Competitive Alkali-metal Flame Reactions: Potassium Atoms with Ethyl Iodide, Cyclopentyl, and Cyclohexyl Chlorides

By E. U. EMOVON and J. F. OJO
(*Department of Chemistry, University of Ibadan, Nigeria*)

THE reactions of potassium atoms with mixtures of ethyl and cyclopentyl chloride and of ethyl iodide and cyclohexyl chloride pairs have been studied by the competitive method developed by Trotman-Dickenson, *et al.*[1] A stream of the mixed organic halide vapours was carried into the Pyrex glass reaction chamber by pure nitrogen, as also were the potassium atoms. The reaction chamber was heated by mercury vapour and its temperature was maintained to within ±0·2°. The mixture of potassium iodide and potassium chloride formed was analysed conductometrically.

The ethyl iodide–cyclopentyl chloride system was studied over the temperature range 199·0—305·2° with reactant ratios, EtI : cyclo-C_5H_9Cl, between 0·68 and 2·88. The relative rate constants (k_1/k_2) for the system

$$K + EtI = KI + Et \qquad (1)$$

$$K + \text{cyclo-}C_5H_9Cl = KI + \text{cyclo-}C_5H_9 \qquad (2)$$

where cyclo-C_5H_9 represents cyclopentyl radical, have been calculated for the 36 runs distributed over 25 groups of temperatures using the same method as Trotman-Dickenson *et al.*[1] The following relative Arrhenius parameters were obtained by the least-squares calculation using the IBM 1620 computer.

$$E_1 - E_2 = 4652{\cdot}6 \pm 185{\cdot}3 \text{ cal./mole}$$
$$\log A_1/A_2 = 2{\cdot}29 \pm 0{\cdot}01$$

The ethyl iodide–cyclohexyl chloride pair represented by

$$\text{K} + \text{EtI} = \text{KI} + \text{Et} \qquad (1)$$
$$\text{K} + \text{cyclo-}C_6H_{11}\text{Cl} = \text{KCl} + \text{cyclo-}C_6H_{11} \qquad (3)$$

where cyclo-C_6H_{11} refers to cyclohexyl radical, was studied between 216·0 and 298·8° with reactant ratios, EtI : cyclo-C_6H_{11}Cl, between 2·00 and 3·57. The following Arrhenius parameters calculated by the method of least squares were obtained from the relative rate constants (k_1/k_3) for 21 runs fairly evenly distributed over 18 temperature groups:

$$E_1 - E_3 = 4984{\cdot}2 \pm 168{\cdot}5 \text{ cal./mole}$$
$$\log (A_2/A_3) = 2{\cdot}74 \pm 0{\cdot}01$$

From the results, the relative Arrhenius parameters for the cyclopentyl–cyclohexyl chlorides pair (2) and (3) can be calculated.

$$\text{Hence } E_2 - E_3 = 331{\cdot}6 \pm 32{\cdot}2 \text{ cal./mole}$$
$$\text{and } \log (A_2/A_3) = 0{\cdot}45 \pm 0{\cdot}00$$

The relative rate constant for this reaction (k_2/k_3) at 246·8° is 2·05 which is in good agreement with the value of 2·16 obtained by Gowenlock *et al.*[2] for the reaction of sodium atoms with cyclopentyl and cyclohexyl bromides. The higher reactivity of the cyclopentanoid system can be explained in terms of the entropy factor[3,4] which is a consequence of the relief of internal strain in the transition state. The entropy effect more than compensates for the small but significantly greater activation energy for the cyclopentyl chloride than the cyclohexyl chloride reactions.[1,5,6]

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