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Preference for Structural versus Geometric Isomerization in the BCl_3-Catalyzed Thermal Isomerizations of Gaseous 1,2-Dimethylcyclopropane

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The thermal isomerization reactions of gaseous *cis*- and *trans*-1,2-dimethylcyclopropane have been studied in the presence and absence of boron trichloride, in a static reactor at $574 < T < 708$ K. Both geometrical (cis ⇄ trans) and structural (→ pentenes and methylbutenes) isomerizations are accelerated by BCl_3, but the normally slower structural rearrangements become the dominant reactions in the presence of catalyst. Mechanistic implications are discussed.

Introduction

Thermal unimolecular isomerizations of gaseous cyclopropanes have been the subject of numerous experimental and theoretical studies.[1-3] The most easily observed reaction of cyclopropane (CP) is the structural isomerization to form propene (P); but suitably labeled cyclopropanes also undergo geometric (cis ⇄ trans) isomerization at rates that are about an order of magnitude more rapid than the structural isomerization rates. A diradical intermediate has been implicated in both processes,[1] but a concerted mechanism for the geometric isomerization has also received some support.[2]

The structural isomerization CP → P in the gas phase is strongly accelerated by both Brønsted acids, e.g., HBr,[4] and Lewis acids, e.g., BCl_3[5,6] and BBr_3.[7] The reaction in thermal reactors is first order in CP and in the acid species and is apparently homogeneous. Structural isomerization of 1,1-dimethylcyclopropane is also accelerated by HCl.[8] These are the only reactions of alkanes thus far reported to be subject to homogeneous, gas-phase acid catalysis. However, since kinetic studies with 1,2-disubstituted cyclopropane–acid gas mixtures have not heretofore been reported, it is not known whether rates of the geometric isomerizations of CP's are accelerated along with the enhancement of the structural isomerization rates. That test is the subject of this report. Starting with *cis*- or *trans*-1,2-dimethylcyclopropane (c-DMCP, t-DMCP), rates of geometric isomerization were also found to be increased by BCl_3, but only at $T < 650$ K. Above that temperature the unimolecular reaction dominates. The structural isomerization, which is slower in the absence of acid catalyst, proceeds about an order of magnitude faster than the geometric isomerization in the presence of BCl_3. Mechanistic implications of this unexpected observation are discussed below.

Experimental Section

Samples containing 10% c-DMCP or t-DMCP (both API Standard Reference Materials) and either 0% or 4.8% or 5% BCl_3 (Matheson CP grade), diluted in Matheson Ultra-High Purity argon, were heated in a well-conditioned 100-cm^3 Pyrex reactor:[6] P(total) = 42–78 Torr; T = 574–708 K; reaction time 20–180 min. Reactants and products were analyzed via vapor-phase chromatography, and rate constants were calculated via a digital integration scheme that converged on a match between calculated and observed concentrations of all products and residual reactant. All reactions were considered to be first order, or pseudo first order with added BCl_3. Only the geometric isomerization was considered reversible. Thirty-six kinetic runs were made.

Results and Discussion

With either c-DMCP or t-DMCP as the reactant, but no BCl_3 present, the principal product was the other geometric isomer, with lesser amounts of structural isomerization products *trans*-2-pentene (t2P), *cis*-2-pentene (c2P), 2-methyl-1-butene (2M1B), and 2-methyl-2-butene (2M2B) present. The results are consistent with results of earlier studies by Flowers and Frey.[9,10] When reactant samples contained BCl_3, the principal products were t2P, c2P, 2M1B, and 2M2B. Unlike the uncatalyzed runs which produced comparable quantities of pentenes and methylbutenes, the catalyzed runs produced pentene/methylbutene ratios as large as 5 from c-DMCP and 8 from t-DMCP. The geometric isomer was also present, but at lower concentrations than the four products of structural isomerization. This also differs from the uncatalyzed runs, which produced much more geometric than structural isomerization products. No new products were observed.

Rate constants for formation of t2P, c2P, t-DMCP (from cis), or c-DMCP (from trans), in the presence and absence of BCl_3, are given for 610 K in Table I and for 673 K in Table II. These values are taken from linear least-squares lines through Arrhenius plots of all data points for each reaction. Rate constants for production of the methylbutenes are not included because of partially overlapping GC peaks and because 2M1B and 2M2B are reported to interconvert in the presence of BCl_3.[11] BCl_3-induced interconversion of cis and trans alkenes also occurs under the conditions of these experiments, but at rates that are less than one-tenth as large as their rates of production from DMCP.

Five observations are apparent from the data in Table I. (a) All reactions of c-DMCP and t-DMCP proceeded faster in the presence of BCl_3. But (b), the structural isomerizations were accelerated much more than was the geometric isomerization. (c) Preferential formation of t2P from c-DMCP, and of c2P from t-DMCP, in the absence of catalyst, was maintained when BCl_3 was added. BCl_3 addition to c-DMCP increased the production of c2P and t2P by virtually equal ratios; likewise for BCl_3-catalyzed production of c2P and t2P from t-DMCP. (d) Rates of geometric isomerization of either reactant were increased by the same relative ratio. But (e), rates of structural isomerizations of t-DMCP appeared to increase 7–8 times as much as rates of structural isomerizations of c-DMCP. Similar observations are apparent from the data in Table II, with the exceptions that the BCl_3-in-

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(1) An excellent review of pre-1976 experimental and theoretical work is provided in: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 117–128.

(2) See also: Berson, J. *Annu. Rev. Phys. Chem.* **1977**, *28*, 111–132.

(3) And for a recent study of geometric isomerization see: Baldwin, J. E.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 6364–6367.

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TABLE I: Ratios of Rate Constants at 610 K for Reactions of c-DMCP and t-DMCP with (k_c) and without (k_u) BCl_3

reaction	k_c/k_u[a]	reaction	k_c/k_u
c-DMCP → t-DMCP	$(5.5 \times 10^{-6})/(9.5 \times 10^{-7}) = 5.7$	t-DMCP → c-DMCP	$(2.1 \times 10^{-6})/(3.8 \times 10^{-7}) = 5.6$
c-DMCP → c2P	$(2.3 \times 10^{-5})/(6.9 \times 10^{-8}) = 3.3 \times 10^2$	t-DMCP → c2P	$(1.0_4 \times 10^{-5})/(4.9 \times 10^{-9}) = 2.1 \times 10^3$
c-DMCP → t2P	$(3.7 \times 10^{-5})/(1.0_1 \times 10^{-7}) = 3.6 \times 10^2$	t-DMCP → t2P	$(8.9 \times 10^{-6})/(3.1 \times 10^{-9}) = 2.9 \times 10^3$

[a] k_c (s^{-1}) = k_2 (L mol^{-1} s^{-1}) × [BCl_3] (mol L^{-1}). Units of k_u are s^{-1}.

TABLE II: Ratios of the Rate Constants at 673 K for Reactions of c-DMCP and t-DMCP with (k_c) and without (k_u) BCl_3

reaction	k_c/k_u[a]	reaction	k_c/k_u
c-DMCP → t-DMCP	$(2.7 \times 10^{-5})/(8.4 \times 10^{-5}) = 0.32$	t-DMCP → c-DMCP	$(1.1 \times 10^{-5})/(3.6 \times 10^{-5}) = 0.32$
c-DMCP → c2P	$(7.8 \times 10^{-5})/(5.7 \times 10^{-6}) = 14$	t-DMCP → c2P	$(4.2 \times 10^{-5})/(6.9 \times 10^{-7}) = 62$
c-DMCP → t2P	$(1.4 \times 10^{-4})/(8.5 \times 10^{-6}) = 16$	t-DMCP → t2P	$(2.9 \times 10^{-5})/(4.3 \times 10^{-7}) = 68$

[a] k_c (s^{-1}) = k_2 (L mol^{-1} s^{-1}) × [BCl_3] (mol L^{-1}). Units of k_u are s^{-1}.

duced rate enhancement of geometric isomerization is barely detectable at 673 K and that the difference between structural isomerization rate enhancements of t-DMCP and c-DMCP at 673 K declines to a factor of 4–5. Any mechanistic interpretation must account for these observations. Five possibilities are considered.

The activation energies for both structural and geometric isomerization of c-DMCP or t-DMCP are 257 (±8) kJ mol^{-1} in the absence of a catalyst.[9,10] With BCl_3 present, data from the present study indicate that the activation energies for both processes drop to 80 (±20) kJ mol^{-1}, slightly less than the ~100 kJ mol^{-1} value deduced for the BCl_3-catalyzed reaction CP → P.[5,6] Since the enthalpy barrier to breaking a C–C bond in CP has been estimated at 226 kJ mol^{-1},[1] the effect of the catalyst must occur in the primary process, not subsequent to the breaking of a C–C bond.

One could speculate that the BCl_3 forms a complex with DMCP which facilitates C–C bond cleavage to form a pentyl 2,4-diradical or a 2-methylbutyl 1,3-diradical, from which H atom migration or methylene rotation occurs enroute to the products. One could further assume that steric hindrance prevents the geometric isomerization rate from being increased by as great a factor as the structural isomerization rate. But then the lack of increased stereoselectivity in the formation of the 2-pentene products is hard to rationalize. A solution is to assume that the recombination rate for the diradical is competitive with the time required to rotate a methylene group with its attached methyl substituent. This would in turn require that the enthalpy barrier for diradical recombination drop to a value close to 0 kJ mol^{-1} in the complexed condition.

Stimson and co-workers[5,7] proposed that the strongly electrophilic acids catalyze CP → P by forming a polarized CP(∂+)–acid(∂–) complex, which facilitates the 1,2 H atom migration. If the catalyzed hydrogen shift preceded the C–C bond-breaking step, then it seems unlikely that the geometric isomerization rate would be affected at all, and the 2-pentenes ought to show greater stereoselectivity then in the absence of BCl_3. Both expectations are contrary to the present results. Thus, the C–C bond cleavage would have to precede the H atom migration. This polarized complex proposal then becomes similar to the complex-induced diradical intermediate mechanism discussed above.

A third speculation is that the BCl_3 reversibly induces singlet-to-triplet conversion of a diradical intermediate. Since CP cannot re-form from triplet trimethylene, this would extend the lifetime of the diradical. The probable effect on the isomerizations is hard to assess. The observed order of catalytic efficiency of CP structural isomerization, BBr_3 > BCl_3 > HBr > HCl, is consistent with the generalization that larger, more polarizable atoms are most efficient at inducing spin conversion. But the low activation energy for the catalyzed reactions is inconsistent with a mechanism in which the spin-conversion interaction occurs after, that is separate from, the bond-breaking step.

A fourth, intriguing, possibility is that the geometric and structural isomerizations of CP may involve different intermediates and that the BCl_3 facilitates the two processes in different ways. The similar relative enhancements of c-DMCP and t-DMCP geometric isomerization, coupled with apparently different relative enhancements of structural rearrangements, support this possibility. However, the observation that all BCl_3-catalyzed reactions of DMCP have similar activation energies indicates that a common intermediate is more likely. Further refinement of the Arrhenius parameters for these reactions is in progress, and this should help to clarify this issue.

A final possibility, that of wall-induced reactions, cannot be absolutely excluded at this time. However, Stimson's observations of overall second-order kinetics and the absence of rate increases in packed vessels,[4,5,7] the similarity in the rate of the BCl_3-induced CP → P reaction measured in two laboratories, and the apparent high degree of selectivity of the catalytic effect[6] mitigate against this interpretation.

At this time, a mechanism in which a DMCP–BCl_3 complex facilitates C–C bond cleavage to form a rotationally hindered diradical or dipolar complex seems most consistent with the available data. Further measurements of the competing rates of reactions of 1,2-disubstituted cyclopropanes, using other substituents and other electrophiles, may provide definitive information on the mechanisms of these reactions. Such work is in progress.

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