

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

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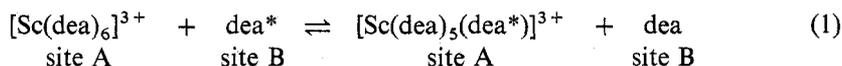
Abstract

The temperature dependence of the site lifetimes, τ_A and τ_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, τ_A and τ_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 observed¹ 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 τ_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 χ_A and χ_B are the mole fractions of X at sites A and B.

¹ 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.

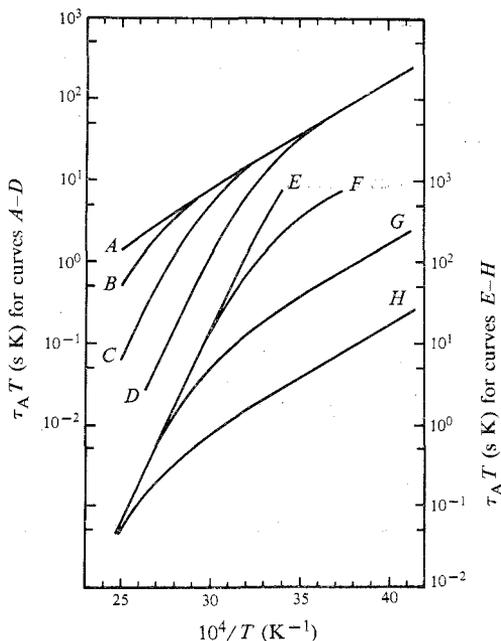


Fig. 1. Variation of $\tau_A T$ with $1/T$ according to equation (2).

Curves A-D

ΔH_1^\ddagger 25 kJ mol⁻¹;
 ΔH_2^\ddagger 90 kJ mol⁻¹;
 ΔS_1^\ddagger -140 J K mol⁻¹;
 ΔS_2^\ddagger 50 J K mol⁻¹.

A, [B] 0.01 mol dm⁻³;

B, [B] 0.1 mol dm⁻³;

C, [B] 1.0 mol dm⁻³;

D, [B] 10 mol dm⁻³.

Curves E-H

ΔH_1^\ddagger 90 kJ mol⁻¹;

ΔH_2^\ddagger 25 kJ mol⁻¹;

ΔS_1^\ddagger 50 J K mol⁻¹;

ΔS_2^\ddagger -140 J K mol⁻¹.

E, [B] 0.01 mol dm⁻³;

F, [B] 0.1 mol dm⁻³;

G, [B] 1.0 mol dm⁻³;

H, [B] 10 mol dm⁻³.

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) ΔH_1^\ddagger and ΔH_2^\ddagger are 25 and 90 kJ mol⁻¹ respectively, ΔS_1^\ddagger and ΔS_2^\ddagger are -140 and 50 J K⁻¹ mol⁻¹ respectively, and $[B]$ is 0.01 mol dm⁻³ 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⁻³, 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 ΔH_1^\ddagger and ΔH_2^\ddagger are 90 and 25 kJ mol⁻¹ respectively, ΔS_1^\ddagger and ΔS_2^\ddagger are 50 and -140 J K⁻¹ mol⁻¹ respectively, and $[B]$ is 0.01 mol dm⁻³ 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⁻³ 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 τ_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 τ_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 τ_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 described²⁻⁴ 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 ΔH_1^\ddagger and ΔH_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] τ_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)⁵ and dimethyl sulfoxide exchange on beryllium(II).⁶

Acknowledgment

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

³ Pitha, J., and Jones, R. N., *Can. J. Chem.*, 1966, **44**, 3031.

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

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

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