

Mechanism of Gas-Phase Hydrogenation of Alicyclic Ketones on Iron Catalyst: Effective Experimental Method on the Basis of Reaction Gas Chromatography/Mass Spectrometry

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Received April 2, 1984; revised October 29, 1984

The mechanism of gas-phase deuterium addition to cyclopentanone and cyclohexanone over fused iron catalyst has been studied by reaction gas chromatography/mass spectrometry (GC/MS) which involves the on-line deuteriogenation and on-column silylation of reaction products. It has been found that in the temperature range of 50–210°C cyclanone hydrogenation proceeds both via ketonic and enolic mechanisms. Also, it has been shown that the method developed can be used for the determination of enolic forms of carbonyl compounds in the gas phase. © 1985 Academic Press, Inc.

INTRODUCTION

Selective hydrogenation may involve two types of surface forms of carbonyl compounds: ketonic and/or enolic forms which in further discussion have been referred to as "ketonic" or "enolic" mechanisms. In earlier works (1–6) hydrogen addition has been shown to proceed exclusively via the ketonic mechanism irrespective of the ketone structure and the experimental conditions, but on heavy Pt, light triad Pd, or Cu catalysts. The reaction mechanism when iron triad is used as catalyst is not very clear. Some researchers (for example (3, 4, 7, 8) have shown that ketonic mechanism is exclusively realized with iron triad. While others (9, 10) have proved that hydrogen can be added to enolic form of carbonyl compounds; the enolic mechanism dominates at high temperatures (150–250°C).

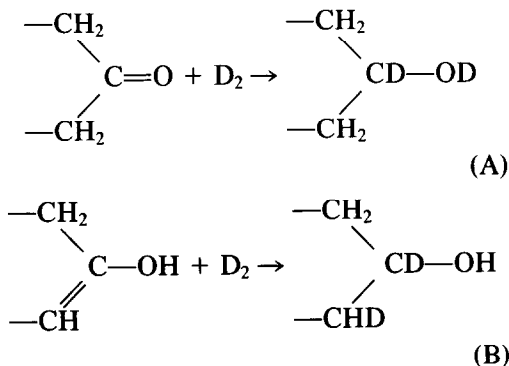
Iron triad catalysts are extensively used in the industry for the hydrogenation of aldehydes and ketones. Therefore, we undertook the study of their reaction mechanism.

This paper deals with the gas-phase hydrogenation mechanism for alicyclic ke-

tones (cyclopentanone and cyclohexanone) over fused iron catalyst. The studies were conducted by reaction gas chromatography/mass spectrometry (GC/MS), involving the use of on-line pulse microreactor located between the injection port and the chromatographic column and of deuterium as carrier and reagent gas (11, 12). The advantage of the method is that it permits the deuteriogenation as well as the chromatographic and mass spectrometric analysis of all reaction products in the same experiment. This method does not demand any additional experiment for preliminary isolation and separation of the reaction products. A scheme of the experimental system is given in Fig. 1.

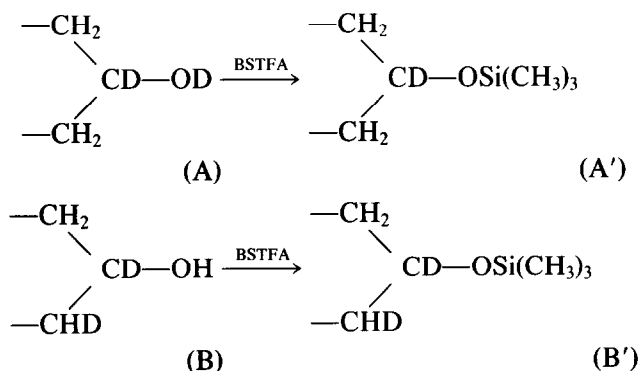
Direct mass spectrometric analysis permits the determination of isotopic content only for ketones whose mass spectra show rather abundant M^{+} ions. Several difficulties have to be overcome when isotopic composition of the resulting alcohols is to be determined mass spectrometrically.

Deuterium addition to unlabeled ketones via ketonic and enolic mechanisms is expected to give rise to deuterated alcohols of the following types



When these alcohols pass through the chromatographic column and interact with the moisture adsorbed on the metallic parts of the mass spectrometer, the deuterioxylys (if present) are partly converted into hydroxylys which may change the actual isotopic content. This is the reason why in

Refs. (4, 6) the alcohols, prior to their mass spectrometric analysis, were washed with water to completely eliminate deuterium from deuterioxylys. The labeled alcohols obtained from unlabeled ketones by the ketonic and enolic mechanisms contain one and two deuterium atoms, respectively. This can be readily detected by mass spectrometry. Using the reaction GC/MS we failed to convert completely deuterioxylys into hydroxylys. Therefore, we decided to take recourse to the recently developed procedure (13) for on-column silylation of alcohols by *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), which permits complete elimination of active hydrogen (deuterium) from hydroxyl group due to the formation of trimethylsilyl ethers:



Another advantage of this technique is that it allows the accuracy of mass spectrometric determination of deuterium content to be increased as the mass spectra of trimethylsilyl derivatives reveal rather abundant M^+ and $[M-\text{CH}_3]^+$ ions (loss of CH_3 radical from the $\text{Si}(\text{CH}_3)_3$ group (Fig. 2). Also, these spectra are free of the $[M-1]^+$ ions, which are generally found in the mass spectra of cycloalkanol.

The studies were conducted in a stainless-steel microreactor having an inlet for BSTFA (Fig. 1). In order to avoid any poisoning of the catalyst, a silylating agent was introduced into the gas flow after the catalytic bed. Figure 2 shows the averaged

mass spectra of the main products obtained in one of the runs.

EXPERIMENTAL

Materials and reagents. The cyclopentanone and cyclohexanone used in our experiments were 99.5% pure. In studying the isotopic exchange of alcohols, cyclopentanol and cyclohexanol of about 99.8% purity were used. The isotopic purity of deuterium gas was over 99.5%. *N,O*-Bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane was procured from Pierce Chemical Company. Fused iron catalyst containing 5% mass of V_2O_5 was investigated (14).

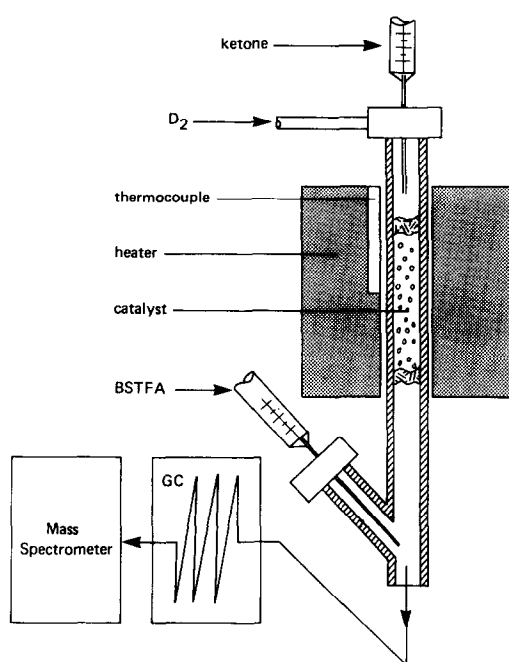


FIG. 1. Schematic of the device used.

Preparation of catalyst. The catalyst (0.05–0.15 g) was placed in a microreactor filled with CO_2 . The granules were 1.5–2.5 mm in diameter. The catalytic bed was about 4 mm in diameter and 5–15 mm in length. Prior to analysis, the catalyst was activated at 450°C in a flow of deuterium (30 ml/min) for 2 h which allowed complete replacement of chemisorbed and dissolved hydrogen.

Reaction gas chromatography/mass spectrometry. The work was performed on a LKB-2091 gas chromatograph/mass spectrometer. The mass spectra were obtained at 70 eV, emission current 25 A, and temperature of ionization chamber and molecular separator 200°C .

In the chromatographic part, the stainless-steel column (1.5 m \times 3 mm) containing 15% Carbowax 20M coated on Chromaton NAW (0.2–0.25 mm) was used. Deuterium was used as the carrier and reagent gas at a flow rate of 10–30 ml/min.

The investigation was done by using the pulse technique in the temperature range of 50 – 210°C . After injecting ketone (0.4–1 μl)

for 2–4 s, 1–3 μl of BSTFA was introduced (see Fig. 1). Subsequent analysis was performed by GC/MS. Because of possible separation of isotopic forms during elution of compounds from the GC column, five 8 scans were made for each chromatographic peak and the recorded mass spectra were averaged. The isotopic composition of the recovered ketones was determined from the intensity ratios of the molecular ion peaks after correcting them for naturally occurring isotopes of carbon, hydrogen, and oxygen. The isotopic composition of trimethylsilyl derivatives was calculated from the intensity ratios of the molecular ion peaks after correcting them for naturally occurring isotopes of C, H, O, and Si.

RESULTS AND DISCUSSION

Results obtained from the deuteriogenation of cyclopentanone and cyclohexanone over fused iron catalyst are presented in Tables 1 and 2. These results are the average of two 4 subsequent pulses. The mole ratio of D_2 to ketone was between 10 and 100.

In order to maintain consistency in discussing the hydrogenation mechanisms we would emphasize the following results:

1. The ketones under study appear to un-

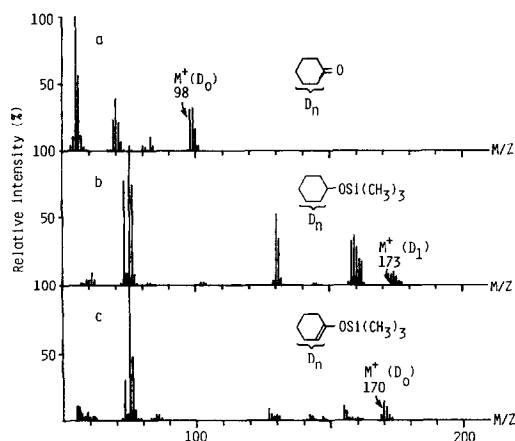


FIG. 2. The mass spectra of deuterated cyclohexanone (a), trimethylsilyl ether of deuterated cyclohexanol (b), and trimethylsilyl ether of deuterated enol (c) registered in one of the runs.

TABLE I
Deuteration of Cyclopentanone on Iron Catalyst

Temp. (°C)	Product composition (%)		Deuterium distribution at the end of catalytic bed (%) ^a										Ketonic-to-enolic mechanism ratio						
	Alcohol	Enol	Ketone			Trimethylsilyl ether of alcohols					Trimethylsilyl ether of enol								
			D ₀	D ₁	D ₂	D ₃	D ₁	D ₂	D ₃	D ₄	D ₅	D ₀		D ₁	D ₂	D ₄			
50	0	0	93 (93.2)	7 (6.6)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
120	64	0.9	40 (42.8)	42 (38.4)	15 (15.1)	3 (3.4)	—	—	—	—	—	—	—	—	—	—	—	—	41:59
150	18	3.0	42 (44)	41 (38)	14 (14.4)	3 (3.1)	—	—	—	—	—	—	—	—	—	—	—	—	41:59
210	25	2.0	43 (43.5)	39 (38.2)	14 (14.6)	4 (3.2)	—	—	—	—	—	—	—	—	—	—	—	—	41:59
120	21	3.4	46 (45.3)	35 (37.8)	16 (13.9)	3 (2.9)	—	—	—	—	—	—	—	—	—	—	—	—	44:56

^a Deuterium distributions calculated according to (15) are given in parentheses.

TABLE 2
Deuteration of Cyclohexanone on Iron Catalyst

Temp. (°C)	Product composition (%)		Deuterium distribution at the end of catalytic bed (%) ^a										Ketonic-to-enolic mechanism ratio					
	Alcohol	Enol	Ketone			Trimethylsilyl ether of alcohol					Trimethylsilyl ether of enol							
			D ₀	D ₁	D ₂	D ₁	D ₂	D ₃	D ₄	D ₅	D ₀	D ₁		D ₂	D ₃			
50	0	1.3	77 (77.2)	23 (18.7)	—	—	—	—	—	—	—	—	—	85 (85.7)	15 (13.1)	—	—	—
70	1.5	1.8	55 (54.4)	31 (34.1)	14 (9.5)	—	—	—	43	45	8	4	—	61 (61.2)	30 (30.9)	9 (6.9)	—	55:45
120	30	1.5	44 (44.9)	38 (37.4)	15 (14.1)	3 (3.1)	—	—	30	23	19	16	12	56 (55.1)	32 (33.9)	13 (9.3)	—	41:59
150	36	3.0	40 (41.1)	39 (38.2)	17 (14.7)	4 (4.0)	—	—	34	27	19	10	10	57 (61.3)	38 (30.9)	5 (6.9)	—	49:51
210	44	2.0	33 (34.1)	38 (38.7)	23 (19.8)	6 (6.0)	—	—	26	33	22	12	7	38 (39.5)	40 (38.6)	18 (16.8)	4 (4.3)	39:61

^a Deuterium distributions calculated according to (15) are given in parentheses.

dergo a considerable H/D exchange in the studied temperature range. The experiments involving large amounts of the catalyst and resulting in a greater conversion of ketones have shown that no more than four hydrogen atoms may be replaced by deuterium. These hydrogen atoms are most likely located at α carbon atoms and, therefore, the isotopic exchange takes place due to enolization of ketones.

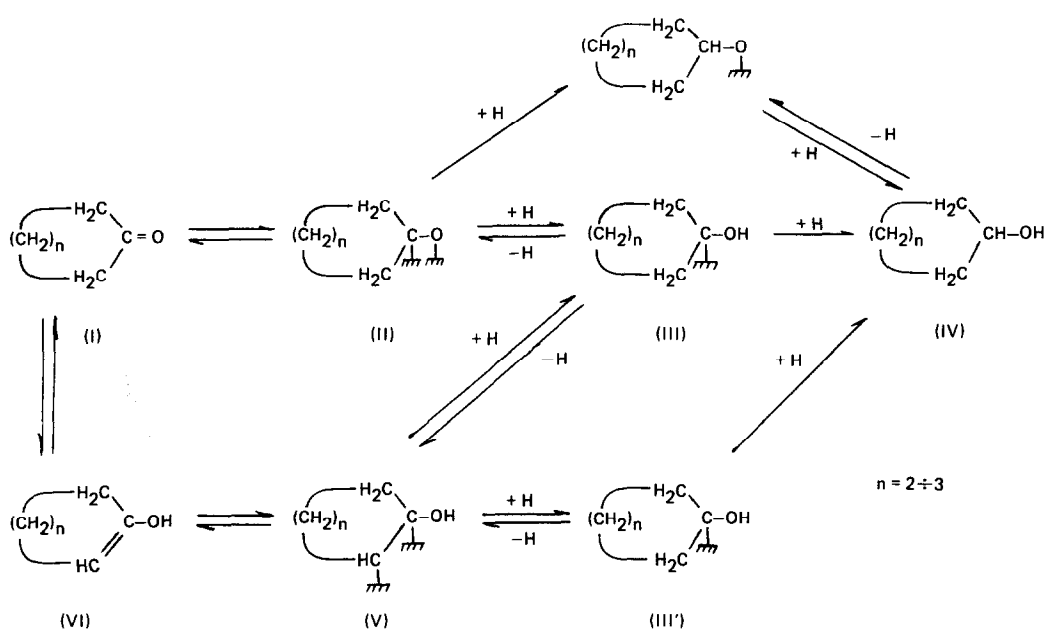
2. Using the relation $(1 - y)^n - y^n n! / (n - i)! i!$ (15) the deuterium distribution for each ketone $C_m H_{n-i} D_i O$ was determined; here, y stands for the atomic portion of deuterium in the substrate. The results obtained are in good agreement with the experimentally found values (see Tables 1 and 2). This enables us to conclude that the isotopic exchange rate is higher than that of ketone hydrogenation under the conditions of our experiment. This is further corroborated by the observation of isotopic exchange in ketones even when alcohols are not formed.

3. To examine whether or not the cycloalkanols undergo H/D exchange, the corresponding alcohols were passed through the catalyst after each run, involving the ketone, under the same conditions. Free alcohols were found to contain nearly 30% D_1 analogs irrespective of the reaction temperature (this value is probably less than the actual because of the on-column isotopic exchange). The mass spectra registered after silylation, however, shows that only a trace (5%) of D_1 -alcohol is formed even at high reaction temperatures. This indicates that isotopic exchange in alcohols takes place mainly at the hydroxyl group without essentially involving the hydrogens at carbon atoms. This is not in accordance with the results reported for iron catalyst (8). The reason may be the different structures of the investigated alcohols and the difference in pulse value (8). The absence of H/D exchange in alcohols facilitates essentially the analysis of experimental results as the isotopic composition of alcohols (determined from the mass spectra of their trimethylsilyl ethers) is believed to be formed

only by the interaction of ketones with deuterium.

4. For the first time direct silylation of reaction products permitted us to detect the enolic forms of ketones (as trimethylsilyl ethers), whose contribution is 1–3.5%. Trimethylsilyl ethers of enols had a lower deuterium content as compared with the unreacted ketones (Tables 1, 2), which is naturally due to loss of label during enolization followed by silylation. The deuterium distribution calculated as per (15) is found to be close to the equilibrium value and, hence, the isotopic compositions of enols and ketones are identical. It is worth mentioning that reaction GC/MS involving the on-column silylation may be applied to the development of a quantitative methodology for the examination of keto-enol tautomerization of carbonyl compounds in the gas phase.

The above discussion reveals that trimethylsilyl ethers of alcohols containing one deuterium atom can result from the addition of deuterium molecule to D_0 -ketones via ketonic mechanism. Ethers containing two deuterium atoms can be obtained by adding deuterium to D_1 -ketones via ketonic mechanism and to D_0 -ketone via enolic mechanism, and so on. Assuming that the deuteriogenation rate does not essentially depend on the isotopic form of ketones, the contribution of ketonic and enolic mechanisms may be approximately evaluated. For calculation, the isotopic compositions of alcohols obtained from the mass spectra of their trimethylsilyl ethers, and the averaged isotopic compositions of ketones within the catalytic bed were used. The results presented in Tables 1 and 2 show that, contrary to the earlier reported data (3, 4, 7, 8), the isotopic composition of alcohols is due to the existence of both enolic and ketonic mechanisms. Taking into account the experimental errors and the accuracy of calculations, it may be concluded that their ratio equals 1 ± 0.25 and does not essentially depend on the reaction conditions and the extent of ketone conversion.



SCHEME 1

The results obtained allow a general scheme to be suggested for isotopic exchange and the hydrogenation of alicyclic ketones over fused iron catalyst (see Scheme 1).

Let us consider the isotopic exchange. On passing through the catalyst in a deuterium stream, ketones undergo rapid isotopic exchange which is close to the equilibrium. This may be attributed to keto-enolic tautomerization facilitated by the catalyst surface (sequence $I \rightarrow VI \rightarrow V \rightarrow III'$). Low concentration of enols in the reaction products and the absence of necessary data (i.e., the rates of keto-enolic interconversions of the ketones studied), however, do not permit this exchange to be considered as the only possible path. That is why, here as well as in (6a), the isotopic exchange is assumed to proceed via another path which leads to ketone exchange in the following sequence ($I \rightarrow II \rightarrow III \rightarrow V$).

Within the framework of the suggested scheme, the hydrogenation of ketone into alcohol via ketonic and enolic mechanisms involves the sequences $I \rightarrow II \rightarrow III \rightarrow IV$

and $I \rightarrow II \rightarrow III \rightarrow V \rightarrow III' \rightarrow IV$, respectively. According to (14), the scheme involves stepwise addition of dissociative chemisorbed hydrogen to the surface intermediate forms of the substrate. It should be noted that for the hydrogenation of ketone the deuterium distribution is naturally different in III and III' and the alcohol molecules derived from them. Hydrogen/deuterium exchange in the hydroxyl group of alcohol may proceed through path $IV \rightarrow VII$. In addition, the fact that hydrogens at the carbon atoms of alcohols are not practically substituted by deuterium, allows one to consider that equilibrium shifts to the right when III and III' change into IV and II into VII.

Practically constant ratio of ketonic and enolic mechanisms in the investigated temperature range suggests that the activation energies for these mechanisms are close to each other.

Our interpretation of the results obtained through ketonic and enolic mechanisms of hydrogenation is not the only possible way, as it cannot be ruled out that the addition of deuterium to the substrate over iron cata-

lyst may involve the π -allylic type surface intermediates (4, 7). In the case of these intermediates the observed enolic-to-ke-tonic mechanism ratio may be easily explained by close probability for the addition of deuterium to the intermediates.

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