Temperature Dependence of Reaction Rate in Crystalline State Racemization

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TEMPERATURE DEPENDENCE OF REACTION RATE IN CRYSTALLINE STATE RACEMIZATION

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Abstract   In crystalline state racemization of cobaloxime complexes, the reaction rate and the reaction cavity, a void space around a reactive group, depend linearly on temperature. The change of the unit cell dimensions did not reveal the true rate when the cavity was large enough. The Arrhenius plot indicated that the activation energy for the crystalline state racemization is 5-9 kJmol^{-1}.

INTRODUCTION

It has been found that the chiral 1-cyanoethyl(ce)-group in some crystals of bis(dimethylglyoximato)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), cobaloxime, complexes are racemized by X-ray exposure without degradation of the crystallinity[1]. The slow rate of the racemization allowed the analysis of several intermediate structures. When the axial base ligand was replaced with other amines and phosphines, a variety of crystalline state racemizations were observed. The racemization processes, roughly speaking, can be divided into three modes. The first mode is the simplest among them, *i.e.* the crystal has only one molecule in its asymmetric unit and the chiral ce-group is racemized to a disordered structure, $R : S = 1 : 1$.

This requires a void space or a reaction cavity around the reactive group if it is to undergo a crystalline state racemization. In this paper, the relationship between temperature dependence of the reaction rates and that of the cavity volumes for three cobaloxime complexes belonging to the first mode are investigated at four
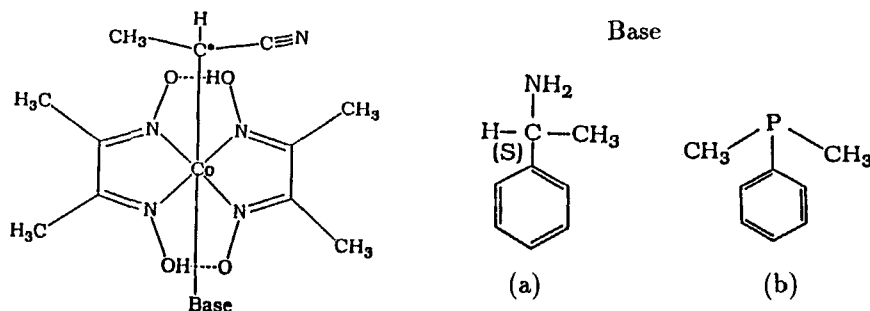
FIGURE 1   Three cobaloxime complexes examined, (a) S-S and R-S complexes and (b) DMP complex.

different temperatures. FIGURE 1 shows three cobaloxime complexes examined, [S-1-cyanoethyl][S-1-phenylethylamine]cobaloxime (S-S complex), [R-1-cyanoethyl][S-1-phenylethylamine]cobaloxime (R-S complex), and [R-1-cyanoethyl][dimethylphenyl-phosphine]cobaloxime (DMP complex). The structures and the racemization processes of these complexes have been reported[2,3,4]. Complexes belonging to the second and third modes will be discussed elsewhere.

REACTION RATE AND CAVITY VOLUME

The volumes of the cavities around ce-groups were determined from the crystal structures for three complexes at four temperatures, 223K, 253K, 298K, and 333K. They are shown in FIGURE 2 by open circles. The change of cell parameters were measured as a function of exposure time. They were well-explained by first-order kinetics. The rate constants were estimated by least squares fitting procedures, using three parameters whose changes are significantly greater than their esd's. They are also shown in FIGURE 2 by close circles.

Cavity volumes gradually expand as the temperature increases for three complexes but the rate constants show significant peculiarities. The rate constant for the S-S complex depends roughly on the size of the cavity. On the other hand, the rate constant for the R-S complex abruptly decreases above room temperature. For the DMP complex, the rate constant does not vary significantly with temperature.

The change of the occupancy factor of the inverted ce-group with exposure time was measured for the R-S complex at 333K. The rate constant deduced from
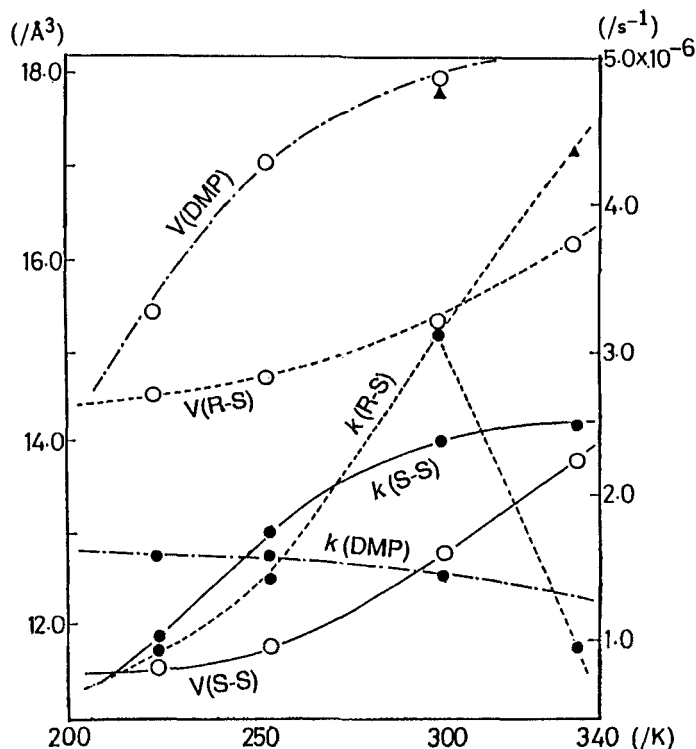
FIGURE 2 Temperature dependence of the rate constant (close circles) and cavity size (open circles) for S-S, R-S, and DMP complexes. Rate constants of racemization determined by occupancy factors are shown by triangles.

the change of occupancy factor is quite large as indicated by a triangle in FIGURE 2. This is approximately the value that is obtained if the plot of rate constants calculated by cell changes is extrapolated to 333K. The structure analysis of DMP complex at the intermediate stage also indicated that the reaction rate from the occupancy factor (triangle in FIGURE 2) is much faster than that estimated from the cell changes.

These results indicate that the rate constant deduced from the cell changes is correlated with the size of the cavity only when the cavity is not too large. When the cavity is greater than about 16Å^3, however, the rate constant cannot be obtained by the change of cell dimensions. If the cavity is large enough, it is not necessary to expand the unit cell in order to accommodate the inverted ce-group. This may be a reason why reactivities estimated by powder patterns are often very complicated.

S-S complex

R-S complex

ACTIVATION ENERGY = 4.8 kJmol^{-1} ACTIVATION ENERGY = 8.9 kJmol^{-1}
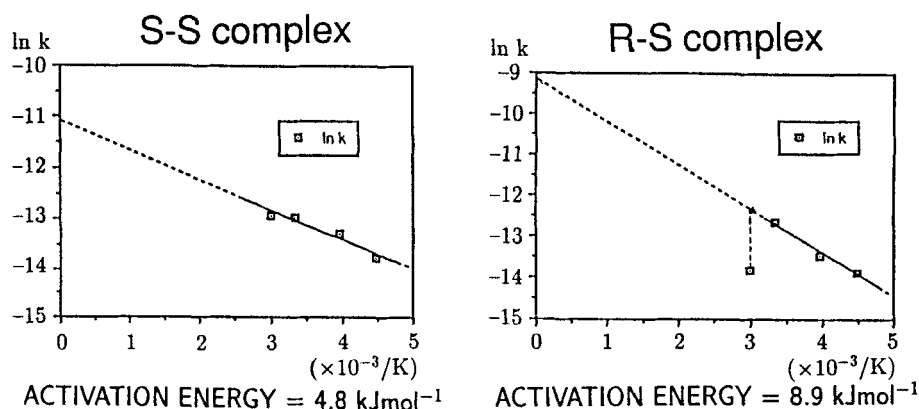
FIGURE 3   Arrhenius plots for S-S and R-S complexes. A triangle indicates the value determined by the occupancy factor.

FIGURE 3 shows Arrhenius plots for S-S and R-S complexes. The activation energies are estimated as 4.8 and 8.9 kJmol^{-1} for S-S and R-S complexes, respectively. Since the activation energy of the R-S complex is greater than that of S-S complex, one might expect the temperature dependence of the cavity size for R-S complex to be greater than that for S-S complex. Opposite results are, however, obtained as shown in FIGURE 2. This may suggest that the effective volume of the cavity as well as the cavity size should be taken into account in order to correlate the cavity volume with the temperature dependence of the reaction rate.

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