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A PROPOSED MECHANISM FOR THE THERMAL REACTIONS IN SOLID COMPLEXES

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ABSTRACT

A general mechanism is proposed for solid state reactions of coordination compounds in which the generation of a point defect is considered as the formation of the transition state. Three types of defects are considered which may apply in different types of reactions. The types of point defects considered are analogous to the Schottky, Frenkel, and substituted ion types occurring in simple crystals. Intramolecular racemization of (+) — $[Co(en)_3]X_3$ (X = Cl, Br, SCN, or I) is shown to be consistent with the substituted ion type of defect, while dehydration of $[Cr(NH_3)_5H_2O]X_3$ complexes is consistent with the formation of a Frenkel type of defect. Energy of the formation of the transition state is discussed in terms of lattice energy and ionic radii.

INTRODUCTION

A large body of literature exists which supports the existence of an "anion effect" in certain solid state reactions involving coordination compounds. This effect comes in the form of reactions like

$$[M(NH_3)_5H_2O]X_3 \xrightarrow{\Delta} [M(NH_3)_5X]X_2 + H_2O \qquad (1)$$

(where M = Cr, Co, or Ru and X = Cl, Br, NCS, I, or ClO_4) which exhibit different activation energies depending on the nature of X [1—12]. A variety of reactions show this dependence on the nature of the anion (or in some cases the cation). Racemization of (+) — $[Co(en)_3]X_3$ depends on the nature of the anion as well [13].

The difficulty in trying to ascribe a mechanism for a solid state reaction on the basis of the experimental rate law has been adequately reviewed [14]. However, even the recent literature persists in trying to describe solid state reactions in terms applicable to processes carried out in the gas phase or in solution. For solids, however, the chemical behavior is often determined by the concentration of various types of defects, not concentrations of reactants [15,16]. It is appropriate, then, to seek mechanistic explanations for solid state reactions in terms of the defect behavior of solids. The purpose of this paper is to present an interpretation of some selected solid state processes in terms applicable to the defect nature of solids.

THE DEFECT-DIFFUSION MODEL

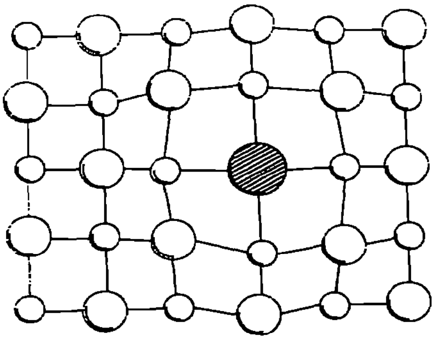
For the purposes of this discussion, we will consider that the initiation of a solid state reaction necessitates the formation of a transition state which causes a point defect in the crystal lattice. Point defects of several types are known, and similar types are presumed to be formed by the transition state. Different types of defects must be invoked to explain different types of reactions. For example, racemizations appear to be a quite different from dehydrations [1,13]. As a simple example of a point defect, we can consider one lattice site to be occupied by an ion of larger size than would normally be found in that site. This substituted ion defect causes an expansion of the lattice around that site of the type shown in Fig. 1. If we presume that the transition state is represented by that larger ion, the lattice expansion is hindered and the degree of hindrance will depend on the lattice energy. The higher the lattice energy, the greater will be the energy of the transition state. Thus, this type of defect formation can serve as a model for the transition state where the reactive species changes structure in a way that leads to a volume increase.

A second type of point defect is the Schottky defect in which an ion is missing from its regular lattice site. To preserve electrical neutrality, this type of defect occurs in pairs. In forming the transition state during a process such as that shown in eqn. (1), we need not consider a pair of defects since the anion vacating a lattice site becomes attached to the complex ion if the process is equivalent to an S_N2 reaction. Therefore, the migration of an anion to the complex could be considered as generating an anion type of Schottky defect as shown in Fig. 2.

The energy for formation of the Schottky type defects can be written as [17]

$$E_s = U\left[1 - \frac{1 - 1/\epsilon}{A\{1 - (1/n)\}}\right] \qquad (2)$$

where ϵ is the dielectric constant, A is the Madelung constant, and n is the



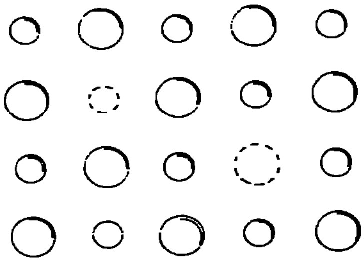


Fig. 1. A substituted ion type of defect in a solid.

Fig. 2. Defects of the Schottky type in a solid.

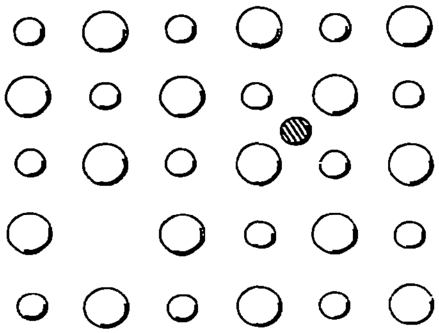


Fig. 3. A Frenkel type of defect in a solid.

exponent of the repulsion term in the lattice energy equation

$$U = \frac{Z_a Z_c A N_0 e^2}{r}\left(1 - \frac{1}{n}\right) \tag{3}$$

The essential feature here is that the energy for the formation of this type of defect is related to the lattice energy for the crystal. This will be explored later in connection with application of this model.

If the reaction under consideration begins with the loss of a volatile ligand from a complex ion in a lattice site, that ligand must be placed in an interstitial position in the lattice. An analogous point defect in a simple crystal is that of the interstitial ion, or Frenkel defect. The transition state thus involves a species having a coordination number one less than that of the original complex ion, with the liberated ligand being in an interstitial position. Creation of this type of defect is equivalent to the initiation of an S_N1 process and is shown in Fig. 3. The ligand causing the defect must now either return to the original complex ion or diffuse through the lattice. Although the process may be S_N1, there will be a difference in the diffusion coefficient of a Frenkel defect through the lattice depending on the relative size of the ions. Thus, the S_N1 process which follows this model will still exhibit rate differences depending on the nature of the ions surrounding the reactive site, and this gives rise to an anion effect on the rate of such a process.

The two properties that are most influential in determining the concentration of point defects are the lattice energy and the relative sizes of the ions (or the lattice spacing). Accordingly, we can consider the lattice energy effects in terms of the Kapustinskii equation

$$U = \frac{287.2 Z_a Z_c m}{r_a + r_c}\left(1 - \frac{0.345}{r_a + r_c}\right) + 2.5 m Z_a Z_c \tag{4}$$

where m is the number of ions in the formula, Z_a and Z_c are charges on the anion and cation, and r_a and r_c are the radii of the anion and cation.

We will now describe selected systems where the defect-diffusion mechanism provides viable alternatives to the conventional mechanisms.

APPLICATIONS OF THE DEFECT-DIFFUSION MECHANISM

Dehydrations

Before proceeding to describe the defect-diffusion mechanism for these reactions, we shall first describe some of the experimental and theoretical

TABLE 1

Kinetic parameters for dehydration of aquo complexes [a]

Complex	E_a (kcal $mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
$[Ru(NH_3)_5H_2O]Cl_3$	22.7	-7.1
$[Ru(NH_3)_5H_2O]Br_3$	23.4	-5.2
$[Ru(NH_3)_5H_2O]I_3$	26.7	5.8
$[Ru(NH_3)_5H_2O](NO_3)_3$	19.3	-15.9
$[Cr(NH_3)_5H_2O]Cl_3$	26.4	-2.53
$[Cr(NH_3)_5H_2O]Br_3$	29.7	9.2
$[Cr(NH_3)_5H_2O]I_3$	32.7	15.4
$[Cr(NH_3)_5H_2O](NO_3)_3$	24.3	-2.49

[a] From ref. 1.

considerations which are relevant. Because the nature of the anion influences the rate, there has been a tendency to call these reactions S_N2. However, ligand exchange processes for Co(III) and Cr(III) are, for the most part, S_N1. In cases of other solid state reactions where the anion effect is slight, the reactions have been labeled S_N1. It must now be considered whether these processes are in fact realistic for solid state processes. An isokinetic relationship has shown that the same mechanism is involved in the dehydration of the series of compounds $[Cr(NH_3)_5H_2O]X_3$, where X = Cl, Br, SCN, or I [18]. However, there is no indication of what this mechanism is. Table 1 shows kinetic parameters for dehydration reactions of this type. Many other data could be listed but this set was chosen for consistency.

For the reaction

$$[Cr(NH_3)_5H_2O]X_3 \xrightarrow[\Delta]{} [Cr(NH_3)_5X]X_2 + H_2O$$

an S_N2 process would require that an anion leave a lattice site and migrate to the complex ion to form a transition state having a coordination number of seven. Two processes are involved here. The first is the vacating of the lattice site by X and the second is the attachment of X to $[Cr(NH_3)_5H_2O]^{3+}$. Vacating a lattice site in an ionic crystal to form a defect is known to be a process requiring considerable energy [17]. Forming a seven-bonded complex is also unfavorable based on a crystal field model, and it requires the sacrifice of about 4.26 Dq, with Dq being about 2100 cm^{-1} for the $[Cr(NH_3)_5H_2O]^{3+}$ ion [19]. This alone would be about 25 kcal $mole^{-1}$ in this case. Thus, the sum of these two events happening in an S_N2 process is significantly greater than the 20—30 kcal $mole^{-1}$ activation energies for reactions of this type [1].

If the process takes place by an S_N1 pathway, the rate determining step is the loss of H_2O from $[Cr(NH_3)_5H_2O]^{3+}$, and the activation energy should be invariant with the nature of the anion. Furthermore, the formation of the five-bonded transition state for a d^3 ion requires giving up 2 Dq if a square based pyramid is formed or considerably more if a trigonal bipyramid is formed [20]. Thus, for $[Cr(NH_3)_5H_2O]^{3+}$, where Dq is about 2100 cm^{-1}, the first of these two cases would correspond to an activation energy of about 12 kcal $mole^{-1}$. This is not sufficiently close to the experimental activation energies for it to be tempting to ascribe the processes as S_N1 with a square based pyramid transition state. The problem with this is, of course, that the activation energy varies depending on the anion present, and therefore the process does not appear to take place by an S_N1 pathway.

For the dehydration to be S_N2, an anion must leave its site in the crystal lattice and enter the coordination sphere of the metal ion. This formation of the transition state would involve the vacating of an anion site with the formation of a Schottky type defect (Fig. 2), and it would be expected that the activation energy would increase with increasing lattice energy in accord with eqn. (2). Since for a given cation the lattice energy would increase as the size of the anion decreases, the chloride compound should have the highest lattice energy. The opposite effect is seen and the dehydration of the chloride salt has a lower activation energy than that of the iodide or bromide [1].

For a given size of cation, diffusion of interstitial defects depends on the size of the anion (or the comparative size of anion and cation) [17]. In fact, interstitial diffusion of Frenkel defects is enhanced by a greater difference in size between cation and anion. The basis for this is that the volume of free space is greater when the cations and anions are of greatly differing sizes. Thus, if water is set free from the complex ion in forming the transition state, the escape of a water molecule will be easiest for the chloride compound since the radius of the cation is about 2.40 Å while that of the Cl^- is 1.81 Å. On the other hand, the radius of I^- is 2.20 Å and the diffusion of interstitial water would be more difficult owing to the smaller free volume. The fact that the perchlorate compound does not dehydrate is in accord with this since the radius of ClO_4^- is 2.36 Å, almost exactly the same as the radius of the cation. The expected difficulty of formation of this type of Frenkel defect should decrease in the order $I^- > Br^- > NO_3^- > Cl^-$. Thus, the expected ease of diffusion of the defect has the iodide compound being the most difficult and the chloride compound being the easiest. This would predict the order of anion effects on the activation energies and this is exactly the order observed. The case of the nitrate compound can be expected not to follow the trend of the remainder of the series because of the structural difference of the anion. With a given cation, the spherical halide ions show a regular effect on the free volume but the effect of the nonspherical NO_3^- will be different. Thus, while the radius of NO_3^- is 1.89 Å, there will be a larger free volume than expected based on size of anion and cation in the nitrate compound since the nitrate ion is not spherical. As far as volume effects are concerned, the nitrate compound should actually behave as though a smaller anion is present, and have a greater free volume. Diffusion of H_2O would be enhanced and the activation energy would be lower than expected on the basis of anion radius, as is observed for both the Cr(III) and Ru(III) complexes.

The entropy effects revealed by the data shown in Table 1 may be explained by the relative sizes of the ions 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 $\Delta S^{\ddagger}$ values for dehydration of aquo complexes of second- and third-row transition metals to be more negative for the chloride and less positive for the iodide. The data shown in Table 1 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 trend in E_a and $\Delta S^{\ddagger}$.

Racemization

The racemization of (+) — $[Co(en)_3]X_3 \cdot n\,H_2O$ (where X = Cl, Br, SCN, or I and $n = 0$ or 1) has been studied in detail by Kutal and Bailar [13]. It was found that the rate of racemization decreases in the order of anions $I^- > Br^- > NCS^- > Cl^-$ for the anhydrous compounds. It was also found that at 127°C the hydrated complexes racemized much faster than the anhydrous ones. However, conclusive evidence was presented to show that the effect was caused by physical modification of the lattice during dehydration. For example, the rate of racemization in solution in a sealed tube was found to be much slower than that for the hydrated solids at the same temperature. However, there was no indication of what the microscopic effects on the lattice were. It was assumed that the changes in ligand field stabilization energy and the ligand—ligand repulsion were constant for the series. The main difference in the series was attributed to the interactions of $[Co(en)_3]^{3+}$ and the anions. It was presumed that hydrogen bonding of the type N—H . . . X was responsible for the differences [13]. However, it may be that factors other than hydrogen bonding are responsible for the rate differences. We now consider this racemization process in terms of the defect-diffusion mechanism.

Since the racemization in this case is known to proceed without rupture of the chelate rings, it is clear that the effect of the anions produces the rate differences. If we accept the evidence that the intramolecular trigonal twist process operates in the cation, then the trigonal transition state is produced only with the expansion of the cation. Thus, a point defect of the type shown in Fig. 1 is produced with the expanded cation behaving as the substituted ion. The difficulty with which this is accomplished increases with increasing lattice energy since we can think of that cation expansion as occurring against the forces generated by the surrounding anions. For a constant cation radius, the lattice energy decreases with increasing $(r_a + r_c)$ according to the Kapustinskii equation. Thus, the formation of the transition state would be easiest in the case of the largest anion. For I^-, Br^-, NCS^-, and Cl^-, the crystallographic radii are 2.20, 1.95, 1.95, and 1.81 Å, respectively, which is exactly in accord with the ease of racemization of the salts of (+) — $[Co(en)_3]X_3$. Thus, for the intramolecular twist to produce a point defect of the type shown in Fig. 1, lattice effects caused by the anions are easily predicted. The fact that Br^- and NCS^- are of similar radii but the compounds racemize at different rates may be because Br^- is spherical while NCS^- is not and, therefore, NCS^- occupies a smaller volume and behaves as a smaller ion as far as lattice expansion is concerned.

The effect of lattice water is also explainable in terms of lattice expansion caused by water escaping during dehydration. As the water diffuses through the lattice, it occupies interstitial positions which causes the lattice expansion to be enhanced and the rate of racemization to be increased. Also, one water molecule diffusing from one unit cell to another could produce a chain effect so that the rate is enhanced greatly as dehydration occurs, exactly as observed. Thus, all the essential features of these racemization processes are accounted for in terms of the defect-diffusion model.

The racemization of 1-*cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ has been interpreted in terms of an aquation—anation pathway [21]. One of the most interesting observations was that nearly complete racemization occurs when a sample is heated slowly at 1—2° C min^{-1} to 180° C but only partial racemization occurs if the compound is heated quickly to 180° C and then held at that temperature for an extended period. Although other explanations are possible, the defect-diffusion mechanism provides a suitable explanation. When heated quickly to 180° C, the loss of water would be rapid and the dehydrated compound would undergo slow racemization owing to the difficulty in forming the transition state of the type shown in Fig. 1. During slow heating, the gradual loss of water to interstitial positions could provide for lattice expansion and relaxation which reduces the lattice energy in the region of the transition state. Hence, the effect is greater than if the water is lost quickly and then a transition state of higher energy must be formed without the assistance of lattice expansion by escaping water.

In this paper, reactions in solids are described in terms of the fundamental processes occurring in the solid state. Using the concepts of defects and diffusion, mechanisms consistent with the experimental observations are found. The appealing nature of this approach lies in the fact that the formation of the transition state does not require the assumption that the same steps are involved in solids as in solutions. Observed anion effects appear therefore as natural consequences of size and lattice energy.

No attempt has been made to examine all the literature available on solid state reactions in light of the proposals made here. Neither is any claim made that the defect-diffusion mechanism applies to all reactions in the solid state. For the reactions examined here, the defect-diffusion mechanism does provide an alternative to traditional labels. Other applications of this model are being considered and the results of these will be reported in future papers.

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