Tetrahedron Letters No.50, pp. 5189-5190, 1968. Pergamon Press. Printed in Great Britain.

EFFECT OF STRUCTURE ON RATE OF REACTION IN HETEROGENEOUS AND HOMOGENEOUS HYDROGENATION OF OLEFINS

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(Received in UK 2 September 1968; accepted for publication 18 September 1968)

Attention has been drawn(1) to the following sequence of rates of hydrogenation at palladised charcoal: bicycloheptadiene > cyclohexene > cycloheptene > cyclopentene > cyclo-octa-1,5-diene > cyclo-octene, and to the parallel between rates and heats of hydrogenation. It has been inferred(1) that hydrogen transfer is the rate-limiting step in these cases. Cyclo-octene, in particular, was shown to be more strongly adsorbed at palladium but slower to hydrogenate than cyclohexene. Other workers(2,3) have found cyclo-octene to hydrogenate more rapidly than cyclohexene. This apparent discrepancy derives, however, from differences in the kinetic situation. Whilst our results refer to the region of pseudo-zero order of reaction, Hussey, Baker and Keulks have identified adsorption as rate-limiting under their conditions using a platinum catalyst. The results of Brown and Brown also evidently refer to conditions of adsorption control. We draw attention to the practical importance of recognising the kinetically controlling step in hydrogenation, and to the importance both of the catalyst metal and the ratio: catalyst/substrate in this context.

It is of interest also to identify the rate controlling factors in homogeneous hydrogenation. Considering a monohydrido-complex [LMH] (M = metal ion, L = stabilising ligands), either complexing of an olefin (S), step (i), or hydrogen transfer, steps (ii) and (iii), may, in principle, be rate-limiting:

$$[\mathrm{LMH}] + \mathrm{S} \xrightleftharpoons{(i)} [\mathrm{LM(S)H}] \xrightleftharpoons{(ii)} [\mathrm{LM(SH)}]$$

$$[\mathrm{LM(SH)}] + \mathrm{H_2} \xrightarrow{(iii)} [\mathrm{LMH}] + \mathrm{SH_2}$$

The existing data(4) for rate order, viz: $\mathrm{R{\cdot}CH = CH_2} > \mathrm{R{\cdot}CH = CH{\cdot}R'}$, observed with $[(\mathrm{PPh_3})_3\mathrm{RuHCl}]$ have been extended to the olefins listed in the table:

Olefin	Rate*	$-\Delta H$(Kcal./mole)	KAg^+(5)
Norbornene	2.13	35	62
Norbornadiene	0.46	35	33.7
Cyclo-octa-1,5-diene	1.99	25	75
Cyclo-octene	0.74	23.0	14.4
Cycloheptene	0.28	25.9	12.8
Cyclohexene	v.slow	27.1	3.6
Cyclopentene	v.slow	25.6	7.3

* Mole hydrogen/min./mole catalyst

Using 4×10^{-4}M. [(PPh$_3$)RuCl$_2$] in ethanol rates of hydrogenation were found to increase linearly with olefin concentration over the range $1 - 8 \times 10^{-2}$M., except for norbornene in the higher concentration range which became self-inhibitory. The rates quoted refer to the slope of the rate *vs*. olefin concentration graphs. We examined also pent-1-ene, hept-1-ene, oct-1-ene and undec-1-ene for which the rate *vs*. concentration graphs gave almost identical slopes of ca. 7.1 mole hydrogen/min./mole [(PPh$_3$)$_3$RuCl$_2$].

The rate of hydrogenation of these olefins is clearly sensitive not only to the degree of substitution at the olefinic bond, but, for similarly substituted olefins, also to the complexing ability of the double bond. We have tabulated values of K_{Ag^+} due to Muhs and Weiss as an approximate index of complexing strength of the olefins. We infer that the complexing stage (i) is rate-determining as in adsorption controlled heterogeneous hydrogenation.

These observations have a direct practical bearing on selective hydrogenation of olefins in both homogeneous and heterogeneous systems.

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