Nickel—Its Intrinsic Acidity and Its Effect on the Hydrogenolysis of 1,1-Dimethylcyclopropane and Ethylcyclopropane

HERMAN PINES AND LEONARDO NOGUEIRA*

The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

The selectivity of hydrogenolysis of 1,1-dimethylcyclopropane and ethylcyclopropane has been studied at 80–150°C in a pulse-microreactor at atmospheric pressure in the presence of hydrogen and nickel containing catalysts. The method of preparation of the catalysts and the supports used can influence the selectivity of 1,2- and 2,3-ring rupture.

In the hydrogenolysis of 1,1-dimethylcyclopropane it was found that nickel oxide catalyst reduced at 400°C yielded a ratio of neopentane/isopentane equal to 0.9 and 3.6, at 80 and 120°C, respectively. A similar catalyst containing 0.05% Na^+ gave ratios of 5.4 and 10.1.

Nickel–kieselguhr 6% catalyst gave a ratio of neopentane/isopentane of 1.3 at 80°C. With catalyst containing 0.1% Na^+ the ratio was 6.1, and with 1.0% Na^+ it amounted to 10.5.

The incorporation of 0.05% of alumina to 6% nickel–silica catalyst greatly enhances the 1,2-ring scission.

Ethylcyclopropane is less sensitive to the changes in the properties of the nickel catalyst.

Mechanism of reaction is discussed and it was shown that the enhancement of 1,2-ring scission can be attributed to the intrinsic acidic sites of the catalysts.

I. INTRODUCTION

The catalytic hydrogenolysis of substituted cyclopropanes has been extensively studied (1). The results reported in the literature defy a reasonable correlation between reaction conditions and product formation. The data from the literature (2–10) on the hydrogenolysis of alkylcyclopropanes over nickel catalysts, Table 1, show that there is a lack of consistency in the selectivity of the ring cleavage. The method of the preparation of nickel catalysts, the nature of the supports, and the pretreatment of the catalysts on the selectivity of the hydrogenolysis of alkylcyclopropane have been ignored.

Recently it has been reported from this laboratory that the method of preparation and of pretreatment of nickel catalysts may affect considerably the course of hydrogenolysis of primary alcohols (11–15). In the presence of hydrogen at atmospheric pressure and at 150–190°C three main reactions were found to occur:

$$RCH_2OH \begin{cases} RCH_3 + H_2O & (1) \\ RH + CH_4 + H_2O & (2) \\ (RCH_2)_2O + H_2O & (3) \end{cases}$$
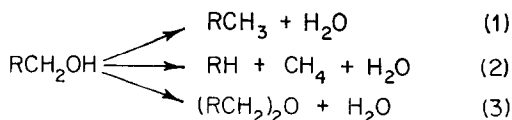
Formation of ether was found to predominate over other reactions when nickel was precipitated on kieselguhr with ammonium carbonate. The yield of ether, however, was lower when potassium carbonate was used as the precipitating agent. A similar observation was made when non-supported reduced nickel oxide was used as catalyst. The formation of ethers was

* Present address: Petrobras, Rio de Janeiro, Brazil.

TABLE 1

Hydrogenolysis of Alkylcyclopropanes on Nickel Catalysts

Reactant	Catalyst	Temp (°C)	Hydrogen pressure (atm)	Distribution of ring cleavage (%)			Ref.
				C_1—C_2	C_1—C_3	C_2—C_3	
(structure)	Ni–kieselguhr	150	1	50	50	0	(2)
(structure)	Ni	100	1	0	0	100	(3)
(structure)	Ni–kieselguhr	180	136	0	0	100	(4)
(structure)	Ni–kieselguhr	150	85	5	5	90	(5)
(structure)	Ni–kieselguhr	50	1	6.5	6.5	87	(6)
(structure)	Ni–kieselguhr	250	190	18	73	9	(7)
(structure)	Ni	100	1	0	0	100	(8)
(structure)	Ni–kieselguhr	250	137	9	45.5	45.5	(9)
(structure)	Ni–evaporated film	0	<1	5	5	90	(10)

attributed to the intrinsic acidic sites of the catalysts (12). It was also observed that the addition of 0.05% by weight of alkali metal ions to a nonsupported nickel catalyst, or 0.5% to a nickel on silica catalyst, greatly influenced the course of the hydrogenolysis reaction (12–14). The presence of acidic sites on a nickel–silica aerogel catalyst was affirmed through infrared studies (16).

The activity and selectivity of a nickel catalyst can be upset by the temperature of reduction of the catalyst with hydrogen. The maximum of selectivity of the nickel for ether formation in the reaction of primary alcohols was achieved by pretreating the nickel oxide with hydrogen at 300–400°C. At this temperature the reduced nickel still contained 1 to 2% of nickel oxide (12). When the temperature was raised to 500°C the total activity of the catalyst dropped and the selectivity of the reaction changed in favor of reductive dehydroxymethylation (Reaction 2).

The present study was undertaken to investigate the effects of the method of preparation of nickel catalysts on the hydrogenolysis of alkylcyclopropanes. Since the selectivity of nickel toward ether formation was due to the presence of intrinsic acidic sites on the catalyst, it was decided to determine whether a similar relationship exists between the acidity of the catalyst and its selectivity toward the hydrogenolysis of 1,1-dimethylcyclopropane and ethylcyclopropane.

If a cation participates in the carbon–carbon scission reaction, then the ring opening would occur in position C_1–C_2 and this reaction would be favored by the acidity of the catalyst. Conversely, the C_2–C_3 bond would undergo hydrogenolysis with a nickel catalyst in which the intrinsic acidic sites were neutralized by alkali metal ions.

II. Apparatus and Procedure

The experiments were conducted using a microreactor described previously (17) A stainless steel reaction tube of 3/8 in. o.d. and 120 mm long was packed with 50 mg of catalyst [200 mg for unsupported

Ni(OH)$_2$] in the form of powder and supported by 100 mm of 40 mesh size glass beads.

Hydrogen was purified over a high pressure deoxo catalyst (Engelhardt Industries, Inc., Newark, NJ) and over a dryer containing molecular sieve 4A (Union Carbide, Linde Div., New York), at liquid nitrogen temperature.

The micropulse reactor was linked to a gas chromatograph. The effluents from the reactor were trapped at liquid nitrogen temperature in a coiled portion of the chromatographic column (17, 18). After all the effluents have been condensed, which normally required 4 min, the liquid nitrogen bath was removed and the coiled portion of the column was allowed to warm up to room temperature. The technique permitted a one-step analysis of gaseous compounds boiling within the range of C$_2$ hydrocarbons and higher molecular weight compounds.

Analyses of the reaction product were performed on a ½ in. × 20 ft column of 33% 2,3-dimethylsulfolane on 80–100 mesh firebrick. Detector block and injector part were maintained at about 25°C. Separation of n-butane from neopentene was performed on a ½ in. × 32 ft column of 15% silicone gum rubber, GE-SE-52 on 60–80 mesh size chromosorb W.

1,1-Dimethylcyclopropane was supplied by Chemical Samples Co., Columbus, OH, and ethylcyclopropane by K and K Labs., Inc., Plainview, NY. Both samples showed the presence of traces of impurities and were used without further purification.

III. Preparation of Catalysts

1. Nickel

To a solution of 20 g Ni(NO$_3$)$_2$6H$_2$O in 80 ml of water was added with stirring 120 ml of 10 M NH$_4$OH. The resulting solution was heated to 80°C and a stream of water vapor was passed through it until ammonia evolution ceased. The precipitated nickel hydroxide was filtered, washed and dried at 140°C for about 12 hr.

The dry Ni(OH)$_2$ was reduced, in $situ$, in a flow of hydrogen, 40 ml/min. The temper-ature was raised from room temperature to 400°C in 80 min and maintained at 400°C for 30 min. The temperature was then lowered to the desired value.

In those experiments designed to study the effect of temperature of reduction of the catalyst on the hydrogenolysis, the Ni(OH)$_2$ was heated at 400°C for 2 hr in a flow of helium. Nickel oxide thus obtained was then cooled to the desired temperature in an atmosphere of helium. At the reaction temperature the flow was switched to that of hydrogen and after 1 hr the experiment was started.

2. Nickel Containing Sodium

Nickel hydroxide prepared as above, 5.53 g, was added to 3.1 ml solutions containing 0.076, 0.152, and 1.50 mmoles of sodium hydroxide, respectively. The mixtures were allowed to stand overnight and then dried at 110°C for several hours. The resultant nickel hydroxides contained 0.05, 0.1, and 1.0% by weight of sodium ions, respectively, based on the nickel content. Each sample of the catalyst was subjected to the same respective treatment as in Sect. III-1.

3. Nickel–Kieselguhr

The catalyst was prepared by the method and from materials described previously (11). Using 12.0 g Ni(NO$_3$)$_2$6H$_2$O and 25.0 g kieselguhr and an excess of (NH$_4$)$_2$CO$_3$·H$_2$O, the dried, at 110°C, nickel carbonate on kieselguhr contained 6% by weight of nickel. The nickel carbonate was subjected to treatment described in Sect. III-1.

4. Nickel–Kieselguhr–Sodium

To 10 ml aqueous solution containing 6.6 × 10^{-2}, 1.32 × 10^{-2}, and 1.356 × 10^{-1} mmoles of sodium carbonate, respectively, were added 10 g of the dry nickel carbonate–kieselguhr. Samples containing 0.05, 0.1, and 1.04% by weight of sodium ions, based on the nickel content, were obtained. The catalysts were prepared by the procedure outlined in Sect. III-1.

5. Silica

Tetraethylsilicate (473 ml) was added to a solution of 250 ml of 0.1 molar hydrochloric acid and 250 ml of ethanol. The solution was neutralized with 250 ml of 0.1 M NH$_4$OH. The precipitated silica gel was allowed to stand overnight, and then washed, dried at 150°C, washed twice with water, dried at 175°C, and calcined at 550°C. Its surface area was 346 m^2/g, and its pore volume was 1.08 ml/g. Before using it as catalyst, the silica was pretreated with hydrogen at 400°C as described in Sect. III-1.

6. Silica–Alumina

The same procedure as described in Sect. III-5 was followed, except that to the solution of tetraethylsilicate 0.11 and 0.55 g of Al(NO$_3$)$_3$H$_2$O were added to obtain silica containing 0.02 and 0.1% by weight of alumina.

7. Nickel–Silica–Alumina

Nickel carbonate was precipitated in the silica–alumina supports using aqueous solutions of nickel nitrate and an excess of ammonium carbonate, as described in Sect. III-3. The resulting samples contained 6% by weight of nickel, and 0.02 and 0.1% alumina, respectively, based on silica. These samples were subjected to treatment with hydrogen as in Sect. III-1.

8. Nickel on Alumina

The preparation of alumina from aluminum isopropoxide was described previously (19). Ni(NO$_3$)$_2$6H$_2$O (5.0 g) was dissolved in 30 ml of water and precipitated on 10 g alumina by the addition of 30 ml of concentrated ammonium hydroxide. The concentration of nickel was 6% by weight based on alumina.

Nickel carbonate was prepared by a similar method, however, potassium carbonate was used as the precipitating agent. The resulting samples were pretreated as described in Sect. III-1.

IV. RESULTS

It has been reported previously and confirmed presently that the hydrogenolysis of the cyclopropane ring catalyzed by nickel is accompanied by demethanation (20). The fragmentation resulted not from the readsorbed alkane, but from a surface residue formed from cycloalkane adsorption. On nickel cyclopropane gave equimolar amounts of ethane and methane (20, 21), while the fragmentation products from methylcyclopropane were composed of equal moles of methane and propane (10). Similar observations were reported previously during the hydrogenolysis of dicyclopropylmethane (6).

The hydrogenolysis of an alkylcyclopropane ring can occur either by 1,2- or by 2,3-carbon–carbon ring cleavage. From the hydrogenolysis of the rings of the two model compounds used in this study the following pentanes were formed:
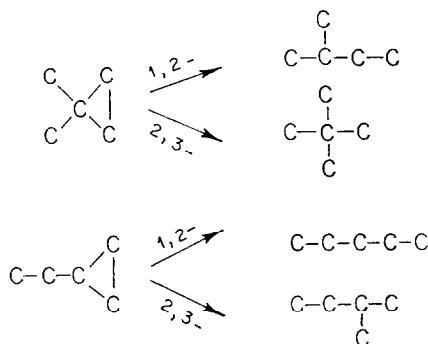
The purpose of this study was therefore to determine the effect of the preparation and the pretreatment of the catalysts on the ratio of 2,3- vs 1,2-ring hydrogenolysis. The calculation of the true ratio of the rupture of cyclopropane ring is difficult to determine on account of the accompanying demethanation reaction, which in the case of 1,1-dimethylcyclopropane forms isobutane and in the case of ethylcyclopropane, n-butane is produced. It is not known to what extent the demethanation accompanies the respective 1,2- and 2,3-ring scission reactions.

1. Reduced Nickel Oxide Catalysts

a. Effect of temperature of reduction. The composition of products obtained from

TABLE 2

EFFECT OF TEMPERATURE OF REDUCTION OF NICKEL CATALYST[a] ON THE HYDROGENOLYSIS OF
1,1-DIMETHYLCYCLOPROPANE[b] AT 80°C

Reduction temp (°C):	250	300	350	400	450
Conversion (mole %):	62.0	53.9	58.7	41.2	40.0
	Product composition (mole %)[c]				
Ethane	0.4	0.3	0.3	0.1	0.1
Propane	0.2	0.4	0.4	0.3	0.4
Isobutane	29.1	28.9	31.7	23.8	20.7
Neopentane	65.9	64.7	60.5	69.6	73.0
Isopentane	4.4	5.7	7.1	6.2	5.8
Neopentane/isopentane	15.0	11.3	8.5	11.2	12.6

[a] Nickel hydroxide (200 mg) decomposed at 400°C in a flow of helium, see III-1.

[b] Hydrogen flow 90 ml/min; injection 10 μl solution of 50% of dimethylcyclopropane in n-hexane.

[c] Based on 100 moles of the title compound reacted.

the hydrogenolysis of 1,1-dimethylcyclopropane over nickel oxide reduced at various temperatures is given in Table 2.

The ratio of C_2–C_3/C_1–C_2 ring rupture, as shown by the ratio of neopentane/isopentane, was changing with the temperature of the reduction of the oxide and reached a minimum value at the temperature of reduction of 350°C. This is the temperature of reduction, which was previously found for the catalyst to develop its optimum intrinsic acidity (12).

b. Effect of sodium ions. The addition of sodium ions in amounts of 0.05 to 0.1% by weight based on the nickel content has an effect on the selectivity of the hydrogenolysis of 1,1-dimethylcyclopropane,

Table 3. The experiments were made at 80 and 120°C, and at these temperatures the ratios of neopentane/isopentane produced were 0.9 and 3.6 in the absence, and 5.4 and 10.1 in the presence of 0.05% of sodium ions. The increase of sodium concentration to 0.1% had no further effect on the selectivity of the product. It appears that 0.05% of sodium was sufficient to neutralize the intrinsic acidic sites which are presumably required to hydrogenolyze 1,2-carbon–carbon ring bond to form isopentane. A similar type of observation was made in the hydrogenolysis studies of alcohols (12). Less pronounced effect was encountered when ethylcyclopropane was used as the substrate, Table 4.

TABLE 3

EFFECT OF SODIUM ON THE HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE IN THE
PRESENCE OF NICKEL CATALYST[ab]

Temp (°C):	80			120		
Sodium (wt %):	0	0.05	0.1	0	0.05	0.1
Conversion (%):	2.6	4.6	3.0	28.5	38.7	26.3
	Product composition[c]					
Ethane				Trace	0.7	0.6
Propane				7.2	0.9	0.3
Isobutane	Trace	5.5	0.9	30.6	34.9	32.2
Neopentane	46.6	79.7	77.5	48.7	57.8	80.7
Isopentane	53.4	14.8	21.6	13.4	5.7	6.2
Neopentane/isopentane	0.9	5.4	3.6	3.6	10.1	9.7

[a] (200 mg) Ni(OH)₂ decomposed and reduced in situ at 400°C, see Sect. III-1.

[bc] Table 2, footnotes b and c.

TABLE 4

EFFECT OF SODIUM ON THE HYDROGENOLYSIS OF ETHYLCYCLOPROPANE IN THE
PRESENCE OF NICKEL CATALYST[ab]

Temp (°C):		80			120	
Sodium (wt %):	0	0.05	0.1	0	0.05	0.1
Conversion:	0.8	2.2	2.5[d]	10.2	28.7	14.8
			Product composition, %[c]			
Ethane				0.2	0.6	0.9
Propane		3.6	Trace	2.6	0.6	0.4
n-Butane		3.5	9.4	10.2	19.7	17.5
Isopentane	57.4	68.3	65.7	72.9	65.8	66.9
n-Pentane	42.6	24.6	25.9	14.1	13.2	14.3
Isopentane/n-pentane	1.3	2.8	2.5	5.2	5.0	4.7

[a] Table 2, footnote a.

[b] Hydrogen: flow 90 ml/min; injection 5 μl of pure ethylcyclopropane.

[c] Table 2, footnote c.

[d] Temperature of reaction 100°C.

2. Nickel–Kieselguhr Catalysts

a. Effect of sodium ions. The experimental results are summarized in Tables 5 and 6. The incorporation of sodium ions into a nickel–kieselguhr catalyst had a favorable effect upon 2,3-ring carbon rupture as determined by the neopentane formed from 1,1-dimethylcyclopropane. The ratio of neopentane to isopentane produced at 80°C increased with the sodium content of the catalyst. The ratios were 1.3, 2.4, 6.1, and 10.5 at the respective sodium concentrations of 0, 0.05, 0.1, and 1% by weight. For a given catalyst the ratios

were not too sensitive to temperatures of reactions. The effect of sodium was attenuated when ethylcyclopropane was used as the substrate.

b. Effect of temperature of reduction. The effect of temperature of reduction of nickel–kieselguhr catalysts on the hydrogenolysis of 1,1-dimethylcyclopropane was studied, Tables 7 and 8.

At each respective temperature of reduction the ratio of neopentane/isopentane was greater when catalyst containing 0.05% of sodium ions was used. In each respective series of experiments the minimum ratio of

TABLE 5

EFFECT OF SODIUM ON THE HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE IN THE
PRESENCE OF NICKEL–KIESELGUHR CATALYST[ab]

Temp (°C):		80				120		
Sodium (wt %):	0	0.05	0.1	1.0	0	0.05	0.1	1.0
Conversion (%):	29.0	33.9	16.9	26.6	33.2	39.1	18.6	30.2
				Product composition[c]				
Ethane					0.1	0.2		
Propane					0.2	0.1		
Isobutane	3.7	9.3	4.7	16.1	24.4	30.1	23.1	28.2
Neopentane	55.1	64.1	81.9	76.6	50.0	51.1	65.8	66.2
Isopentane	41.2	26.6	13.4	7.3	25.3	18.6	11.1	5.6
Neopentane/isopentane	1.3	2.4	6.1	10.5	2.0	2.7	6.0	11.7

[a] 50 mg of NiCO₃ on kieselguhr, decomposed and reduced *in situ* at 400°C, see Sect. III-4.

[bc] Table 2, footnotes b and c.

TABLE 6
EFFECT OF SODIUM ON THE HYDROGENOLYSIS OF ETHYLCYCLOPROPANE IN THE
PRESENCE OF NICKEL–KIESELGUHR CATALYST[ab]

Temp (°C):	80				120			
Sodium (wt %):	0	0.05	0.1	1.0	0	0.05	0.1	1.0
Conversion (%):	26.3	31.0	15.5	23.5	32.3	39.0	19.7	26.8
				Product composition[c]				
Ethane	0.1	0.2		0.4	0.5	0.7	0.5	0.5
Propane	0.1	0.2		0.5	0.5	0.5	0.4	0.5
Butane	11.7	15.9	11.0	23.9	23.7	24.9	18.8	25.6
Isopentane	69.6	69.1	76.6	62.7	58.4	58.3	64.9	60.8
n-Pentane	18.4	15.6	12.2	12.5	16.9	15.6	15.4	12.6
Isopentane/n-pentane	3.8	4.4	6.3	5.0	3.5	3.7	4.2	4.8

[a] Table 3, footnote a.
[bc] Table 2, footnotes b and c.

TABLE 7
EFFECT OF TEMPERATURE OF REDUCTION OF NICKEL–KIESELGUHR CATALYST[a] ON THE
HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE AT 80°C[b]

Temp (°C):	250	300	350	400	450	500
Conversion (mole %):	25.3	27.0	29.4	28.3	31.1	28.0
			Product composition (mole %)[c]			
Isobutane	16.5	15.5	14.1	10.1	9.2	9.7
Neopentane	60.1	57.5	51.7	61.4	40.5	39.3
Isopentane	23.4	27.0	34.2	28.5	50.3	51.0
Neopentane/isopentane	2.6	2.1	1.5	2.2	0.8	0.8

[a] NiCO$_3$ (50 mg) on kieselguhr decomposed in situ in a flow of helium at 400°C; see Sect. III-4.
[bc] Table 2, footnotes b and c.

TABLE 8
EFFECT OF TEMPERATURE OF REDUCTION OF NICKEL–KIESELGUHR–SODIUM CATALYST[a] ON THE
HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE AT 80°C[b]

Temp (°C):	250	300	350	400	450	500
Conversion (mole %):	29.8	33.3	34.0	25.2	24.1	24.8
			Product composition (mole %)[c]			
Ethane	—	—	0.1	—	—	—
Propane	—	—	Trace	—	—	—
Isobutane	21.1	24.8	24.3	14.6	15.0	14.5
Neopentane	69.7	64.9	64.4	68.1	69.3	70.5
Isopentane	9.2	10.3	11.2	17.3	15.7	15.0
Neopentane/isopentane	7.6	6.3	5.7	3.9	4.4	4.7

[a] Table 5, footnote a.
[bc] Table 2, footnotes a and b.

TABLE 9

EFFECT OF ALUMINA ON THE HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE ON NICKEL–SILICA CATALYST[a] AT 80°C[b]

Alumina (wt %):	0	0.02	0.1
Conversion (mole %)[b]	100	81.7	98.6
Ethane	0.3	Traces	Traces
Propane	0.2	Traces	Traces
Isobutane	39.3	23.8	28.1
Neopentane	54.2	67.4	53.0
Isopentane	6.0	8.8	18.9
Neopentane/isopentane	9.0	7.7	2.8

[a] $NiCO_3$ (50 mg) on silica decomposed and reduced, in situ, in a flow of hydrogen, the concentration of nickel is 6 wt %, see Sects. III-5 and 6.

[b] Table 2, footnotes b and c.

NOTE: (i) A silica-(0.1%) alumina catalyst under the same conditions gave the following result: Conversion (mole %) = 72; Product distribution, isobutylene trace, 2-methyl-1-butene, 11.3%; and 2-methyl-2-butene, 88.7%. (ii) Pure silica used to prepare the above catalysts did not promote any reaction in the range of 80-150°C.

2,3-/1,2-bond rupture occurred when the catalysts were reduced at 350 to 400°C. These results can be related to the development at these temperatures of optima in-

trinsic acidic sites on the catalysts as was demonstrated with nonsupported nickel (12).

3. Nickel–Silica. Effect of Alumina

The results of hydrogenolysis of 1,1-dimethylcyclopropane over 6% by weight nickel on silica catalyst are given in Table 9. The ratio of 2,3-/1,2-cyclopropane ring scission, as indicated by the neopentane and isopentane formed, was 9.0. The addition of 0.02 and 0.1 wt % of alumina, respectively, greatly enhances the rupture of the cyclopropane ring in 1,2-position. These results are not too surprising because traces of alumina added to nickel–silica generally impart to the latter acidic properties (13).

Pure silica, used to prepare the catalysts, did not promote any reaction in the range of 80 to 150°C, while silica containing 0.1% alumina isomerized 1,1-dimethylcyclopropane through ring opening at C_1–C_2 bond (footnote b, Table 9).

4. Nickel–Alumina

Alumina prepared from aluminum isopropoxide, and which was shown previously to contain intrinsic acidic sites (19),

TABLE 10

HYDROGENOLYSIS OF 1,1-DIMETHYLCYCLOPROPANE IN THE PRESENCE OF NICKEL–ALUMINA CATALYST[ab]

Nickel from:	$Ni(OH)_2$[c]			$NiCO_3$[d]		
Temp (°C):	80	120	150	80	120	150
Conversion (mole %):	37.6	44.3	47.5	33.0	40.1	43.9
	Product composition (mole %)[e]					
Ethane	—	0.2	0.3	—	0.2	0.4
Propane	—	0.1	0.2	—	0.1	0.5
Isobutane	8.4	28.4	36.1	4.9	23.8	34.8
Neopentane	85.9	65.3	57.1	92.3	71.3	58.8
Isopentane	5.7	6.0	6.3	2.8	4.6	5.5
Neopentane/isopentane	15.1	10.9	9.1	32.9	15.5	10.7

[a] $NiCO_3$ or $Ni(OH)_2$ (50 mg) on alumina "A" decomposed and reduced, in situ, in a flow of hydrogen at 400°C; concentration of nickel based on alumina is 6 wt %.

[b] Table 2, footnote b.

[c] From nickel nitrate and ammonium hydroxide, see Sect. III-8.

[d] From nickel nitrate and potassium carbonate, see Sect. III-8.

[e] Table 2, footnote c.

NOTE: Alumina used to prepare the above catalysts gave the following result under the same conditions: Conversion (mole %) = 2.9, 3.9, and 9.6 at 80, 120, and 150°C, respectively. Product distribution is 2-methyl-1-butene, 14.5, 23.3, and 26.6%; 2-methyl-2-butene, 85.5, 76.7, and 73.4% at the respective temperatures.

TABLE 11

HYDROGENOLYSIS OF ETHYLCYCLOPROPANE IN THE PRESENCE OF NICKEL–ALUMINA "A" CATALYST[a]

| Nickel from:	Ni(OH)$_2$			NiCO$_3$		
Temp (°C):	80	120	150	80	120	150
Conversion (mole %):	32.7	37.0	42.9	23.2	39.6	46.9
	Product composition (mole %)					
Ethane	0.3	0.7	0.8	0.1	0.6	0.8
Propane	0.3	0.7	0.8	0.1	0.6	0.9
n-Butane	17.0	24.7	25.5	8.0	21.5	22.9
Isopentane	69.2	61.6	60.6	81.0	65.3	63.3
n-Pentane	13.1	12.3	12.3	10.8	12.0	12.1
Isopentane/n-pentane	5.3	5.0	4.9	7.5	5.4	5.2

[a] Same footnotes as for Table 9.

was used as support for the nickel. The latter was deposited from nickel nitrate using either ammonium hydroxide or potassium carbonate as the precipitating agents. The effect of the method of precipitation on the selectivity of the hydrogenolysis of 1,1-dimethylcyclopropane is shown in Table 10. The ratio of neopentane to isopentane was doubled from 15.1 to 32.9 when the precipitating agent was changed from ammonia to potassium carbonate, and it can be assumed that the presence of traces of potassium ions was sufficient to neutralize the intrinsic acidic sites of the support. This effect was less pronounced when ethylcyclopropane was used as the substrate, Table 11.

tion of the catalyst and on the supports used, and they were all related to the intrinsic acidic sites of the catalysts. The acidity of the catalysts was to a great extent responsible for the 1,2-ring opening in 1,1-dimethylcyclopropane.

The neutralization of the acidic sites of the catalyst through the incorporation of small amounts of sodium ions greatly inhibited the 1,2-ring cleavage. The imparting, however, of acidic sites to a nickel on silica catalyst by the introduction of 0.1% of alumina greatly enhanced the 1,2-ring rupture.

The products from the hydrogenolysis of 1,1-dimethylcyclopropane can be explained by the following scheme:
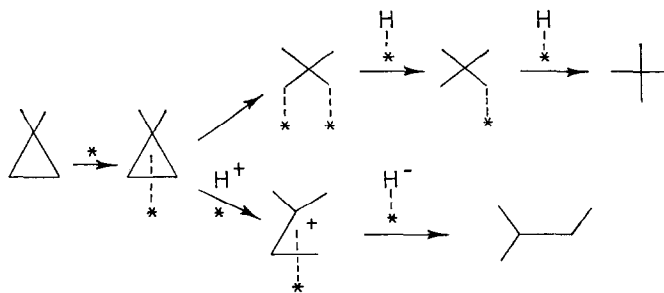
V. DISCUSSION OF RESULTS AND MECHANISM

The experimental data have demonstrated that the selectivity of the alkanes produced from the hydrogenolysis of 1,1-dimethylcyclopropane in the presence of nickel catalysts depended on the methods of prepara-

The olefinic character of the ring enables it to form a π-bonded intermediate as the first step. This intermediate has been invoked to explain the difference in activities of various metals toward hydrogenation reactions (22).

A protonic ring opening mechanism has

been proposed to account for the results of isomerization of alkylcyclopropanes over a silica–alumina catalyst (23, 24).

The protons required for the cleavage of C_1–C_2 bond are most probably derived from the heterolytic dissociation of hydrogen molecule on the Lewis acid and base sites of the catalyst. Such a dissociation has been previously suggested to occur on alumina (25). Sodium ions can act as poisons for such a reaction by preventing the hydrogen from being adsorbed on the surface as ions.

The intrinsic acidity of a nonsupported reduced nickel catalyst was attributed to the presence of nickel oxide, in concentration of 1 to 2% (12). The number of acidic sites on this catalyst is relatively small and therefore 0.05% of Na^+ was sufficient to cause a drastic change in the selectivity of the products obtained from the hydrogenolysis of 1,1-dimethylcyclopropane, Table 3.

On steric grounds, ethylcyclopropane can form π-bond intermediate on the surface more readily than the 1,1-dimethylcyclopropane, but the gain in energy in the formation of a tertiary carbonium ion from the latter more than offsets the unfavorable approach of it to the surface. As a probe molecule therefore 1,1dimethylcyclopropane is better suited than ethylcyclopropane to correlate small changes in preparation of nickel catalysts with selectivity of ring cleavage. A comparison of data in Tables 5 and 6 revealed that with 1,1-dimethylcyclopropane in the presence of nickel-kieselguhr catalyst with 0 to 1.0% sodium ions, the ratio of 2,3- vs 1,2-ring cleavage, as determined by the ratio of neopentane/isopentane produced varied from 1.3 to 10.5. For the same catalysts ethylcyclopentane gave ratios in the range of 3.8 and 5.0.

In the suggested mechanistic scheme, it is proposed that the protonolyzed π-bond intermediate does not undergo demethanation and forms only isopentane. The cation can either accept a hydride and desorb as isopentene, or produce an olefin that, under reaction conditions, will ultimately yield isopentane. This is based on the findings that the products from the reaction of 1,1-dimethylcyclopropane on silica containing

0.1% alumina formed methylbutenes, while ethylcyclopropane, under the same conditions, yielded n-pentenes, without any fragmentation.

The preferential rupture of C_2–C_3 position in 1,1-dimethylcyclopropane in the absence of acidic sites can be attributed to the two geminal methyl groups which are considered to exert an inductive effect on the cyclopropane ring so as to increase the electron density in the carbon–carbon bonds adjacent to the point of substitution (26, 27). In ethylcyclopropane, where there is only one alkyl substituent in the ring, the inductive effort is less pronounced, and the ring scission is less selective.

REFERENCES

1. NEWHAM, J., Chem. Rev. 63, 123–137 (1963).
2. SLOBODIN, Y. M., GRIGO'YEVA, V. I., SHMULYAKOVSKY, Y. E., Zh. Obshch. Khim. 23, 1480 (1953); Chem. Abstr. 48, 11358 (1954).
3. ROSANOV, N. A., J. Russ. Phys.-Chem. Soc. 48, 168 (1916); Chem. Abstr. 11, 454 (1917).
4. SHORTRIDGE, R. W., CRAIG, R. A., GREENLEE, K. W., DERFER, J. M., AND BOORD, C. E., J. Amer. Chem. Soc. 70, 946 (1948).
5. VOLKENBERG, VAN R., GREENLEE, K. W., DERFER, J. M., AND BOORD, C. E., J. Amer. Chem. Soc. 71, 3595 (1949).
6. BURWELL, R. L., JR., AND NEWHAM, J., J. Phys. Chem. 66, 1431 (1962).
7. KELSO, R. G., GREENLEE, K. W., DERFER, J. M., AND BOORD, C. E., J. Amer. Chem. Soc. 74, 287 (1952).
8. KISHNER, N., J. Russ. Phys.-Chem. Soc. 44, 165 (1912); Chem. Abstr. 6, 1431 (1912).
9. KELSO, R. G., GREENLEE, K. W., DERFER, J. M., AND BOORD, C. E., J. Amer. Chem. Soc. 77, 1751 (1955).
10. ANDERSON, J. R., AND AVERY, N. R., J. Catal. 8, 48 (1967).
11. PINES, H., AND STEINGASZNER, P., J. Catal. 10, 60 (1968).
12. PINES, H., AND KOBYLINSKI, T., J. Catal. 17, 375 (1970).
13. KOBYLINSKI, T., AND PINES, H., J. Catal. 17, 384 (1970).
14. HENSEL, J., AND PINES, H., J. Catal. 24, 197 (1972).

15. PINES, H., HENSEL, J., AND SIMONIK, J., *J. Catal.* **24**, 206 (1972).

16. PERI, J. B., *Discuss. Faraday Soc.* **41**, 121 (1965).

17. STEINGASZNER, P., AND PINES, H., *J. Catal.* **5**, 356 (1966).

18. STEINGASZNER, P., *in* "Ancillary Techniques of Gas Chromatography" (L. S. Ettre and W. H. McFadden, eds.), pp. 37–39. Wiley, New York, 1969.

19. PINES, H., AND HAAG, W. O., *J. Amer. Chem. Soc.* **82**, 2488 (1960).

20. TAYLOR, W. F., YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **4**, 374 (1965).

21. KNOR, Z., POMEC, V., HERMAN, Z., DOTEJSEK, Z., AND CERNY, S., *J. Catal.* **2**, 299 (1963).

22. SINFELT, J. H., YATES, D. J., AND TAYLOR, W. F., *J. Phys. Chem.* **69**, 1877 (1965).

23. HIGHTOWER, J. W., AND HALL, W. K., *J. Amer. Chem. Soc.* **90**, 851 (1968).

24. HIGHTOWER, J. W., AND HALL, W. K., *J. Amer. Chem. Soc.* **89**, 778 (1967).

25. PINES, H., AND RAVOIRE, J., *J. Phys. Chem.* **65**, 1859 (1961).

26. BOND, G. C., AND NEWHAM, J., *Trans. Faraday Soc.* **56**, 1501 (1960).

27. BOND, G. C., "Catalysis by Metals." Academic Press, New York, 1962.