and intermediate species present in high-energy chemical systems.

Acknowledgments. The author gratefully acknowledges the assistance of Mr. William Frasure who helped with many of the electronic modifications in the experimental apparatus and Dr. Jacob Schaefer for his many helpful suggestions during the course of these experiments. Thanks are also due to Professors John Baldeschwieler and Gene Futrell for their helpful discussions with the author on the experimental and chemical systems used and to Dr. M. B. S. Munson for critically evaluating the manuscript and making several most useful suggestions.

Tracer Studies of Acid-Catalyzed Reactions. VII. Mechanism of Alkylcyclopropane Isomerization over Silica–Alumina

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Abstract: The olefin products from the isomerization of several alkylcyclopropanes over silica–alumina have furnished information regarding the Brønsted or Lewis nature of the active sites. Only normal olefins were formed from methylcyclopropane. The product ratios (~50% *trans*-, ~25% *cis*-2-butene, and ~25% 1-butene) were essentially independent of the extent of conversion and reflected the lower activation energy (~0.8 kcal/mole) for the formation of *trans*-2-butene. The pressure dependence of the isomerization rate was less than first order in methylcyclopropane or in cyclopropane. Tracer experiments with both compounds revealed that one hydrogen (or deuterium) atom was transferred intermolecularly in each isomerization act. A small inverse isotope effect indicated, however, that carbon–hydrogen bond rupture was not rate limiting. Both normal and branched olefins were formed from either *cis*- or *trans*-1,2-dimethylcyclopropane, but no 2-methyl-1-butene was detected. Only branched olefins resulted from *gem*-1,1-dimethylcyclopropane isomerization, but no 3-methyl-1-butene was formed. All of these data were consistent with a Brønsted ($c\text{-}C_nH_{2n+1}^+$ intermediate) rather than the bimolecular Lewis acid mechanism ($c\text{-}C_nH_{2n-1}^+$ intermediate) which has been suggested for cyclopropane. Microcatalytic deuterium tracer experiments demonstrated that the protonic sites were associated with carbonaceous residue ("coke") formed by reaction of substrate with the catalyst surface.

Although both Lewis and Brønsted acid sites appear to exist on aluminum silicates,[1] there has been considerable uncertainty concerning the function of these sites in chemisorption[2] and in the catalysis of specific hydrocarbon reactions.[3] Recently, we have presented evidence that Brønsted protons, furnished by a carbonaceous residue, serve as sites for the formation of the *sec*-butylcarbonium ion,[4] which in turn acts as a common intermediate in the interconversion of the *n*-butenes over silica–alumina.[5] This model predicted semiquantitatively the selectivities and their temperature dependencies, explained the relative reactivities, and provided reasonable values of certain thermodynamic-state functions between the three isomers. The purpose of the present paper is to present evidence that such Brønsted acid sites are also responsible for the formation of carbonium ion intermediates during alkylcyclopropane isomerization to olefins over a similar catalyst.

Larson, Gerberich, and Hall[3] used deuterium isotopes in microcatalytic experiments to demonstrate that one hydrogen atom was exchanged intermolecularly during cyclopropane isomerization to propylene over silica–alumina. These data could be explained by either a bimolecular hydride transfer (I) or a protonic mechanism (II) and would require either a $C_3H_5^+$ (Lewis site) or a $C_3H_7^+$ (Brønsted site) intermediate surface complex, respectively. Studies[6] of the isomerization of methylcyclopropane (MCP), ethylcyclopropane (ECP), and the three dimethylcyclopropanes (DMCP) have now enabled us to distinguish between these possibilities on the basis of product distributions.

Experimental Section

Catalysts and Pretreatment. Houdry M-46 silica–alumina (12.5% Al_2O_3) was used in all experiments. The catalyst had a surface area of 270 m^2/g and was ground and sieved to 40–60 mesh. Pretreatment included slowly increasing the temperature to 530° during evacuation, treatment with O_2 for 2 hr at 530°, and overnight evacuation at the same temperature to a "sticking" McLeod vacuum. The catalyst was cooled to reaction temperature and contacted with flowing helium (microcatalytic experiments) or cooled to −195° under vacuum where a measured quantity of reactant was frozen into the reaction vessel which was then rapidly warmed to reaction temperature (static experiments).

Gases. All gases were obtained from commercial sources: cyclopropane from Ohio Chemical & Surgical Equipment Co.; methylcyclopropane from API standard samples; and cyclobutane, cyclopropane-d_6, and methyl cyclopropane-d_8 from Merck Sharp and Dohme of Canada, Ltd. The latter compound was purified by semipreparative-scale glpc, and all gases were twice distilled from −78 to −195° and thoroughly outgassed before use. The *trans*-2-butene-d_8 was prepared by exchange with D_2 over a pure

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

(2) (a) R. P. Porter and W. K. Hall, *J. Catalysis*, **5**, 366, 544 (1966); (b) A. E. Hirschler, *ibid.*, **5**, 390 (1966).

(3) J. G. Larson, H. R. Gerberich, and W. K. Hall, *J. Am. Chem. Soc.*, **87**, 1880 (1965).

(4) J. W. Hightower and W. K. Hall, *ibid.*, **89**, 778 (1967).

(5) J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, **71**, 1014 (1967).

(6) H. R. Gerberich, J. W. Hightower, and W. K. Hall, *J. Catalysis*, **8**, 391 (1967).

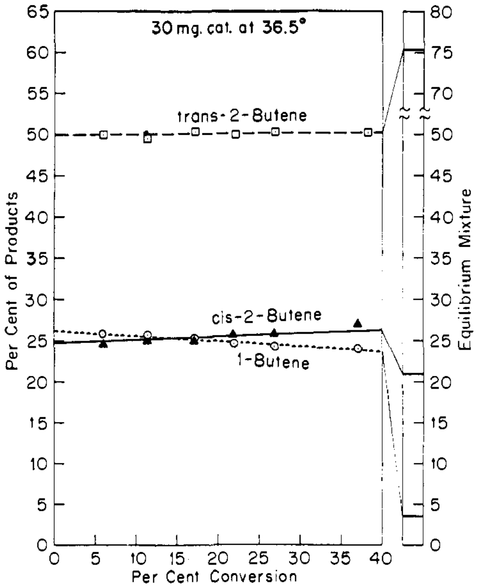

Figure 1. Products from methylcyclopropane isomerization over silica–alumina in a static reactor.

alumina catalyst[7] and separated from the other butenes by glpc. It, too, was distilled and outgassed. The Airco helium used in the microcatalytic experiments was passed through an activated charcoal trap thermostated at −195°.

Equipment and Procedures. The 300-cc static reactors were connected through a stopcock and standard taper to a standard vacuum system. Carefully weighed catalyst samples were placed in the bottom of a 20-mm o.d. well which extended 4 in. below the main part of the reactor and which could be surrounded by a furnace during pretreatment. Reaction temperatures were regulated to within ±0.5° by means of a water bath (below 100°) or a furnace controlled by a Thyratron resistance regulator (above 100°). The gases were stirred by convection currents within the reactor. Gaseous samples amounting to from 1 to 5% of the reaction mixture were periodically removed by expansion and separated by glpc, and the products were individually trapped at −195° in the tracer experiments for mass spectral analysis.

In the microcatalytic experiments, 5.0-cc slugs of reactant were injected into the helium carrier stream by manipulation of stopcocks in a doser[8] and passed over the catalyst. The products were collected for 30 min in a −195° trap before being flashed into the chromatographic column. As before, the separated products could be collected for mass spectral analysis.

The semipreparative-scale chromatographic column used was a 30-ft, 1/2-in. copper spiral filled with 35% (by weight) propylene carbonate on 80–100 Gas Chrom R.[9] It was thermostated at 0°, and all C_4H_8 isomers except *cis*-2-butene and cyclobutane were completely resolved. For analysis of the dimethylcyclopropanes and the C_5 olefins, a 10-ft column packed with the same material and thermostated at 25° was employed. A silver nitrate–ethylene glycol column[10] was used where necessary for final resolution of certain C_5 olefins from the cyclic paraffins.

The products were analyzed in a Nuclide 6-in. radius mass spectrometer using low-energy electrons (10–15 ev). Under these conditions, fragmentation was less than 10%. After standard corrections were made for the C^{13} isotopic impurity, the data were corrected for fragmentation based on statistical hydrogen–deuterium loss, as calculated from the experimental fragmentation patterns of the lightweight molecules.

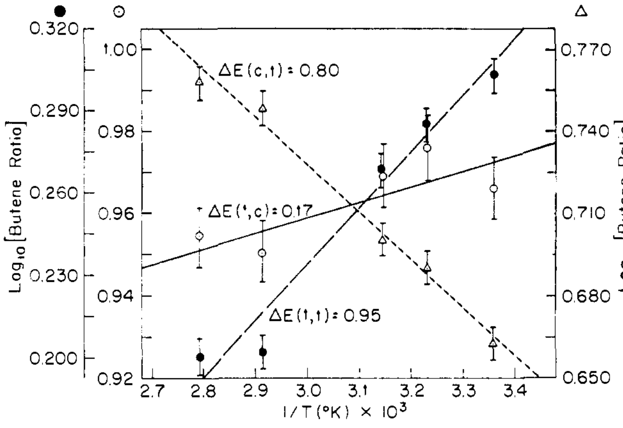

Figure 2. Arrhenius plots for activation energy differences during methylcyclopropane isomerization to *n*-butenes over silica–alumina in a static reactor.

Results

Methylcyclopropane Isomerization. The only gaseous products observed from the isomerization of MCP over silica–alumina between 0 and 100° were the three *n*-butenes. Never was any detectable cyclobutane nor isobutene formed in either the microcatalytic or static experiments. Figure 1 shows the percentage of each butene product as a function of MCP conversion in a static reactor at 36.5°. Even though the butenes were not formed in thermodynamic equilibrium with each other, their ratios did not change significantly until most of the MCP had disappeared. The slowness of secondary reaction is indicated by the slight slope of the curve for 1-butene which, on the basis of previous work,[4,5] would react the fastest of the three *n*-butenes.

Several experiments between room temperature and 85° gave similar plots, and the zero conversion intercepts varied with temperature in a systematic manner. The ratios of these intercepts were plotted according to the Arrhenius equation (Figure 2) to determine the activation energy differences between paths leading to each of the three *n*-butene products. The values derived were in good cyclic agreement; the sum of ΔE values between 1-butene and *cis*-1-butene and between *cis*- and *trans*-2-butene (0.17 + 0.80 = 0.97 kcal/mole) was nearly the same as the ΔE value between 1-butene and *trans*-2-butene (0.95 kcal/mole). This agreement may be fortuitous because we estimate the maximum possible error in these figures to be about 0.2 kcal/mole. Nevertheless, it is clear that the activation energy for the formation of *trans*-2-butene was significantly lower than it was for formation of the other two butenes. The apparent activation energies for the disappearance of MCP and 1-butene were 12.6 ± 0.7 and 11.5 ± 0.5 kcal/mole, respectively (Figure 3). Both sets of experiments were carried out in static reactors using the same unreactivated 30-mg sample of catalyst M-46 which showed reproducible activity from day to day.

The over-all energy profile for interconversion of the C_4H_8 isomers is shown in Figure 4, the ΔE values for *n*-butene interconversion having been reported earlier.[4]

Order of the Reactions. Both MCP and cyclopropane followed kinetics which were about half order in reactant pressure, and the apparent order decreased with increasing pressure. Both reactants showed a curvature which indicated an order less than unity

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(7) J. G. Larson, J. W. Hightower, and W. K. Hall, *J. Org. Chem.*, 31, 1225 (1966).

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

(9) J. A. McKenna, Jr., and J. A. Idleman, *Anal. Chem.*, 31, 2000 (1959).

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Table I. Coisomerization of Cyclopropane-d_0 and -d_6 over Silica-Alumina in a Static Reactor[a]

Reaction time, hr	Product	% each product	% each isotopic species							Atoms exchanged/ molecule	Light molecules/ heavy molecules
			d_0	d_1	d_2	d_3	d_4	d_5	d_6		
0.0	CP	100.0	51.7	...	...	...	0.2	3.6	44.5	0.040	1.070
0.5	P	1.5	27.8	16.1	1.0	0.4	2.6	25.9	26.2	0.498	0.822
	CP	98.5	49.7	0.7	0.1	...	0.2	4.3	45.0	0.057	1.023
1.5	P	6.4	27.6	16.5	2.1	0.5	3.1	24.8	25.4	0.532	0.867
	CP	93.6	47.9	2.5	0.2	...	0.4	5.8	43.2	0.095	1.027
2.5	P	11.9	26.0	18.2	2.1	0.5	3.5	24.7	25.0	0.558	0.871
	CP	88.1	47.3	4.3	0.3	...	0.6	7.1	40.4	0.132	1.079
3.5	P	15.8	25.0	18.6	2.6	0.6	4.0	24.7	24.5	0.583	0.868
	CP	84.2	44.1	7.7	0.2	0.2	1.1	9.8	36.9	0.208	1.085
4.5	P	20.8	24.2	18.9	3.2	0.8	4.7	24.6	23.6	0.618	0.876
	CP	79.2	43.3	8.4	1.0	0.2	1.3	10.3	35.5	0.238	1.119
5.5	P	25.5	...	...	...	...	...	...	...	...	...
	CP	74.5	41.9	9.6	1.2	0.2	1.5	11.2	34.4	0.267	1.117
6.5	P	29.5	21.8	19.2	4.4	1.3	6.0	24.9	22.4	0.687	0.854
	CP	70.5	37.8	16.2	1.4	0.3	1.9	11.7	30.7	0.354	1.250

[a] 25 cc of cyclopropane, 225°, 4 mg of catalyst.

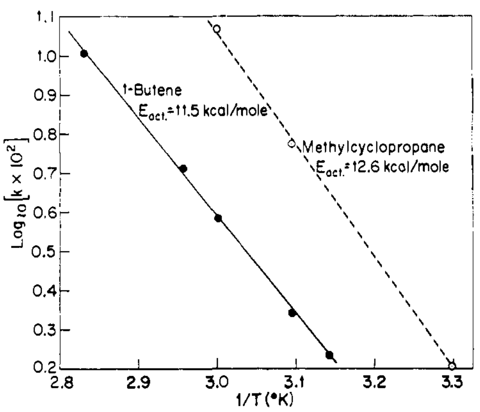

Figure 3. Arrhenius plots for isomerization of methylcyclopropane and 1-butene over 30 mg of M-46 silica-alumina in a static reactor.

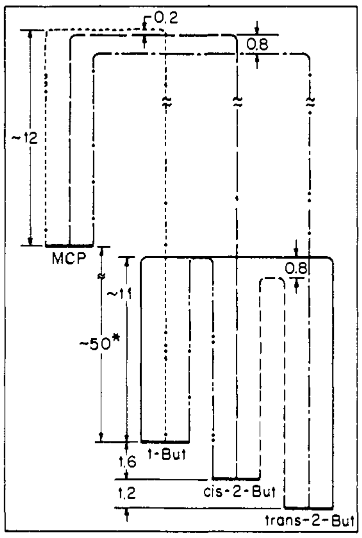

Figure 4. Activation energy profile for interconversion of C_4H_8 isomers over silica-alumina (* see ref 18).

when plotted according to the first-order equation

$$\log(100 - X) = -\frac{kt}{2.303} + \log(100) \qquad (1)$$

Here X is the per cent conversion, t the time in hours, and k the first-order rate constant. Furthermore, the initial slopes of such plots were dependent on the initial pressure, their ratio being about proportional to the reciprocal square root of the pressure ratio. These static results were confirmed in both steady-state flow and microcatalytic experiments which also indicated that the cyclopropane reaction was about half order in reactant. It will be shown later[11] that these observations conform to Langmuir-Hinshelwood kinetics.

Coisomerization of Cyclopropane-d_0 and -d_6. Two static experiments involved coisomerization of cyclopropane-d_0 and -d_6 (about 1:1 mixtures) over silica-alumina at 100 and 225°; the results at the higher temperature are given in Table I, and they are quite similar to those observed at the lower temperature. These experiments were designed to examine intermolecular hydrogen exchange and isotope effects.

The "exchange concentration" (the number of atoms exchanged/molecules) curves plotted in Figure 5 were determined from

$$\sum_{i=0}^{3} iN_i + \sum_{i=4}^{6}(6 - i)N_i \qquad (2)$$

where N_i is the mole fraction of each isotopic species containing i deuterium atoms. The "exchange" apparently present in the starting material (Table I) reflected the d_7 isotopic impurity in the perdeuteriocyclopropane; this amount was subtracted to obtain the values plotted. The zero conversion intercept of nearly 0.5 for the product propylene indicates that one

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[11] J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, in press.

Table II. Coisomerization of Methylcyclopropane-d_8 and -d_0 over Silica–Alumina in a Static Reactor[a]

Reaction time, hr	Product	% each product	% each isotopic species d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	Atoms exchanged/ molecule	Light molecules/ heavy molecules
0.0	MCP	100.0	47.8	0.1						5.7	46.4	0.060	0.92
1.0	MCP	94.8	47.8		0.1					5.7	46.4	0.060	0.92
	B	1.2	32.4	17.6	0.5		0.9	1.0	3.4	26.0	18.2	0.574	1.02
	C	1.3	28.5	18.0	0.6	0.2	0.3	0.4	3.7	29.9	18.4	0.596	0.90
	T	2.7	28.0	16.6	0.4	0.2	0.3	0.3	3.4	28.5	22.3	0.555	0.83
3.0	MCP	84.7	48.2	0.2	0.1	0.1	0.1		0.1	5.7	45.5	0.070	0.95
	B	3.7	32.3	18.2	0.5	0.1	0.6	0.5	3.5	26.1	18.2	0.566	1.06
	C	4.1	28.0	18.2	0.8	0.2	0.4	0.2	3.9	29.9	18.4	0.603	0.90
	T	7.5	26.4	18.2	0.6	0.2	0.3	0.3	3.7	30.1	20.2	0.597	0.83
5.0	MCP	73.7	48.4	0.2	0.1		0.1		0.1	5.8	45.3	0.068	0.95
	B	6.5	31.1	17.5	0.6		0.7	0.8	3.6	26.8	18.9	0.578	0.98
	C	7.1	26.4	17.7	0.8	0.2	0.4	0.4	4.1	30.7	19.3	0.618	0.83
	T	12.7	26.4	18.0	0.7	0.1	0.3	0.3	3.8	30.0	20.4	0.597	0.83
7.0	MCP	64.4	48.6	0.3		0.1	0.1		0.1	5.8	45.0	0.070	0.96
	B	8.7	30.3	17.7	0.7		0.6	0.8	3.9	27.1	18.9	0.588	0.95
	C	9.5	26.3	17.9	1.0	0.2	0.4	0.4	4.2	30.6	19.0	0.620	0.84
	T	17.4	26.1	18.3	0.8	0.1	0.2	0.3	4.2	30.0	20.0	0.603	0.83
11.0	MCP	46.2	49.3	0.6	0.1	0.1			0.1	6.0	43.8	0.076	1.01
	B	13.3	...	...	...	...	...	...	...	...	...	...	...
	C	14.5	25.2	17.9	1.3	0.2	0.4	0.4	4.6	31.0	19.0	0.643	0.81
	T	26.0	25.2	17.9	1.1	0.2	0.3	0.4	4.5	30.4	20.0	0.625	0.80
13.0	MCP	38.6	50.2	0.7	0.1				0.1	6.0	42.9	0.070	1.04
	B	14.4	30.2	18.0	1.0		0.7	0.8	4.2	26.6	18.5	0.601	0.97
	C	17.0	27.4	19.1	1.5	0.2	0.4	0.6	4.9	28.9	17.0	0.649	0.94
	T	30.0	26.4	18.7	1.1	0.2	0.3	0.4	4.5	29.2	19.2	0.618	0.87
22.5	MCP	9.9	52.9	2.4				0.1	0.2	6.5	37.9	0.097	1.24
	B	19.5	29.2	18.4	1.8		0.6	0.9	5.0	26.7	17.4	0.626	0.98
	C	25.8	25.8	18.9	2.3	0.2	0.3	0.6	6.0	29.1	16.8	0.683	0.90
	T	44.7	25.7	19.0	1.9	0.2	0.3	0.5	5.5	29.2	17.7	0.670	0.88
28.8	MCP	0.9	57.5	3.6						7.0	31.9	0.106	1.57
	B	19.1	28.1	18.6	2.5	0.1	0.6	1.2	5.8	26.4	16.7	0.679	0.98
	C	29.3	25.0	19.2	3.0	0.3	0.4	0.9	7.0	28.2	16.0	0.727	0.91
	T	50.7	25.6	19.4	2.5	0.3	0.3	0.8	6.4	28.2	16.5	0.700	0.92
46.5	MCP	0.0	...	...	...	...	...	...	...	...	...	...	...
	B	11.5	22.4	19.5	5.5	0.8	0.5	2.3	9.3	25.5	14.2	0.859	0.94
	C	34.2	21.7	20.2	5.2	0.8	0.5	1.8	9.9	26.3	13.6	0.868	0.93
	T	54.3	22.5	19.8	4.3	0.7	0.5	1.5	8.9	27.0	14.8	0.815	0.90

[a] 15 cc of methylcyclopropane, 40°, 30 mg of catalyst.

hydrogen atom per molecule was transferred during isomerization at both temperatures. The much steeper slope for propylene at 100° than at 225° indicates that the propylene underwent further exchange which was independent of and had a lower activation energy than did cyclopropane isomerization. There was also considerable exchange into the unisomerized cyclopropane, but the superposition of the points at both temperatures indicates that this exchange process had the same activation energy as did isomerization.[3]

It was also possible to calculate an isotope effect from the relative reactivities of the two species, as judged from the ratio of "light material"

$$^1/_2N_3 + \sum_{i=0}^{2} N_i$$

to "heavy material"

$$^1/_2N_3 + \sum_{i=4}^{6} N_i$$

in the propylene. These ratios are recorded in the last column of Table I. In this treatment, all molecules with fewer than three D atoms were assumed to stem from the d_0 material and all with more than three D atoms from the d_6 material. Molecules with three D atoms were assumed to come equally from both sources.

Coisomerization of Methylcyclopropane-d_0 and -d_8. Two static coisomerization experiments similar to those with cyclopropane were carried out with 1:1 = d_0:d_8 MCP mixtures at 40 and 100°; the results at both temperatures were quite similar, and those at 40° are given in Table II. The exchange concentration intercepts near 0.5 for all three *n*-butenes (Figure 6) clearly show that isomerization involved intermolecular hydrogen transfer. The small slope of the curves indicates that there was very little further scrambling among the products; this is consistent with the lack of change in the product distribution (Figure 1) with conversion until most of the MCP had disappeared. There was much

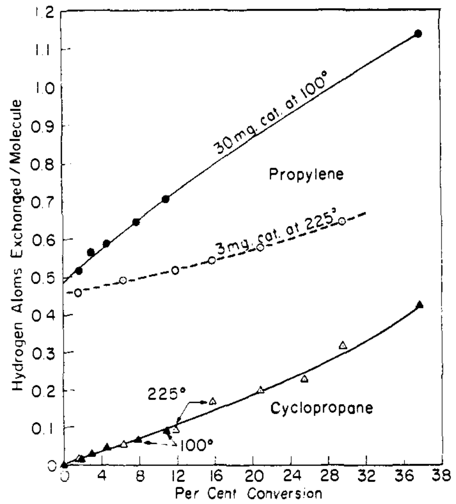


Figure 5. Exchange concentration curves for coisomerization of cyclopropane-d_0 and -d_6 over silica–alumina in a static reactor.

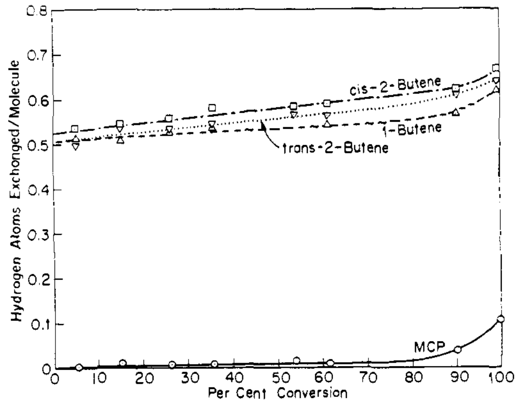


Figure 6. Exchange concentration curves for coisomerization of methylcyclopropane-d_0 and -d_8 over silica–alumina in a static reactor at 40°.

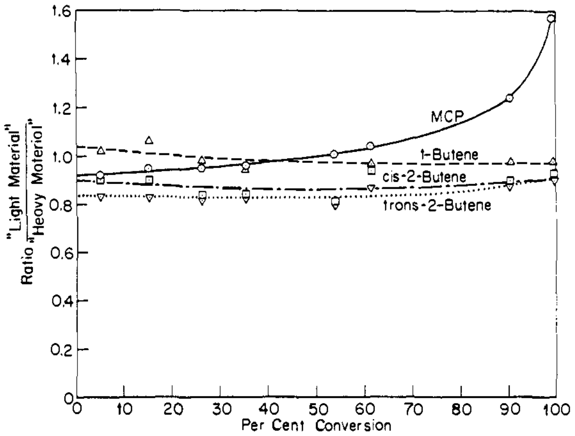


Figure 7. Isotope effects during coisomerization of methylcyclopropane-d_0 and -d_8 over silica–alumina in a static reactor at 40°.

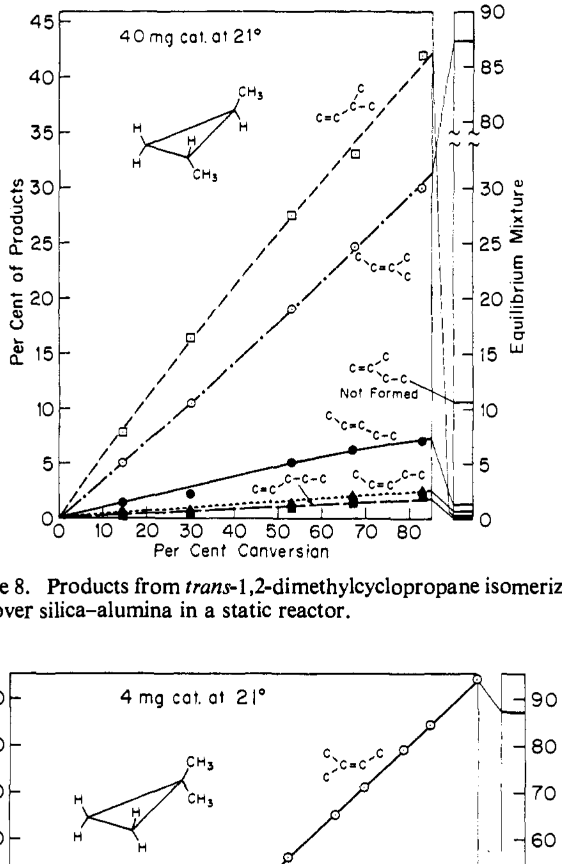


Figure 8. Products from *trans*-1,2-dimethylcyclopropane isomerization over silica–alumina in a static reactor.

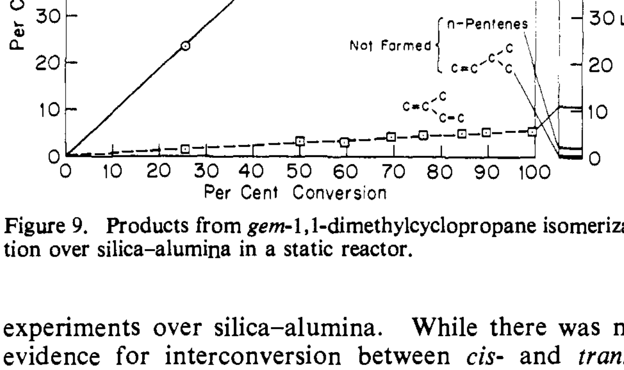


Figure 9. Products from *gem*-1,1-dimethylcyclopropane isomerization over silica–alumina in a static reactor.

less exchange into the unisomerized MCP than occurred in the case of cyclopropane.

There appeared to be a small inverse isotope effect in the formation of the 2-butenes, but a slight direct isotope effect in 1-butene formation (Figure 7). Although scatter in the data made it impossible to attach quantitative significance to these numbers, the isotope effect was in any case relatively small, the ratio k_H/k_D after normalization[4] being between 0.9 and 1.1 for all processes.

Exchange with Residue. Table III contains results of a microcatalytic experiment in which two slugs of *trans*-2-butene-d_8 were first passed at 25° over 0.25 g of freshly pretreated M-46 to lay down a deuterated residue containing about 7 × 10^{13} butene molecules/cm^2 of surface. Two slugs of MCP-d_0 were then passed successively over the catalyst. The isomerized products showed considerable exchange with the deuterated residue, but the exchange was limited almost exclusively to one atom/molecule. There was no evidence of displacement of the heavy molecules (appearance of d_7 or d_8 molecules) from the surface. All three *n*-butene products underwent about the same amount of hydrogen exchange with the residue, but there was very little exchange into the unisomerized MCP.

Dimethylcyclopropane Isomerization. All three dimethylcyclopropanes isomerized quite readily in static experiments over silica–alumina. While there was no evidence for interconversion between *cis*- and *trans*-1,2-DMCP, both straight-chain and branched olefins

Table III. Exchange of H Atoms with Deuterated Residue during Methylcyclopropane Isomerization over Silica–Alumina in a Microcatalytic Reactor[a]

Slug no.	Reactant[b]	Total rec, cc	% conversion	Product	% each product	% each isotopic species d_0	d_1	d_2	d_7	d_8	Atoms exchanged/ molecule	No. D atoms exchanged × 10^{-18}
1	*trans*, d_8[c]	3.5	~1.5	B	...	...	...	...	...	...	...	
				T	98.5	...	...	...	6.7	93.3	...	
				C	1.5	...	...	...	7.5	92.5	...	
2	*trans*, d_8[c]	4.7	~1.0	B	...	...	...	...	...	...	...	
				T	99.0	...	...	...	6.9	93.1	...	
				C	1.0	...	...	...	...	...	...	
3	MCP	4.9	46.5	B	10.9	78.7	20.7	0.6	...	...	0.22	2.9
				T	24.5	82.5	17.1	0.4	...	...	0.18	5.0
				C	11.1	79.5	19.8	0.7	...	...	0.21	2.7
				MCP	53.5	99.7	0.3	...	...	...	0.00	...
4	MCP	5.0	35.3	B	8.2	85.0	14.5	0.5	...	...	0.15	1.6
				T	18.2	86.2	13.1	0.7	...	...	0.15	3.6
				C	9.1	83.5	15.6	0.9	...	...	0.17	2.0
				MCP	64.5	99.9	0.1	...	...	...	0.00	...

[a] Conditions: 0.25 g of M-46, 10 psig, 25 cc/min, He flow. [b] Slug size: 5.0 cc (NTP). [c] Isotopic purity: 99.2% D.

resulted from isomerization of both compounds; products from the *trans* isomer are shown in Figure 8. There was only one significant difference in the results from *cis*-DMCP; *viz.*, the ratio of 3-methyl-1-butene to 3-methyl-2-butene was inverted (from 1.35 to 0.5). In neither case was 2-methyl-1-butene observed among the products.

As shown in Figure 9, *gem*-DMCP gave exclusively branched olefins, but no 3-methyl-1-butene was detected.

Ethylcyclopropane Isomerization. The only products observed from the isomerization of ECP were the three *n*-pentenes in the approximate ratio 1-pentene:*cis*-2-pentene:*trans*-2-pentene = 1:8:8 at room temperature. These ratios were temperature dependent, and the activation energy for 1-pentene formation was about 1 kcal/mole higher than the activation energy for formation of either 2-pentene. The experimental activation energy profile for interconversion of the C_5H_{10} isomers is shown in Figure 10. Kazanskii and co-workers[12] have also reported that *n*-pentenes resulted from ECP isomerization over silica–alumina.

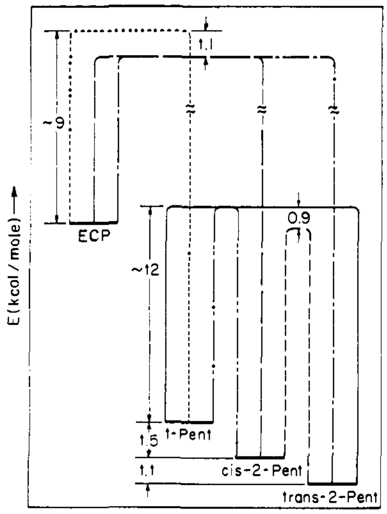


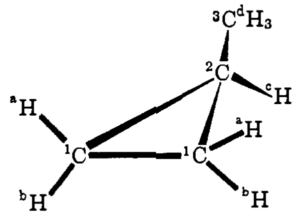
Figure 10. Activation energy profile for interconversion of C_5H_{10} isomers over silica–alumina.

Cyclobutane Isomerization. Whereas all the alkylcyclopropanes isomerized readily at room temperature, cyclobutane did not begin to react until the temperature exceeded 400°. All four butenes, butadiene, saturated C_4 compounds, and cracking products (propane, propylene, ethane, ethylene, and methane) were formed slowly at 425° in a static reactor.

Discussion

The similar behavior of cyclopropane and MCP during isomerization over silica–alumina suggests that both reactions occurred by the same type of mechanism. Because there was no possibility of studying selectivity in cyclopropane isomerization (propylene was the only product formed), it was not possible to distinguish between the $C_3H_5^+$ Lewis surface complex of mechanism I and the $C_3H_7^+$ Brønsted intermediate of mechanism II.[3] However, the multiplicity of possible products from alkylcyclopropane isomerization offered an additional probe which may be a function of the mechanism.[6]

Consider the isomers resulting from isomerization of by classical mechanisms, making the single assumption that primary carbonium ions will not be formed.



Mechanism I. (a) Loss of either ${}^aH^-$ (or either ${}^bH^-$) would yield a secondary ion which would rearrange through ${}^1C$–${}^2C$ cleavage to a butenyl or an allylic carbonium ion and ultimately form one of the three *n*-butenes.

(12) M. Yu. Lukina, S. V. Zotova, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, 123, 105 (1958); *Chem. Abstr.*, 53, 6055 (1959).

(b) Loss of $^{c}H^{-}$ would result exclusively in formation of isobutene through ^{1}C–^{1}C cleavage.

(c) Loss of one of the $^{d}H^{-}$ ions would produce a primary carbonium ion which might be stabilized by resonance as a bicyclobutonium ion.[13–15] Return of this species to the gas phase should yield only cyclobutane and/or 1-butene as primary products.

Mechanism II. (a) Proton addition to ^{1}C would always result in formation of *n*-butenes through ^{1}C–^{2}C cleavage.

(b) Proton addition to ^{2}C is not allowed since it would involve formation of an unstable primary carbonium ion.

Since only the *n*-butenes were formed as primary products in the approximate ratio 1-butene:*cis*-2-butene:*trans*-2-butene = 1:1:2, only mechanisms Ia and IIa are plausible. However, if the hydride abstraction mechanism I were operative, the *least likely* hydrogens to be lost are $^{a}H^{-}$ and $^{b}H^{-}$. Loss of $^{c}H^{-}$ would leave a relatively stable tertiary carbonium ion, and loss of $^{d}H^{-}$ would produce an ion stabilized by resonance as the ring-expanded nonclassical bicyclobutonium ion.[13–15] Since isobutene was not observed and cyclobutane was neither formed nor reacted under conditions of MCP isomerization, there is no reason to suppose that mechanism Ia is operative.

On the other hand, the proton addition mechanism II will account qualitatively for all the observed products and, in addition, will rationalize the absence of isobutene. Furthermore, it will explain the absence of 2-methyl-1-butene among the olefins produced from *cis*- or *trans*-1,2-DMCP isomerization, as well as the absence of 3-methyl-1-butene from products of the 1,1-DMCP reaction. In all of these cases, formation of the absent olefins would have required either an unstabilized primary carbonium ion intermediate or an intramolecular hydride shift, whereas the observed products could be explained solely on the basis of secondary or tertiary carbonium ion intermediates. Finally, by mechanism II no 1-pentene should be formed from ECP isomerization. A small amount was formed as a primary product but its concentration (about 6%) was considerably less than the amount of the terminal olefin product (about 25%) formed from MCP. The higher E_{act} to form 1-pentene than to form the 2-olefins indicates that the former was in fact the more difficult reaction.

Protons induced in the carbonaceous residue served as sites for interconversion of the *n*-butenes,[5] and it appears that such sites are also operative in the alkylcyclopropane reactions. In their microcatalytic experiments, Larson, Gerberich, and Hall[3] found considerable exchange into both the product propylene and the unisomerized cyclopropane when the latter was passed over a catalyst containing a deuterated residue. In the present work, under similar circumstances, all three *n*-butene products from MCP isomerization contained considerable deuterium (Table III), thus indicating direct participation of deuterium atoms from residue. Presumably, the active sites were induced protons in the residue which formed carbonium ion surface complexes with the substrate.

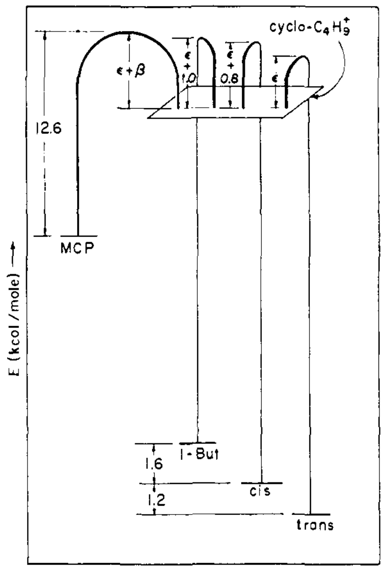
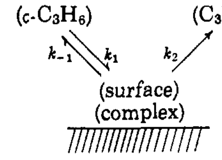


Figure 11. Energy profile for interconversion of methylcyclopropane and the *n*-butenes over silica–alumina.

A detailed description of the isomerization kinetics for cyclopropane and MCP is the subject of a future communication,[11] but certain pertinent features are presented here. All of the results can be reasonably well interpreted on the basis of a pseudo-equilibrium between cyclopropane and a surface species, *viz.*



(3)

where the surface complex has the choice of returning to the gas phase either as unisomerized cycloalkane through k_{-1} or as an isomerized olefin *via* k_2. Baird and Aboderin[16] postulated a nonclassical cyclopropylcarbonium ion (c-$C_3H_7^+$) to explain the distribution of deuterium in the products during solvolysis of cyclopropane in D_2SO_4. The same surface complex formed by interaction of the substrate with a proton supplied by the residue will also explain our results provided that the activation energy for its formation is similar to that for isomerization. Such a picture accounts for the scrambling in the unisomerized cyclopropane, as well as for the intermolecular exchange during each isomerization act. It offers an explanation for the apparent reaction order being less than first order and increasing with increasing temperature. Finally, it explains the absence of a large primary kinetic isotope effect, since the rate-controlling step is probably C–C rather than C–H bond cleavage. Rabinovich, *et al.*,[17] also observed a small inverse isotope effect in the thermal isomerization of cyclopropane.

Assuming similar considerations apply to the alkylcyclopropanes, the energy profile of Figure 4 for MCP can be transformed into that shown in Figure 11, where the "energy platform" represents the level for the c-$C_4H_9^+$ complex. The product selectivities are determined by the relative heights of the barriers leading to

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[13] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

[14] E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

[15] C. Y. Wu and R. E. Robertson, *ibid.*, **88**, 2666 (1966).

[16] R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252, 2300 (1964).

[17] B. S. Rabinovich, P. W. Gilderson, and A. T. Blades, *ibid.*, **86**, 2994 (1964).

each of the *n*-butenes.[5] If it is assumed that no geometric or statistical factors are involved, the product ratios corresponding to the energy barrier height differences should be 1-butene:*cis*-2-butene:*trans*-2-butene = 15:18:67 at 36.5°; the observed ratios were 26:24:50. When this treatment was applied to ECP (Figure 10), the predicted product ratios at room temperature were 1-pentene:*cis*-2-pentene:*trans*-2-pentene = 8:46:46; the observed ratios were 6:47:47. It is quite clear, therefore, that the selectivities in these reactions, as in the isomerization of butenes[4,5] over the same catalyst, are largely controlled by the relative heights of the activation energy barriers.

In conclusion, there is reason to suppose that the reaction of MCP does not pass through the same intermediate species present in the isomerization of the *n*-butenes over silica–alumina. From our earlier studies[5] of butene isomerization over the same catalyst in the same temperature range, it was concluded that the product selectivities were controlled by a statistical factor and the relative barrier heights between the intermediate *sec*-butylcarbonium ion and the several products. From these data it can be estimated that if the same metastable state were present along the reaction coordinate, the product ratios should be 1-butene:*cis*-2-butene:*trans*-2-butene = 1:1.2:1.2. The observed product ratios (*ca.* 1:1:2) differed significantly from these, even though they too resulted mainly from differences in activation energy. The (c-$C_4H_9^+$) ion suggested in Figure 11 must be located at much higher energy than is the *sec*-butyl ion because of the thermodynamic instability of MCP relative to the butenes.[18]

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[18] Estimated from the data of O. N. Kachinaskaya, *Vestn. Mosk. Univ., Ser. II: Khim.*, **16**, 69 (1961); *Chem. Abstr.*, **56**, 9506 (1962).

Kinetics of Copper(II)–Glycine Interactions in Aqueous Solution

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Abstract: Rate constants for the formation of copper(II) complexes with the glycine anion have been measured by a combination of temperature-jump and close-to-equilibrium stopped-flow techniques. Measurements were carried out in moderately acid solutions to avoid complications due to copper–hydroxy species. Relaxation times, in the millisecond time region, could be interpreted only as reactions between metal ion and free anion, even though the zwitterion predominated at the pH's used. The forward rate constants for the mono and bis complexes with glycine were found to be 4×10^9 and 4×10^8 M^{-1} sec^{-1}, respectively, at 25° and $I = 0.1$. These constants, although large, were consistent with the Eigen–Tamm mechanism for the formation of metal complexes wherein the release of a water molecule from the inner hydration sphere of the metal ion is the rate-determining step. The unimolecular rate constants for ligand penetration into the inner hydration sphere of the copper ion were estimated to be 2×10^9 and 5×10^8 sec^{-1} for the first and second steps, respectively.

The development of relaxation techniques[2] has resulted in the characterization of many fast reactions which were previously inaccessible using classical techniques. The study of metal–ligand interactions should provide some necessary information which could be used by chemists involved in examining more complex biochemical systems. To date, particular emphasis has been placed upon Mg^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} because these metals react with ligands under particularly favorable conditions: the rate constants are easily accessible, hydroxy species do not interfere (except for Fe^{3+}) at normal pH's, and often large changes in light transmission occur upon reaction. A compilation of rate data by many techniques for metal–ligand reactions was recently given by Eigen and Wilkins.[3] The measured forward rate constants for complex formation were interpreted as favoring S_N1 mechanisms since these constants depended primarily on the metal ion and did not vary greatly with the ligand.

This study was undertaken to help clarify the nature of metal–ligand reactions involving copper. Copper has not been so extensively studied as many of the other transition elements, presumably because of its rapid water exchange rate,[4] $>10^8$ sec^{-1}, and ease of formation of hydroxy species even at relatively low pH's. The results of this study show that even when the ligand is almost completely in the zwitterion form, the rate for copper recombination with the anion can be directly determined.

Experimental Section

Materials. Matheson Coleman and Bell reagent grade $Cu(NO_3)_2 \cdot 3H_2O$, Fisher reagent grade KNO_3, and Nutritional Biochemicals glycine were used without further purification. All solutions were prepared with degassed Stokes distilled water.

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[1] To whom all correspondence should be addressed.

[2] *E.g.*, M. Eigen and L. De Maeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter XVIII, and references contained therein.

[3] M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

[4] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).