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Low Pressure Hydrogenation of Ketones with Platinum Metal Catalysts

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Aliphatic, aromatic, and α,β-unsaturated ketones were hydrogenated at atmospheric pressure and room temperature in a number of solvents by palladium, platinum, rhodium, and ruthenium on high-surface carbon. Conditions for rapid and selective hydrogenation were determined.

Ketones have often been hydrogenated with platinum metal catalysts, but no previous systematic study has been made of the interdependence of solvent and catalyst on the rate and selectivity of hydrogenation. This paper examines the rate and course of low pressure hydrogenations in various solvents of three types of ketones by palladium, platinum, rhodium, and ruthenium on high-surface carbon.

From the results, a combination of catalyst and solvent that will give rapid and selective hydrogenation of aliphatic, aromatic, or α,β-unsaturated ketones can be chosen. The work was directed mainly toward laboratory preparations, and factors such as resistance to poisoning, catalyst life; effect of temperature and pressure, which would be of interest in commercial applications, was not examined. For convenience a large ratio of catalyst to substrate was used in determining the rates, but experience has shown the relative effectiveness of the various catalysts will be maintained, when a ratio more suitable for synthesis is used.

EXPERIMENTAL

The catalysts studied were all commercial preparations, manufactured by Engelhard Industries, of 5% reduced metal on high-surface carbon (Norit), and carried the designating numbers, 5% Pd-#3433, 5% Pt-#3635, 5% Rh-#3525, 5% Ru-#2403. Ruthenium catalysts were activated immediately before use by shaking the catalyst and solvent together under one atmosphere pressure of hydrogen for 1 hr., after which the flask was flushed with nitrogen and the substrate was added. The other catalysts were used directly as received. Electrolytic hydrogen and reagent grade solvents were used without further purification. The substrates were redistilled before use.

Rate measurements were made by a differential manometer using sensitive strain gauges with an electronic recording potentiometer. One arm of the manometer was connected to a flask containing the catalyst, solvent, and substrate, and the other arm to a flask containing only catalyst and solvent. Any contribution to the rate by adsorption of hydrogen on the catalyst was thus eliminated. All rate measurements were at 25° and an initial pressure of 1 atm., with 300 mg. of catalyst, 0.004 mol. of substrate, and 100 ml. of solvent. During the course of the experiment the pressure fell 5 to 10%. In all cases agitation by shaking was sufficiently vigorous to eliminate any contribution of hydrogen transport on the observed reaction rates. Identification of the product was made by comparison of the infrared spectrum with that of known samples. In the rate experiments a large amount of catalyst, relative to the substrate, was used to provide a convenient rate and to minimize the chance of a small amount of poison materially affecting the rate. One hydrogenation was made with each catalyst and with each compound using double the amount of substrate (and hence double any poison), but no appreciable change in rate was observed.

RESULTS AND DISCUSSION

In Table I the rates[1] of hydrogenation of cyclopentanone, cyclohexanone, and methyl isobutyl ketone are given.

All reductions were continued, except when the rate was very slow, until hydrogenation ceased. A few reactions, noted in Table I by p′, showed evidence of poisoning and the rate gradually declined. These experiments showing gradual poisoning are reproducible. The shape of the rate curve was unaltered by doubling the amount of solvent. All other rates were zero order over almost the entire range. Under the conditions employed no hydrogenolysis occurred and the alcohol was the only product. The rates of hydrogenation of these ketones depend markedly on catalyst, substrate, and solvent.

Palladium was ineffective in all solvents tested,[2] with the technique used. The failure of palladium to hydrogenate these aliphatic ketones might be attributed to exceptionally strong adsorption of the ketone, if the ketone were added dropwise instead of all at once to the palladium in solvent, hydrogenation would proceed at a slow but tolerable rate. Palladium has been used to hydrogenate ketones, but usually at elevated temperature and pressures and for long periods of time. This is not the catalyst of choice.

Platinum in aqueous acid hydrogenated all three compounds satisfactorily, but, in base, poisoning was observed with cyclopentanone and methyl isobutyl ketone. This poison is formed during the hydrogenation and is not initially in the substrate; when the ratio of substrate and solvent to catalyst was doubled, the rate curve was unchanged. A similar poisoning of platinum in neutral or basic solution was observed in the hydrogenation of

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[1] The rate is expressed in ml. of hydrogen absorbed per min. p′ indicates poisoning. A slow decline in rate was observed as reduction progressed.

[2] Colloidal platinum and palladium have also been found ineffective for carbonyl reduction in alcohol and acetic acid. Z. Csuros and I. Sello, *Hung. Acta Chim.*, I, 27 (1949).

TABLE I

RATE[1] OF HYDROGENATION OF ALIPHATIC KETONES

	Catalyst											
	5% Pd/C			5% Pt/C			5% Rh/C			5% Ru/C		
Solvent	I	II	III	I	II	III	I	II	III	I	II	III
CH_3COOH	0.2	0.0	0.0	0.2	7	0.3	0.2	11	p′	0.0	0.0	0.0
H_2O	0.0	0.1	0.0	6	22	18	16	25	15	26	24	11
0.5N NaOH	0.2	p′	0.2	p′	20	p′	20	26	22	14	24	45
0.5N HCl	0.0	0.1	0.1	11	22	10	5	16	4	0.2	p′	0.2
CH_3OH	0.0	0.2	0.0	0.2	0.2	0.3	0.1	0.3	0.3	p′	0.1	p′
$CH_3CO_2C_2H_5$	0.0	0.1	0.0	0.2	0.3	0.2	0.0	0.2	0.0	0.0	0.1	0.0

I = Methyl isobutyl ketone. II = Cyclohexanone. III = Cyclopentanone.

TABLE II

RATE[1] OF HYDROGENATION OF AN UNSATURATED KETONE AND ALCOHOL

		Catalyst							
		5% Pd/C		5% Pt/C		5% Rh/C		5% Ru/C	
Solvent		I	II	I	II	I	II	I	II
CH_3COOH	C=C	55	45	44	23	44	42	0.0	0.0
	C=O	0.2	—	0.1	—	0.2	—	0.0	—
H_2O	C=C	55	21	44	23	44	23	28	16
	C=O	0.0	—	6	—	10	—	7	—
0.5N NaOH	C=C	45	9	8	6	20	16	16	7
	C=O	0.2	—	p′	—	20	—	16	—
0.5N HCl	C=C	60	32	40	25	36	16	p′	p′
	C=O	0.0	—	12	—	5	—	0.1	—
CH_3OH	C=C	65	—	56	—	48	—	10	—
	C=O	0.0	—	0.1	—	0.1	—	p′	—
$CH_3COOC_2H_5$	C=C	80	20	60	20	80	21	0.0	0.3
	C=O	0.0	—	0.0	—	0.0	—	0.0	—

I = Mesityl oxide. II = 4-Methyl-3-pentene-2-ol.

oximes,[3] and unsaturated amines.[4] In these instances poisoning was reasonably attributed to formation of the strongly basic amine, but other compounds formed in the reduction may have also contributed to the poisoning.

Rhodium and ruthenium, unlike platinum, hydrogenate most rapidly in neutral or basic solution and are relatively slow in acid. In favorable environment both rhodium and ruthenium were exceptionally active for carbonyl reduction, and are certainly the most desirable metals to use in a nonacidic solution. The statement[5] has been made that rhodium will not hydrogenate ketones unless they are activated. This conclusion was reached because alcohol was used exclusively as the solvent.

Cyclohexanone hydrogenates more rapidly than methyl isobutyl ketone, perhaps because of less steric hindrance. Except in alkaline solution, cyclohexanone also hydrogenates more rapidly than cyclopentanone. The more rapid reduction of cyclohexanone is in accord with the generalization,[6] based partly upon kinetics, that exo double bonds in 5-membered rings are relatively stable; exo double bonds in 6-membered rings, relatively unstable.

α,β-Unsaturated Ketones. The effect of conjugation on the rate of reduction of an α,β-unsaturated ketone and the best way of achieving a selective hydrogenation was examined using mesityl oxide. This material could be reduced to the saturated alcohol by several routes, but, in fact, reduction proceeded entirely through the saturated ketone. In Table II, the rates of hydrogenation of 4-methyl-3-pentene-2-ol, and of mesityl oxide are given. The rate of absorption of the second mole of hydrogen by mesityl oxide is, in general, that to be expected if the intermediate product is methyl isobutyl ketone. The reduction is in all cases highly selective. When the reaction was interrupted after absorption of one mole of hydrogen, only methyl isobutyl ketone was found; there was no saturated or unsaturated alcohol.

The rate of absorption of the first mole of hydrogen is, therefore, the rate of olefin saturation. These data do not preclude the possibility that the carbonyl was involved in the olefin reduction through 1,4 addition. In every case the rate of hydrogenation of the olefin is faster for the unsaturated ketone than it is for the unsaturated alcohol, although both probably have similar steric requirements.

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[3] E. Breitner, E. Roginski, and P. N. Rylander, *J. Chem. Soc.*, in press.

[4] J. M. Devereux, K. R. Payne, and E. R. A. Peeling, *J. Chem. Soc.*, 2845 (1957).

[5] W. P. Dunworth and F. F. Nord, *J. Am. Chem. Soc.*, **74**, 1459 (1952).

[6] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

TABLE III

RATE[1] OF HYDROGENATION OF ACETOPHENONE

Solvent		Catalyst			
		5% Pd/C	5% Pt/C	5% Rh/C	5% Ru/C
CH_3COOH	C=O	30	p′	⎧26	0.0
	CH—OH	3	p′	⎨26	0.0
	ring	0	p′	⎩7	0.0
H_2O	C=O	11	10	⎧26	9
	CHOH	0	1	⎨26	⎧2
	ring	0	—	⎩11	⎩2
0.5*N* NaOH	C=O	3	4	⎧13	9
	CHOH	0	0	⎨4	⎧2
	ring	0	—	⎩4	⎩1
0.5*N* HCl	C=O	24	12	⎧11	0.1
	CHOH	0	12	⎨7	0
	ring	0	2	⎩3	0
CH_3OH	C=O	24	12	⎧11	0.1
	CHOH	0	12	⎨7	0
	ring	0	2	⎩3	0
$CH_3COOC_2H_5$	C=O	0.8	2	⎧22	0.1
	CHOH	0	1	⎨8	0
	ring	0	0	⎩6	0

The rate curves for hydrogenation by rhodium and ruthenium in base are interesting. These catalysts hydrogenate at constant rate over the entire reaction, which would imply that 2 mol. of hydrogen are absorbed by the substrate in a single residence on the catalyst and give the saturated alcohol directly. This was not the case, however. When the reaction was stopped after 1 mol. of hydrogen was absorbed, methyl isobutyl ketone was the only product. The constant rate arose fortuitously because mesityl oxide and methyl isobutyl ketone hydrogenate separately at the same rate. But in competition with mesityl oxide, methyl isobutyl ketone is not hydrogenated at all, because of the much stronger adsorption of the unsaturated ketone by the catalyst. Even when the initial reaction mixture consisted of three parts methyl isobutyl ketone and one part mesityl oxide, the olefin was first completely reduced and subsequently the carbonyl.

AROMATIC KETONES

Selective hydrogenation of aromatic ketones presents a more difficult problem than selective hydrogenation of aliphatic or α,β-unsaturated ketones. In aromatic ketones hydrogenolysis and reduction of the ring occur readily, as can be seen from the data for the hydrogenation of acetophenone[7] given in Table III.

Because two or more reactions do occur simultaneously, the inflections in the rate curves do not always occur at integral numbers and, furthermore, the change in rate is not always abrupt. To this extent the rates given in Table III are idealized and thus some of the rates in the table were put in brackets indicating concurrent reductions. Pure products cannot be expected in these cases, although one may be preponderant. However, they adequately describe the extent of hydrogenation and give approximately the relative rates of formation of phenylethyl alcohol (1 mol. of hydrogen absorbed), ethylbenzene (2 mol.), α-cyclohexylethanol (4 mol.), and ethylcyclohexane (5 mol.). Platinum in acetic acid hydrogenated acetophenone at a rapid but constantly declining rate; it is noted, therefore, only by p′.

Palladium is the best catalyst for side-chain hydrogenation without ring saturation. Under these conditions acetophenone does not absorb more than 2 mol. of hydrogen, and by using the proper solvent it stops abruptly after 1 mol. to give phenylethyl alcohol. The much faster reduction by palladium of aromatic ketones compared to aliphatic is striking, especially when contrasted with the much smaller, and sometimes opposite, changes with the other catalysts.

Rhodium is seen to be very active for ring hydrogenation,[8] and would be the catalyst of choice for total reduction. Reductions with rhodium, stopped after 1, 2, or 3 mol. of hydrogen absorption gave mixtures in which some ring hydrogenation occurred. When the reduction was done without solvent or in methanol and stopped after four moles about an 80% yield of cyclohexyl methylcarbinol was obtained.

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(7) The hydrogenation of acetophenone in dioxane and acetic acid with palladium and platinum black has been studied, W. Theilacker and H. G. Drossler, *Chem. Ber.* **87**, 1676 (1954). The course of hydrogenation was shown to be profoundly influenced by acids and bases.

(8) a. H. A. Smith and R. G. Thompson, "Advances in Catalysis," Academic Press Inc., New York, 1957, Vol. IX, P. 727. b. G. Gilman and G. Cohn, "Advances in Catalysis," p. 733.