Hydrogen Chloride Catalyzed Isomerization of 1,1-Dimethylcyclopropane

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Abstract: Gaseous 1,1-dimethylcyclopropane (DMC) isomerizes in the presence of HCl at 420–476° to a nonequilibrium mixture of the three isomeric methylbutenes. The reaction is apparently homogeneous and nonradical and, for $p_{DMC} = 2–33$ cm and $p_{HCl} = 2–24$ cm, follows the rate law $-d[DMC]/dt = k_u[DMC] + k_c[DMC][HCl]$. The results are consistent with the occurrence of two concurrent processes: (i) a unimolecular isomerization[2] (rate, k_u[DMC]) mainly to 2-methylbut-2-ene (2MB2) and 3-methylbut-1-ene (3MB1), and (ii) a HCl-catalyzed isomerization (rate, k_c[DMC][HCl]) mainly to 2-methylbut-1-ene (2MB1). There is subsequent isomerization among the methylbutenes toward an equilibrium mixture, this process also being HCl catalyzed. Values of k_u for process i are in good agreement with the findings of other workers.[2] It is proposed that process ii is bimolecular and the formation of 2MB1 proceeds *via* a six-centered transition state[3] which may be quasi-heterolytic. The variation of k_c with temperature is expressible as $k_c = 2.3 \times 10^{18} \exp(-53{,}800/RT)$ sec^{-1} ml mole^{-1}. There is evidence that at pressures of DMC below 20 mm, isomerization in the presence of HCl also proceeds *via* a free-radical process.

The study described in this paper arose from an earlier study on the pyrolysis of gaseous neopentyl chloride[4,5] at 400–500°. Hydrogen chloride and 1,1-dimethylcyclopropane (DMC) appear as reaction products, and a knowledge of their chemical interaction was necessary for the elucidation of the mechanism of the main pyrolysis reaction.

In recent years there have been many studies of hydrogen halide catalysis of gas-phase reactions particularly by Maccoll, Stimson, and coworkers.[6-8] The HBr-catalyzed isomerization of gaseous cyclopropane to propene has been reported by Ross and Stimson:[9] at 440° the rate of isomerization in the presence of 100 mm of HBr is about 50 times the uncatalyzed rate. These authors have proposed an ion-pair transition state with a protonated cyclopropane[10] as the cation, *viz.* (cyclopropane H)$^+$–Br$^-$; however, the catalyzed reaction is retarded by propene and free radicals may be involved. Maccoll and Ross[11] have studied the HBr-catalyzed isomerization of but-1-ene to but-2-enes at 286–383°; their results are consistent with a bimolecular mechanism, but more recently Bridge and Holmes[12] have proposed that free radicals may also be involved in this reaction.

The thermal isomerization (uncatalyzed) of gaseous 1,1-dimethylcyclopropane at 447–511° has been studied by Flowers and Frey.[2] The products are 51% 3-methylbut-1-ene (3MB1), 48% 2-methyl-2-ene (2MB2), and 1% 2-methylbut-1-ene (2MB1). The reaction is apparently unimolecular, and the variation of rate coefficient with temperature is expressible as

$$k = 1.12 \times 10^{15} \exp(-62{,}600/RT) \text{ sec}^{-1}$$

The main products may be justified in terms of a mechanism involving ring rupture associated with the migration of a hydrogen atom between two adjacent carbon atoms on the ring; 2MB1 may be formed by the less likely intramolecular transfer of a hydrogen atom from a methyl group to either of the carbon atoms in the ring positions 2 or 3.

Experimental Section

Materials. DMC was prepared from 1,3-dibromo-2,2-dimethylpropane by reduction with Zn, according to the method of Shortridge, *et al.*[13] 3MB1, 2MB2, and 2MB1 were purchased from Fluka AG Buchs SG (Switzerland). HCl, isobutylene, and 3MB1 were purchased from Matheson Co. in research grade gas cylinders. 3-Chloro-2-methylpropene was from Koch Light Co. Gaseous synthetic NH_3 (in cylinders) was purchased from Imperial Chemical Industries, A.N.Z., Ltd.

The purity of all substances (except NH_3 and HCl) was checked by gas chromatography. Final purification in the vacuum system was effected by trap-to-trap distillation.

Apparatus and Procedure. Reactions were mostly carried out in a cylindrical Pyrex glass vessel (volume 400 ml; surface/volume = 0.8 cm^{-1}) coated with the pyrolysis products of 3-chloro-2-methylpropene at 450° and "seasoned" with DMC and its decomposition products at the same temperature. A packed vessel (vol 257 ml; surface/volume = 4.7 cm^{-1}), coated and seasoned in the same way, was used to test for surface effects. The apparatus and experimental methods have been described elsewhere.[5,14] For a kinetic run, HCl was added first to the reaction vessel, followed by DMC. After the desired reaction time, NH_3 gas was added in slight excess to the HCl, and the entire reaction mixture was rapidly transferred to a sampling vessel cooled in liquid nitrogen. The sample vessel was allowed to warm to room temperature, and analysis of the organic products was carried out by gas chromatography. (The addition of NH_3 prior to sampling was to prevent the facile addition reaction of HCl with the methylbutenes.)

A flame-ionization type gas chromatograph was used for analysis with the following columns:[15] (i) 20% w/w Squalane with 1%

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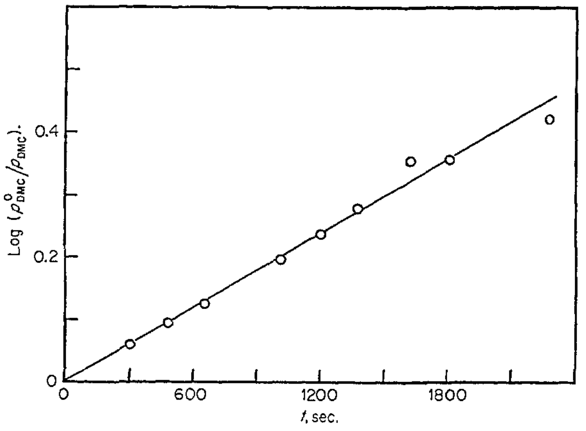

Figure 1. First-order plot for the isomerization of 1,1-dimethylcyclopropane in the presence of HCl (temperature, 450°; initial pressure of each reagent, 100 mm).

w/w Tween 20 on Celite at 25° (4 ft), (ii) 5% w/w Dow Corning high-vacuum silicone grease, 5% w/w silicone oil F 96 (General Electric), 0.3% w/w Aptet 800, and 0.1% Alketerge on Celite at 0° (12 ft.).

Kinetic Measurements and Results. Over the temperature range 419–476° the reaction products consisted of nonequilibrium mixtures of the three isomeric methylbutenes. No other products were formed in significant amounts.

Table I. Kinetic Data for the HCl-Catalyzed Decomposition of DMC at 450° [a]

Initial pressures of reactants, mm HCl	DMC	$10^{-2}k_c$, sec^{-1} ml $mole^{-1}$
98	30	1.41
109	47	1.32
109	51	1.34
110	75	1.51
99	98	1.36
96	151	1.42
102	175	1.45
104	210	1.38
102	247	1.25
110	296	1.23
105	328	1.36
30	107	1.28
56	99	1.22
70	101	1.34
77	100	1.29
89	100	1.36
106	108	1.51
114	100	1.38
129	102	1.26
151	100	1.31
169	101	1.50
194	100	1.42
213	100	1.36
238	116	1.42

[a] See eq 2.

For a fixed concentration of DMC and HCl, the disappearance of DMC followed a first-order kinetic law as illustrated by the data shown in Figure 1. Values of the first-order rate coefficients, $k_{overall}$, calculated from graphs such as Figure 1 were found to depend upon the total pressure of hydrogen chloride in the manner shown in Figure 2, provided the partial pressure of DMC was above 20 mm. From Figures 1 and 2 it follows that the rate of disappearance of DMC may be represented by eq 1 as the sum of an uncatalyzed reaction of the first order in DMC, and a catalyzed reaction of mixed second order, being first order in each of DMC and HCl. Values of k_u, either estimated from kinetic runs in the absence of HCl or extrapolated from data such as in Figure 2, were in good agreement with the findings of Flowers and Frey.[2] Thus at 464°, 10^4k_u (in absence of HCl) = 2.9 sec^{-1}, and at 450°, 10^4k_u (from extrapolation) = 1.0 sec^{-1}; these compare with the respective values of 3.0 and 1.3 sec^{-1} as estimated from the results of Flowers and Frey.

$$-d[DMC]/dt = k_u[DMC] + k_c[DMC][HCl] \quad (1)$$

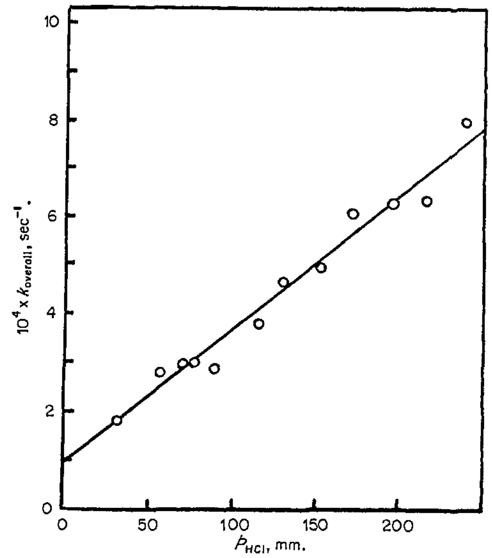

Figure 2. Variation of $k_{overall}$ with changes in the pressure of HCl (temperature 450°; initial pressure of 1,1-dimethylcyclopropane, 100 mm).

Table I lists, for individual runs at 450.1°, values of k_c estimated

$$k_c = [(1/t)\ln(p^0_{DMC}/p_{DMC}) - k_u]/[HCl] \quad (2)$$

by means of eq 2 (derived from eq 1) where p^0_{DMC} is the initial partial pressure of DMC and p_{DMC} the partial pressure after reaction time, t. It is clear that k_c remains sensibly constant over a wide range of pressures of both reactants. The addition of isobutylene (a radical-chain inhibitor[16]) to the normal reaction mixture caused no significant change in the rate of isomerization of DMC (see Table II), and runs in a packed vessel did not differ appreciably from those in the unpacked vessel (see Table III). The data shown in Tables I–III are for temperatures near 450°, but similar behavior was evidenced at other temperatures. Mean values of k_c (with 90% confidence limits of the mean) at six temperatures are given in Table IV. From these data, a least-squares plot of log k_c against $1/T$ yielded the following values (with 90% confidence limits) for the constants in the Arrhenius equation, $k_c = A\exp(-E/RT)$: E = 53,800 ± 980 cal $mole^{-1}$ and log A = 18.37 ± 0.30, ($A = 2.3 \times 10^{18}$ sec^{-1} ml $mole^{-1}$).

Table II. Effect of Added Isobutylene upon DMC Isomerization[a]

Initial pressures of reactants, mm Isobutylene	HCl	DMC	$10^{-2}k_c$, sec^{-1} ml $mole^{-1}$
13	8	7	1.41[b]
9	9	12	1.48
9	25	20	1.42
10	18	24	1.54
9	19	31	1.40
7	40	57	1.43
14	54	44	1.51
10	74	79	1.49
46	156	20	1.51

[a] Temperature 450.7°. [b] For runs at 450.7° in the absence of isobutylene, $10^{-2}k_c$ = 1.41 sec^{-1} ml $mole^{-1}$ provided the initial pressures of HCl and DMC were above 20 mm.

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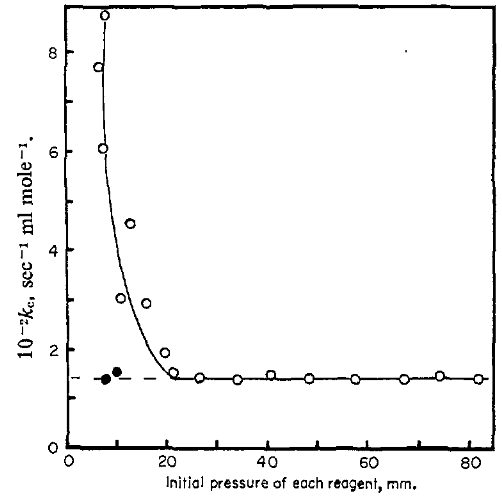


Figure 3. Variation of k_c with changes in the initial pressures of 1,1-dimethylcyclopropane and HCl (temperature, 450°; equal initial pressures of both reagents): ●, runs in the presence of 10 mm of isobutylene.

The data in Tables I–IV are for kinetic runs in which the partial pressure of DMC was greater than 20 mm. As shown in Figure 3, increasingly higher values of k_c were recorded as the partial pressure of DMC was dropped below this value. This rise in k_c values was found to occur below the same pressure at all temperatures and to be accentuated by increasing the surface/volume of the reaction vessel. Addition of isobutylene to the reactants in the "low-pressure region" restored k_c to the normal "high-pressure" value (see Figure 3).

Table III. HCl-Catalyzed Isomerization of DMC in a Packed Vessel[a]

Initial pressures of reactants, mm HCl	 DMC	$10^{-2}k_c$, sec^{-1} ml mole^{-1}
100	95	1.41[b]
99	110	1.29
100	101	1.38
96	92	1.40
105	102	1.52
102	109	1.54
101	103	1.46
103	104	1.41
99	101	1.62
97	109	1.47

[a] Temperature 451.7°. [b] For runs at 451.7° in an unpacked vessel $10^{-2}k_c$ = 1.48 sec^{-1} ml mole^{-1} provided the initial pressures of HCl and DMC were above 20 mm.

Table IV. Temperature Dependence of Rate Coefficient, k_c

Temp, °C	No. of runs	$10^{-2}k_c$,[a] sec^{-1} ml mole^{-1}
420.3	16	0.260 ± 0.008
430.8	13	0.483 ± 0.024
440.3	11	0.790 ± 0.041
450.1	80	1.294 ± 0.024
459.5	13	2.136 ± 0.038
472.4	10	4.085 ± 0.051

[a] Mean values and 90% confidence limits of the mean.

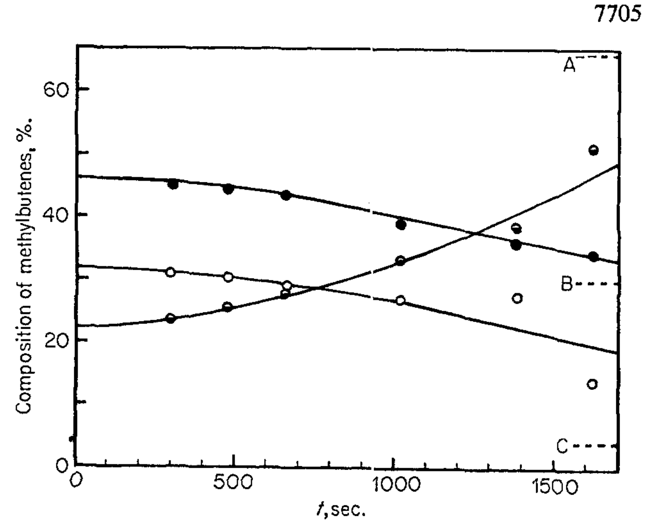


Figure 4. Composition of the methylbutenes at different stages of the isomerization of 1,1-dimethylcyclopropane in the presence of HCl (temperature 450.7°; initial pressure of each reagent, 100 mm): ●, 2-methylbut-1-ene (2MB1); ○, 3-methylbut-1-ene (3MB1); ◒, 2-methylbut-2-ene (2MB2); A, equilibrium percentage of 2MB2; B, equilibrium percentage of 2MB1; C, equilibrium percentage of 3MB1.

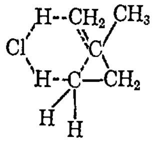
Figure 4 shows the composition of the methylbutenes as observed at different stages of the isomerization of 100 mm of DMC in the presence of 100 mm of HCl at 450.7°. The initial composition of methylbutenes formed was 23% 2MB2, 46% 2MB1, and 31% 3MB1 compared with the equilibrium composition[4] of 66% 2MB2, 30% 2MB1, and 4% 3MB1 at the same temperature. For 100 moles of total methylbutenes produced in this reaction, runs in the absence of HCl showed that the uncatalyzed isomerization of DMC would have produced approximately 35 moles of methylbutenes consisting of 17 moles of 2MB2, <1 mole of 2MB1, and 18 moles of 3MB1. It is clear that the catalyzed isomerization of DMC produced mainly 2MB1. The quantities of the other methylbutenes produced in smaller amounts in the catalyzed process could not be assessed with accuracy because of the difficulties of analysis in the early stages of the reaction and because of some isomerization among the methylbutenes, a process which is also HCl catalyzed. Separate studies of the isomerization reactions of the methylbutenes in the presence of HCl showed that after 500 sec at 450° these reactions would have proceeded by less than 5% for the conditions under which the HCl-catalyzed isomerization of DMC was studied (refer to Figure 4). Attempts to study the isomerization reactions of the methylbutenes quantitatively were largely unsuccessful owing to irreproducible kinetics and to the reactions being partly heterogeneous in character.

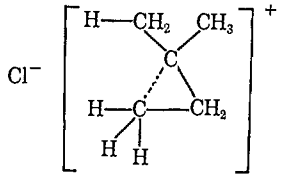
Product analyses for the HCl-catalyzed isomerization of DMC in the "low-pressure region" showed that the exceptionally high values of k_c were accompanied by a disproportionate increase in the production of 2MB2. Thus, for 10 mm partial pressures of both reactants, 2MB2 accounted for nearly 40% of the methylbutenes formed. Addition of 10 mm of isobutylene to the reaction mixture, however, not only effected a reduction in the value of k_c, but also restored the relative proportions of methylbutenes near to those values observed in the "high-pressure region."

Discussion

The kinetic evidence for the isomerization of 1,1-dimethylcyclopropane is consistent with the occurrence of two concurrent processes: (i) a unimolecular isomerization producing mainly 2-methylbut-2-ene and 3-methylbut-1-ene, as observed by other workers,[2] and (ii) a bimolecular HCl-catalyzed isomerization producing mainly 2-methylbut-1-ene for partial pressures of reactants above 20 mm. A bimolecular gas-phase mechanism for process ii is supported by the observation of mixed second-order kinetics and by the lack of sensitivity of the second-order rate coefficient to the addition of olefinic inhibitor or to an increase in the surface area of the vessel. The production of 2-methylbut-1-ene *via* process ii may be explained in terms of a six-centered transition state (I). Similar transition states have been proposed by

Maccoll, *et al.*,[3] for the hydrogen halide catalyzed dehydration of alcohols,[6] for the hydrogen bromide catalyzed isomerization of but-1-ene,[11] and for the pyrolysis of 1-chloro-*cis*-but-2-ene.[17] Transition states of this type may be quasi-heterolytic[3] as represented by II in the case of the 1,1-dimethylcyclopropane reaction.





The Arrhenius preexponential factor for the catalyzed isomerization ($A = 2.3 \times 10^{18}$ sec^{-1} ml mole^{-1}) is significantly larger than for most bimolecular reactions. High A factors are not uncommon for the gas-phase reactions of cyclopropane compounds (*e.g.*, $A = 2.6 \times 10^{16}$ sec^{-1} for *trans*- to *cis*-1,2-dideuteriocyclopropane,[18] and $A = 2.8 \times 10^{15}$ sec^{-1} for methylcyclopropane[19] to a mixture of butenes) and are indicative of a positive entropy of activation for these reactions which involve the loosening of tight ring structures.

The marked change in character of the isomerization behavior of 1,1-dimethylcyclopropane in the presence of hydrogen chloride for reactant pressures below 20 mm suggests that a free-radical process may be dominant in this region. This type of reaction would be supressed by a sufficiently high concentration of 1,1-dimethylcyclopropane, methylbutene, or isobutylene, as these substances should act as efficient radical-chain inhibitors.[16] A radical-chain reaction at low pressures could therefore be self-inhibiting at higher pressures of reactant permitting the molecular processes to become predominant. The behavior shown in Figure 3 is similar to that reported by Barton and Howlett[20] for the inhibiting effect of propene upon the pyrolysis of 1,2-dichloroethane.

Further work is proceeding on the HCl-catalyzed isomerization of alkylcyclopropanes and related compounds.

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Shock Tube *cis–trans* Isomerization Studies

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Abstract: An 0.75-in. i.d. single pulse shock tube is described. This instrument was used to determine that the first-order rate constants for *cis–trans* 2-butene isomerization is $k = 10^{13.38}e^{-61,600/RT}$ sec^{-1}; and that for 1,2-difluoroethylene, $k(cis \rightarrow trans) = 10^{13.17}e^{-62,800/RT}$ sec^{-1}, while $k(trans \rightarrow cis) = 10^{12.98}e^{-60,100/RT}$ sec^{-1}. A relative rate method was used.

Thermal *cis–trans* isomerization reactions are of considerable theoretical interest. This paper presents new high-temperature data on the 2-butene isomerization and relative isomerization rates for 1,2-difluoroethylene which have not been previously reported.

Early studies[1-3] yielded surprisingly low values for the frequency factor and activation energy for the 2-butene isomerization, and these were interpreted in terms of a triplet state intermediate. Later investigations showed conclusively that the singlet mechanism predominates, but the several studies were not in complete agreement.[4-6] It appeared that despite the apparent simplicity of the unimolecular isomerization process, significant difficulties were encountered in a conventional experimental analysis of these systems. A high-temperature (1000–1250°K) shock tube study[7] of the 2-butene isomerization in the unimolecular high-pressure region showed no significant side products due to free radicals. Although there was considerable scatter of the shock tube data, combining these with the low-temperature (683–749°K) conventionally determined

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