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Catalytic Hydrogenation of Cycloalkanones on Pt/SiO_2 and Ru/SiO_2

The Effects of Ring Size

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The hydrogenations of cycloalkanones (C_4–C_9) in the liquid phase on Pt/SiO_2 and Ru/SiO_2 have been studied from 0.1 to 150 bar in cyclohexane as solvent. Using competitive kinetic methods through the R_{AB} parameter, a scale of reactivity is proposed. Adopting the value of 1 for cyclohexanone, we found 7.1 for cyclobutanone, 6.9 for cyclopentanone, 13.8 for cycloheptanone, 19.2 for cyclooctanone, and 17.9 for cyclononanone on Pt/SiO_2. These results when compared with the relative rates for BH_4^- nucleophilic addition reactions on carbonyl compounds and with the corresponding rates for chromic acid oxidation of cycloalkanols give a good indication for a slow step in the catalytic hydrogenation in liquid phase corresponding to the fixation of the first hydrogen atom to a Π-adsorbed species, the hybridization of the C atom passing from sp^2 to sp^3.

INTRODUCTION

Numerous investigations have aimed at establishing the mechanism of hydrogenation of ketones in the liquid phase. In particular, the possibility of the intervention of enol intermediates likely to be readily adsorbed on the catalyst has been considered, but discounted principally on the basis of H–D exchange studies (*1–5*). Studies of the exchange which takes place on certain metals (rhodium and palladium) (*3*), hydrogenolysis and ketalization reactions (*6*), as well as comparisons between olefin and carbonyl reactions (*7–8*), have on the other hand led to an overall conception of the mechanism for this reaction (*3, 7–10*) based on the general scheme represented by the Horiuti–Polanyi-type reaction mechanism.

The slow step of the reaction depends on the nature of the organic reactant and the metal (*7, 10, 11*) and may correspond to the attachment of either the first or the second hydrogen atom. Thus the influence of the nature of the ketone is exemplified by comparing the kinetic results obtained for acetone (*12*) with the cycloalkanones (*13–15*). Acetophenone and cyclohexanone (*4*) differ in that their kinetic orders with respect to hydrogen are 1 and $\frac{1}{2}$, respectively. This latter observation suggests that hydrogenation of cyclohexanone could proceed by steps IIα and IIIα, and acetophenone by steps IIβ and IIIβ, the rate-determining step being the attachment of a hydrogen to the carbonyl carbon, i.e., steps IIα and IIIβ, in either case (*3, 7–10*) (Fig. 1).

We wish to report new results obtained by studying the effect of variation of ring size on reactivity. This effect, not only extensively studied with respect to homo-

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geneous phase nucleophilic additions to carbonyl (*16–19*), but also for the reverse reaction, i.e., oxidation of cycloalkanols (*20*) as well as solvolysis reactions (*21*), has provided insight into the mechanisms of these reactions. No comparable study of catalytic hydrogenation reactions has been reported to date, although the greater reactivity of cyclohexanone compared to cyclopentanone has been noted (*1, 13*).

METHODS

Within the framework of Langmuir's hypothesis for isothermal adsorption, the rate equation for a reaction $A + H_2 \rightarrow$ products may be written:

$$r_A = \frac{k_A b_A b_{H_2} C_A C_{H_2}}{(1 + b_A C_A + b_{H_2} C_{H_2} + \Sigma b_n C_n)^2}$$

where k_A and b's are, respectively, the kinetic rate constant and the adsorption constants.

This expression, under conditions close to the initial conditions and in the absence of solvent adsorption, can be reduced to

$$r_A = \frac{k_A b_A b_{H_2} C_A C_{H_2}}{(1 + b_A C_A + b_{H_2} C_{H_2})^2}.$$

Where two organic reactants of the same type are under investigation, it will be advantageous to subject the compounds to competitive hydrogenation, for under such circumstances a parameter R_{AB} may be defined (*22*) such that

$$R_{AB} = \frac{r_A}{r_B} = \frac{-dC_A/dt}{-dC_B/dt} = \frac{k_A b_A C_A}{k_B b_B C_B},$$

$$R_{AB} = \frac{\ln (C°_A/C_A)}{\ln (C°_B/C_B)} = \frac{k_A b_A}{k_B b_B},$$

which means that in the case of two compounds simultaneously hydrogenated a plot of $\log C_A$ versus $\log C_B$ is linear and the slope provides the competition ratio R_{AB}. This parameter should be independent of the mass of the catalyst, of the concentration of the organic reactants of foreign substances in a particular solvent, as well as the rate of stirring. For the hydrogenation reactions of olefins (*23, 25*), a variety of aromatic compounds (*24, 26*) and several substituted cyclohexanones (*27*), this independence has already been verified.

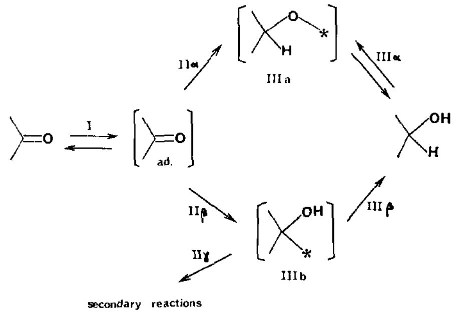


FIG. 1. General mechanism of the hydrogenation reaction.

We have carried out competitive hydrogenation of cycloalkanones (from cyclobutanone to cyclononanone) in the pressure range 0.1 to 150 bar, using Pt/SiO_2 and Ru/SiO_2 as catalysts and cyclohexane as solvent under conditions which have been described previously (*4*).

We had available to us two types of apparatus, one for working at pressures below 1 atm (*23*) and the other, an "Engineers Autoclave" for higher pressures. The catalysts were prepared from hexachloroplatinic acid and from ruthenium ammonium oxychloride by depositing 5% by weight (of metal) on a previously fractionated Davison silica (grain size 0.05–0.125 mm, i.e., 18–22 mesh). The catalysts were subsequently reduced under a current of hydrogen at 350°C for Pt and 450°C for Ru.

The cycloalkanones used were commercial products (Fluka) and their corresponding alcohols were obtained by reduction in methanolic sodium. The composition of individual reaction samples was determined by G.L.C. using either

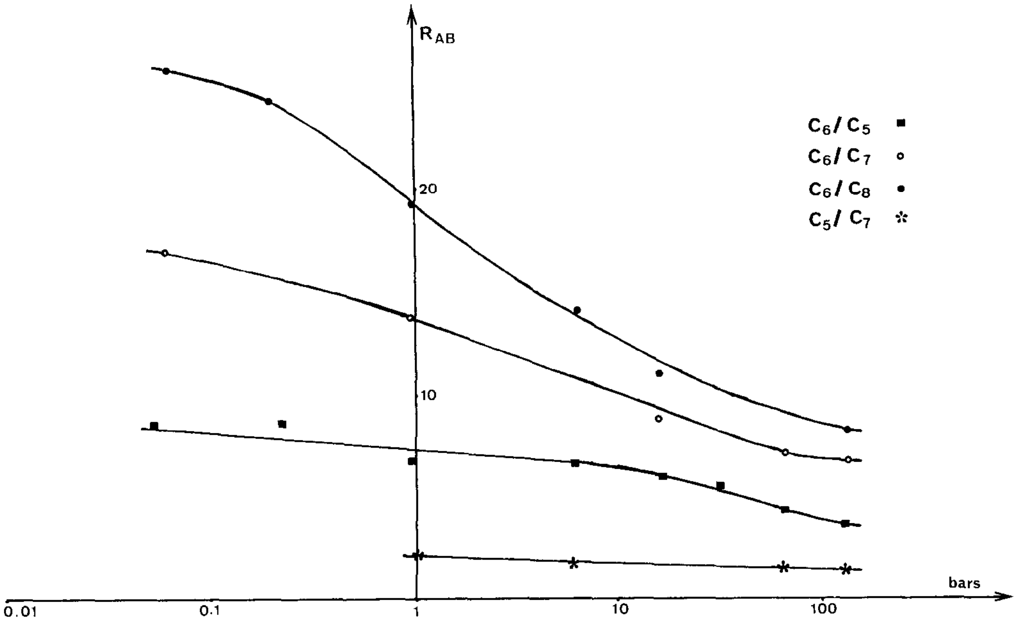


FIG. 2. R_{AB} versus log P_{H_2} (Pt/SiO$_2$).

a Varian Aerograph model 1200 or a Girdel series 3000; the ketones and their respective alcohols were all readily separable on a 10% carbowax 20M on chromosorb W column, using temperature programming (100–240°C).

RESULTS

For a pair of similar ketones subjected to competitive hydrogenation, R_{AB} ought in theory to be independent of hydrogen pressure. The results of the measurement of R_{AB} for each pair of ketones, as a function of this parameter, which are assembled in Figs. 2 and 3, show that this is not in practice universally true. For the catalyst Pt/SiO$_2$ (Fig. 2) only at pressures above 100 bar, and to a lesser extent at pressures below 1 bar it can be said that R_{AB} tends to be independent of pressure. We believe that the explanation given for curves of a similar nature observed with olefins (*23*) and aromatic hydrocarbons (*26*), namely, that the rate-determining step changes with changing pressure, is equally applicable to our results. Thus at low pressure the reaction between adsorbed species is rate determining, while at high pressures the adsorption process itself becomes rate limiting. The kinetic orders in ketone which are observed in these reactions, i.e., approaching zero at low pressure and unity at high pressure, support this conclusion.

For the Ru/SiO$_2$ catalyst the observed results (Fig. 3) show a similar overall trend to those of the Pt/SiO$_2$.

Ring size has a particularly marked effect on reactivity. In all cases cyclohexanone is the most reactive ketone, although R_{6j} (j = 4, 5, 7–9) does diminish with increasing pressure. In the absence of a definite constancy of the R_{6j} value at low hydrogen pressures, where the rate-determining step for the two ketones is the reaction between adsorbed species, the scale of relative reactivity for the cycloalkanones ought to be established at the lowest hydrogen pressure possible. We propose (Fig. 4) a scale of reactivity for these ketones, calculated on the basis of the observed R_{6j} values at a pressure of

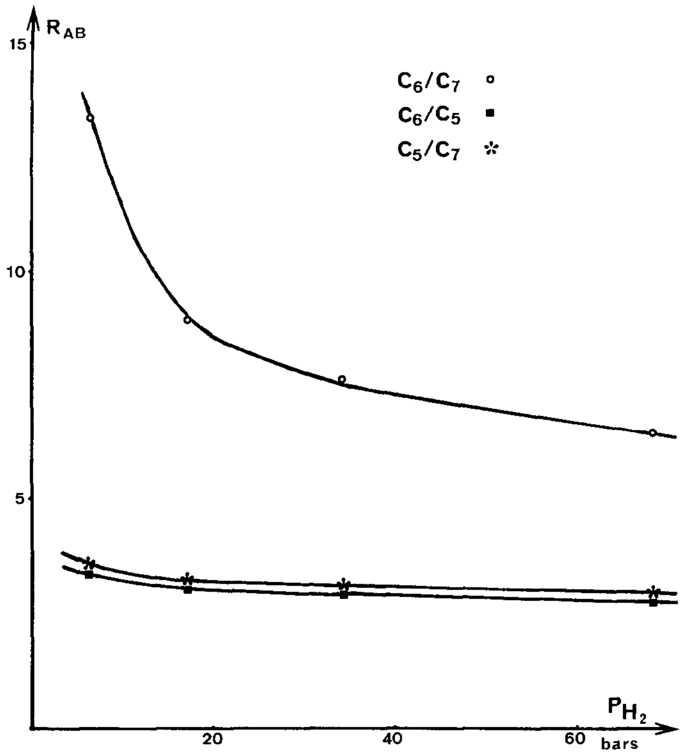


FIG. 3. R_{AB} versus P_{H_2} (Ru/SiO$_2$).

one atmosphere, values which are readily reproducible when using the same lot of catalyst.

DISCUSSION

Comparison of the reactivity of cycloalkanones towards BH_4^-, where the reacting carbon undergoes a change of hybridization from sp^2 to sp^3 (*17*, *18*), with the reverse reaction, i.e., chromic acid oxidation of the corresponding secondary alcohols, which involves the opposite change in hybridization (*28*), reveals similar trends (Table 1). The origin of the differences in reactivity between these molecules in either case lies principally with the change in internal strain (I-strain (*16*)) that accompanies the change in hybridization on proceeding from the initial state to the transition state.

Our catalytic hydrogenation reactions display very similar behavior, so that it would appear that the rate-determining step must involve a similar change in hybridization and that the structure of the transition state must resemble that of a semihydrogenated intermediate whose carbon is sp^3 hybridized. The latter necessarily implies a prior II-adsorption of the reactant.

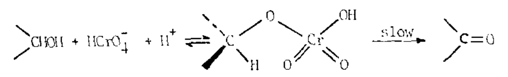
TABLE 1

Comparison of the Reactivity of Cycloalkanones and Cycloalkanols

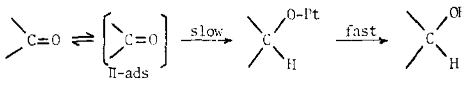
Cyclo-alkanones	R_{6j} BH_4^- (*16*)	R_{6j} Oxidation (*20*)	R_{6j} This work
C_4	0.6	2.3	7.1
C_5	23	2.1	6.9
C_6	1	1	1
C_7	157	4.9	13.8
C_8	2000	5.3	19.2
C_9	5000	5.1	17.9

The observed decrease in R_{6j} with increasing pressure supports this conclusion, for this decrease in importance of ring size as the adsorption becomes the rate controlling factor indicates that the transition state becomes more and more ketone-like (*17*).

Comparison of the relative rates of catalytic hydrogenation with the corresponding rates of chromic acid oxidation, already referred to (Table 1, Fig. 5), reveals a very close parallel between these two reactions. In fact, for the entire series of compounds the relative rates of the two reactions differ by virtually a constant factor of 3. Now it is well known (*28*) that in the latter reaction the slow step corresponds to the passage from chromic ester to ketone according to the following scheme:



It is entirely conceivable that Pt, like Ru, could form a similar –O– metal bond, and thus we believe that for this catalyst the following mechanism of reaction applies:



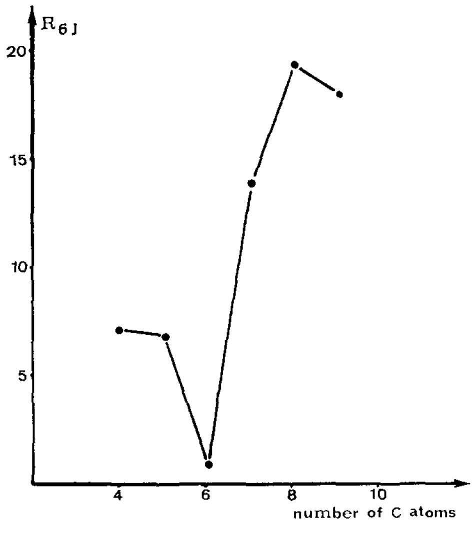


FIG. 4. Catalytic hydrogenation of cycloalkanones over Pt/SiO$_2$ at atmospheric pressure. The effects of ring size.

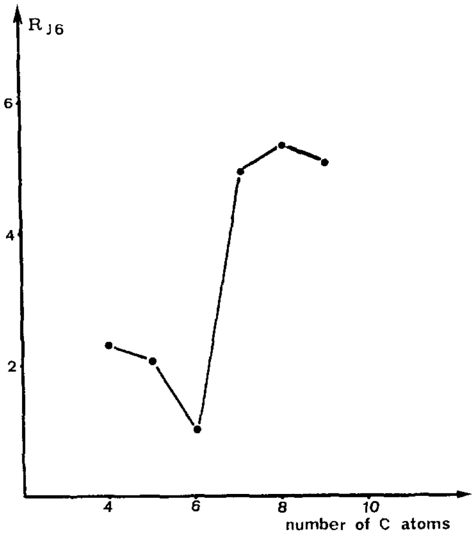


FIG. 5. Chromic acid oxidation reaction for cycloalkanols. The effects of ring size.

This is in accord with the previously proposed mechanism (*3*, *7–10*) for the case where there is no hydrogenolysis, and the slow step corresponds to fixation of the first hydrogen atom to a previously Π-adsorbed species, the reacting carbon passing from sp^2 to sp^3 in this step.

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