

Tracer Studies of Acid-Catalyzed Reactions.

I. The Isomerization of Cyclopropane over Silica-Alumina

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When small slugs of cyclopropane were passed over exhaustively deuterated silica-alumina catalysts, deuterium atoms were introduced into only about 10% of the product propylene molecules; the unisomerized cyclopropane was exchanged to about the same extent. Multiple deuteration was not appreciable except when D_2O was added back or when the ratio of catalyst to cyclopropane was made high. When exposed to the catalyst under identical conditions, propylene became deuterated to an extent comparable with the propylene produced by isomerization. Evidently, most of the deuterium which appears in these hydrocarbons results from an exchange process separate from the isomerization mechanism. When equimolar mixtures of cyclopropane and cyclopropane- d_6 were passed over the catalyst, both the propylene and the residual cyclopropane became extensively deuterated. It was shown that multiple deuteration of the cyclopropane occurred by a stepwise process and that the initial (low conversion) distribution of the product propylene contained approximately equimolar amounts of C_3H_6 , C_3H_5D , C_3D_5H , and C_3D_6 . The isomerization and isotope mixing reactions had the same activation energy. There were no first-order isotope effects. The results may be interpreted alternatively in terms of a carbonium ion mechanism, making repeated use of a small number ($\leq 10^{12}/cm.^2$) of catalyst protons or cocatalytic hydroxyl groups, or as a bimolecular hydride transfer mechanism involving cyclopropyl ($C_3H_5^+$) carbonium ions. Alumina was a somewhat poorer catalyst for isomerization, but a better catalyst for exchange; silica gel was not a catalyst and did not undergo exchange with cyclopropane up to 500° .

Introduction

The highly strained cyclopropane ring has properties which render this molecule particularly attractive for mechanistic studies. The homogeneous gas phase reaction has been studied by several workers¹⁻⁶ and, while disagreement exists concerning whether the reaction proceeds via a trimethylene biradical^{4,5,7,8} or by a concerted intramolecular hydrogen shift,^{2,3,6,9} it is generally believed to be a unimolecular process having an activation energy of 65 kcal./mole. Blades⁶

reported an isotope effect of 1.98 for the coisomerization of cyclopropane and cyclopropane- d_6 at 482° ; no isotopic mixing occurred.

The heterogeneous, acid-catalyzed isomerization has also been studied.¹⁰⁻¹² The reaction goes at comparable rates at considerably lower temperatures (150 vs. 600°) and with a much lower apparent activation energy (ca. 17 kcal./mole over silica-alumina); the rate is first order in cyclopropane pressure and appears to parallel the "water content" of the catalyst.¹² These facts are consistent with the suggestion of Roberts¹⁰ that the cyclopropane ring is opened when a catalyst proton is attached to a ring carbon forming a *n*-propylcarbonium ion; since the added proton forms a methyl group, the isomerization is completed by loss of another proton to the catalyst surface. The purpose of the present work was to test this hypothesis.

The Roberts mechanism¹⁰ predicts that when a completely deuterated catalyst is contacted with cyclopropane, the initial product propylene should contain nearly one deuterium atom per molecule; deuteration of unreacted cyclopropane is not anticipated. A primary isotope effect would be expected for the isomerization reaction, i.e., $k_H/k_D \sim 2$. Two limiting cases can be visualized when small slugs of cyclopropane are passed over an exhaustively deuterated catalyst using the microcatalytic technique,¹³ depending upon the ratio of cyclopropane molecules, n_g , per slug to the available D^+ , n_a . If $n_a \gg n_g$, a plot of the fraction of C_3H_5D in the product propylene vs. slug number should have a gentle slope; if $n_a \ll n_g$, the slope should be high, the fraction of deuterated propylene falling nearly to zero with the first several slugs. Either curve should extrapolate to unity at zero slug number. As revealed in a preliminary account of this work,¹⁴ this behavior pattern was not followed.

After completion of our work, a report of some studies of the solvolysis of cyclopropane in D_2SO_4 was published.¹⁵ In agreement with the above predictions, the net uptake by the carbon skeleton was 1.01 ± 0.05 atoms of deuterium per molecule of 1-propanol formed. Also, the solvolysis rate was 1.5 times faster in H_2SO_4 than in D_2SO_4 . The tracer atom was not localized in the methyl group, however, but was distributed over all three carbon atoms in a way which could be explained if the carbonium ion intermediate were a nonclassical hydrogen-bridged, rather than the *n*-propyl or a methyl-bridged, ion.

(1) T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 399 (1934).

(2) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953).

(3) W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 609 (1961).

(4) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(5) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

(6) A. T. Blades, *Can. J. Chem.*, **39**, 1401 (1961).

(7) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(8) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962).

(9) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

(10) R. M. Roberts, *J. Phys. Chem.*, **63**, 1400 (1959).

(11) D. W. Bassett and H. W. Habgood, *ibid.*, **64**, 769 (1960).

(12) W. K. Hall, F. E. Lutinski, and H. R. Gerberich, *J. Catalysis*, **3**, 512 (1964).

(13) W. K. Hall and P. H. Emmett, *J. Am. Chem. Soc.*, **79**, 2091 (1957).

(14) W. K. Hall, H. R. Gerberich, and J. G. Larson, *ibid.*, **85**, 3711 (1963).

(15) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252, 2300 (1964); *Tetrahedron Letters*, No. 4, 235 (1963).

The effect of this is to allow exchange of the cyclopropane hydrogen without ring opening, as observed.¹⁵

Experimental

Catalysts. Most of the experiments were made with samples of Houdry M-46 silica-alumina, taken from the batch used by Larson and Hall¹⁶ in their studies of the chemisorption of isobutane. This catalyst contains about 12.5% Al_2O_3 and has a surface area of 270 m^2/g . Its principal impurities are iron (0.1%), alkali metals (0.03%), and alkaline earth metals (0.1%). A pure silica gel (S-6-2) was prepared by the neutral hydrolysis of ethyl orthosilicate. Spark spectral analysis indicated a total of less than 10 p.p.m. of metallic impurities. Its surface area was 565 m^2/g . Other properties are reported elsewhere.¹⁷

A sample of an alumina,¹⁸ prepared from the neutral hydrolysis of aluminum isopropoxide, was studied. Its total metallic impurity level was less than 50 p.p.m. and its surface area was 158 m^2/g . X-Ray measurements, made as the catalyst was dehydrated during the final stages of its preparation, revealed that it was probably a mixture of η - and γ -alumina.

Catalyst Pretreatment. It was customary to treat catalyst samples in flowing oxygen at 515° for 16 hr. to remove adsorbed carbonaceous residues. When the experiment required an undeuterated catalyst, this treatment was followed by an overnight evacuation at this temperature. When a deuterated catalyst was needed, the oxygen-treated sample was repeatedly contacted with large excess amounts of D_2O at 140°¹⁹; it was then given the final overnight evacuation at 515°. For convenience, this condition will be referred to as *dry catalyst*, even though it contains about 0.7% D_2O as terminal OD groups.¹⁷ In a few experiments, D_2O was *added back* to dry catalyst using the procedures of Haldeman and Emmett.¹⁹

The effectiveness of the deuteration procedure was checked in several instances by circulating D_2 over dry catalyst at 515° with a constant bleed into a mass spectrometer. It was concluded that the H/D ratio left in the catalyst was ≤ 0.01 . Furthermore, the surface concentration of OD groups ($1.5 \pm 0.5 \times 10^{14}/\text{cm}^2$) found earlier¹⁷ was approximated in the present work. The catalyst could be repeatedly used (with regeneration equivalent to the pretreatment) without substantially changing this value. At the end of more than a dozen experiments with the same sample, the surface deuterium concentration was determined to be $1.0 \times 10^{14}/\text{cm}^2$. In several instances, additional steps were required for special purposes. These are noted in the text.

Gases. Airco helium (nominal purity, 99.997 mole %) was used as carrying gas. It was passed through a Pyrex, glass wool trap cooled to -78° and a series of two traps filled with activated charcoal thermostated at -195° before use.

The cyclopropane was supplied by the Ohio Chemical and Surgical Equipment Co.; it had a nominal purity of 99.5%, the principal impurities being propylene and

H_2 . To ensure removal of traces of H_2O and other oxygenated compounds, it was passed over NaH. Slugs of this gas revealed only traces of propylene and butane when chromatographed. The cyclopropane- d_6 and propylene- d_6 were obtained from Merck Sharp and Dohme of Canada. These were stored in glass vessels fitted with stopcocks. Prior to use, the gases were condensed at -195° while the vessels were evacuated to a residual pressure of about 10^{-5} torr. As required, aliquots of these compounds were then distilled (at -78°) into the evacuated gas handling system. The D_2O used for deutering the catalysts was obtained from the General Dynamics Corp. Its specified isotopic purity was 99.5%.

Equipment and Procedures. The all-glass micro-catalytic apparatus has been detailed elsewhere¹³; it was integrated with a conventional high vacuum system. A 27-ft. dimethylsulfolane-hexamethylphosphoramide on firebrick chromatographic column was used at 28° and provision was made to recover samples of the propylene and the residual cyclopropane, separately, as they were eluted from the column. These were transferred into glass sample tubes for mass spectrometric analysis.

The purified reactant gas was put into an evacuated gas buret of a B.E.T.-type system. When blends were required, they were mixed by compression-expansion (ten times) at this stage. Reactant gas was transferred to the evacuated glass stopcock dosing device¹³ and carried over the catalyst with purified helium at a flow rate of 37 cc. (NTP)/min. When blends of cyclopropane and cyclopropane- d_6 were passed through the system without catalyst, subsequent mass spectrographic analyses of samples collected in the usual way showed no isotopic mixing. Similarly, when such blends were passed over silica gel, no mixing occurred.

The catalyst volume was about 3 cc. except where otherwise noted. In order to obtain good separation, the gases emerging from the catalyst were held up in a -195° trap for a period of 15 min. and then, after removal of the liquid nitrogen, flashed onto the column by heating electrically. The chromatographic separation and the transfer of samples to the mass spectrometer tubes required about 1 hr. Thus, in experiments where alternate slugs of C_3H_6 and C_3D_6 were passed, the material from the first slug which desorbed in the second, etc., had been on the catalyst for about this period.

Treatment of the Mass Spectrometric Data. Samples of cyclopropane and propylene were analyzed with a Consolidated 21-103C mass spectrometer. In experiments where only monoexchanged species appeared, the data were simple to treat. In samples where only C_3H_6 and $\text{C}_3\text{H}_5\text{D}$ species were present, the ratio of m/e peaks $^{43}/_{42}$ was taken as the ratio of $\text{C}_3\text{H}_5\text{D}/\text{C}_3\text{H}_6$, after subtraction of the contribution to m/e 42 by the $\text{C}_3\text{H}_4\text{D}^+$ ion and the usual C^{13} corrected. The former correction was determined by multiplying the C^{13} corrected m/e -43 peak by $^{5}/_6$ of the m/e - $^{41}/_{42}$ peak ratio in pure C_3H_6 . In cases where only C_3D_6 and $\text{C}_3\text{D}_5\text{H}$ were present, the m/e - $^{47}/_{48}$ peak ratio after C^{13} correction gave the $\text{C}_3\text{D}_5\text{H}/\text{C}_3\text{D}_6$ ratio directly. In samples where all species from d_0 through d_6 were present, cracking patterns for each were determined. Samples of the pure compounds were used to obtain patterns for

(16) J. G. Larson and W. K. Hall, *J. Am. Chem. Soc.*, **85**, 3570 (1963).

(17) W. K. Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *J. Catalysis*, **2**, 506 (1963).

(18) W. K. Hall and F. E. Lutinski, *ibid.*, **2**, 518 (1963).

(19) R. G. Haldeman and P. H. Emmett, *J. Am. Chem. Soc.*, **78**, 2917, 2922 (1956).

cyclopropane, cyclopropane- d_6 , propylene, and propylene- d_6 . Since the various other isotopic species were not available, the cracking patterns for d_1 through d_5 species were calculated utilizing the patterns for the pure d_0 and d_6 compounds by a method similar to that used by Schissler, Thompson, and Turkevich²⁰ for methanes. While such methods are frequently found rather poor, the evidence cited below indicates that this method gave reasonably accurate results in our system. When utilizing the patterns so determined, it was found that m/e peaks 38 to 41 essentially vanished when the contributions from all species had been subtracted. Furthermore, it was found that the sum of the partial pressures of the various isotopic species, as determined from peak heights (assuming the same sensitivity as the pure calibration gases), yielded values in good agreement with the measured inlet pressure. The analysis of samples of propylene obtained by equilibrating a mixture of propylene and propylene- d_6 to varying extents gave hydrogen balances which agreed with that present in the original mixture to within 1%. In an experiment over alumina, a mixture of cyclopropane and cyclopropane- d_6 was essentially equilibrated. Mass spectral analysis gave virtually identical isotopic distributions for the unconverted cyclopropane and the propylene formed by isomerization: for example, for cyclopropane (d_0 through d_6), 8.5, 20.2, 33.2, 24.0, 11.2, 3.0, and 0.1 mole %, respectively; and for propylene, 8.8, 21.8, 32.2, 24.2, 10.3, 2.5, and 0.3 mole %. The calculated equilibrium distribution for this H/D ratio (1.75) turns out to be 6.7, 22.8, 32.5, 24.8, 10.6, 2.4 and 0.2 mole %, respectively, for d_0 through d_6 . The average mole per cent difference between mass spectral results and the calculated equilibrium distribution was about 1 mole %. This close agreement, together with the above-mentioned criteria, gives considerable confidence to the method used to analyze the mass spectral data.

Results

Microcatalytic results for the isomerization of cyclopropane over silica gel and silica-alumina are presented in Table I. The former is not a catalyst for this reaction, no propylene being formed below 500°. Above this temperature, the homogeneous reaction sets in, as in the empty tube.

When the same amount of cyclopropane was passed over a comparable surface area of silica-alumina, a substantial conversion was obtained at 149°. These results are in good agreement with earlier work.¹⁰⁻¹² With silica gel, the hydrocarbon was virtually quantitatively recovered, while with silica-alumina, a sizeable fraction of the first slug disappeared from the mass balance. The cumulative loss (Table IB) over the experiment amounted to 2 cc. (NTP) or 1.2×10^{13} molecules/cm.². This property became more pronounced when the ratio of catalyst to cyclopropane was increased (Table IC). Here, most of the first slug and sizeable portions of the subsequent slugs disappeared. At the end of the experiment, however, the specific loss was about the same, *i.e.*, 1×10^{13} /cm.². As these figures are sums, including small differences of large numbers, they should be regarded,

(20) D. Schissler, S. Thompson, and J. Turkevich, *Discussions Faraday Soc.*, 10, 46 (1951).

Table I. Microcatalytic Behavior in Cyclopropane Isomerization^a

Slug no.	Catalyst temp., °C.	—Amounts recovered, cc.— (NTP)			Loss to catalyst, cc. (NTP)	Fraction isomerized, % propylene
		Cyclopropane	Propylene	Total		
A. 0.64 g. of Silica Gel; 8.0-cc. (NTP) Dose						
1	149	7.9	0	7.9	...	0
2	149	7.9	0	7.9	...	0
3	301	7.9	0	7.9	...	0
4	299	8.0	0	8.0	...	0
5	567	7.7	0.3	8.0	...	4
6	569	7.6	0.3	7.9	...	4
B. 1.65 g. of Silica-Alumina; 8.0-cc. (NTP) Dose						
1	148	2.5	4.1	6.6	1.4	62
2	148	3.8	3.7	7.5	0.5	49
3	150	3.8	4.1	7.9	0.1	52
4	149	4.0	4.0	8.0	0	50
5	149	4.0	4.0	8.0	0	50
C. 6.24 g. of Silica-Alumina; 2.7-cc. (NTP) Dose						
1	123	0	tr.	...	2.7	..
2	123	1.1	0.5	1.6	1.1	31
3	123	1.3	0.7	2.0	0.7	35
4	123	1.5	0.7	2.2	0.5	32
5	123	1.6	0.7	2.3	0.4	30
6	123	1.6	0.7	2.3	0.4	30
7	123	1.5	0.6	2.1	0.6	29

^a Flow rate of He carrying gas was 37 cc. (NTP)/min.

at best, as semiquantitative estimates. During such experiments, catalysts became colored from cream to yellow, the catalyst becoming darker the larger the loss. Qualitatively, the loss increased somewhat with the catalyst water content and with its activity level, *i.e.*, with temperature. Alumina behaved more like silica gel than silica-alumina in this respect. Although a detailed study was not made, the available data suggest that at the lower temperatures very little hydrocarbon was desorbed after the 15-min. collection period; at higher temperatures, some additional desorption may have occurred during the remaining 45 min. in flowing He between slugs. This would have escaped detection.

When slugs of cyclopropane were passed over an exhaustively deuterated catalyst (Table IB), cyclopropane- d_1 and propylene- d_1 appeared; multiply deuterated products were not formed in appreciable amounts. The mole fractions of cyclopropane- d_1 and propylene- d_1 are plotted (squares) in Figure 1. Evidently, only about 10% of the product propylene and 5% of the cyclopropane underwent exchange, and only 6×10^{18} of the 6×10^{20} available D atoms appeared in the total recovered products. In this type of experiment, the extent of deuteration did not increase in proportion to the isomerization rate on raising the temperature. This behavior should be contrasted with the results from blends of cyclopropane and cyclopropane- d_6 (see later).

When the hydrogen content of the catalyst was lowered nearly 10-fold by raising the evacuation temperature to 900°, the extent of deuteration was correspondingly reduced (triangles of Figure 1). In this case, however, it was necessary to raise also the reaction temperature (to 200°) in order to effect a comparable isomerization rate (*ca.* 35% propylene).

Table II. Effect of Adding Back D₂O on Isotopic Distributions in Propylenes and Cyclopropanes Formed in Microcatalytic Experiments^a

	Cyclopropane, %				Propylene, %				
	1	2	3	1 ^c	1 ^b	1	2	3	1 ^c
C ₃ D ₆	0.3
C ₃ D ₅ H	0.3	2.1	0.5
C ₃ D ₄ H ₂	0.4	3.1	0.8	0.1
C ₃ D ₃ H ₃	1.4	0.2	7.4	2.2	0.5	0.2	0.2
C ₃ D ₂ H ₄	5.5	2.2	1.3	0.4	19.4	8.0	3.8	1.8	0.9
C ₃ DH ₅	21.8	12.1	7.1	4.4	36.3	27.2	20.2	14.4	8.6
C ₃ H ₆	70.5	85.5	91.5	95.2	31.4	61.4	75.4	83.6	91.3

^a Houdry M-46 (1.46 g.) was cooled from 500 to 200° in 25 mm. of D₂O; it was then evacuated at 200° for 1 hr. This should leave the catalyst with about 1.0% D₂O.¹⁹ Except as otherwise noted, 8.0-cc. (NTP) slugs of cyclopropane were passed over the catalyst at 125° and a flow rate of 37 cc. (NTP)/min.; fraction isomerized was about 70%. ^b Same as above except slug was passed at 150° where virtually all the cyclopropane was isomerized. ^c Same as *b* except the catalyst was dry (515° evacuation) and 4-cc. (NTP) slugs, *i.e.*, 8 cc. at 0.5 atm., were used. For a comparison at 165°, see Table IV.

In this experiment, only about 0.1% of the resulting cyclopropane and 0.2% of the propylene were C₃H₅D.

An experiment was made to assess the possibility that sites for reaction are formed from residues corresponding to the hydrocarbon which disappeared from the mass balance of Table I. The deuterated catalyst was treated with propylene-*d*₆ at 155° for about 20 min. During this treatment, the gas phase was monitored with a mass spectrometer and the formation of higher molecular weight hydrocarbons was observed. About 1.6 cc. (NTP) of propylene disappeared, corresponding to a surface coverage of 8 × 10¹² molecules/cm.². Further losses were not found in the subsequent isomerization reaction, the results of which are presented (circles) in Figure 1. In the control experiment, 8-cc. (NTP) slugs of cyclopropane were passed over a catalyst containing sufficient deuterium to monodeuterate about 24 cc. of propylene; the catalyst pretreated with propylene-*d*₆ also contained this amount plus about 50% more bound to the chemisorbed residues. Multiply deuterated species did not appear in the products of this experiment in detectable amounts. Although the extent of deuteration in the products was somewhat higher than usual, the data do not indicate that the chemisorbed propylene acts as sites for reaction.

As shown elsewhere,¹² the isomerization rate was enhanced when small amounts of D₂O were added back to the catalyst. To obtain a rate comparable with the experiments of Figure 1, it was necessary to lower the reaction temperature to 125°. Isotopic distributions from such an experiment are listed in Table II where they may be compared with data taken at 150 ± 2° for a dry catalyst and for an experiment where D₂O was added back. In the latter case, the isomerization was nearly complete so that data for only propylene are given. In the experiments with added-back D₂O, 8.0-cc. (NTP) slugs were used, but the total available deuterium content was about 1.67 times larger than with the dry catalyst. Therefore, with the dry catalyst control the concentration of cyclopropane in the slug was reduced to compensate for this factor. Other comparisons may be made with the data of Figure 1 (Table IB) and of Table IV.

When D₂O was added back, multiple deuteration was found in both the propylene and the residual cyclopropane, but the major species was C₃H₆. The distribution of deuterium in the two compounds was remarkably similar and, with increasing throughput,

shifted toward that found with the dry catalyst. The propylene distribution from the experiment made at 150° (sixth column of Table II) was also similar to the corresponding first slug at the lower temperature (column 7). It was, however, generally richer in deuterium, a fact which is in disagreement with the Roberts mechanism because, for a given number of acid sites available for the ring opening reaction, the concentration of deuterium in the propylene should be highest when the amount of cyclopropane isomerized is the smallest.

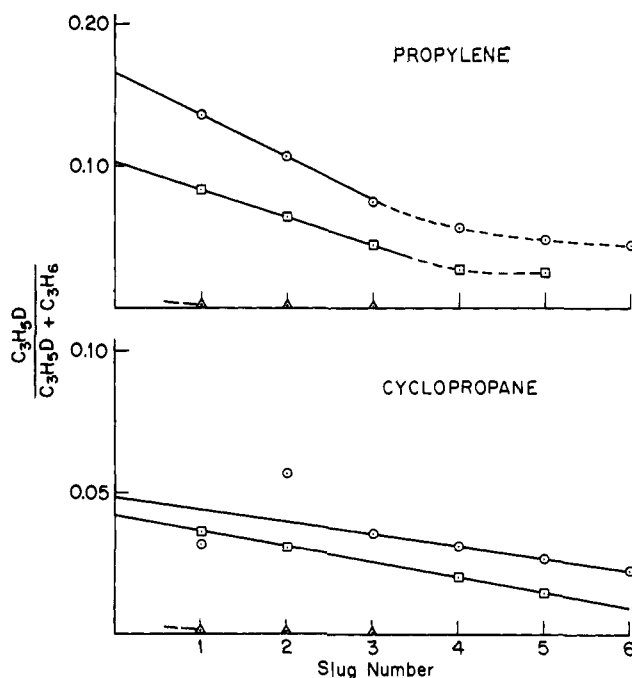


Figure 1. Deuteration during isomerization: ○, preadsorbed propylene-*d*₆; □, control (Table IB); △, dehydrated catalyst.

When the ratio of catalyst to gas was increased, the results were analogous to those where D₂O was added back. In the experiments of Table IC, slugs of cyclopropane-*d*₆ were passed over the undeuterated catalyst. The propylene product consisted of about 50% C₃D₆, about 35% C₃D₅H, and 15% C₃D₄H₂, and the residual cyclopropane of 60% C₃D₆, 25% C₃D₅H, and 15% C₃D₄H₂.

Table III. Reaction of Propylene with Deuterated Silica-Alumina^a

	Slug no.			
	1	2	3	4 ^b
	% Propylene			
C ₃ D ₃ H ₃	0.2
C ₃ D ₂ H ₄	1.2	0.6	0.4	0.2
C ₃ DH ₅	10.1	4.8	4.8	3.8
C ₃ H ₆	88.6	94.6	94.8	95.9
	% D			
	2.2	1.0	0.9	0.7

^a Propylene slugs (8.0 cc. (NTP)) were passed over 1.46 g. of Houdry M-46 at 165°; catalyst had been evacuated at 515° following deuteration. ^b This propylene was formed by isomerization of cyclopropane under the same conditions; it was 85% isomerized.

propane and samples of these gases were taken for mass spectrometric analysis. An experiment was made to see if the products from a given slug contained hydrocarbon chemisorbed from the preceding slug. Also tested was the degree of isotopic mixing from equimolar slugs of cyclopropane and cyclopropane-*d*₆ at several temperatures. This experiment is outlined in the first four lines of Table IV, where the isotopic distributions in the products are also listed. The first four slugs were all passed at the same temperature and, after the first slug, gave approximately the same isomerization rate. The isotopic distribution corresponding to the first slug is typical of the results of

Table IV. Results of Experiments Showing Interaction of Labeled Cyclopropanes^a

Slug no.	1	2	3	4	5	6	7	Blank
Gas used	C ₃ H ₆	C ₃ D ₆	C ₃ H ₆	Mixt.	Mixt.	Mixt.	Mixt.	Mixt.
Temp., °C.	165	165	165	165	150	130	110	
% isomerized	64.5	56.0	58.7	54.2	42.3	23.0	10.5	
	Analysis of Cyclopropanes, Mole %							
C ₃ D ₆		75.80	0.23	24.52	29.92	38.62	42.99	47.08
C ₃ D ₅ H		14.19	0.27	13.59	11.40	7.60	5.31	2.60
C ₃ D ₄ H ₂		5.18	0.15	5.60	4.00	1.45	0.35	
C ₃ D ₃ H ₃			0.09	2.39	1.38	0.52	0.17	
C ₃ D ₂ H ₄	0.26		0.63	4.38	3.02	1.15	0.44	
C ₃ DH ₅	4.15	2.39	6.72	13.11	10.62	5.97	3.35	
C ₃ H ₆	95.6	2.44	91.91	36.14	39.65	44.71	47.39	50.31
% C ₃ H ₆ exchanged	4.4		8.1	33.90	26.54	14.17	7.57	0.00
% C ₃ D ₆ exchanged		20.0		45.39	34.99	19.43	11.80	5.54
	Analysis of Propylenes, Mole %							
C ₃ D ₆		62.42	0.11	11.98	13.72	16.23	19.36	
C ₃ D ₅ H		26.08	0.44	18.69	19.26	20.07	22.28	
C ₃ D ₄ H ₂		7.08	0.23	13.46	12.80	11.70	9.79	
C ₃ D ₃ H ₃	0.08	0.00	0.14	8.29	7.84	6.40	2.48	
C ₃ D ₂ H ₄	0.57	0.83	2.00	10.59	10.38	8.68	6.36	
C ₃ DH ₅	7.17	3.29	10.85	18.82	18.07	17.92	18.46	
C ₃ H ₆	92.20	0.29	86.30	18.19	17.92	18.97	21.27	
H/D ratio ^b				1.082	1.012	0.953	0.899	
% C ₃ H ₆ exchanged	7.8		13.7	64.88	64.35	61.10	55.06	
% C ₃ D ₆ exchanged		34.1		75.21	72.39	68.30	63.29	

^a At NTP 8.0-cc. slugs were passed over 1.46 g. of deuterated Houdry M-46 catalyst at a flow rate of 37 cc./min. ^b (C₃H₆ + C₃H₅D + C₃H₄D₂ + 0.5C₃D₃H₃)/(C₃D₆ + C₃D₅H + C₃D₄H₂ + 0.5C₃D₃H₃).

It was shown in our preliminary communication¹⁴ that slugs of propylene became deuterated to about the same extent as the propylene produced by the isomerization of cyclopropane when passed over the catalyst under identical conditions. Some additional results (at 165°) are given in Table III. The fourth slug contained cyclopropane rather than propylene; the deuterium content of the propylene formed did not differ significantly from the propylene passed in the third slug.

When the isomerization was carried out over a catalyst which had been treated with D₂ for 4 hr. at 500° following its original deuteration with D₂O, the products actually contained less deuterium than those of the experiment of Figure 1 (squares). Adding D₂ to the cyclopropane produced no increase in exchange and had no effect on the isomerization rate.

The time of contact of a slug with the catalyst under the conditions of our experiments was a matter of a few seconds. About 1 hr. elapsed between slugs, however, during which time the product propylene was chromatographically separated from residual cyclo-

exchange experiments with deuterated catalysts, *e.g.*, those of Figure 1. The loss from the mass balance of this slug amounted to 2.6 cc. (NTP) or to a coverage of about $1.6 \times 10^{13}/\text{cm}^2$. About 0.3 cc. of the loss was recovered as *d*₀, *d*₁, and *d*₂ products from the second slug. A substantial amount of C₃D₅H was also produced from the cyclopropane-*d*₆ of the second slug, even though no hydrogen was originally present in the catalyst. The residual chemisorbed hydrocarbon (2.3 cc.) was more than adequate to supply the hydrogen required for the C₃D₅H plus C₃D₄H₂ produced (2.2 cc.). Data for the third slug generally confirm these results. In viewing these data, it must be remembered that the accuracy of the analysis decreases with increasing number of hydrogen atoms per molecule. Thus, the deuterium distribution in the cyclopropanes and propylenes from the third slug demonstrate the *overlap* most unambiguously. This overlap is indicative of bimolecular interactions.

The mass spectrographic analysis of the nearly equimolar mixture used in slugs 4-7 is given in the last column of Table IV. In these experiments, the extent

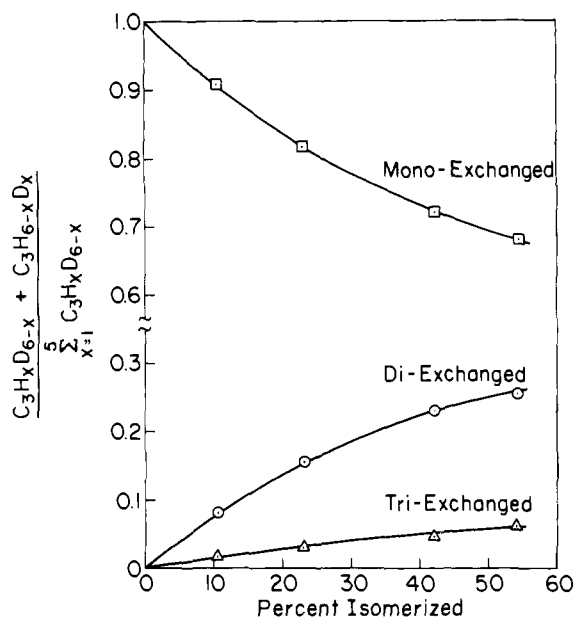


Figure 2. Proof that isotope mixing of cyclopropanes occurs *via* a monoexchange species. The abscissa was varied by changing the temperature (data from Table IV).

of isomerization was varied by changing the temperature. It is evident that a considerable amount of isotopic mixing occurred. As the temperature was increased, the $C_3D_3H_2$, $C_3H_3D_3$, and $C_3D_2H_4$ fractions increased at the expense of the parent compounds and (with propylene) the monoexchanged compounds. When the cyclopropane data for slugs 4-7 (Table IV) were plotted *vs.* the number of deuterium atoms per molecule, the curves were convex to the abscissa; the equilibrium distribution would be concave. Thus, a stepwise process far from equilibrium is indicated; this is demonstrated in Figure 2 where it is shown that the initial cyclopropanes are monoexchanged species.

The data for the propylenes are not so easy to interpret. The ratio of C_3H_6 to C_3H_5D was nearly unity in all cases; the ratio of C_3D_3H to C_3D_6 decreased from about 1.5 to nearly unity as the extent of isomerization approached zero. Considerably larger amounts of propylene- d_3 were produced than cyclopropane- d_3 in the same experiment. Thus, the observed distributions are closer to equilibrium than those from the cyclopropanes. Mechanistic reasons may exist for the approach to unity of the ratios of monoexchanged to unexchanged propylenes with small isomerization. As shown in Figure 3, the initial product contained approximately equimolar amounts of monoexchanged ($d_1 + d_3$) and unexchanged ($d_0 + d_6$) propylenes. Multiply exchanged species were not present to an important extent in the initial product. It is therefore significant that the products stemming from cyclopropane- d_0 were approximately equal to those stemming from cyclopropane- d_6 (dashed and dotted lines). This experiment was repeated, omitting the first three steps to avoid carry-over of residues from slug 3 (C_3H_6) into the products from the mixtures used in slugs 4-7. The results completely confirmed the data of Table IV; in fact, the ratios of isotopic propylenes ($C_3D_6:C_3D_3H$ and $C_3H_6:C_3H_5D$) were somewhat closer to unity at all conversions than those shown here.

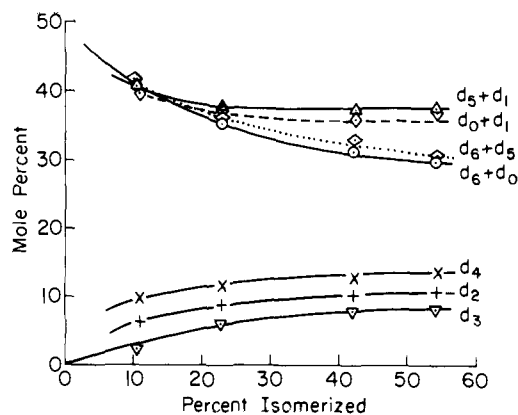


Figure 3. Isotope distribution in the propylene fraction at various extents of isomerization. The abscissa was varied by changing the temperature (data from Table IV).

The ratio of the amount of propylene formed from cyclopropane- d_0 to the amount formed from cyclopropane- d_6 is given following the analysis of the propylenes in Table IV (H/D ratio). These data, when plotted *vs.* per cent isomerized, form a good straight line with an intercept of $0.85 = R_H/R_D$. This small inverse isotope effect may be compared with a normal kinetic isotope effect of about three²¹ in this temperature range. Exactly the same conclusion is reached if one examines the residual cyclopropane.

Careful experiments in which cyclopropane was isomerized repeatedly, first over a deuterated surface, then over the same catalyst in the hydrogen form and *vice versa*, revealed no significant difference in rate. When it was recalled that no more than 10% of the propylene formed was monodeuterated, however, it was concluded that if there were an isotope effect for addition of a proton *vs.* a deuteron to the ring, the effect would not be measurable because 90% of the reaction would utilize protons furnished indirectly by substrate. By the same reasoning, a strong isotope effect, if one existed, should have shown up in the experiments of Table IV where alternate slugs of cyclopropane and cyclopropane- d_6 were passed. It was concluded, therefore, that the isotope effect was negligible.

Still another possible isotope effect (for the mixing of isotopes in the unisomerized cyclopropanes) can be derived from Figure 4. Here, the fraction of the cyclopropane which has undergone isotope mixing but has not been isomerized (Table IV) is plotted against the over-all per cent isomerized. (The points for the cyclopropane- d_6 curve have been corrected for the cyclopropane- d_3 present initially.) Cyclopropane- d_6 appears to be slightly more reactive for exchange than is cyclopropane- d_0 , but when the ratio of rates for these compounds (R_H/R_D) is plotted *vs.* per cent isomerized, the intercept is slightly greater than unity. Hence, all that can be said is that whatever the effect, it is small. The similarity of the several types of isotope effects suggests an intimate relationship between the isomerization and mixing reactions.

The variables of Figure 4 were altered by changing the temperature. Since linear curves resulted, it follows that the isomerization and mixing reactions

(21) Extrapolated from the data of Blades.⁶

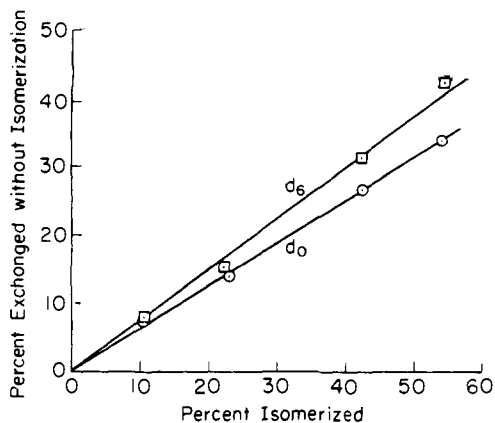


Figure 4. Proof that isotope mixing in the unisomerized cyclopropane occurs with the same activation energy as isomerization. Both variables were altered together by changing the temperature (data taken from Table IV and corrected for initial cyclopropane- d_6 content).

have the same activation energy; otherwise, the ratio of their rates would be an exponential function of temperature leading to decided curvature. Whereas the two activation energies could be closely similar by accident, this finding suggests that the two processes involve the same intermediate.

When equimolar blends of propylene and propylene- d_6 were passed, the results were quite analogous to those described above for cyclopropane. As shown in Figure 5, the exchange was a stepwise process, having a rate comparable with that of isomerization and exchange of cyclopropane, *i.e.*, the data of Figure 5 were taken in the same temperature range as the corresponding cyclopropane data of Figure 2. (The data of Figure 5 were taken at 165, 146, 124, and 105°; the corresponding data for cyclopropane were 165, 150, 130, and 110°.)

As shown in Table I, small amounts of isomerization could be effected over silica gel above 550°. When equimolar slugs of cyclopropane and cyclopropane- d_6 were co-isomerized, no isotopic mixing took place; the reaction behaved exactly as the homogeneous reaction in the empty tube. A normal isotope effect of $1.64 = R_H/R_D$ was obtained in fair agreement with the data of Blades (1.79).

Over alumina, isotopic equilibrium was obtained among the cyclopropanes, propylenes, and the hydroxyl groups of the catalyst surface even when the extent of isomerization was as low as 17%. As shown elsewhere,¹² the kinetic characteristics of the isomerization over alumina are closely similar to the behavior over silica-alumina.

Discussion

The present work bears on two important questions: the mechanisms of the isomerization and exchange reactions and the nature of the sites and intermediates involved. The data may be rationalized in several different ways, none of which is completely satisfactory. The likely possibilities will be presented and their consequences discussed. If future work can distinguish among them, considerable progress will have been made toward the understanding of acid-catalyzed reactions.

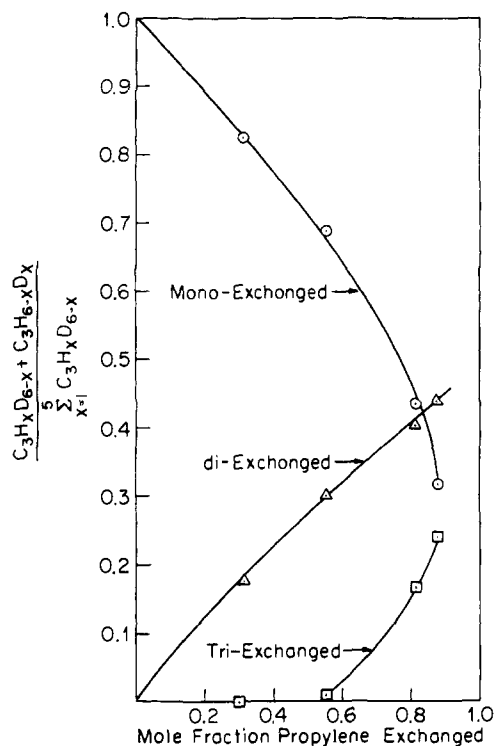


Figure 5. Proof that isotopic mixing between propylene and propylene- d_6 over silica-alumina is a stepwise process. The abscissa was varied by changing the temperature.

The available information concerning the mechanism of the catalytic isomerization of cyclopropane is summarized below, *viz.*:

(1) The reaction is first order in cyclopropane pressure.^{11,12}

(2) It has an apparent activation energy of from 16 to 19 kcal./mole.¹⁰⁻¹²

(3) The rate is approximately proportional to the catalyst "water content"; the rates may be further increased by "adding back" water.¹² Although surface hydroxyl groups may be a necessary, they are not a sufficient condition for catalytic activity. Silica gel is not a catalyst but contains an equal number of spectroscopically identical OH groups.¹⁷

(4) There is no primary isotope effect, *i.e.*, where $k_H/k_D \approx 2$.

(5) Monodeuteriopropylene does not appear to be the initial product when the isomerization is carried out over a deuterated catalyst; if it were, the mole fraction propylene- d_1 vs. slug number plots (*e.g.*, Figure 1) should extrapolate to unity at zero slug number.

(6) Cyclopropane is exchanged to about the same extent as the propylene formed or as propylene when passed over the catalyst under the same conditions.

(7) Isomerization and the mixing of isotopes in the cyclopropane products from the co-isomerization of cyclo- C_3H_6 and cyclo- C_3D_6 over silica-alumina have the same activation energy and may be presumed to occur *via* the same intermediate. Distinction should be made here between "mixing" and "exchange with catalyst hydrogen." Although mixing might occur *via* exchange with a small portion of the catalyst hydrogen, it is much faster than exchange with most of it. The latter process is so favorable over alumina that "mixing" may occur by this route.

(8) The mixing of isotopes is a stepwise process, which occurs with propylenes as well as cyclopropanes.

(9) Equimolar quantities of C_3H_6 , C_3H_5D , C_3D_5H , and C_3D_6 olefins are produced as initial products of co-isomerization.

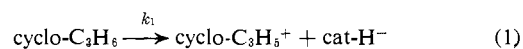
(10) When a slug passes the catalyst, both cyclopropane and propylene are evolved from substrate chemisorbed from a previous slug.

Recently¹² we reported that the rates of cyclopropane isomerization correlated well with the hydrogen content of silica-alumina and that this correlation extended both to lower and higher hydrogen contents obtained by dehydrating the catalyst at higher temperature than usual (525°) or by adding back H_2O according to methods ascribed by earlier workers¹⁹ to cause enhanced activity for hydrocarbon reactions. Since the rate increased by 25-fold¹² as the hydrogen content was increased from 0.1 to 2.5×10^{14} OH/cm.², a substantial fraction of the propylene formed by isomerization over a deuterated catalyst should be monodeuterated, on the basis of the Roberts mechanism, when the number of gaseous molecules isomerized per slug, n_g , is adjusted to a number of catalyst deuterons, n_a , falling in this range. In most of the present work, 8 cc. (NTP) of cyclopropane was passed over 1.65 g. of silica-alumina whose hydrogen content had been found¹⁷ to be approximately 15 cc. (NTP)/g. (as OH). Thus, if a major fraction (say, 20%) of the catalyst hydrogen were acidic, it should have been readily apparent. When $n_a/n_g \sim 2$, a large fraction of the propylene formed from the first slug should be monodeuterated. The actual fraction of propylene- d_1 should depend on a number of factors including the fraction of the slug which is isomerized and the relative accessibility of various portions of the total surface area. Nevertheless, the fraction of propylene- d_1 appearing in the second slug should be a correspondingly smaller fraction of that from the first slug; *i.e.*, the propylene slug number plot should extrapolate to unity at zero slug number and its slope should depend upon the magnitude of n_a/n_g and on the fraction of the cyclopropane isomerized. Thus, if 10% of the product from the first slug is propylene- d_1 , no more than 1% of the product from the second slug should become deuterated, etc. Reference to Figure 1 shows that this behavior was not followed. The propylene curves cannot be extrapolated to unity. Moreover, the unchanged cyclopropane was exchanged to nearly the same extent as the propylene formed in the reaction; slugs of propylene became deuterated indistinguishably from propylene produced by isomerization. Finally, the expected large isotope effect was not found. It is therefore clear that the experimental results do not conform to the simple picture of Roberts.¹⁰ The same objections can be raised against a concerted mechanism in which a catalyst deuterium is added to one carbon of the cyclopropane ring while a hydrogen is lost from another as the ring opens.¹² If the non-classical carbonium ion (cyclo- $C_3H_7^+$) of Baird and Aboderin¹⁵ is invoked, the only difference is that exchange can occur without ring opening. The fraction C_3H_5D vs. slug number plots (*e.g.*, Figure 1) should still extrapolate to unity and H^+ should add to the ring much faster than D^+ .

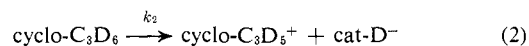
In the protonic mechanisms, the isomerization is

supposed to be a unimolecular process where the carbonium ion concentration is proportional to the gas pressure, implying that only a small portion of the available acid sites are covered. This picture does not accord with the exchange data nor with the evidence that the reaction involves bimolecular interactions. As indicated in Table I, $\sim 10^{13}$ /cm.² molecules of cyclopropane disappeared from the mass balance and are thought to have remained on the catalyst in some form. Small amounts of both cyclopropane and propylene from previous slugs were found in the products of later slugs; *e.g.*, it is estimated that several per cent of the products from the third slug of Table IV stemmed from the second slug. This amounted to $\sim 10^{12}$ /cm.² molecules, *i.e.*, an appreciable fraction of the "loss." It is therefore believed that an amount of hydrocarbon of this order of magnitude is held on the catalyst in an active form which may be released, either as propylene or as cyclopropane, when contacted with the latter gas. Larson and Hall¹⁶ reported similar bimolecular interactions during the exchange of isobutane with deuterated cracking catalysts.

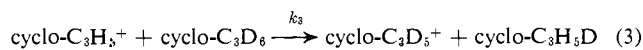
A scheme which fits most of our data involves a bimolecular hydride transfer to a $C_3H_5^+$ carbonium ion formed on the catalyst surface in a way similar to that observed for triphenylmethane and cumene.²² Accordingly



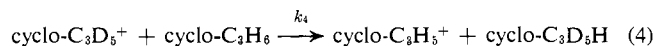
and



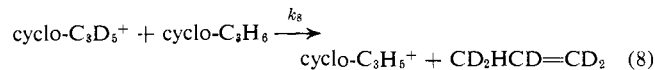
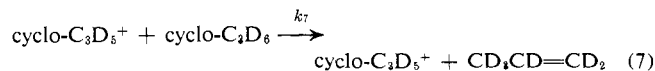
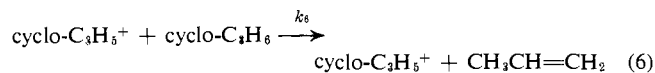
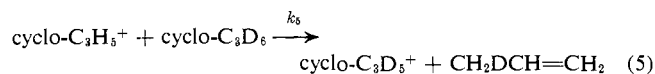
These reactions are taken to be fast (not rate determining) and, at constant temperature, irreversible. They may be thought of as initiation reactions, as they provide the reactive intermediate species required for isomerization or exchange. These reactions are followed by hydride transfer from gaseous or physically adsorbed cyclopropane. If the hydride ion is transferred to the carbonium ion carbon, exchanged but unisomerized cyclopropane is evolved, *i.e.*



and



When, on the other hand, the hydride ion is transferred to either of the other carbon atoms, propylene is formed, *i.e.*



In this way, equimolar portions of the four indicated olefins may be obtained in the initial product, pro-

(22) H. P. Leftin and W. K. Hall, *Congr. Intern. Catalyse*, 2^e, Paris, 1960, 1, 1353 (1961).

viding that isotope effects may be neglected. As demonstrated by the work of Ausloos and co-workers,²³ no isotope effect is found for reactions of the type considered here, presumably because the activation energy for hydride transfer is very low. In the gas phase, these workers report $k_{\text{H}}/k_{\text{D}} = 0.83$ for the reactions



and



This small secondary isotope effect is, perhaps fortuitously, in nearly perfect agreement with that found here (0.85). A similar low value (0.8) was found by Rabinovitch, Gilderson, and Blades²⁴ in studies of the thermal isomerization of cyclopropane at very low pressures where the reaction was thought to be wall activated. The primary isotope effect (1.96) found for the thermal isomerization of cyclopropane at high pressures corresponds to the rate limited by rearrangement of the activated complex; at low pressure where collisional activation limits the rate, the higher density of quantum statistical energy states for deuterated molecules leads to the inverse isotope effect.

If there is no activation energy for hydride transfer, how can the experimental activation energy (~ 17 kcal./mole) be explained? The rate of propylene production, r , is given by

$$r = k(\text{C}_3\text{H}_5^+)_s P_{\Delta} \quad (11)$$

where $(\text{C}_3\text{H}_5^+)_s$ is the surface concentration of carbonium ions and P_{Δ} is the cyclopropane pressure. Since the experimental activation energy is much too high to correspond to the temperature coefficient of k , it must be attributed to the formation of the C_3H_5^+ ion. The implication is that this is an endothermic process so that its surface concentration is increased with temperature, perhaps reflecting an increasing density of sites.

The bimolecular scheme outlined in eq. 3-8 provides for a stepwise isotopic mixing in both the cyclopropane and propylene products; it accounts for the uniform initial distribution of the product propylenes and for the small-inverse isotope effect; it accounts for the carry-over of chemisorbed cyclopropane from one slug into the products of the next. It does not account for the correlation of the reaction rate with the catalyst hydrogen content. Conceivably, this could be explained through an increased surface density of carbonium ions with increased hydrogen content, although we have no evidence that this is the case.

The data of Table III and Figure 5 show that the exchange and isotope mixing processes taking place with propylene are very similar to those which occur with cyclopropane. It is natural, therefore, to suppose that the intermediates, as well as the mechanisms, are analogous. Thus, if a bimolecular, hydride transfer mechanism operates for cyclopropane, one is forced to suppose that an allylic ion is the active intermediate when propylene is passed. Similarly, this same ion may form if the cyclo- C_3H_5^+ ion undergoes

a monomolecular rearrangement. The only way that the postulate of an allylic ion can be avoided is by a mechanism involving protons. Although the concept of the allylic intermediate has not been generally accepted, Leftin and Hermana²⁵ have recently presented spectroscopic evidence supporting their postulate that the butenylcarbonium ion is the intermediate in the double bond isomerization of butene-1.

If catalyst protons are involved in the isomerization mechanism, their presence is obscured by an exchange reaction between hydrocarbon molecules and the catalyst hydroxyl groups, *i.e.*, the concentration of Brønsted acid can be no larger than several per cent of the catalyst hydroxyl content. This same conclusion was reached earlier from n.m.r. studies.¹⁷ If the unreasonable assumption is made that 10% of the propylene formed from the first slug of Figure 1 involved acidic deuterons, an upper limit can be calculated, *viz.*, 8 cc. (NTP) of cyclopropane \times 50% isomerized \times 10% = 0.4 cc. (NTP). This corresponds to about $2 \times 10^{12}/\text{cm}^2$, a value at least an order of magnitude lower than the upper limit established by n.m.r.¹⁷ A similar calculation for the result of the experiment where a larger amount of catalyst and a smaller slug size were used yielded a value $\sim 10^{11}/\text{cm}^2$, a value which is lower than current estimates of either Brønsted or Lewis acidity.^{17,22,26-28} Likewise, in the experiment with a catalyst dehydrated to 900° (triangles of Figure 1), no more than $7 \times 10^{10} \text{ D}^+/\text{cm}^2$ could have been present, initially. Thus, the surface density of Brønsted sites is evidently less than that of Lewis sites. This is consistent with the view that hydrocarbon molecules chemisorb on electrophilic sites which polarize the molecule sufficiently to allow carbonium ion formation by reaction with adjacent hydroxyl groups.^{12,29} It is, of course, also possible that isomerization occurs *via* the cyclo- C_3H_7^+ ion, as in aqueous H_2SO_4 , with protons provided by carbonaceous residues held on Lewis sites. Such suggestions have been advanced recently for the double bond isomerization of butene-2.^{30,31}

When water was added back under conditions that maximized the exchange rate between isobutane and deuterated catalysts,¹⁹ $\sim 10^{14}/\text{cm}^2$ of additional D atoms were introduced into the catalyst. It has been frequently argued that Lewis sites are converted into Brønsted acids under these circumstances. The rate of isomerization of cyclopropane was increased approximately fourfold by this treatment.¹² Although the deuteration rate was also increased, the data of Table II indicate no change in mechanism, and, in fact, when the temperature was further lowered to obtain about 50% isomerization, the distribution of deuterium in the products was not greatly different from that for the dry catalyst at the same activity level. It is therefore quite evident that a 1:1 correspondence between H_2O molecules added and protons produced does not exist. These

(25) H. P. Leftin and E. Hermana, Preprints of Papers, 3rd International Congress on Catalysis, Amsterdam, July 1964.

(26) H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, **66**, 1457 (1962).

(27) W. K. Hall, *J. Catalysis*, **1**, 53 (1962).

(28) A. E. Hirschler, *ibid.*, **2**, 428 (1963); A. E. Hirschler and J. O. Hudson, *ibid.*, **3**, 239 (1964).

(29) M. R. Basila, T. R. Kantner, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

(30) A. Ozaki and K. Kimura, *J. Catalysis*, **3**, 395 (1964).

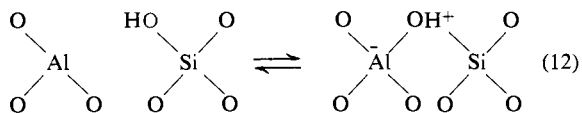
(31) B. J. Joice and J. J. Rooney, *ibid.*, **3**, 565 (1964).

(23) R. P. Borkowski and P. Ausloos, *J. Chem. Phys.*, **40**, 1128 (1964); P. Ausloos and R. Gordon, *ibid.*, **41**, 1278 (1964).

(24) B. S. Rabinovitch, P. W. Gilderson, and A. T. Blades, *J. Am. Chem. Soc.*, **86**, 2994 (1964).

data are consistent with the observation of Basila, *et al.*,²⁹ that pyridinium ions are formed reversibly when H₂O is added to Lewis-bound pyridine on cracking catalysts. Thus, if a C₃H₇⁺ carbonium ion is an intermediate in any of the chemistry of interest here, it is probably the nonclassical ion of Baird and Aboderin,¹⁵ formed by interaction of Lewis-bound cyclopropane with hydroxyl hydrogen.

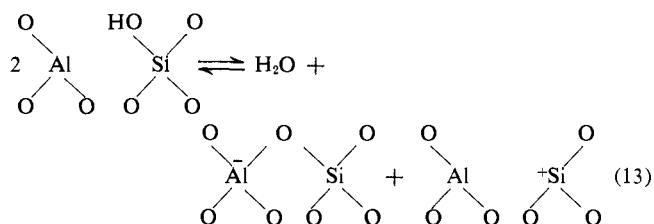
As pointed out earlier,¹² silica-alumina catalysts may contain a Brønsted function by virtue of a reversible reaction between a trigonal aluminum ion and an adjacent SiOH group, *i.e.*



A change in coordination number of aluminum from 3 to 4 will occur whenever the tetrahedra so formed can be screened by a stable ion, *e.g.*, Na⁺, NH₄⁺, or a carbonium ion; the four-coordinated aluminum is unstable only when the screening cation is a proton. This chemistry is inferred from consideration of the changes which must occur during decationation of the X and Y zeolites. In the sodium forms, the aluminum is entirely tetrahedrally coordinated; it so remains as Na⁺ ions are replaced by NH₄⁺. On heating, ammonia is evolved and the remaining proton attacks the lattice, breaking an AlOSi bond to form the entity indicated by the left-hand member of eq. 12. Presumably, if a molecule is chemisorbed on the trigonal aluminum ion, it may become protonated by the adjacent hydroxyl group. On a silica-alumina catalyst, the structure is not so well organized as with a zeolite. Hence, several hydroxyl (or deuterioxyl) groups may be adjacent to the same site and the behavior shown on Figure 1 could conceivably result. A slow rearrangement of the surface could similarly mislead us. Water presumably could function as cocatalyst as well as OH groups. Unfortunately, the model affords no explanation of the much more favorable ratio of

isomerization to exchange over silica-alumina than over alumina or why no isotope effect was observed.

Pairs of sites represented by the left-hand member of eq. 12 can be dehydroxylated, creating strongly electrophilic sites, *i.e.*



The strongly electrophilic defect sites, where an oxygen is missing, predominate in decationated zeolites after pretreatment equivalent to that used in the present work.³² Presumably, analogous sites could function in silica-alumina.

In the present work, direct evidence for acidic protons was sought but not obtained; it cannot be categorically stated, however, that a protonic acid of concentration less than 10¹²/cm.² is not present. Until the basic question concerning the nature of the acid function of silica-alumina and alumina is settled, little real progress can be made towards a detailed understanding of the mechanisms of reactions occurring on these surfaces. This is demonstrated by the alternative mechanisms for the several types of intermediates considered herein. It is hoped that further work will lead to distinction among these possibilities.

Acknowledgment. Thanks are due to the Radiation Laboratories of the Mellon Institute for use of their mass spectrometer and assistance with isotopic analysis. We are also indebted to Mr. R. L. Fischer for assistance in carrying out the experiments. This work was sponsored by the Gulf Research and Development Company as part of the research program of the Multiple Fellowship on Petroleum.

(32) J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, *J. Phys. Chem.*, in press.

The Preparation of Fluorodiazonium Hexafluoroarsenate (N₂F⁺AsF₆⁻) from *cis*-Difluorodiazine¹

David Moy and Archie R. Young, II

Contribution from the Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey. Received December 23, 1964

cis-Difluorodiazine and arsenic pentafluoride react at or below ambient temperature to yield a 1:1 solid adduct. The adduct is stable under an atmosphere of dry nitrogen to 150°. It reacts violently with water but is soluble and stable in anhydrous hydrogen fluoride. Although no stable derivative of the fluorodiazonium cation (N₂F⁺) has been reported previously, the F¹⁹ nuclear magnetic resonance spectrum and X-ray diffraction

pattern of the adduct strongly suggest an ionic constitution (N₂F⁺AsF₆⁻) in hydrogen fluoride and in the solid state.

Introduction

Difluorodiazine was first prepared by Haller² in 1942. Its electron diffraction pattern is consistent

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) J. Haller, Doctoral Dissertation, Cornell University, Ithaca, N. Y., Sept. 1942.