

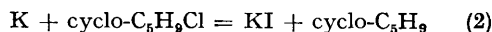
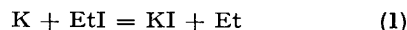
Competitive Alkali-metal Flame Reactions: Potassium Atoms with Ethyl Iodide, Cyclopentyl, and Cyclohexyl Chlorides

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 $\pm 0.2^\circ$. 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-C₅H₉Cl, between 0.68 and 2.88. The relative rate constants (k_1/k_2) for the system



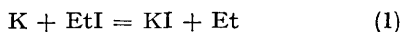
where cyclo-C₅H₉ represents cyclopentyl radical, have been calculated for the 36 runs distributed over 25 groups of temperatures using the same

method as Trotman-Dickenson *et al.*¹ The following relative Arrhenius parameters were obtained by the least-squares calculation using the IBM 1620 computer.

$$E_1 - E_2 = 4652.6 \pm 185.3 \text{ cal./mole}$$

$$\log A_1/A_2 = 2.29 \pm 0.01$$

The ethyl iodide-cyclohexyl chloride pair represented by



where cyclo-C₆H₁₁ refers to cyclohexyl radical, was studied between 216.0 and 298.8° with reactant ratios, EtI : cyclo-C₆H₁₁Cl, 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:

$$E_1 - E_3 = 4984.2 \pm 168.5 \text{ cal./mole}$$

$$\log (A_2/A_3) = 2.74 \pm 0.01$$

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

$$\text{Hence } E_2 - E_3 = 331.6 \pm 32.2 \text{ cal./mole}$$

$$\text{and } \log (A_2/A_3) = 0.45 \pm 0.00$$

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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⁴ C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell, London, 1957, 3rd edn., pp. 410-412.

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⁶ A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, 1951, 19, 329.