

## Site Lifetime Temperature Variations in Intermolecular Exchange Processes Characterized by a Two-Term Rate Law

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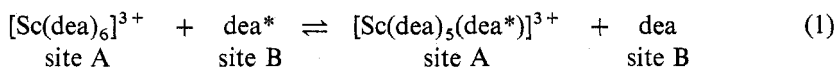
### Abstract

The temperature dependence of the site lifetimes,  $\tau_A$  and  $\tau_B$ , characterizing the intermolecular exchange of X between sites A and B through simultaneous first-order and second-order processes as expressed in the rate law

$$1/\tau_A = \chi_B/\chi_A\tau_B = k_1 + k_2[B]$$

and the treatment of such data determined by nuclear magnetic resonance spectroscopy are discussed.

The site lifetimes,  $\tau_A$  and  $\tau_B$ , characterizing the intermolecular exchange of X between sites A and B exhibit an Eyring temperature-dependence for a single-term first or higher order exchange rate law. Under the usual circumstances where the ground state and transition state heat capacities are temperature-independent this results in a linear dependence of  $\ln(\tau_A T)$  and  $\ln(\tau_B T)$  on the reciprocal of temperature,  $1/T$ . However, for a two-term rate law containing a first-order and a second-order term with dissimilar activation enthalpies the dependence of  $\ln(\tau_A T)$  and  $\ln(\tau_B T)$  on  $1/T$  may become non-linear as recently observed<sup>1</sup> for the exchange of *N,N*-diethylacetamide (dea) on  $[\text{Sc}(\text{dea})_6]^{3+}$  shown schematically in equation (1) (where the asterisk is a typographical distinction only)



and as predicted by the two-term Eyring equation (2) for  $\tau_A$ :

$$\begin{aligned} 1/\tau_A &= k_1 + k_2[B] \\ &= (k_B T/h) \{ \exp(-\Delta H_1^\ddagger/RT + \Delta S_1^\ddagger/R) + [B] \exp(-\Delta H_2^\ddagger/RT + \Delta S_2^\ddagger/R) \} \end{aligned} \quad (2)$$

In equation (2)  $k_1$  and  $k_2$  are first-order and second-order rate constants,  $[B]$  is the concentration of X at site B, the subscripted activation parameters refer to the similarly subscripted rate constants, all other symbols have their usual meaning, and

$$\tau_A = \tau_B \chi_A / \chi_B$$

where  $\chi_A$  and  $\chi_B$  are the mole fractions of X at sites A and B.

<sup>1</sup> Pisaniello, D. L., and Lincoln, S. F., *Inorg. Chem.*, 1981, 20, 3689.

The simulation of the variation of  $\ln(\tau_A T)$  with  $1/T$  through equation (2) for two different sets of activation parameters and over a range of  $[B]$  is shown in Fig. 1.

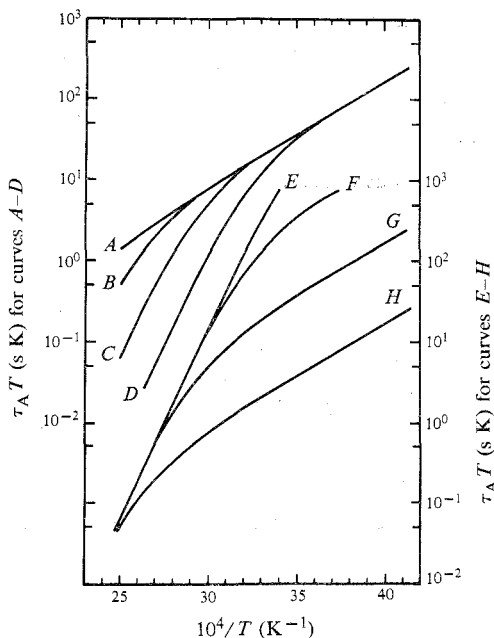


Fig. 1. Variation of  $\tau_A T$  with  $1/T$  according to equation (2).

Curves A-D

$\Delta H_1^\ddagger$  25 kJ mol<sup>-1</sup>;

$\Delta H_2^\ddagger$  90 kJ mol<sup>-1</sup>;

$\Delta S_1^\ddagger$  -140 J K mol<sup>-1</sup>;

$\Delta S_2^\ddagger$  50 J K mol<sup>-1</sup>.

A,  $[B]$  0.01 mol dm<sup>-3</sup>;

B,  $[B]$  0.1 mol dm<sup>-3</sup>;

C,  $[B]$  1.0 mol dm<sup>-3</sup>;

D,  $[B]$  10 mol dm<sup>-3</sup>.

Curves E-H

$\Delta H_1^\ddagger$  90 kJ mol<sup>-1</sup>;

$\Delta H_2^\ddagger$  25 kJ mol<sup>-1</sup>;

$\Delta S_1^\ddagger$  50 J K mol<sup>-1</sup>;

$\Delta S_2^\ddagger$  -140 J K mol<sup>-1</sup>.

E,  $[B]$  0.01 mol dm<sup>-3</sup>;

F,  $[B]$  0.1 mol dm<sup>-3</sup>;

G,  $[B]$  1.0 mol dm<sup>-3</sup>;

H,  $[B]$  10 mol dm<sup>-3</sup>.

Two major points emerge from an examination of the Figure. The first is that the nature of the non-linearity is markedly dependent on the magnitudes of the activation parameters and  $[B]$ . Thus when in equation (2)  $\Delta H_1^\ddagger$  and  $\Delta H_2^\ddagger$  are 25 and 90 kJ mol<sup>-1</sup> respectively,  $\Delta S_1^\ddagger$  and  $\Delta S_2^\ddagger$  are -140 and 50 J K<sup>-1</sup> mol<sup>-1</sup> respectively, and  $[B]$  is 0.01 mol dm<sup>-3</sup> it is seen in curve A that there is a linear dependence of  $\ln(\tau_A T)$  on  $1/T$  at low temperature where the  $k_1$  term dominates and non-linearity only becomes pronounced at higher temperatures where the  $k_2$  term becomes significant in the exchange process. When  $[B]$  is 10 mol dm<sup>-3</sup>, however, the domination of the exchange process by the  $k_1$  term is restricted to a smaller range at low temperature in which  $\ln(\tau_A T)$  is linearly dependent on  $1/T$  and as the temperature increases the  $k_2$  term becomes dominant such that a second range in which  $\ln(\tau_A T)$  is linearly dependent on  $1/T$  occurs at high temperatures as seen in curve D. When  $\Delta H_1^\ddagger$  and  $\Delta H_2^\ddagger$  are 90 and 25 kJ mol<sup>-1</sup> respectively,  $\Delta S_1^\ddagger$  and  $\Delta S_2^\ddagger$  are 50 and -140 J K<sup>-1</sup> mol<sup>-1</sup> respectively, and  $[B]$  is 0.01 mol dm<sup>-3</sup> it is seen in curve E that there is a linear dependence of  $\ln(\tau_A T)$  on  $1/T$  at high temperatures where the  $k_1$  term dominates and non-linearity only becomes pronounced at low temperatures where the  $k_2$  term becomes significant in the exchange process which is the reverse of the situation shown by curve A. When  $[B]$  is 10 mol dm<sup>-3</sup> the domination of the exchange process by the  $k_2$  term results in a considerable low-temperature range in which  $\ln(\tau_A T)$  is linearly dependent on  $1/T$  and it is only at higher temperatures that the  $k_1$  term makes a significant contribution to the exchange process with the resultant non-linearity shown by curve H.

The second major point emerging from Fig. 1 is that in nuclear magnetic resonance experiments at a given frequency the temperature ranges over which  $\tau_A$  can be determined may differ considerably for different values of  $[B]$ . Apart from the errors

inherent in extrapolation procedures, the non-linearity of the dependence of  $\ln(\tau_A T)$  on  $1/T$  renders any attempt to extrapolate such  $\tau_A$  data obtained at different  $[B]$  values into a common temperature range (in order to derive  $k_1$ ,  $k_2$ , and their associated activation parameters) particularly subject to error. Such errors may be avoided if the surface defined by the complete experimental data set  $\tau_A$ ,  $T$ , and  $[B]$  is simulated through equation (2) by use of a statistically weighted non-linear least squares method which minimizes the residuals between the experimental and simulated surfaces. Such general data analysis methods have been previously described<sup>2-4</sup> and have been adapted to the above circumstances in our program DATAFIT.

Should a two-term rate law of the form of equation (2) operate with similar  $\Delta H_1^\ddagger$  and  $\Delta H_2^\ddagger$  magnitudes the dependence of  $\ln(\tau_A T)$  on  $1/T$  will be linear as will also be the case if the rate law contains only the second-order term. In both of these cases it is also probable that over a significant variation of  $[B]$   $\tau_A$  will not be determined over a common temperature range for each magnitude of  $[B]$  studied. As linearity is simply a limiting case of non-linearity, DATAFIT, or a similar program, may be used to advantage in determining activation parameters in such cases also, as has been demonstrated for hexamethylphosphoramide exchange on zinc(II)<sup>5</sup> and dimethyl sulfoxide exchange on beryllium(II).<sup>6</sup>

#### Acknowledgment

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<sup>2</sup> Wolberg, J. R., in 'Prediction Analysis' (Van Nostrand: Princeton, New Jersey, 1967).

<sup>3</sup> Pitha, J., and Jones, R. N., *Can. J. Chem.*, 1966, **44**, 3031.

<sup>4</sup> Dye, J. L., and Nicely, V. A., *J. Chem. Educ.*, 1971, **48**, 443.

<sup>5</sup> Tkaczuk, M. N., and Lincoln, S. F., *Aust. J. Chem.*, 1980, **33**, 2621.

<sup>6</sup> Tkaczuk, M. N., and Lincoln, S. F., *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 433.