Letters

Rate laws for the racemization of co-ordination compounds in the solid state

THE kinetics of solid-state processes is a complicated and contentious subject; it is, however, well documented in the literature of ceramics and chemical engineering.[1-6] In the light of this it is surprising that the vast majority of studies of the reactions of co-ordination compounds in the solid state are dominated by interpretations based on concepts and models more appropriate for homogeneous gas- and solution-phase kinetics. The purpose of this Letter is to reconsider in detail the recently reported [7,8] kinetics of thermal racemization of the tris-chelated complexes of 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) with nickel(II) and iron(II) in the solid state. It is shown that a more accurate model of the kinetics of these reactions is available in well known equations for the kinetics of solid-state processes and that subsequently the correlation of activation parameters with elementary chemical processes is fraught with difficulties.

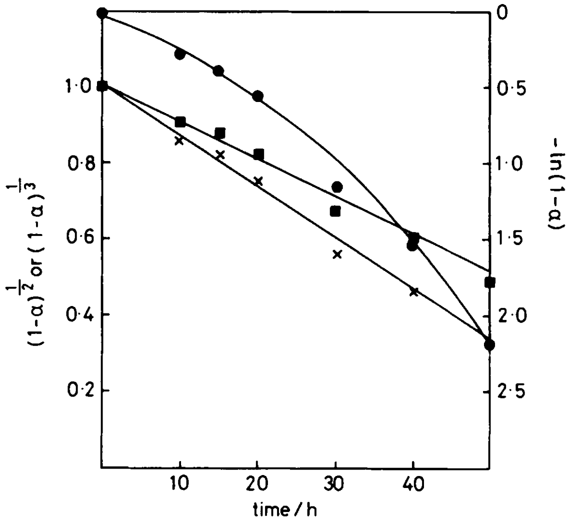
Some commonly used equations for solid-state reactions are in the Table; only in the case of random nucleation is a first-order model (F_1) appropriate, and in this case plots of $\ln(1-\alpha)$ *versus* time should be collinear with the origins.[5] This is clearly not the case in the work of Yamamoto and co-workers. One implication of this is that another rate law may be more appropriate. An investigation of the earlier data of Yamamoto and co-workers fully published in ref. 7 was undertaken.

Some commonly used solid-state reaction rate equations

Mechanism [a]	Integrated form [b]	Notation [b]	m [b,c]
d.c., 1 dimension	$\alpha^2 = (k/x^2)t$	$D_1(\alpha)$	0.62
d.c., 2 dimensions	$(1-\alpha)\ln(1-\alpha) + \alpha = (k/r^2)t$	$D_2(\alpha)$	0.57
d.c., 3 dimensions	$(1-2\alpha/3) - (1-\alpha)^{2/3} = (k/r^2)t$	$D_4(\alpha)$	0.57
p.b.c., 2 dimensions	$1-(1-\alpha)^{1/2} = (u/r)t$	$R_2(\alpha)$	1.11
p.b.c., 3 dimensions	$1-(1-\alpha)^{1/3} = (u/r)t$	$R_3(\alpha)$	1.07
First order (r.n.)	$\ln(1-\alpha) = -kt$	F_1	1.00
n.g., 2 dimensions	$[-\ln(1-\alpha)]^{1/2} = kt$	$A_2(\alpha)$	2.00
n.g., 3 dimensions	$[-\ln(1-\alpha)]^{1/3} = kt$	$A_3(\alpha)$	3.00

[a] d.c. = Diffusion control, p.b.c. = phase-boundary control, r.n. = random nucleation, n.g. = nucleation and growth. [b] Notation of Sharp and co-workers (ref. 6) is used; t = time. [c] Slope of plot of $\ln[-\ln(1-\alpha)]$ *versus* $\ln t$, see ref. 3.

Various methods have been suggested for assigning the rate law of solid-state processes. Brindley *et al.*[6] have shown the utility of a reduced time plot; such plots have markedly different shapes for different reaction types. Hancock and Sharp [3] have advocated the use of plots of $\ln[-\ln(1-\alpha)]$ *versus* $\ln t$; the gradient of such plots in the region $0.1 < \alpha < 0.5$ is characteristic of the type of mechanism. Briefly, for the gradient *m ca.* 1, the concept of an order of reaction is valid, for *m ca.* 0.5 diffusion control dominates, and for $m > 2$ nucleation and growth (Avrami/Erofeyev) kinetics apply. Finally, the correlation of plots of integrated rate equations against time may be compared statistically. These three methods have been applied to our study of Yamamoto's data, each leading to essentially the same conclusions.



Kinetics of racemization of anhydrous $[Fe(phen)_3][ClO_4]_2$; graphical representation of various rate laws: (●) $-\ln(1-\alpha)$, (■) $(1-\alpha)^{1/2}$, (×) $(1-\alpha)^{1/3}$

Considering each complex in turn, for $[Fe(phen)_3]$-$[ClO_4]_2$ we find *m ca.* 1 at all temperatures, suggesting that the concept of an order of reaction is valid. A statistical and graphical analysis of the results (Figure) leads to the conclusion that a phase-boundary controlled process in two dimensions (R_2) best describes the kinetics. The results of our calculations are similar for $[Ni(phen)_3][ClO_4]_2$.

For the bipyridyl complexes the gradients of $\ln[-\ln(1-\alpha)]$ *versus* $\ln t$ are much steeper, suggesting nucleation and growth kinetics are appropriate; for none of these complexes are Yamamoto's plots of $\ln(1-\alpha)$ *versus* time collinear with the origin, and many also show marked curvature. The slopes of the $\ln[-\ln(1-\alpha)]$ plots lead to the conclusion that nucleation and growth in two dimensions occurs for the nickel complex and in three for the iron complex. For all four complexes reduced time plots indicate that the reactions belong to the type postulated above. The quantity of data available is rather limited both in terms of α *versus* time and temperature range; however, it seems clear that there is little theoretical justification for the use of a first-order rate law. The suggested mechanisms involve control of reaction rate by physical factors and not by elementary chemical steps; the correlation of rates or related activation parameters with fundamental chemical steps is hence unreliable.

The nature of racemization in the solid state also calls for a careful consideration to be made of the relationship between the rate constant for racemization (whatever the mechanism) with that for interconversion of the enantiomorphs. When the racemization of optically active materials in dilute solutions prepared with achiral solvents is studied, it is usual and correct to explain the relationship between inversion and racemization as shown below (L and D are enantiomorphs,

$$\left.\begin{array}{ll} 2\text{L} \xrightarrow{k_{\text{rac.}}} \text{L} + \text{D} & \text{racemization} \\ \text{L} \overset{k_{\text{inv.}}}{\rightleftharpoons} \text{D} & \text{inversion} \end{array}\right\} k_{\text{inv.}} = k_{\text{rac.}}/2$$

$k_{\text{inv.}}$ and $k_{\text{rac.}}$ the rate constants for inversion and racemization respectively).

In the solid state we are dealing with the racemization of the compound within the asymmetric matrix of the crystal; optically pure and racemic compounds are not isomorphous, so simple correlations of inversion and racemization rate constants are hence not valid. These complexes racemize with phase-boundary or nucleation and growth control of reaction rate, *i.e.* the rate-determining step is not necessarily the inversion itself but is concerned with physical processes within the crystal. It thus seems intrinsically unreasonable to equate the rate constants for racemization and interconversion in the way earlier workers have. In many ways this view is similar to that recently advocated by House.[9]

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FUJIWARA and YAMAMOTO reply. In our previous study of the solid-state racemization of halide salts of tris-complexes of phenanthroline and 2,2′-bipyridyl with nickel(II) and iron(II) ions, these complex salts were found to undergo a rapid initial loss of optical activity and subsequently to racemize according to a first-order process as shown in Figure 1 of ref. 1. Such an initial loss was reported for the complex salts $K_3[Cr(C_2O_4)_3]$ [2] and $[Co(en)_3]X_3$(en = ethylenediamine).[3] In addition, an induction period which evidently divides the initial process from the subsequent first-order process was observed for $(-)$-$[Ni(phen)_3]I_2$, see Figure 2 of ref. 1. In the case of the perchlorates of nickel(II) and iron(II) complexes,[4] however, the three processes (initial, induction, and first-order) did not appear clearly under the experimental conditions and the apparently linear relationship [$\ln(1 - \alpha)$ *versus* time] through overlapping of the three processes was considered to be valid. Kutal and Bailar [3] have pointed out that lattice defects play an important role in the initial racemization of $(+)$-$[Co(en)_3]X_3$. On the other hand, the subsequent racemization for $(-)$-$[Ni(phen)_3]X_2$ and $(+)$-$[Fe(phen)_3]X_2$ obeys a distinct first-order rate expression as found in our study [1] as well as that for $K_3[Cr(C_2O_4)_3]$.[2] This may be the case of random nucleation. However, the first-order racemization does not appear to be appreciably related to physical processes within the crystal lattice. If the physical processes alone give a definite effect on the racemization of these solid complexes, the expected difficulty of the lattice expansion during the racemization (or $\Delta H^{\ddagger}$), related to the lattice energy as pointed out by House,[5] should increase with the lattice anion in the order $X = ClO_4^- < I^- < Br^- < Cl^-$. However, the reverse order in $\Delta H^{\ddagger}$ was observed in our study ($Cl^- < Br^- < I^- < ClO_4^-$).[1] This fact indicates that the chemical interaction of the halide ions with the chelate cations should be reflected on the racemization process with a first-order expression. Moreover, $\Delta H^{\ddagger}$ values for all the iron complex salts were found to be identical.[1] O'Brien's letter does not explain the difference in the anion effect on $\Delta H^{\ddagger}$ between the nickel and iron complexes. We consider that the physical factors alone (lattice energy and ionic radii) [5] could not explain this difference and so the chemical factor, donicity of lattice anions or the interaction of anions with chelate cations, should be important in determining the anion effect on racemization. In addition, the solid samples of the anhydrous complexes were confirmed to be amorphous by *X*-ray powder photographs.[1]

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