region, the diffusion of a volatile product through a solid product phase may limit the rate of reaction.

Reactions may not show all the steps illustrated in Fig. 1. In fact, the majority do not show desorption of gas, and although induction periods are fairly common, they are by no means universal. Consequently, it is frequently observed that the reaction starts off at its maximum rate. It is also sometimes observed that the reaction never progresses to $\alpha = 1$, for several reasons. One of the most common is the retention of a gaseous product in the solid product or reactant phases. Retention is regarded as the adsorption or chemisorption of a volatile product. The coalesence of particles due to sintering reduces surface area and increases the possibility that volatile products may be retained. Because of these factors, it is frequently found that a single rate law does not represent the entire reaction.

2.2 *Factors affecting reaction rates*

Reactions of materials in the solid state are strongly influenced by a variety of factors, and complete treatment of this vast subject is beyond the scope of this review [17,18]. If the reaction takes place on the surface of the solid, the particle size may be important because the smaller the particles, the larger the surface area for a given volume of material. However, in many cases the reaction rate is independent of particle size, even when a volatile product is liberated. For example, the dehydration of $CaC_2O_4 \cdot H_2O$, a model system for testing kinetic methods for reactions in solids, is independent of particle size [19,20]. For specific systems, it is not always possible to ascribe kinetic differences between samples to particle size variations, although it is frequently tempting to do so.

The nature of the surface itself is frequently important since the reaction is controlled by the topochemistry, the nature of the reactant/product interface. Solid state reactions may also depend on the formation and growth of active sites called nuclei. For some kinetic models, the geometric nature of the growth of these nuclei determines the form of the rate law for the reaction. Phase boundary advancement from these nuclei is another factor of importance. It is apparent that the rate of diffusion of material may play an important role in the kinetic behavior of the reaction. Lattice defects are also important since these defects promote diffusion and reactivity in general because they represent high-energy centers in the solid. Finally, the historical treatment of the sample up to the time when its reaction is studied may be significant. This treatment may cause surface damage, cracks, pores, etc. Also, defects may have been quenched in by the preparative methods or they may have been annealed out. For example, it has recently been found that aging of $CaC_2O_4 \cdot H_2O$ for one year causes the dehydration to occur more easily [20]. It appears that this effect is caused by changes in cracks and pores in the crystals. All of these factors make it quite likely that materials having the same apparent composition may react in somewhat different ways or at different rates.

2.3 Rate laws

Rate laws for reactions in the solid state may be grouped into several categories. In some cases, these groupings are based on the nature of the α vs. time curve. For example, those having maximum rates initially which decrease thereafter are called deceleratory rate laws. Those which have sigmoidal-shaped α vs. time curves are referred to as sigmoidal rate laws. A third (but small) category is that which follows an acceleratory rate law. Space does not permit the derivation of these rate laws based on model processes [21], but 17 rate laws are usually tabulated [22].

If a reaction follows a first-order rate law and W_0 represents the amount of reactant initially present, it is easy to show that

$$\ln(W_0/W) = kt \tag{3}$$

and the fraction reacted, α, is

$$\alpha = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0}$$

so that

$$-\ln(1-\alpha)=kt \tag{4}$$

For spherical particles ($V=4\pi r^3/3$) reacting so that the reaction takes place on the surface ($S=4\pi r^2$)

$$-\frac{\mathrm{d}V}{\mathrm{d}t}=kS=4\pi k\left(\frac{3V}{4\pi}\right)^{2/3}=k'V^{2/3}$$

The rate law is said to be "2/3-order" or a contracting volume rate law. From this equation, one can easily derive the equation

$$V_0^{1/3}-V^{1/3}=\frac{kt}{3}$$

Now

$$\alpha=\frac{V_0-V}{V_0}=1-\frac{V}{V_0}$$

so that

$$1-(1-\alpha)^{1/3}=k''t \tag{5}$$

where $k''=k'/V_0^{1/3}=[4k\pi(3/4\pi)^{2/3}]/3V_0^{1/3}$. Similar procedures could be used to derive other deceleratory rate laws and those based on diffusion control.

When the rate of the reaction depends on nucleation on the surface of the particles, several cases result from the random nucleation rate law [21]. The general form of the rate law is

$$[-\ln(1-\alpha)]^{1/n}=kt \tag{6}$$

where n is called the index of reaction. The Avrami–Erofeev rate laws are of this type with indices of 1.5, 2, 3, or 4. Sigmoidal α vs. time plots characterize these rate laws designated as A1.5, A2, A3, and A4, respectively. While the A1.5 case is referred to as a one-dimensional growth of nuclei model, it has also been shown to be related to diffusion [23]. The A2 and A3 cases are called the two- and three-dimensional growth of nuclei models, respectively.

Table 1 summarizes 17 rate laws which have applicability to solid state reactions. It is apparent that several of these rate laws have very similar mathematical forms. The nature of sample-to-sample variation for kinetic runs is such that a single rate law is unambiguously identified only very rarely [24–27]. Consequently, it is necessary to make a large number of kinetic runs to obtain a clear indication of which rate law fits the majority of experiments. This fact is frequently overlooked as is the fact that one must test a variety of rate laws. It appears that, in some older work to be discussed later, only the familiar "order"-type rate laws were considered.

TABLE 1

Mechanisms of solid state reactions $f(\alpha) = kt$

Name of the function	f(α)
1. Acceleratory α-time curves	
Power law	$\alpha^{1/2}$
Exponential law	$\ln \alpha$
2. Sigmoidal α-time curves	
A1.5 Avrami–Erofeev one-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{2/3}$
A2 Avrami–Erofeev two-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{1/2}$
A3 Avrami–Erofeev three-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{1/3}$
A4 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/4}$
B1 Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
3. Deceleratory α-time curves	
3.1 Based on geometrical models one-dimensional contraction	$1-(1-\alpha)^{2/3}$
R2 contracting area	$1-(1-\alpha)^{1/2}$
R3 contracting volume	$1-(1-\alpha)^{1/3}$
3.2 Based on diffusion mechanisms	
D1 one-dimensional diffusion	α^2
D2 two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3 three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$
D4 Ginstling–Brounshtein	$[1-(2\alpha/3)]-(1-\alpha)^{2/3}$
3.3 Based on order of reaction	
F1 first order	$-\ln(1-\alpha)$
F2 second order	$1/(1-\alpha)$
F3 third order	$[1/(1-\alpha)]^2$

2.4 The anion effect in anation reactions

By the term "anion effect" is usually meant a difference in the kinetics of an anation reaction when different anions are present with the same cation. One of the earliest observations on the anion effect involved the deaquation–anation reactions of $[M(NH_3)_5H_2O]X_3$ where M = Co, Cr, or Ru and X = Cl, Br, I, or NO_3. Wendlandt and Bear studied these reactions of $[Cr(NH_3)_5H_2O]X_3$ compounds [28] and reported that the reactions take place between 50 and 150°C. The order of stability of the compounds was given as chloride < nitrate < bromide < iodide. The rate of water loss was followed by observing the change in vapor pressure with time. Because plots of $\log[p_f/(p_f - p_t)]$ (where p_f is the final pressure and p_t is the pressure at time t) vs. t were linear, the reactions were all presumed to be first order [28]. Activation energies were reported to be 75 ± 8, 103 ± 13, 75 ± 8, and 67 ± 8 kJ mol^{-1}, for the chloride, bromide, iodide, and nitrate compounds, respectively.

The $[Cr(NH_3)_5H_2O]X_3$ compounds were also studied by Tsuchiya et al.

[29]. Thermal stability was reported to vary as nitrate < chloride < bromide < iodide with activation energies of 67, 111, 155, and 79 kJ mol^{-1}, respectively, for the deaquation–anation reactions. A first-order process was presumed to represent the reactions. Tsuchiya et al. also studied the dehydration–anation reactions of the sulfate and sulfite compounds and found activation energies of 160 and 136 kJ mol^{-1}, respectively.

Negase and Yokobayashi also studied the deaquation–anation reactions of the $[Cr(NH_3)_5H_2O]X_3$ compounds using TGA and DSC [30]. It was reported that the initial mass loss occurs at 75, 51, 56, 76, and 83°C for the nitrate(I), nitrate(II), chloride, bromide, and iodide complexes, respectively. The nitrate(I) and nitrate(II) were samples described as more (I) and less (II) crystalline. The reactions were followed by means of vapor pressure measurements and all but that for the nitrate(I) were analyzed using the first-order, $\ln(1-\alpha)$, rate expression. Curves for the nitrate(I) compound were sigmoidal and were analyzed by means of the Prout–Tompkins rate law, $\ln[\alpha/(1-\alpha)]$. Activation energies for the anation reactions were reported as 144.3, 101.7, 110.5, 124.3, and 136.8 kJ mol^{-1} for the nitrate(I), nitrate(II), chloride, bromide, and iodide compounds, respectively.

Studies on the $[Co(NH_3)_5H_2O]X_3$ compounds began with the perchlorate [31]. Thermal studies indicated that this compound does not lose the coordinated water at temperatures up to 200°C. Smith and Wendlandt studied the compounds $[M(NH_3)_5H_2O](ClO_4)_3$ where M = Co, Cr, or Rh and reported that only the rhodium compound dehydrated to give $[M(NH_3)_5ClO_4](ClO_4)_2$ [32]. Later, Wendlandt and Bear studied aquapentamminecobalt(III) chloride, bromide, iodide, and nitrate [33]. It was reported that the temperatures at which dehydration began were 40, 50, 70, and 80°C for the chloride, nitrate, iodide, and bromide compounds, respectively. Kinetic studies were carried out by measuring the increase in pressure due to water loss in a closed system. It was reported that the anation reactions were first order since plots of $\log[p_f/(p_f-p_t)]$ were linear. However, there was no indication that other rate laws were tested. Deaquation–anation of the chloride, bromide, and nitrate has activation energies of 80, 105, and 130 kJ mol^{-1}, respectively. Gore and Wendlandt used mass loss data to determine activation energies of 155, 130, and 138 kJ mol^{-1} for the anation reactions of the chloride, bromide, and iodide compounds, respectively [34].

One of the most interesting studies on deaquation–anation reactions is that of Ohyoshi et al. [35]. In that work, the behavior of aquapentammineruthenium(III) complexes was studied and compared with that of the chromium(III) and cobalt(III) complexes. The kinetic analysis was performed using the rate law $\log[M_0/(M_0-M_t)] = kt$ where M_0 is the initial mass and M_t is the mass at time t. Table 2 shows some of the data for the Ru(III), Cr(III), and Co(III) complexes.

The data shown in Table 2 indicate that, in general, the activation energies for the anation reactions for each series of metal complexes increase in the order $NO_3 < Cl < Br < I$. The activation energies decrease as $Ru < Co < Cr$ when the

TABLE 2

Kinetic parameters for the deaquation of aqua complexes[a]

Complex	k, $10^4\ s^{-1}$ (Temp., °C)	E_a ($kJ\ mol^{-1}$)	$\Delta S^\ddagger$ (e.u.)
$[Ru(NH_3)_5H_2O]Cl_3$	1.12(43)	95.0	−7.1
$[Ru(NH_3)_5H_2O]Br_3$	0.77(40)	97.9	−5.2
$[Ru(NH_3)_5H_2O]I_3$	0.71(40)	111.7	5.8
$[Ru(NH_3)_5H_2O](NO_3)_3$	2.38(41)	80.8	−15.9
$[Cr(NH_3)_5H_2O]Cl_3$	2.41(65)	110.5	−2.53
$[Cr(NH_3)_5H_2O]Br_3$	2.43(76)	124.3	9.2
$[Cr(NH_3)_5H_2O]I_3$	1.61(82)	136.8	15.4
$[Cr(NH_3)_5H_2O](NO_3)_3$	1.38(55)	101.7	−2.49
$[Co(NH_3)_5H_2O]Cl_3$	4.27(86)	79	—
$[Co(NH_3)_5H_2O]Br_3$	4.79(85)	105	—
$[Co(NH_3)_5H_2O](NO_3)_3$	2.51(85)	130	—

[a] Data from ref. 35.

different metal ions are considered. Further, the $\Delta S^\ddagger$ values show an increase in the series as $NO_3 < Cl < Br < I$. These observations led Ohyoshi et al. to propose the two possible mechanisms shown below.

Mechanism I (S_N1)
$[Ru(NH_3)_5H_2O]X_3 \rightarrow [Ru(NH_3)_5X_3 + H_2O$
$[Ru(NH_3)_5]X_3 \rightarrow [Ru(NH_3)_5X]X_2$
Mechanism II (S_N2)
$[Ru(NH_3)_5H_2O]X_3 \rightarrow [Ru(NH_3)_5(H_2O)X]X_2$
$[Ru(NH_3)_5(H_2O)X]X_2 \rightarrow [Ru(NH_3)_5X]X_2 + H_2O$

If the loss of water is the rate-determining step, as shown in Mechanism I, kinetics of the anation should not depend on the anion. If, however, coordination of the anion is the rate-determining step, the nature of the anion would affect the reaction rate, as is observed. Accordingly, it was concluded that the deaquation–anation reactions are S_N2 [35].

The studies described in this section have clearly demonstrated an anion effect in the deaquation–anation reactions of complexes having the formula $[M(NH_3)_5H_2O]X_3$. Also, the rate of racemization of (+)-$[Co(en)_3]X_3$ (where X = Cl, Br, I, or NCS) in the solid state has been shown to decrease in the order $I > Br > NCS > Cl$ [13]. Since this review is concerned with anation reactions, racemization reactions will not be discussed further. A detailed review of solid-state racemizations is available [36]. Because of the inherent difficulties in considering anation reactions as S_N1 or S_N2 based on principles of solid state chemistry, a more realistic explanation of the origin of the anion effect was sought. A brief description of this model will now be provided [37].

3. THE DEFECT-DIFFUSION MODEL AND ITS APPLICATIONS

3.1 The defect-diffusion model

When a reaction takes place in a solid, the formation of the transition state results in a point defect in the lattice. These defects are analogous to the substituted ion, Schottky, and Frenkel defects which are familiar in solid state science [38]. While racemization reactions are not being considered here, such a process taking place by a twist mechanism [39–41] could be considered as producing a distorted ion which differs from the ion normally present at that site. Thus, it behaves as a substituted ion type of defect which occupies a different volume and causes lattice distortion at the site. If lattice expansion results, the formation of the transition state will be hindered when the lattice energy is higher. Thus, the ease of racemization of (+)-$[Co(en)_3]X_3$ compounds decreases in the order I > Br ≫ Cl since the lattice energy is greater for smaller anions for a given size of the cation [13].

In an anation reaction, an anion must leave its site in the crystal lattice and migrate to the complex cation. This leaves a missing ion or Schottky type of defect. Formation of Schottky defects involves an energy, E_s, which can be written as [42]

$$E_s = U\frac{1-[1-(1/D)]}{A[1-(1/n)]} \tag{7}$$

where U is the lattice energy, D is the dielectric constant, A is the Madelung constant, and n is the exponent in the repulsion term of the lattice energy equation

$$U = \left[\frac{Z_a Z_c A N_0 e^2}{r}\right]\left[1 - \frac{1}{n}\right] \tag{8}$$

When a volatile ligand is lost from a complex in a cation site, the free ligand is forced into an interstitial position in the lattice. Such a situation is analogous to the formation of a Frenkel defect. If this occurs before the anion enters the coordination sphere of the metal, a dissociative mechanism is being followed. The volatile ligand may either diffuse through the lattice or return to the coordination sphere of the metal ion. The diffusion coefficient for the volatile ligand through the lattice will depend on the fraction of free space, which in turn depends on the relative sizes of the ions. It can be shown that the fraction of free space in a crystal increases as the difference between the size of the cations and anions increases [43]. Accordingly, even if the anation reaction follows a dissociative pathway there will be an anion effect. For example, it has been shown that the fraction of free space in the lattices of $LiNO_3$ and $Sr(NO_3)_2$ alters the way in which NO_2^- and O fragments from NO_3^- dissociated by X-rays recombine [44]. In a similar way, the tendency for the liberated ligand to reattach to the metal ion should decrease as the fraction of free space increases. These events are more in line with the principles of solid state chemistry than are the S_N1 and S_N2 labels which can be used for reactions taking place in solution.

If a reaction such as

$$[Co(NH_3)_5H_2O]X_3(s) \rightarrow [Co(NH_3)_5X]X_2(s) + H_2O(g) \tag{9}$$

were to take place by an S_N2 process, it would be unusual since most substitution reactions in Co(III) complexes follow an S_N1 pathway. In an S_N2 process, an anion would have to leave an anion site and migrate to the complex cation to form a seven-bonded transition state. In the case of $[Cr(NH_3)_5H_2O]Cl_3$, the activation energy is about 110 kJ mol^{-1}. Formation of the transition state would require the loss of 4.26 Dq [45] with Dq being about 2100 cm^{-1} for $[Cr(NH_3)_5H_2O]^{3+}$ [46]. The crystal field activation energy alone would amount to 105 kJ mol^{-1}. However, the formation of the Schottky defect by moving the anion from its lattice position is known to involve a high energy for compounds with high lattice energy [42].. Therefore, the observed activation energy of 110 kJ mol^{-1} appears to be much too low for an S_N2 process. For an S_N2 pathway, the migration of an anion from its lattice site would require the sacrifice of part of the lattice energy. Therefore, the reaction rates should decrease as the lattice energy increases, which occurs with a given cation as the sizes of the anions decrease. For the $[M(NH_3)_5H_2O]X_3$ complexes, the trend in activation energies is exactly opposite to this prediction.

If the dehydration–anation of $[Co(NH_3)_5H_2O]X_3$ takes place by the loss of water from $[Co(NH_3)_5H_2O]^{3+}$, the nature of the anion should not affect the activation energy. If a square-based pyramid transition state is formed, 4 Dq of CFSE is lost. If a trigonal bipyramid transition state is formed, 11.48 Dq of CFSE is lost [45]. Since Dq is about 2290 cm^{-1} for $[Co(NH_3)_5H_2O]^{3+}$ [47], these losses of CFSE amount to 110 and 314 kJ mol^{-1}. When the formation of a Frenkel type of defect by the liberated water is considered, the total activation energy would be quite high. However, as shown in Table 2, the activation energy for the anation reaction of $[Co(NH_3)_5H_2O]Cl_3$ is only 79 kJ mol^{-1}. From these considerations, it appears that neither the S_N1 nor the S_N2 pathway is consistent with the observations on these reactions.

3.2 The role of free space

Diffusion of interstitial defects depends on the comparative size of the anion and cation [42]. The greater difference between the size of the cation and anion, the greater the fraction of free space in the crystal. If water is set free from the complex ion and enters interstitial positions, the diffusion of water through the crystal will be easiest when the difference between the sizes of the cation and anion is largest. The radius of $[Co(NH_3)H_2O]^{3+}$ is about 240 pm, while that of the Cl^- ion is about 181 pm. On the other hand, the radius of I^- is 220 pm. Accordingly, the loss of water would be easiest for the chloride compound and most difficult for the iodide, exactly as is observed (see Table 2). The radius of ClO_4^- is 236 pm, almost exactly the same as the radius of the cation. Since the fraction of free space is much lower when the cations and anions are of equal size, the perchlorate compounds should undergo deaquation–anation with difficulty. This is also what is observed experimentally [31,48]. The expected difficulty for accommodating water in interstitial positions in the $[Co(NH_3)_5H_2O]X_3$ compounds should be $ClO_4^- > I^- > Br^- > NO_3^- > Cl^-$. The nitrate compound appears to be out of order. However, the thermochemical radius of NO_3^- is 189 pm. In the case of the nitrate compound, there will be a larger free volume than expected based on the size of the anion and cation since the NO_3^- ion is not spherical. Thus, the actual order with respect to ease of the deaquation–anation reaction is $ClO_4^- > I^- > Br^- > Cl^- > NO_3^-$, exactly as predicted on the basis of the defect-diffusion model. The anion effect can be explained on the basis of free volume without attaching a label such as S_N2 to the reaction.

The entropy effects shown by the data given in Table 2 may be explained by the relative sizes and the free volume. Where there is a large difference between the size of the cation and anions, as in $[Cr(NH_3)_5H_2O]Cl_3$, the water molecule may be able to slip into an interstitial position, causing little or no lattice distortion. Therefore, the entropy of activation is small and negative. Where the cation and anions are of approximately the same size, water can occupy an interstitial position only with considerable lattice expansion so that the entropy of activation is positive. If this is, in fact, the case, one would expect the $\Delta S^‡$ values for dehydration of aqua complexes of the second- and third-row transition metals to be more negative for the chloride and less positive for the iodide. The data shown in Table 2 show that this is, in fact, the case. Again, the case of the nitrate compounds reveals that NO_3^- generates an anion effect similar to that produced by a smaller anion owing to its smaller volume. Hydrogen bonding of the liberated water may also play a role in assisting the molecules to enter interstitial positions. Again, the Ru(III) complexes follow the same trends in E_a and $\Delta S^‡$.

3.3 *Anation reactions and the defect-diffusion model*

In describing the defect-diffusion model, its application to the anation reactions of the $[M(NH_3)_5H_2O]X_3$ compounds has been illustrated. However, there are many other anation reactions for which this approach can be used to explain trends in the data. A small number of these reactions will be described here.

Recently, a study of the kinetics of the anation reactions of $[Ir(NH_3)_5H_2O]X_3$ (where $X = Cl$, Br, or I) was conducted [49]. In this study, it was found that the reactions followed an Avrami rate law (A2.5 for the chloride and bromide, and A2 for the iodide). The activation energies for the anation reactions reported were 75, 105, and 120 kJ mol^{-1}, respectively [49]. With the $[Ir(NH_3)_5H_2O]^{3+}$ cation, the greatest fraction of free space would be present in the chloride and the smallest fraction would be present for the iodide. Therefore, the expected order of activation energies for the anation reactions is chloride < bromide < iodide, exactly as is observed. It appears that the diffusion of water through interstitial positions correlates with the free space in the crystals.

Heating compounds having the formula $[M(NH_3)_5H_2O][Co(CN)_6]$ (where M = Co(III), Rh(III), or Ir(III)) results in an anation reaction in which a cyanide bridge forms [50–52].

$$[M(NH_3)_5H_2O][Co(CN)_6](s) \rightarrow [(NH_3)_5M{-}NC{-}Co(CN)_5](s) + H_2O(g) \qquad (10)$$

Ribas and Monfort studied these reactions and reported that, when M = Co(III), the reaction follows an Avrami A1.5 rate law, $[-\ln(1-\alpha)]^{2/3}$. This rate law was also indicated for the M = Rh(III) case but a zero-order or power law gave an equally good fit to the data. For the Ir(III) compound, the best fitting rate law was A3: $[-\ln(1-\alpha)]^{1/3}$ or a power law, P2: $\alpha^{1/2}$. Thus, none of the reactions appear to follow a first- or second-order rate law.

Activation energies of 129, 110, and 94 kJ mol^{-1} were reported for M = Co(III), Rh(III), and Ir(III), respectively [52]. This trend is expected on the basis of free space since the anion $[Co(CN)_6]^{3-}$ is the same in all cases and the cations increase in size for the series of complexes Co(III) < Rh(III) < Ir(III). Therefore, the rate of diffusion of water would be expected to vary for the series in the reverse order, which accounts for the observed activation energies.

Ribas et al. have studied the anation reactions of compounds having the formula $[M(NH_3)_5H_2O][Cr(CN)_6]$ and $[M(NH_3)_5H_2O][CrNO(CN)_5]$ where M = Cr(III), Co(III), Rh(III), or Ir(III) [53]. These anation reactions lead to compounds containing M–NC–Cr linkages. It was reported that the reactions gave the best fit with an Avrami rate law of the type A*n* where *n* varied from 1 to 2. It was stated that the rate plots were sigmoidal and that an average value of $n = 2$ gave the most consistent fit to the rate data. There was no indication that a first- or second-order rate law represented the data for these reactions. However, the activation energies for the anation reactions are as follows:

$[Co(NH_3)_5H_2O][CrNO(CN)_5]$	104.1 ± 5 kJ mol^{-1}
$[Rh(NH_3)_5H_2O][Cr(CN)_6]$	114.5 ± 2 kJ mol^{-1}
$[Rh(NH_3)_5H_2O][CrNO(CN)_5]$	118.6 ± 1 kJ mol^{-1}
$[Ir(NH_3)_5H_2O][Cr(CN)_6]$	135.2 ± 5 kJ mol^{-1}
$[Ir(NH_3)_5H_2O][CrNO(CN)_5]$	127.8 ± 5 kJ mol^{-1}

For this series of compounds, there is not a very large variation in activation energies. It appears, however, that in this case the availability of free space is not controlling the reactions since the greatest difference in cation and anion size would be for the Ir(III) complexes. Since Ir(III) is a third row transition metal ion, it may be that crystal field effects are more important than free space because of the increase in Dq values for metals in the order third row > second row > first row. More information is needed to explain the observed trend in activation energies.

Corbella and Ribas have studied the deaquation–anation reactions of *trans*-$[Cr(en)_2H_2OF]X_2$ where en = ethylenediamine and X = Cl, Br, I, or $(1/2)S_2O_6$ [54]. For these complexes, the activation energies reported were 107.6, 125.9, 152.0, and 148.5 kJ mol^{-1} for the chloride, bromide, iodide, and dithionate complexes, respectively. For the complexes in the same order, the values for $\Delta S^{\ddagger}$ were −13.2, −6.75, 15.3, and 12.4 cal mol^{-1} K^{-1}. It was found that the kinetic data were modeled best by a power law or by an A1.5 Avrami rate law except for the iodide compound. These observations are consistent with the defect-diffusion model rather than a reaction based on the concept of order. While the data will not be discussed here, complexes having 1,3-diaminopropane and 1,2-diaminocyclohexane were also studied with similar results [54]. Complexes containing cations with mixed diamine ligands have also been studied and the kinetic results are consistent with the free space model [55].

While the studies described thus far have shown the effect of varying the entire anion in a compound, a similar effect exists when the anion is a complex ion and some of the ligands are altered. An illustration of this is provided by the work on the complexes $[Co(NH_3)_5H_2O][CoX(CN)_5]$ where X = CN, Cl, Br, I, NO_2, or N_3 [43]. The deaquation reaction in this case leads to the formation of cyanide bridges of the type $[(NH_3)_5Co{-}NC{-}Co(CN)_4X]$. For all of the reactions except that of the azide, an Avrami A1.5, $[-\ln(1-\alpha)]^{2/3}$ rate law, gave the best fit to the kinetic data. In the case of the azide compound, the best fit was provided by an A2.5 rate law. The activation energies reported were as follows for the various identities of X: CN, 124.0; Cl, 120.5; Br, 91.8; NO_2, 84.0; N_3, 70.2; I, 63.5 kJ mol^{-1} [43]. When X is one of the smaller ligands such as CN or Cl, the cation and anion are approximately of equal size. As X is changed to the larger ligands such as N_3 or I, the overall size of the anion increases and the difference between the size of the cation and anion increases. Accordingly, the removal of water and placing it in an interstitial position becomes easier and the activation energy decreases. This is precisely the effect seen from the trend in activation energies.

Ribas et al. have studied the loss of water from $[Co(NH_3)_5H_2O]_2[M(CN)_4]_3$ compounds where M = Ni, Pd, or Pt leading to complexes of type $[(NH_3)_5Co{-}NC{-}M(CN)_3]_2[M(CN)_4]$ [56]. It was found that the activation energies for the dehydration reactions were 117.4, 131.0, and 66.7 kJ mol^{-1} for the Ni, Pd, and Pt complex anions, respectively. This is in accord with the expected order except for the Pt complex. In the case of the $Pt(CN)_4^{2-}$ anion, Pt–Pt interactions distort the lattice, resulting in easier diffusion of water through the lattice. However, the kinetic data obtained were shown to fit sigmoidal (α, t) plots and Avrami or growth rate laws. Consequently, these deaquation–anation processes are not S_N1 or S_N2 reactions. An additional study of this type involved the preparation of $[(NH_3)_5M'{-}CN{-}M(CN)_3]_2[M(CN)_4]_3$ by the dehydration of $[M'(NH_3)_5H_2O]_2$-

$[M(CN)_4]_3$ where $M' = Rh$ or Ir and $M = Ni$, Pd, or Pt [57]. In this case, the activation energies for the Rh complexes were 105, 115, and 90 kJ mol^{-1} for the $Ni(CN)_4^{2-}$, $Pd(CN)_4^{2-}$, and $Pt(CN)_4^{2-}$ compounds, respectively. For the Ir complexes, the corresponding values were 107, 118, and 92 kJ mol^{-1}, respectively. The low value for the Pt complex was interpreted in terms of the Pt—Pt interaction. The activation energies for dehydration of the Rh and Ir complexes presumably are lower than those for the Co complexes because there is a greater difference between the size of the anion and cation in those cases.

The effects of lattice anions on the ligand substitution reactions of the type

$$[M(phen)_3]X_3(s) \rightarrow [M(phen)_2X_2](s) + phen \tag{11}$$

have been investigated where M = Fe(II), Co(II), or Ni(II); X = Cl, Br, I, or (1/2)SO_4; and phen = 1,10-phenanthroline [58]. Kinetic analysis was carried out using a procedure which tests most of the rate laws shown in Table 1 [59]. For the Fe(II) complexes, the activation energies were as follows: chloride 164 kJ mol^{-1}, bromide 239 kJ mol^{-1}, iodide 335 kJ mol^{-1}, and sulfate 368 kJ mol^{-1}. For the Ni(II) complexes in the same order, the activation energies were reported to be 98, 183, 206, and 227 kJ mol^{-1}. Activation energies for the Co(II) complexes showed little variation with the nature of the anion. The data for the Fe(II) and Ni(II) complexes are consistent with the fact that the smaller the size of the anion, the larger the volume of free space and the lower the expected activation energy for the loss of a volatile ligand [58].

An extensive, highly replicated study of the deaquation–anation reaction of $[Co(NH_3)_5H_2O]Cl_3$ has recently been completed using both isothermal and non-isothermal methods [60]. Two independently prepared batches of $[Co(NH_3)_5H_2O]Cl_3$ were used. When studied non-isothermally (32 runs using each batch), kinetic analysis showed that the most appropriate rate law was either A1.5 or A2 with A1.5: $[-\ln(1-\alpha)]^{2/3}$ giving the best fit to more of the runs. For the 32 isothermal experiments on one batch, 26 gave the best fit with the A1.5 rate law and four gave the best fit with the A2 rate law. These results show clearly that the reaction

$$[Co(NH_3)_5H_2O]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s) + H_2O(g) \tag{12}$$

has been misinterpreted as S_N1 or S_N2 for many years, probably because of incomplete kinetic analysis of the data. However, LeMay and Babich have made important contributions to understanding these reactions by studying the effects of procedural variables on the processes [61]. The results of that study showed that particle size, sample size, sample bed thickness, heating rate, and nature of the atmosphere around the sample can all affect the kinetics of the reaction.

Studies have also been conducted using hexammine complexes. Ohyoshi et al.

have studied reactions of the type

$$[Cr(NH_3)_6]X_3(s) \rightarrow [Cr(NH_3)_5Cl]Cl_2(s) + NH_3(g) \qquad (13)$$

(where X is Cl or Br) in the solid state using thermal methods [62]. It was reported that the reaction "can be regarded as a first-order reaction with respect to the reactant" on the basis of linear $\log[a/(a-x)]$ plots, where a is the initial mass and $(a-x)$ is the mass at time t. The activation energies reported were 126 kJ mol^{-1} for the chloride compound and 180 kJ mol^{-1} for the bromide compound. These results are in agreement with the fact that there is less free space when the larger bromide ion is present.

This study is typical of many of those in the earlier literature in that there is no indication that the kinetic data were tested with the wide range of rate laws shown in Table 1, which are known to apply to processes in the solid state. Many of the earlier studies were based on the assumption that anation reactions should be described in terms of first- or second-order rate laws based on the anion effect. Also, many of the activation energies reported in the literature are questionable, having been based on very few experiments. It has been amply demonstrated that highly replicated kinetic studies are necessary to identify consistent rate laws and to determine accurate activation energies [24–27]. It is clear that the mechanisms of reactions of coordination compounds in the solid state are different from those proposed for the corresponding reactions in solutions. In many cases, it appears that the defect-diffusion model can provide realistic approaches to interpreting kinetic results [36,37].

There has been rapid improvement in the instruments and data analysis techniques used to study solid state reactions, including those of coordination compounds. The use of established principles of solid state science to answer questions about reactions of coordination compounds in the solid state is becoming more widespread. Since such reactions are important for synthetic purposes and as processes necessary to prepare a wide range of materials, it is inevitable that this area will receive increased attention in the future.

REFERENCES

1 S.M. Jorgensen, J. Prakt. Chem., 18 (1878) 209.
2 P. Pfeiffer, Berichte, 33 (1900) 2686.
3 P. Pfeiffer, P. Koch, G. Lando and A. Treischmann, Berichte, 37 (1904) 4256, 4269, 4277.
4 C.L. Rollinson and J.C. Bailar, Jr., J. Am. Chem. Soc., 66 (1941) 641.
5 C.L. Rollinson and J.C. Bailar, Jr., Inorg. Synth., 2 (1946) 196.
6 T.D. O'Brien and J.C. Bailar, Jr., J. Am. Chem. Soc., 67 (1945) 1856.
7 H.E. LeMay, Jr. and J.C. Bailar, Jr., J. Am. Chem. Soc., 89 (1967) 5577.
8 H.E. LeMay, Jr. and J.C. Bailar, Jr., J. Am. Chem. Soc., 90 (1968) 1729.
9 J.E. House, Jr. and J.C. Bailar, Jr., J. Am. Chem. Soc., 91 (1969) 67.
10 J.E. House, Jr. and J.C. Bailar, Jr., Inorg. Chem., 8 (1969) 672.
11 E.P. Hertzenberg and J.C. Bailar, Jr., Inorg. Chem., 10 (1971) 2371.

12 E.P. Hertzenberg and J.C. Bailar, Jr., Inorg. Chem., 10 (1971) 2377.
13 C. Kutal and J.C. Bailar, Jr., J. Phys. Chem., 76 (1972) 119.
14 T. Fujiwara and J.C. Bailar, Jr., Inorg. Chem., 25 (1986) 1806.
15 T. Fujiwara and J.C. Bailar, Jr., Bull. Chem. Soc. Jpn., 61 (1988) 849.
16 T. Fujiwara and J.C. Bailar, Jr., Bull. Chem. Soc. Jpn., 61 (1988) 857.
17 D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966.
18 M.E. Brown, D. Dollimore and A.K. Galway, in C.H. Bamford and D.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1972.
19 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48 (1981) 137.
20 J.E. House, Jr. and R.W. Eveland, J. Solid State Chem., in press.
21 D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966, Chap. 2.
22 M.E. Brown and C.A.R. Phillpotts, J. Chem. Educ., 55 (1978) 556.
23 E.A. Secco, J. Inorg. Nucl. Chem., 41 (1979) 607.
24 J.E. House, Jr., Thermochim. Acta, 47 (1981) 379.
25 J.E. House, Jr. and L.A. Marquardt, J. Solid State Chem., 89 (1990) 155.
26 J.E. House, Jr., R.J. Webb, K.A. Kemper and H.M. Fogel, Thermochim. Acta, 118 (1987) 261.
27 J.E. House, Jr., K.A. Kemper and H.M. Fogel, Thermochim. Acta, 129 (1988) 263.
28 W.W. Wendlandt and J.L. Bear, J. Inorg. Nucl. Chem., 22 (1961) 77.
29 R. Tsuchiya, Y. Kaji, A. Uehara and E. Kyuno, Bull. Chem. Soc. Jpn., 42 (1969) 1881.
30 K. Nagase and H. Yokobayashi, Bull. Chem. Soc. Jpn., 47 (1974) 2036.
31 M. Mori, R.T. Takemura and E. Matsuda, Bull. Chem. Soc. Jpn., 34 (1961) 1757.
32 J.S. Smith and W.W. Wendlandt, Nature, 201 (1964) 291.
33 W.W. Wendlandt and J.L. Bear, J. Phys. Chem., 65 (1961) 1516.
34 R.H. Gore and W.W. Wendlandt, Thermochim. Acta, 1 (1970) 491.
35 A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata and J. Oda, Bull. Chem. Soc. Jpn., 48 (1975) 262.
36 P. O'Brien, Polyhedron, 2 (1983) 233.
37 J.E. House, Jr., Thermochim. Acta, 38 (1981) 59.
38 A.R. West, Solid State Chemistry and its Applications, Wiley, New York, 1984, pp. 318–333.
39 J.C. Bailar, Jr., J. Inorg. Nucl. Chem., 8 (1958) 165.
40 P. Ray and N.K. Dutt, J. Indian Chem. Soc., 20 (1943) 81.
41 C.S. Springer, Jr. and R.E. Sievers, Inorg. Chem., 6 (1967) 853.
42 H. Schmalzreid, Solid State Reactions, Verlag Chemie, Weinheim, 2nd edn., 1974, pp. 24–27.
43 J. Casabo, T. Flor, F. Teixidor and J. Ribas, Inorg. Chem., 25 (1986) 3166.
44 D. Bhatta, J.K. Mishra and S.R. Mohanty, Indian J. Chem., 23A (1984) 1030.
45 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reaction, Wiley, New York, 2nd edn., 1967, Chap. 3.
46 J.E. Huheey, Inorganic Chemistry, Harper and Row, New York, 2nd edn., 1978, p. 363.
47 C.K. Jorgensen, Modern Aspects of Ligand Field Theory, Elsevier, New York, 1971, pp. 347–348.
48 M. Mori and R.T. Tsuchiya, Bull. Chem. Soc. Jpn., 33 (1960) 841.
49 J. Ribas and M. Monfort, Thermochim. Acta, 91 (1985) 115.
50 R.A. Castello, C.P. MacColl, N.B. Egan and A. Haim, Inorg. Chem., 8 (1969) 699.
51 J.E. House, Jr. and B.J. Smith, J. Inorg. Nucl. Chem., 39 (1977) 777.
52 J. Ribas and M. Monfort, Thermochim. Acta, 76 (1984) 201.
53 J. Ribas, A. Escuer and M. Monfort, Inorg. Chem., 24 (1985) 1874.
54 M. Corbella and J. Ribas, Inorg. Chem., 25 (1986) 4390.
55 M. Corbella and J. Ribas, Inorg. Chem., 26 (1987) 3589.
56 J. Ribas, M. Serra and A. Escuer, Inorg. Chem., 23 (1984) 2236.

57 J. Ribas, M. Serra and A. Escuer, Inorg. Chim. Acta, 116 (1986) 157.
58 S. Yamasaki, T. Fujiwara and Y. Yamamoto, Bull. Chem. Soc. Jpn., 60 (1987) 2565.
59 L. Reich and S.S. Stivala, Thermochim. Acta, 34 (1979) 287.
60 D.G. Beck, M.S. Thesis, Illinois State University, Normal, 1991.
61 H.E. LeMay, Jr. and M.W. Babich, Thermochim. Acta, 48 (1981) 147.
62 A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata and J. Oda, Bull. Chem. Soc. Jpn., 48 (1975) 230.