Homogeneous and Heterogeneous Hydrogenation: a Kinetic Correlation

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Summary Hydrogen transfer is rate-limiting in homogeneous hydrogenation of cycloalkenes by [py_2(dmf)$RhCl_2(BH_4)$] in dimethylformamide (dmf) solution, as in heterogeneous hydrogenation.

HETEROGENEOUS hydrogenation of cycloalkenes, *e.g.* at Pd–C, is typically zero order in the alkene with hydrogen-transfer as the rate-limiting step.[1] By contrast, the homogeneous hydrogenation of a group of cycloalkenes using [$(PPh_3)_3RuCl_2$] is concentration-dependent, and the relative rates for different cycloalkenes reflect the complexing constant of the olefin.[2] We were therefore interested to find that homogeneous hydrogenation of a group of cycloalkenes using the complex[3] [py_2(dmf)$RhCl_2(BH_4)$] in dimethylformamide (dmf) solution reproduces the type of rate *vs.* concentration relation (*cf.* Figure 1) found[1] in heterogeneous hydrogenation, and the same rate order,[1] viz.: norbornene cyclohexene > cycloheptene > cyclopentene > cyclooctene. Significantly, in the higher concentration range, where hydrogen-transfer is clearly rate-limiting, log rate *vs.* heat of hydrogenation is found to be linear (*cf.* Figure 2). We infer that the transition state for hydrogenation is

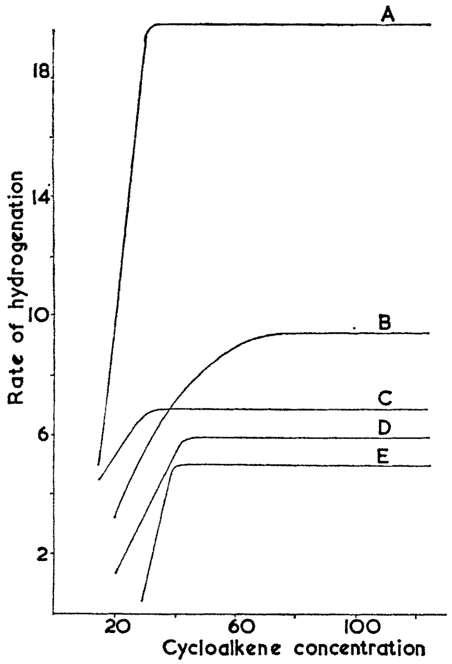


FIGURE 1. *Rates of hydrogenation* (*c.c./min.*) vs. *concentration* 10^{-2}M) *with* [py_3RhCl_3] ($3{\cdot}7 \times 10^{-3}$M) *and* $NaBH_4$ ($22{\cdot}0 \times 10^{-3}$M) *in dmf* (12 *c.c.*): (*A*) *norbornene*, (*B*) *cyclohexene*, (*C*) *cycloheptene*, (*D*) *cyclopentene and* (*E*) *cyclo-octene.*

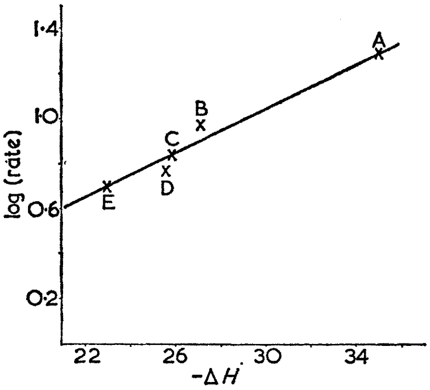
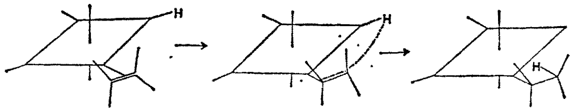


FIGURE 2. *Relationship between log* (*rate of hydrogenation*) *and heat of hydrogenation* (*kcal./mole*): (*A*) *norbornene*, (*B*) *cyclohexene*, (*C*) *cyclo-heptene*, (*D*) *cyclopentene and* (*E*) *cyclo-octene.*



(I) (II) (III)

alkene-like, as in (II), and hence the energetics of the $sp^2 \rightarrow sp^3$ transformation controls the activation energy. We regard these results as important in completing the bridge between heterogeneous and homogeneous catalysis.

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[1] I. Jardine and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1966, 458.

[2] I. Jardine and F. J. McQuillin, *Tetrahedron Letters*, 1968, 5189.

[3] I. Jardine and F. J. McQuillin, *Chem. Comm.*, 1969,