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Influence of a Second Reducible Function on the Mechanism of the Hydrogenation of an Ethylenic Double Bond

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The hydrogenation of 2-cyclohexenone and 2-methyl-2-cyclohexenone was carried out with a Pt/SiO_2 catalyst under stirred batch reactor conditions. The selectivity in the hydrogenation of the double bond is very high (>90%). A negative order in ketone is observed, in contrast with the positive experimental order for olefins like cyclohexene, but in accordance with the negative order already found for 1,4-cyclohexanedione and acetophenone. Comparison with the hydrogenation of 3,4-dihydro-2*H*-pyran whose behavior is identical to that of cyclohexene (kinetic order: + 1.0) shows that the juxtaposition of electrons in α position to the double bond does not change the kinetic parameters which are modified when there is a second reducible function (C=O). This result is probably due to an interaction of the π system of the second function with the active sites of the catalyst leading to an inhibition by the reactant itself.

INTRODUCTION

Hydrogenation of carbon–carbon multiple bonds of alkenes, alkynes, and aromatics, or of the C=O bond, generally gives reaction orders which are either positive or zero with respect to the reactant at all hydrogen pressures, whereas the hydrogenation of the bifunctional derivatives gives negative orders in reactant.

In 1965 Bond *et al.* (*1*) found that depending on the nature of the catalyst the order in 1,3-butadiene varied from 0 to −1 (−0.7 for platinum) and the order in hydrogen remained constant at about 1 at low pressures. In the hydrogenation of bicyclo-{2.2.1}-heptadiene-1,5 and of cyclohexene on a Pd/C catalyst, Jardine and McQuillin (*2*) found a diminution of the specific rate of hydrogenation of the diene whereas the rate of hydrogenation of the olefin increased with increasing reactant concentration (first order). Recently, for the hydrogenation of 1,3-butadiene on copper catalyst at low pressures Nishimura *et al.* (*3*) proposed a rate equation with a reaction order of 1 in hydrogen and −2 in reactant. Finally, Wells *et al.* (*4, 5*) working at low hydrogen pressure on the deuteriation of 1,2-propadiene with a Pd/Al_2O_3 catalyst and the hydrogenation of 1,3-butadiene with a rhenium catalyst showed negative orders with respect to reactant of −0.4 and −0.5, respectively.

These results demonstrate that the behavior of dienes is different from that of simple olefins.

For ketone hydrogenation, similar results have been found at low and medium hydrogen pressures, in which the order in hydrogen is close to 1. Thus, although the order in reactant is positive and close to $\frac{1}{2}$ for monofunctional compounds such as cyclanones (*6*), the existence of another carbonyl function (1,4-cyclohexanedione) or a phenyl ring (acetophenone) gives a negative order −0.6 for the former (*7*) and −0.3 for the latter (*8*).

It seems of interest then to study more precisely the influence of the reducible function C=O in α position to a double bond by an examination of the hydrogenation of 2-cyclohexenone and its methyl homolog, comparing its behavior in the same experimental conditions (Pt/SiO_2 and

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liquid phase) to that of cyclohexene and 3,4-dihydro-2*H*-pyran.

EXPERIMENTAL

Apparatus. We used two different types of apparatus: the first, used for reactions at hydrogen pressures less than one atmosphere, has been previously described (*7, 12*); the second, used for higher pressures, consisted of an autoclave (Autoclave Engineers type Magnedrive) with a capacity of 0.3 liter and a system for sampling of liquid during the course of the reaction without stopping the agitation.

Materials. All the compounds were commercial products (Merck) except the 2-methyl-2-cyclohexenone and 2-methyl-2-cyclohexenol. 2-methyl-2-cyclohexenone was obtained from 2-methylcyclohexanone (*9*), by chlorination of the ketone and dehydrochlorination of the resulting 2-chloro-2-methylcyclohexanone, bp 55°C/10 mm; 2-methyl-2-cyclohexenol was obtained by reduction of 2-methyl-2-cyclohexenone by the method of Dauben and Berezin (*10*). The product was isolated by chromatography on silica, bp 80°C/18 mm.

The catalysts ($\mathrm{Pt/SiO_2}$, $\mathrm{Ir/SiO_2}$, and $\mathrm{Ru/SiO_2}$) were prepared by impregnation. An aqueous solution of hexachloroplatinic or hexachloroiridic acid or ruthenium red (products Fluka or Merck) was first prepared, weighing the necessary amount to give 5% in weight of metal in the finished catalyst. The support, which was the fraction between 0.05 and 0.125 mm particle size (18–22 mesh) of a crushed Davison silica for chromatography (initially 28–200 mesh), was then added and the mixture was agitated for 2 h before evaporating to incipient wetness. Then the catalysts were dried in an oven at 80°C for 18 h.

After heating at 200°C under a stream of nitrogen (4 liters/h) for 1 h, the catalysts were reduced under a stream of hydrogen (4.5 liters/h) at 250°C for 6 h and then cooled under a stream of hydrogen. Finally, the catalysts were maintained in a stream of nitrogen for 1 h. The Ru catalyst was first calcined under a stream of air (6 liters/h) at 250°C for 6 h, then reduced under flowing hydrogen at 450°C.

Operating procedure. For the reactions at low pressure the apparatus was purged with nitrogen after introduction of the catalyst. For hydrogen pressures less than one atmosphere, the reaction was run in a mixture of hydrogen and nitrogen with the total pressure equal to 1 atm: after a while, a portion of the solvent (20 ml) was added and shaken for 1 h. Afterwards, the reactant, diluted with solvent, was added. The total amount of the liquid phase was 40 ml. In the case of reactions at high pressure, the catalyst, the reactant, and the solvent were placed directly in the autoclave. After 10 purges with nitrogen, a period of agitation of 1 h under a nitrogen pressure of 8 atm, and evacuation of the gas, the hydrogen was introduced at the desired pressure.

Analysis. The different samples were analyzed by gas chromatography on a Girdel 3000 apparatus with a flame ionization detector.

2-Cyclohexenone, cyclohexanone, and cyclohexanol were separated on a Carbowax 20 M column (10% on Chromosorb W, 3 m, ⅛″). The conditions used were: injector 250°C, detector 270°C, temperature program from 100 to 185°C at 10°C/min. The carrier gas was nitrogen at 30 ml/min.

2-Methylcyclohexanone, 2-methylcyclohexanol, 2-methyl-2-cyclohexenone, and 2-methyl-2-cyclohexenol were separated on a Carbowax 20 M column (10% on Chromosorb W, 3 m, ⅛″). The conditions for the separation were: injector 250°C, detector 270°C, column isothermal at 120°C, and nitrogen carrier gas at 30 ml/min.

In the case of competitive hydrogenations, the cyclohexenones and the corresponding cyclanones and alcohols were separated on an OV 225 Pyrex column (3% on Chromosorb WHP 100/120; 2.1 m, ⅛″). The conditions used for the separation were: injector 250°C, detector 290°C, temperature program from 50 to 60°C at 1°C/min followed by an isothermal period of 10 min at 60°C. Nitrogen at 30 ml/min was used as the carrier gas.

Tetrahydropyran and 3,4-dihydro-2*H*-pyran were separated on an FFAP column (15% on Chromosorb W DMCS, 3 m, ⅛"). The conditions of separation were: injector 150°C, detector 150°C, isothermal at 50°C. Nitrogen was used as the carrier gas at 20 ml/min.

In the case of the competitive hydrogenation, 3,4-dihydro-2*H*-pyran, tetrahydropyran, cyclohexene, and cyclohexane were separated on an FFAP column (15%, 3 m, ⅛") using the same conditions as above.

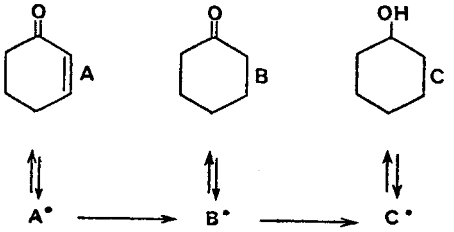
RESULTS AND DISCUSSION

A kinetic study of the catalytic hydrogenation of α,β-unsaturated ketones has not previously been reported. Stereochemical studies, however, have indicated an influence of the medium, depending upon whether the solvent was acidic, basic, or neutral (*11*). We therefore chose to work with a neutral solvent (hydrocarbon) and Pt/SiO_2 as catalyst, by analogy with previous studies with olefins (*12–18*).

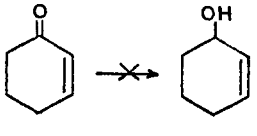
The results of the hydrogenation of 2-cyclohexenone A to give cyclohexanone B and cyclohexanol C will be analyzed in terms of the rate of the reaction (disappearance of cyclohexenone) and the selectivity of the reaction to give product B.

Selectivity

In the case of compounds containing two reducible functions, we can envisage the following scheme



since, as we will see, there is no reduction of the 2-cyclohexenone to 2-cyclohexenol.



The selectivity of the reaction in *B* can be expressed as a function of τ, where τ represents the number of moles of hydrogen consumed per mole of ketone *A*: $\tau = (n_B + 2n_C)/n_A^0$. Here, τ can vary between 0 and 2.

Moreover, the plots of molar percentages of B or C versus τ have the advantage of eliminating the time factor and permit a more precise determination of the initial selectivity S_B^0 of ketol. The tangents of these curves as shown in Fig. 1 (*18a, 18b*) give intercepts at $\tau = 1$, which determine two line segments AB and CD such that AB = 2CD = 2*x* and thus, the initial selectivity S_B^0 is defined as: $S_B^0 = dn_B/dn_C = (1 - 2x)/x$.

The maximum molar % in cyclohexanone B can be determined directly from the diagram of molar % = $f(\tau)$.

We note also that, at 50% reaction, a value of $\tau = 0.5$ represents a reaction which goes in two steps: A → B → C whereas a direct reaction of A to C would give a value of $\tau = 1$ at the half-reaction.

Influence of the Amount of Catalyst

In the kinetic studies of the hydrogenation of 2-cyclohexenone, no kinetic order satisfactorily accounts for the observed results, because, as in the case of olefins (*16, 17*), the initial rate, at both high and low pressures, is proportional, not directly to the amount of catalyst *m* but to $m - m_0$,

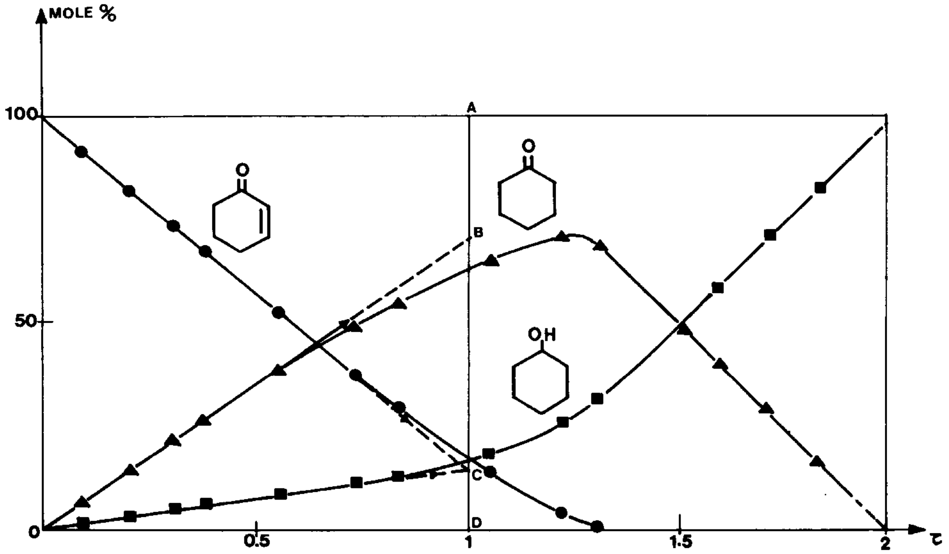


FIG. 1. Consecutive process in the catalytic hydrogenation of 2-cyclohexenone; $\tau = (n_B + 2n_C)/n_A{}^0$ with n_i = molar fraction of the species i at time t. Catalyst, Pt/SiO$_2$; temperature, 22°C; p_{H_2} = 77 atm; solvent, cyclohexane.

where m_0 represents the inactive mass of the catalyst. The initial rate may be expressed as:

$$r_A{}^0 = k(m - m_0)$$

where, for example, $k = 3 \times 10^{-3}$ mole min^{-1} (g cata)$^{-1}$ and $m_0 = 0.08$ g for a Pt/SiO$_2$ catalyst at 5% by weight, an initial concentration n_0 in ketone of 3.64×10^{-2} mole, a temperature of 22°C, and a p_{H_2} of 77 atm in cyclohexane as solvent.

This result is probably due to a partial poisoning of the catalyst before the reaction takes place. It must be noted that this effect does not affect the selectivities.

Influence of the Hydrogen Pressure

Determination of the order in hydrogen. The variations of the specific rate $\{r_S = r_A{}^0/(m - m_0)\}$ for the hydrogenation of 2-cyclohexenone were studied as a function of hydrogen pressure, keeping all other factors constant. An examination of Figs. 2 and 3 shows that between 0.03 and 0.21 atmosphere (low-pressure region) the reaction order is near 1 (1.1), becoming 0 at high pressures (between 30 and 100 atm), where probably the surface is fully covered by H atoms.

The results are thus identical to those previously found for the hydrogenation of olefins (*13, 16, 17, 19, 20*). The addition of a carbonyl group α to a carbon–carbon double bond does not modify the reaction order in hydrogen.

Influence of hydrogen pressure on the initial selectivity and the percentage of ketone. A graph of the initial selectivity, $S_B{}^0$ vs hydrogen pressure (Fig. 4) shows a loss of selectivity with increasing hydrogen pressure and finally a flat region corresponding to an initial selectivity in cyclohexanone of 6.

At low pressures of hydrogen ($p_{H_2} < 1$ atm) the results are different; there is an infinite initial selectivity and a very high maximum percentage of cyclohexanone is obtained. The Pt/SiO$_2$ catalyst is both active and selective at low pressures of hydrogen.

Influence of the Amount of 2-Cyclohexenone

We studied the changes in the specific rate as a function of the concentration of 2-

TABLE 1

Influence of the Amount of 2-Cyclohexenone Reactant[a]

Amount of reactant (g)	Initial selectivity S_B^0	Percentages of cyclohexanone at $\tau = 1$
2.499	6	64
2.999	6	67
3.499	8	73

[a] Catalyst, 0.150 g of Pt/SiO_2 at 5% by weight; temperature, 22°C; P_{H_2} = 77 atm; solvent, 80 ml of cyclohexane.

cyclohexenone for varying amounts of catalyst keeping the hydrogen pressure constant at 77 atm. The graph of the logarithm of the specific rate vs the logarithm of the reactant concentration gives a negative reaction order of -1.4 in reactant. This result is similar to those found with bifunctional compounds such as dienes (*1*, *2*), 1,4-cyclohexanedione (*7*), or acetophenone (*8*). However, the initial selectivity S_B^0 and the percentage of cyclohexanone formed are almost independent of reactant concentration (Table 1).

Influence of Other Parameters on the Rate of Hydrogenation of 2-Cyclohexenone

Effect of another ketone. The addition of

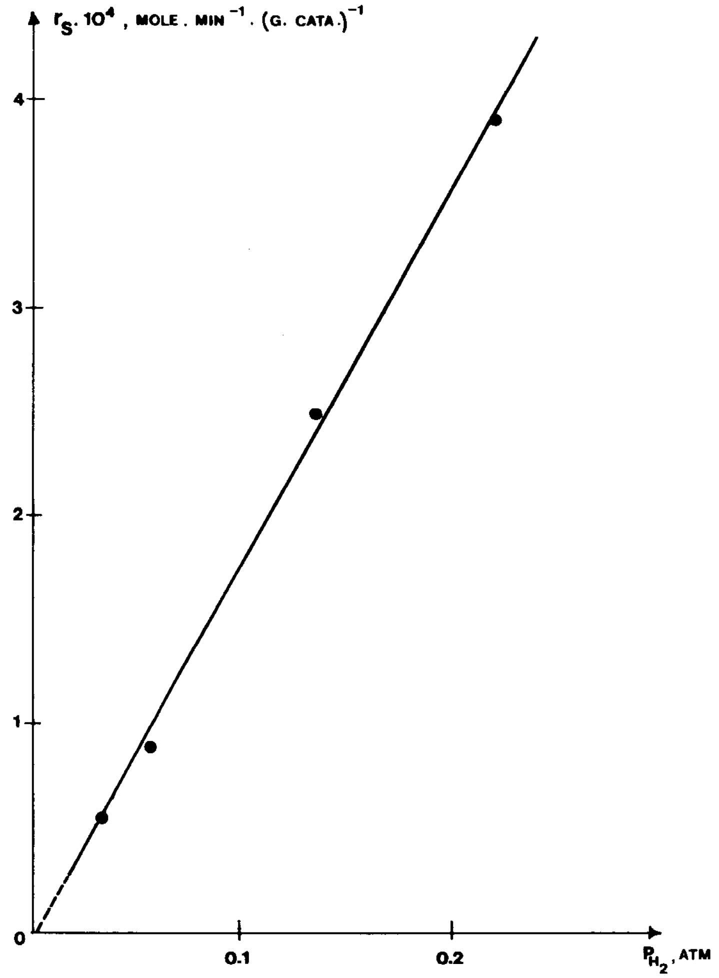


FIG. 2. Specific rate of hydrogenation of 2-cyclohexenone versus the pressure of hydrogen (region of low pressure). Catalyst, Pt/SiO_2; temperature, 22°C; solvent, cyclohexane.

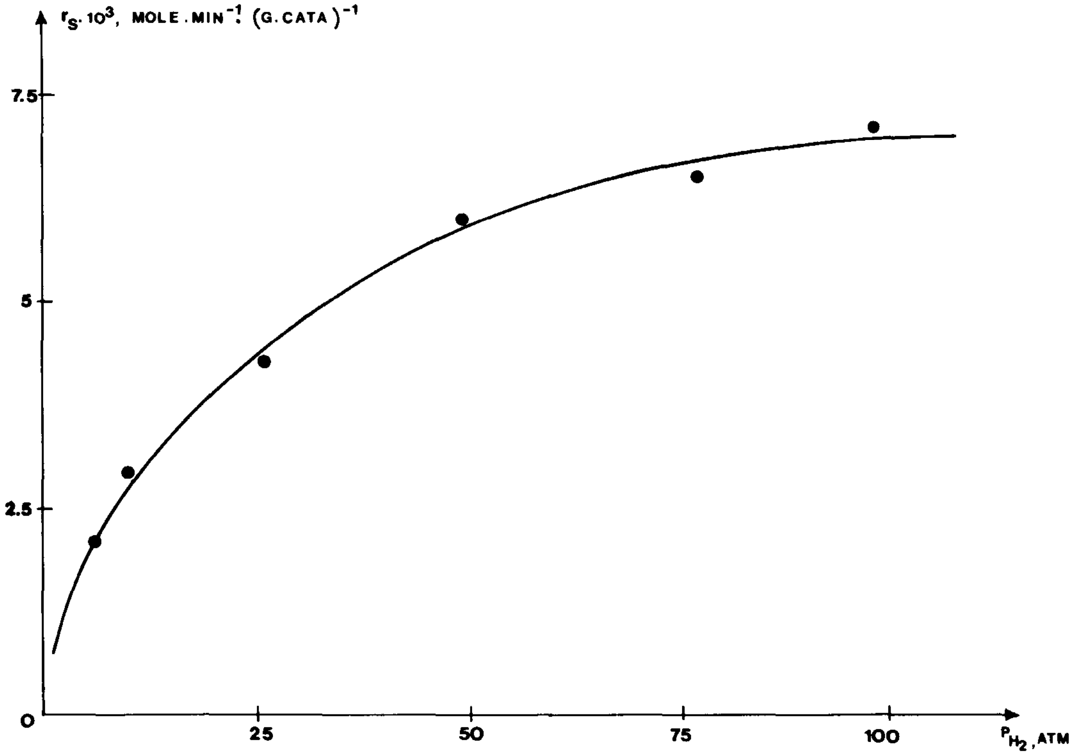


FIG. 3. Specific rate of hydrogenation of 2-cyclohexenone versus the pressure of hydrogen (region of high pressure). Catalyst, Pt/SiO_2; temperature, 22°C; solvent, cyclohexane.

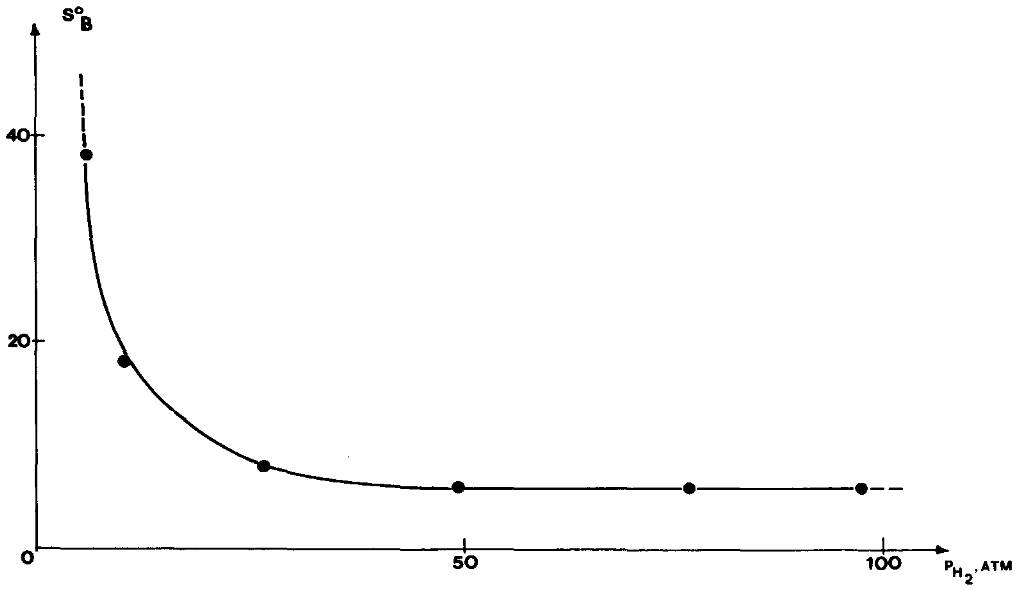


FIG. 4. Initial selectivity in cyclohexanone versus the pressure of hydrogen (region of high pressure). Catalyst, Pt/SiO_2; temperature, 22°C; solvent, cyclohexane.

TABLE 2

Influence of the Addition of Cyclopentanone[a]

Amount of reactants (g)	Initial rate $r_A^0 \times 10^5$ (mol/min)	Initial selectivity S_B^0	Percentage of cyclohexanone at $\tau = 1$
1.000 (2-Cyclohexane)	2.6	Very high	93
1.001 (2-Cyclohexane) 0.216 (Cyclopentanone)	2.0	Very high	94

[a] Catalyst, 0.400 g of Pt/SiO_2 at 5% by weight; temperature, 21°C; P_{H_2} = 0.055 atm; solvent, 40 ml of cyclohexane.

cyclopentanone which is not hydrogenated in our conditions does not modify the initial rate to any appreciable extent. The results at low pressure are presented in Table 2. Consequently, we can consider that the cyclohexanone formed in the course of the hydrogenation of 2-cyclohexenone probably has no effect on the rate of hydrogenation.

Effect of the nature of the metal. We compared the behavior of different metal catalysts, under identical conditions, namely, the same support (silica) and the same percentage by weight of metal (5%). From Table 3 it appears that the initial selectivity and the percentage of cyclohexanone at $\tau = 1$ are identical on platinum and ruthenium. Iridium is less selective. Thus in the hydrogenation of 2-cyclohexenone, the selectivity increases in the order Ir $\ll$ Pt $\simeq$ Ru.

Hydrogenation of 2-Methyl-2-cyclohexenone

Substituted olefins generally show the same behavior as olefins (*12–18*). We now wish to determine whether the results we obtained for 2-cyclohexenone at elevated pressures of hydrogen apply to 2-methyl-2-cyclohexenone.

As in the case of 2-cyclohexenone, the diagrams of molar % vs time do not permit a determination of the order in reactant. However, in contrast to the hydrogenation of 2-cyclohexenone where we found no trace of 2-cyclohexenol, the hydrogenation of 2-methyl-2-cyclohexenone is slightly modified giving small amounts ($\simeq$3%) of 2-methyl-2-cyclohexenol in the solution.

The competitive hydrogenation of the C=O function is probably due to the diminution of the specific rate of hydrogenation of the methylated double bond which changes from 15×10^{-3} in the case of 2-cyclohexenone to 0.7×10^{-3} mole min^{-1} (g cata)$^{-1}$ for an initial concentration of 1.4×10^{-2} mole.

The initial selectivity in methylcyclohexanone ($S_B^0 = 2$) and the percentage of this product at $\tau = 1$ (40%) are lower than the corresponding results for the hydrogenation of 2-cyclohexenone (S_B^0 = 6, 70%). These results are in agreement with those obtained with olefins by Maurel *et al.* (*12–18*) who showed that the hydrogenation of a double bond is very sensitive to steric hindrance and in particular to the presence of a substituent directly on the double bond.

TABLE 3

Influence of the Nature of Metal[a]

Metal of 5% by weight	Amount of catalyst (g)	Initial rate $r_A^0 \times 10^4$ (mol/min)	Initial selectivity S_B^0	Percentage of cyclohexanone at $\tau = 1$
Pt/SiO_2	0.150	1.3	17	85
Pt/SiO_2	0.300	3.6	18	85
Ir/SiO_2	0.151	12	4	65
Ru/SiO_2	0.301	1.2	18	87

[a] Amount of 2-cyclohexenone, 2.000 g; temperature, 27°C; P_{H_2} = 6.3 atm; solvent, 80 ml of cyclohexane.

As far as the kinetic order in hydrogen is concerned, its value is zero in the range of pressures studied (6–100 atm). Whatever the amount of catalyst, the variation of the logarithm of the specific rate as a function of the logarithm of the concentration of 2-methyl-2-cyclohexenone gives a straight line and a reaction order in reactant of -1.1 at a pressure where the order in hydrogen is zero.

We then find the same kinetic results as for the hydrogenation of 2-cyclohexenone: direct substitution by a methyl group of the olefin does not modify the kinetics of hydrogenation of an α,β-unsaturated ketone. The only change comes from the reactivity in competitive hydrogenation; 2-cyclohexenone is more reactive than 2-methyl-2-cyclohexenone using the experimental determination of the parameter R_{AB} defined previously as $R_{AB} = k_A b_A / k_B b_B$ where k and b are, respectively, the kinetic rate constant and the adsorption constant (6). The variation of R_{AB} with hydrogen pressure (Fig. 5) shows the existence of two regions of pressure where R_{AB} is constant suggesting that the slow step of the reaction is not the same at low and high pressure.

The results obtained with 2-cyclohexenone and 2-methyl-2-cyclohexenone show that the presence of a reducible function α to a double bond modifies the kinetics of hydrogenation of the simple olefin. As indicated in the introduction, there are differences in the kinetic order in reactant between bifunctional compounds and their monofunctional derivatives (dienes versus olefins, 1,4-cyclohexanedione and acetophenone versus cyclanones).

The negative order in reactant could be due to an interaction of the π system of the second reducible function with the active sites of the catalyst leading to an inhibition by the reactant itself.

Hydrogenation of 3,4-Dihydro-2H-pyran

We wondered, therefore, if it was necessary to have a reducible function such as the C=O group or only another kind of potentially electron donor group such as the heteroatom of oxygen to induce the observed modification of the kinetic results.

We chose then to study the hydrogenation of 3,4-dihydro-2*H*-pyran in the liquid phase on Pt/SiO_2 using the same conditions

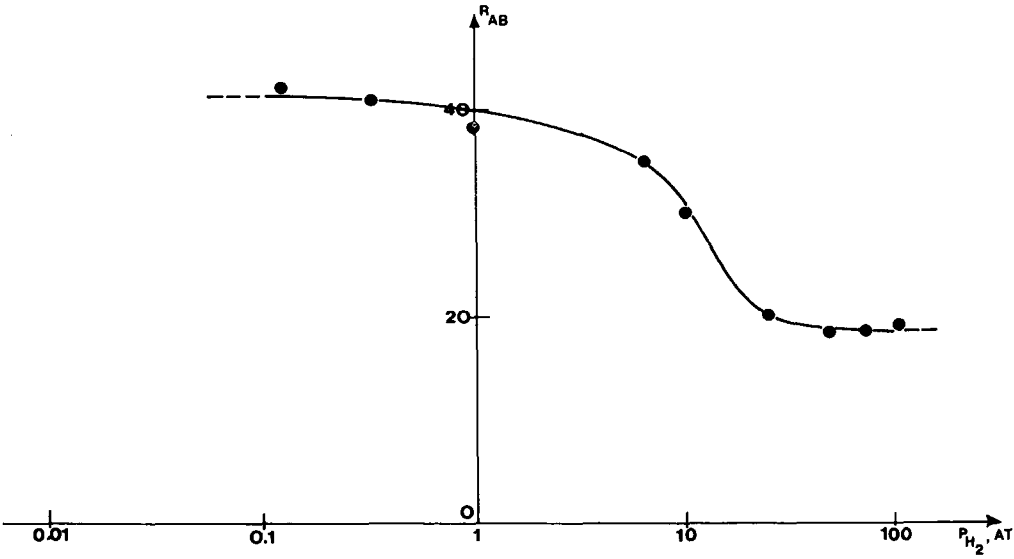


FIG. 5. R_{AB} (cyclohexenone/methylcyclohexenone) versus the pressure of hydrogen. Catalyst, Pt/SiO_2; temperature, 22°C; solvent, cyclohexane.

TABLE 4

Relative Reactivities R_{AB} of 3,4-Dihydro-2*H*-pyran and Cyclohexene[a]

Amount of 3,4-dihydro-2*H*-pyran (g)	Amount of cyclohexene (g)	Amount of catalyst (g)	P_{H_2} (atm)	R_{AB}
1.027	1.005	1.002	77	9
0.454	1.006	1.017	77	11
0.517	0.980	1.472	2	13
0.481	0.952	1.501	2	13

[a] Catalyst, Pt/SiO$_2$ at 5% by weight; temperature, 27°C; solvent, 60 ml of *n*-hexane.

as before. This compound possesses free pairs of electrons to the olefinic double bond whose influence on the kinetic results could be compared to that of the C=O group of the molecule of 2-cyclohexenone.

As regards the kinetic order in hydrogen the results are similar giving an order of zero in the range of 10–100 atm. However, as regards the kinetic order in reactant, the results are definitely different giving a positive order of 1 in pyran. The behavior is then analogous to that observed for single olefins such as cyclohexene (*16*).

If we go further in the comparison with this olefin studying competitive hydrogenation with 3,4-dihydro-2*H*-pyran (Table 4), it turns out that at low pressure as well as at high pressure, the molecule of pyran reacts faster than cyclohexene in agreement with the results of Kieboom and van Bekkum (*21*) for their analysis of the electronic effects of substitution on the adsorption and hydrogenation of substituted olefins.

In contrast, a comparison of the initial rates of hydrogenation of 2-cyclohexenone and cyclohexene,[2] which under identical conditions give a ratio of about 6 in favor of cyclohexene (Table 5), seems to show that the electronic effect of the oxygen atom in 3,4-dihydro-2*H*-pyran favors the reaction and the presence of a second reducible function disfavors it.

CONCLUSION

Hydrogenation of 2-cyclohexenone and its 2-methyl derivative leads to saturated ketones without concurrent hydrogenation of the carbonyl group according to a consecutive reaction scheme. These results are analogous to those found previously with 1,4-cyclohexanedione (*7*) and acetophenone (*8*). In the latter two compounds, the kinetic order in the reactant is negative with no hydrogenation of the phenyl group in the case of acetophenone, and the reduction of only one carbonyl group of 1,4-cyclohexanedione. It appears that the π electrons of a second functional group which is, in principle, reducible, but is not reduced during the course of the reaction, can interact with the metal and cause the observed kinetics. The work with 2,4-dihydro-2*H*-pyran shows that the p electrons on oxygen do not behave similarly to a

TABLE 5

Hydrogenation Rate of 2-Cyclohexenone and Cyclohexene[a]

Amount of reactant (g)	Initial rate $r_A{}^0 \times 10^3$ (mol/min)
2.000 (2-Cyclohexenone)	0.5
2.001 (Cyclohexene)	3.0

[a] Catalyst, 0.400 g of Pt/SiO$_2$ at 5% by weight; temperature, 30°C; P_{H_2} = 6 atm; solvent, 80 ml of *n*-hexane.

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[2] It is not possible to carry out a competitive hydrogenation of cyclohexene and 2-cyclohexenone since at high pressure the slow step of the two reactions is not identical.

second reducible group, since in this case the kinetic behavior is similar to that of cyclohexene.

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