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TRANSITION STATE VARIATION IN THE MENSHUTKIN REACTION?

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Data for reaction of CH_3I and CD_3I with substituted pyridines were previously argued ^{3}to indicate a variant transition state as rate of reaction was varied, but the fact that both sets of results follow LFER's may be taken as evidence against such a conclusion.

Recently, variable isotope effects were reported[1] for reaction between CH_3I, CD_3I and pyridines 3-X, 5-Y-C_6H_3N in 2-nitropropane at 25°, interpreted as indicating variation in transition state structure as rate was varied, in contrast to Arnett's conclusions[2] We present here arguments which possibly serve to show these results may indicate the opposite that the transition state model applied to this reaction requires that it is constant.

As Figure 1 shows, log k_{CH_3I} and log k_{CD_3I} produce LFER's when plotted against pK_a for the appropriate pyridine[3] Changes in the alkylating group by isotopic substitution lead to changes in rate, due to, in this case, the minor variations in proximity effects, solvent interactions and the like, factors which are found from general experience to produce variation of ρ values in LFER's for both kinetic and equilibria data.

We introduce a potentially variable steric interaction S into eq 1 for the correlation between log k (CH_3I or CD_3I) and pK_a.

$$\log k = \rho(pK_a) + S + \log k_o \qquad (1)$$

$$d \log k/d(pK_a) = \rho + dS/d(pK_a) \qquad (2)$$

Linearity of both plots indicate that the second term of the right hand side of eq 2 is zero, implying a constant transition state for the molecular model.

Writing the individual correlations in the form of eqs 3 and 4

$$\log k_{CH_3I} = \rho_{CH_3I}(pK_a) + S_{CH_3I} + \log(k_o)_{CH_3I} \qquad (3)$$

$$\log k_{CD_3I} = \rho_{CD_3I}(pK_a) + S_{CD_3I} + \log(k_o)_{CD_3I} \qquad (4)$$

we obtain eq 5

$$\log(k_{CH_3I}/k_{CD_3I}) = (\rho_{CH_3I} - \rho_{CD_3I})(pK_a) + \Delta S + \log(k_o)_{CH_3I}/(k_o)_{CD_3I} \qquad (5)$$

where $\Delta S = S_{CH_3I} - S_{CD_3I}$.

Thus: $$d \log(k_{CH_3I}/k_{CD_3I})/d(pK_a) = (\rho_{CH_3I} - \rho_{CD_3I}) + d\Delta S/d(pK_a) \qquad (6)$$

The linearity of the plot of eq 5 would again demonstrate the second term of the right side of eq 6 to be zero, but here small deviations from the individual Bronsted plots in Figure 1 create large random errors in log (k_{CH_3I}/k_{CD_3I})

We conclude that there may be no reason to assume that Arnett's deductions[2] are incorrect. It would be of great interest to see if a finite value for the final terms of eqs 2 and 6 could be found for a greater range of pyridinium pK_a values, but our opinion based on related phenomena is that this is unlikely to be the case.[5]

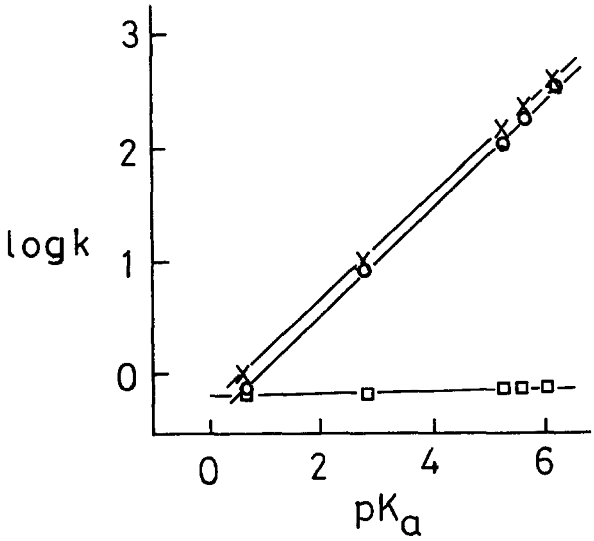

FIGURE 1

Log k_{CH_3I} O and log k_{CD_3I} x plotted against pK_a (pyridinium) Slope of the former, ρ_{CH_3I}, is 0 476 (correlation coeff. 0 9997, SD 0.007) and the latter, ρ_{CD_3I}, is 0.469 (0.9999, SD 0.004). □ Log k_{CH_3I} - log k_{CD_3I} plotted against pK_a on the same scale.

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