

SOLVENT EFFECTS ON THE RACEMIZATION OF THE  
TRIS-(1,10-PHENANTHROLINE)NICKEL(II) ION\*

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Leffler (1955) has drawn attention to the implications of a linear relationship  $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$  between the enthalpies ( $\Delta H^\ddagger$ ) and entropies ( $\Delta S^\ddagger$ ) of activation in a study of a large number of organic reactions in which solvent or structure of the reactant was varied.  $\beta$  has the dimensions of absolute temperature and is known as the isokinetic temperature. Provided that  $\beta$  was sufficiently different from the mid-point of the temperature range of the reaction then a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  was expected only if a similar mechanism persisted. An application of this isokinetic relationship proves helpful in interpreting the effects of solvent changes on inorganic reactions.

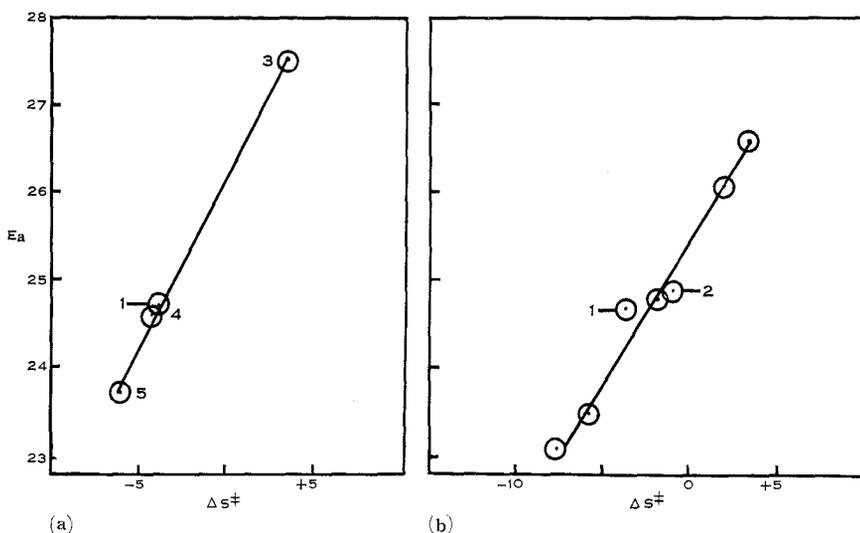


Fig. 1(a) and (b).—Points 1–5 correspond respectively to ethanol, water, ethyleneglycol, n-propanol, and methanol. (b) From top to bottom the unlabelled points on the curve correspond to 5, 10, 40, 70, and 90% mole-fraction ethanol-water mixtures.

The effects of a change in solvent on the racemization rate of the tris-(1,10-phenanthroline)nickel(II) ion have been studied in detail by Davies and Dwyer (1954). In ethanol-water mixtures remarkable variations in the rate constant were observed. The rate of racemization at first decreased, then increased, and finally decreased again as the ethanol content was increased. Similar behaviour was found in water-methanol and water-acetone solvent mixtures. Rate studies in different nonaqueous

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solvents could not be correlated with the solvent viscosities or dielectric constants, two factors of theoretical importance in rate theory. A dissociation mechanism of racemization is known to be present in aqueous solution and also in ethanol, 0.7 mole-fraction ethanol-water, and nitrobenzene (Wilkins and Williams 1957). Dissociation would thus appear to be a likely mechanism in all the organic solvents studied. The isokinetic relationship provides a means of checking the constancy of the dissociation mechanism in the various solvents for which dissociation data are lacking. If the solvents perform closely similar roles in the reaction then a linear relationship between  $E_a$  (experimental activation energy) and  $\Delta S^\ddagger$  is to be expected.

Good linear relationships are obtained for the results of Davies and Dwyer in various alcohols, Figure 1(a), and in ethanol-water solvents Figure 1(b). A fit to the same isokinetic line is not expected when gross changes in the solvent are made, for example water and nitrobenzene. The  $\Delta S^\ddagger$  values have been calculated by the method of Glasstone, Laidler, and Eyring (1941) and are approximately two entropy units more negative than those quoted elsewhere (Stranks 1960).

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