

Rates of Reactions of Cyclopropane, Cyclobutane, Cyclopentene, and Cyclohexene in the Presence of Boron Trichloride

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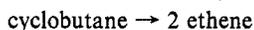
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Cyclopropane (CP), cyclobutane, cyclopentene, and cyclohexene were heated, with added BCl_3 , in a static reactor to 628–748 K. The latter three were also heated with BCl_3 to 939–1435 K in a single-pulse shock tube; a shock tube study of CP with BCl_3 was reported earlier. In the static reactor CP isomerization to propene was greatly accelerated by BCl_3 as previously reported, but none of the other reactants appeared to be affected by the catalyst. In the shock tube the BCl_3 also appeared to have no effect on the primary decomposition reactions studied, but some changes in rates of side product formation were noted. Mechanistic implications of the high degree of specificity, shown by BCl_3 toward reactions of cyclic hydrocarbons, are offered.

Introduction

The subject of this paper is the catalysis of reactions of gaseous organic molecules by strong Lewis acids. From work in static systems at 500–800 K, Stimson and co-workers¹ have shown that HCl , HBr , BCl_3 , and BBR_3 greatly accelerate the rates of many decomposition or rearrangement reactions of hydrocarbons, alcohols, ethers, and halides. Other groups² have begun to examine the influence of these gaseous acids on reactions induced by intense infrared laser beams.

We have become interested in answering the following questions about these systems: (a) Does the catalytic effect extend to very high temperatures (>1000 K) at which extents of molecular vibrational excitation are similar to those produced in multiphoton excitation experiments? (b) What types of molecules are subject to the catalysis, and, equally important, what molecules are not? (c) What are the specific mechanisms of catalysis? To answer these questions, we have begun studying reaction rates of a wide variety of organic molecules in the presence of Lewis acids, in both a static reactor ($T \geq 625$ K) and a single-pulse shock tube ($T \geq 900$ K). The first result, that BCl_3 does not accelerate the structural isomerization of cyclopropane at $T > 900$ K, appeared recently.³ In the present paper we report a confirmatory study of the catalytic effect of BCl_3 on cyclopropane isomerization at lower temperatures, and studies that show the absence of a major influence of BCl_3 on three other reactions of cyclic hydrocarbons at either low or high temperatures:



These prototype reactions were chosen because their unimolecular decomposition kinetics have been extensively studied over a wide range of temperatures.

Experimental Section

The lower temperature reaction rate studies were carried out (by B.L.K.) in a conventional vacuum system. The reaction cell was a 2.54 cm i.d. Pyrex cylinder 11 cm long, enclosed in an aluminum furnace which was heated electrically by four 300-W cartridge heaters. The furnace was insulated by a Fiberglas jacket. Temperatures were measured to ± 0.75 °C with a digital ther-

mometer (Omega Engineering Model 650-J-D). The cell and furnace were so positioned as to leave about 5 cm between either cell end wall and the furnace extremities. Reaction times ranged from 5 to 400 min, after which products were quickly frozen into a removable U-tube or 50-cm³ bulb, each fitted with stopcocks, for transfer to the gas chromatograph.

The higher temperature reaction studies were performed (by D.K.L. et al.) in a 2.54 cm i.d. Pyrex single-pulse shock tube. A complete description of the device and operating procedures has appeared previously.^{3,4}

Analyses of reactants and products were performed in a Varian 1440 chromatograph equipped with flame ionization detector. For the cyclopropane and the cyclobutane studies, column packing was Poropak Q. Products from the studies of the cyclopentene and cyclohexene reactions were separated by a column containing 20% poly(propylene glycol) saturated with silver nitrate, on Chromosorb W.

The gaseous reagents BCl_3 ($\geq 99.9\%$), cyclopropane ($\geq 99\%$), ethene, propene, and butadiene (all Matheson CP grade) were used as obtained from lecture bottles for preparation of reaction mixtures and gas chromatograph calibration mixtures. Liquid reagents cyclobutane (Columbia Chemical Co., $\geq 99\%$), cyclopentene (Aldrich, $\geq 99\%$), and cyclohexene (Fisher reagent grade, $\geq 98\%$) were evaporated into evacuated bulbs on the vacuum line and then subjected to one or more trap-to-trap distillations under vacuum before use. Dicyclopentadiene (Eastman technical grade $\geq 85\%$) was cracked to the monomer by distillation at atmospheric pressure and then distilled under vacuum. Sample mixtures were prepared manometrically by successive additions to previously evacuated 3- or 5-L bulbs. Matheson ultrahigh-purity argon ($\geq 99.999\%$) was used as the diluent in all mixtures prepared for shock tube studies, and in some mixtures prepared for the static reactor studies. Mixtures were either mixed with internal stirring mechanisms or allowed to equilibrate 2 or more days before use. Experimental conditions for the rate measurements are summarized in Tables I and II. In the shock tube studies of each reaction, mixtures with and without BCl_3 were run on the same day.

Calculations and Results

Cyclopropane—Static Reactor Study. The only product observed in the thermal reaction of cyclopropane, both in the presence and in the absence of boron trichloride, was propene. Small amounts of propene (1.60–3.00%) were found to be present in the cyclopropane–boron trichloride mixture at room temperature. These amounts were subtracted from the amount of propene produced in the catalyzed reaction and the resulting values were

(1) (a) Johnson, R. L.; Stimson, V. R. *Aust. J. Chem.* **1975**, *28*, 447. (b) Stimson, V. R.; Taylor, E. C. *Ibid.* **1976**, *29*, 2557. (c) See also earlier work referenced therein.

(2) (a) Danen, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 1187. (b) Zare, R. N., private communication.

(3) Lewis, D. K.; Bosch, H. W.; Hossenlopp, J. M. *J. Phys. Chem.* **1982**, *86*, 803.

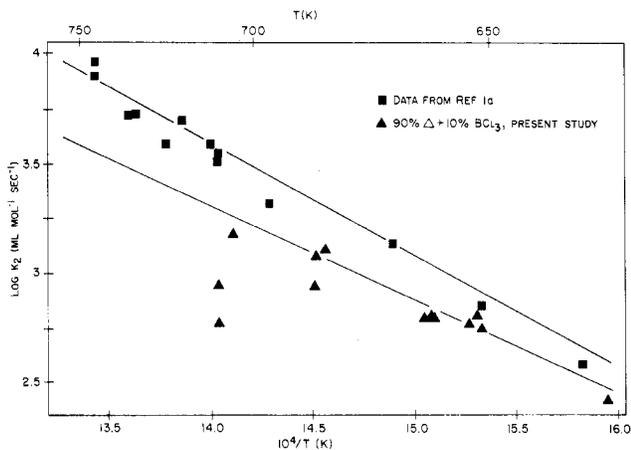
(4) Lewis, D. K.; Giesler, S. E.; Brown, M. S. *Int. J. Chem. Kinet.* **1977**, *9*, 387.

TABLE I: Summary of Experimental Conditions for Static System (Lower Temperature) Rate Studies

reaction	no. of runs	% reactant	% BCl ₃	P, torr	diluent	t, min	T, K
cyclopropane → propene	13	90	10	12–28		20–35	628–712
cyclobutane → 2 ethene	14	60	40	16–25		12–46	644–750
cyclopentene → cyclopentadiene + H ₂	6	5	0.81/5	38.5–68.4	Ar	76–395	701–738
cyclohexene → ethene + 1,3-butadiene	7	10	5	37–53	Ar	10–180	710–748

TABLE II: Summary of Experimental Conditions for Shock Tube (Higher Temperature) Studies

reaction	no. of runs	% reactant	% BCl ₃	diluent	P, atm	T, K
cyclobutane → 2 ethene	8	2.0	0 or 1.0	Ar	2–3	939–1089
cyclopentene → cyclopentadiene + H ₂	17	1.7 or 2.0	0 or 1.0	Ar	2–3	1094–1465
cyclohexene → ethene + 1,3-butadiene	21	1.0	0 or 1.0	Ar	~2	966–1190

Figure 1. Second-order rate constants for the BCl₃-catalyzed isomerization of cyclopropane in the static reactor.

used in the calculation of the rate constants at various temperatures. For the 13 experiments run, second-order rate constants, k_2 , were determined from the equation

$$\text{rate} = k_2[\text{BCl}_3][\text{c-C}_3\text{H}_6] = k_1[\text{c-C}_3\text{H}_6] \quad (1)$$

The pseudo-first-order rate constants $k_1 (=k_2[\text{BCl}_3])$ were calculated from the integrated first-order rate expression

$$\ln(C/C_0) = -k_1 t \quad (2)$$

where C_0 and C are the concentrations of cyclopropane before and after the reaction, respectively.

The Arrhenius plot for the catalyzed isomerization of cyclopropane in the static reactor is shown in Figure 1. A least-squares line is drawn on the basis of $\log k_2$ values at temperatures below 708 K only, to avoid the undue weighting of the three highly scattered data points at higher temperatures. The values for the Arrhenius frequency, A , and the activation energy, E (cal/mol), calculated from this graph give the following rate equation:⁵

$$k_2 = 1.68 \times 10^9 \exp(-19500/RT) \text{ s}^{-1} \text{ mL mol}^{-1} \quad (3)$$

The $\log k_2$ values obtained by Johnson and Stimson^{1a} are also plotted against $1000/T$ in Figure 1. The least-squares values from these data yield $A = 2.3 \times 10^{11} \text{ s}^{-1} \text{ mL mol}^{-1}$ and $E = 25.4 \text{ kcal/mol}$. From the corresponding values of $A = 1.58 \times 10^{15} \text{ s}^{-1}$ and $E = 65.0 \text{ kcal/mol}$ for the uncatalyzed first-order reaction,⁶ the catalytic effect of boron trichloride on the isomerization of cyclopropane is quite obvious. To further show this effect, pseudo-first-order rate constants, k_1 , are given in Figure 2, along with the Arrhenius line for the uncatalyzed reaction⁶ and the previously reported shock tube data with and without BCl₃.³

Cyclobutane—Static Reactor Study. The only product in the “catalyzed” and uncatalyzed thermal decomposition of cyclobutane was found to be ethene. Unlike in the case of cyclopropane, no reaction product was found in the cyclobutane–boron trichloride

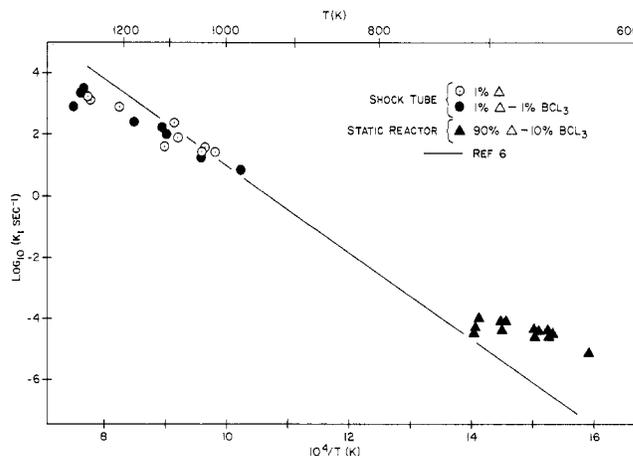


Figure 2. First-order rate constants for cyclopropane isomerization (pseudo first order, for the static reactor data).

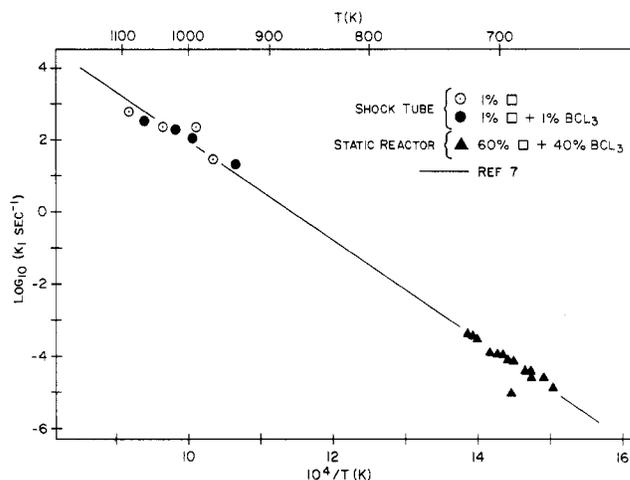


Figure 3. First-order rate constants for cyclobutane dissociation.

mixture at room temperature. The values of first-order rate constants for the decomposition of cyclobutane in the presence and in the absence of boron trichloride are plotted in Figure 3. These values for k_1 were obtained via eq 2 from the chromatographic peak heights of cyclobutane and ethene in product samples: $C = \% \text{ c-C}_4\text{H}_8$; $C_0 = \% \text{ c-C}_4\text{H}_8 + 1/2(\% \text{ C}_2\text{H}_4)$. Rate constants for the uncatalyzed reactions are given by⁷ $\log k = 15.6 - 62500/4.58T$ as reported from shock tube studies by Barnard et al. and Lewis et al. The present data indicate the lack of any significant extent of the catalyzed reaction, a result that is quite different from that obtained for the cyclopropane reaction.

Cyclobutane—Shock Tube Study. Chromatographic analysis of the 2% reactant mixtures with and without BCl₃ showed that both contained about 0.1% *n*-butane (5% of the cyclobutane

(5) In all least-squares calculations in this paper, all variance was ascribed to the Y axis ($\log k$) variable.

(6) (a) Bradley, J. N.; Frend, M. A. *Trans. Faraday Soc.* **1971**, *67*, 72. (b) Jeffers, P. M.; Lewis, D. K.; Sarr, M. S. *J. Phys. Chem.* **1973**, *77*, 3037.

(7) (a) Barnard, J. A.; Cocks, A. T.; Lee, R. Y.-K. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1782. (b) Lewis, D. K.; Feinstein, S. A.; Jeffers, P. M. *J. Phys. Chem.* **1977**, *81*, 1877.

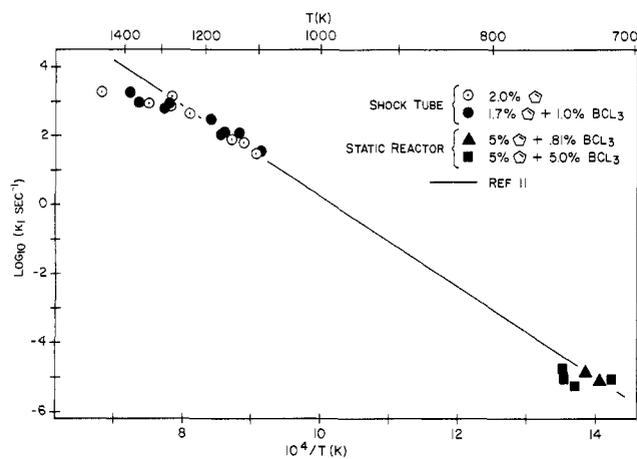


Figure 4. First-order rate constants for cyclopentene dehydrogenation.

concentration). To avoid complications due to reaction of this impurity, shock temperatures were kept below 1100 K. Eight runs were made, covering 939–1089 K. Ethene was the only detectable product produced. Rate constants were calculated from analyses of product samples via eq 2, as described above.⁸ This procedure assumes mass balance but eliminates possible errors associated with contamination of sample by driver gas (helium) and errors in determining the exact pressures of samples injected into the chromatograph. Note that for the low-conversion runs especially, small errors in determining absolute percentages of cyclobutane in product samples would lead to large errors in deduced rate constants.

Temperatures behind reflected shocks were calculated from incident shock velocities as previously described.³ Heat capacity polynomials for cyclobutane and BCl_3 were calculated from published vibrational frequencies.^{9,10}

The data obtained are shown in Figure 3. As previously reported for cyclopropane isomerization at high temperatures,³ the rate constants for runs with and without BCl_3 are well mixed and in agreement with expected values for the homogeneous reaction, documenting the absence of a catalytic effect under these conditions.

Cyclopentene—Static Reactor Study. Below 700 K, no reaction was observed; between 700 and 750 K, cyclopentadiene was the only observed product. It was assumed that H_2 was produced in equal amounts, but this could not be verified with the present chromatograph. First-order rate constants for seven runs were calculated from product samples via eq 2, with $C = \% \text{c-C}_5\text{H}_{10}$ and $C_0 = \% \text{c-C}_5\text{H}_{10} + \% \text{c-C}_5\text{H}_8$; they are plotted in Figure 4, along with the Arrhenius line $\log k = 13.35 - 60000/4.58T$ obtained from studies of the uncatalyzed reaction in a static reactor^{11a} and in a shock tube.^{11b} Large fluctuations in room temperature during this work, coupled with long run times, led to variations in reactor temperature perhaps as large as 3°C during some runs. This may have contributed to the larger than routine scatter of the data points. Nevertheless, the absence of significant catalysis of the primary or side reactions by BCl_3 under the conditions used in this study is evident from the results.

Cyclopentene—Shock Tube Study. Chromatographic analysis of both reactant mixtures showed cyclopentene to be the only detectable organic material. In shock-heated samples, cyclopentadiene was the main product, as expected; lesser amounts of ethene, propene, propyne, allene, and butadiene were present, as previously reported.^{11b} Linear five-carbon compounds were also

(8) For this shock tube, under the present operating conditions, $t = (8 \pm 1) \times 10^{-4}$ s. The average value was used in all calculations.

(9) Shimanouchi, T. "Tables of Molecular Vibrational Frequencies, Part 2"; U.S. Government Printing Office: Washington, DC, 1967; NSRDS-NBS 11, p 35.

(10) Stull, D.; et al. "JANAF Thermochemical Tables"; U.S. Government Printing Office: Washington, DC, 1971; NSRDS-NBS No. 37.

(11) (a) Tanji, H.; Uchiyama, M.; Amano, A.; Tokuhisa, J. *J. Chem. Soc. Jpn., Ind. Chem. Sect.* **1967**, 70, 307. (b) Lewis, D.; Sarr, M.; Keil, M. *J. Phys. Chem.* **1974**, 78, 436.

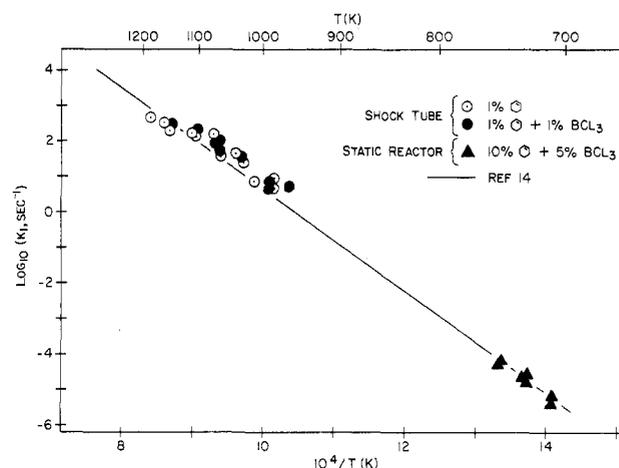


Figure 5. First-order rate constants for cyclohexene decomposition.

believed to be present in minor amounts but were not resolved and quantified.¹²

Rate constants were calculated from cyclopentene and cyclopentadiene concentrations in product samples via eq 2, as described above, and are displayed in Figure 4. As in the cyclobutane study, temperatures were calculated from incident shock wave velocities; heat capacity polynomials for cyclopentene and BCl_3 , required for shock speed–temperature relationship calculations, were obtained from vibrational frequencies in the literature.^{10,13}

As is evident from Figure 4, the rate constants for cyclopentene dehydrogenation, in samples with and without BCl_3 , were as expected for the homogeneous unimolecular reaction. There were, however, small but significant differences in concentrations of some side products, comparing runs with and without catalyst. On one day, samples run with BCl_3 produced larger amounts of ethene and propene, smaller amounts of butadiene, and approximately equal amounts of propyne and allene; differences were less than a factor of 2. On a second day of runs, 1 week later, using the same two reactant mixtures, concentrations of all side products from runs with catalyst were slightly smaller than from runs without catalyst. No direct cause of these small differences was evident.

Cyclohexene—Static Reactor Study. Chromatographic analysis of reactant samples showed no evidence of reaction with BCl_3 , at room temperature. After heating, product samples were found to contain primarily ethene, butadiene, and unreacted cyclohexene, with trace amounts of cyclohexadienes. First-order rate constants were calculated from butadiene and cyclohexene concentrations in product samples and are shown in Figure 5, along with the Arrhenius line $\log k = 15.15 - 66560/4.58T$, for the homogeneous uncatalyzed reaction, as deduced from static reactor^{14a} and shock tube^{14b} studies. There is no evidence of BCl_3 catalysis of the primary or secondary reactions of cyclohexene, under the conditions of this study.

Cyclohexene—Shock Tube Study. When the uncatalyzed mixture was shock heated to temperatures up to 1110 K, the only observed products were ethene and 1,3-butadiene; at higher temperatures, traces of methane and propene were also observed. Results with the catalyzed mixture were generally similar, except that traces of methane were evident in product samples at all temperatures, and some ethyne was also produced at the highest temperatures. From previous work with cyclohexene,¹⁵ we know that traces of cyclohexadienes and benzene (and H_2 , which cannot be detected by the GC system used) are also produced from cyclohexene pyrolysis at high temperatures. Since the retention

(12) These side products have been quantified in a subsequent study: Lewis, D.; Batchelor, P.; VanPraagh, A.; Kalra, B., in preparation.

(13) Furuyama, S.; Golden, D.; Benson, S. W. *J. Chem. Thermodyn.* **1970**, 2, 161.

(14) (a) Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, 68, 1878. (b) Tsang, W. *J. Chem. Phys.* **1965**, 42, 1805.

(15) Lewis, D.; Siegal, M.; Williams, L., unpublished.

times of these organic species are very long in the column used for measuring ethene and butadiene, these species, and the influence of BCl₃ on their rates of production, were not monitored.

Temperatures behind reflected shocks were calculated from incident shock velocities. Shock speed-temperature relationships were estimated from the previously calculated values for cyclopentene and cyclopentene/BCl₃ mixtures, assuming 1% cyclohexene = 1.2% cyclopentene to compensate for the differences in heat capacities. Integrated first-order rate constants were calculated from eq 2, with C_0 = % cyclohexene in unshocked mixtures, and C = C_0 - % 1,3-butadiene in post-shock samples. The resulting data are shown in Figure 5. Again, the runs with and without BCl₃ are well mixed; BCl₃ does not significantly affect the primary decyclization of cyclohexene under the conditions of this study.

Discussion

The results of this work may be summarized as follows. In the temperature/pressure ranges covered in the static reactor experiments, the structural isomerization of cyclopropane to propene was the only reaction accelerated by BCl₃. Neither primary nor secondary reactions of cyclobutane, cyclopentene, or cyclohexene were observed to be influenced in any important way by BCl₃. For the cyclopropane isomerization, second-order rate constants were similar to those reported earlier by Stimson and co-workers.¹ A lower activation energy was deduced in the present study; the standard deviations of E from the former work (± 0.4 kcal/mol) and the present work (± 2.0 kcal/mol) are sufficiently large that the E values are different at the 68% confidence level but not the 95% level. Another plausible interpretation is that the lines in Figure 1 are parallel, within experimental error, and that one static reactor study or the other was subject to a systematic temperature error of a few (≤ 10) degrees, resulting in the slight leftward or rightward displacement of one set of data from the other. HCl is a trace contaminant in CP-grade BCl₃, and additional amounts of HCl may be formed in reaction mixtures as a result of reaction of BCl₃ with water adsorbed on metal surfaces. However, the Brønsted acids have been found to be less effective catalysts than the corresponding Lewis acids (HCl vs. BCl₃; HBr vs. BBr₃),¹ so the presence of small to moderate quantities of HCl should have had no significant effect on reaction rates in the two studies being compared.

At the higher temperatures achieved behind reflected shocks, in the previous study of cyclopropane³ and in the present work, the primary reactions of all four subject molecules appeared to be unaffected by the presence of BCl₃. In the case of cyclopropane (or the other reactants, for that matter), this does not mean that the catalyzed reaction did not occur at all; it only means that any catalyzed process proceeded at a rate too slow to appreciably increase the overall rate of reaction. As noted previously,³ pseudo-first-order rate constants for the BCl₃-catalyzed cyclopropane isomerization at temperatures and densities of the shock tube study, predicted from Johnson and Stimson's data,¹⁸ lie at least 1 order of magnitude below true first-order rate constants for the unimolecular reaction. The catalyst did appear to influence the production of side products somewhat, especially at the higher temperatures studied. In the previously reported cyclopropane study,³ relatively minor changes in amounts of various side products were noted above 1300 K, where substantial quantities of radicals are no doubt present. No side products were observed from cyclobutane pyrolysis, because of the relatively low temperature range to which experiments were restricted. With cyclopentene, small differences in amounts of side products were again noted, with and without BCl₃, but they could not be reproduced from day to day. Since the cyclopentene used in both mixtures came from the same bulk sample and distillation process, it is unlikely that an organic contaminant is the cause. If any HCl were present in the BCl₃, dissociation at $T > 1150$ K could induce additional decomposition of cyclopentene in the catalyzed mixture, via previously described mechanisms.^{11b,16} Alternatively,

a small air leak into one or the other mixtures might have caused the difference. The slight but reproducible increase in side products from cyclohexene pyrolysis with added BCl₃ is not presently explained. Possibly the ethyne is due to enhanced production of 1,4-cyclohexadiene, and subsequent symmetry-allowed decomposition of that species;¹⁵ this is a question to be resolved in future work.

The reader will note, in Figures 2-5, the apparent falloff of unimolecular rate constants at the highest temperatures. This observation, due to a combination of true unimolecular falloff and experimental errors that magnify at high temperatures (i.e., at large extents of reaction in a fixed reaction time device), is familiar in shock tube data and has been addressed previously.³ Its presence in no way clouds the conclusions presented above. It also will be noted that the shock tube data in Figure 5 lie slightly above the line representing earlier studies.¹⁴ This is believed to be a systematic error in the present analyses, due either to estimations used in developing the shock speed-temperature relationships or to the method of calculating C and C_0 in eq 2. In the cyclohexene work, C_0 was calculated from an unshocked sample, C from a shocked sample; in all other studies, both C and C_0 were calculated from relative percentages of two species in a single shocked sample.

The selectivity exhibited by acid catalysts such as BCl₃ toward certain molecules and reactions may, when extended to a broader range of examples, have commercial utility. This selectivity may also be of some help in answering mechanistic questions.

The mechanism of acid catalysis of cyclopropane \rightarrow propene has long been in question. The uncatalyzed reaction has been interpreted as occurring via (a) a C-C bond cleavage to form a diradical, followed by (b) a hydrogen atom migration to form the product;¹⁷ deuterium labeling studies have shown $k_a/k_b \sim 7$,¹⁸ establishing the latter process as essentially rate limiting. Early catalysis studies with HBr¹⁹ led to the suggestion that the catalyst was facilitating the atom transfer by forming a four-center transition state. However, it has since been determined that DBr accelerates cyclopropane isomerization without producing deuterated propene²⁰ and that BCl₃ and BBr₃ are even more effective catalysts than the hydrogen halides.¹ Thus, the catalysis seems to occur via the formation of Lewis acid-base adducts which cause sufficient polarization of the reactant to facilitate reaction.¹ But the following questions remain: What are the structures and energetics of these complexes, and how do they facilitate the cyclopropane isomerization while not affecting many other hydrocarbon reactions?

Recently, two methods have been used to detect and characterize complexes of cyclopropane with hydrogen halides. Buxton et al.²¹ and Legon et al.²² obtained rotational (microwave spectroscopy) spectra for CP-HF and CP-HCl complexes, respectively. These complexes were observed to have C_{2v} structures, with the HX proton lying between the halogen atom and the cyclopropane ring, along a line bisecting the carbon-carbon axis. The nature of interaction is apparently hydrogen bonding between the electrophilic H-X proton and the electron density lying outside, and in the plane of, the cyclopropane ring.

Truscott and Ault²³ have also found evidence for the formation of complexes containing one or two HCl or HBr molecules with cyclopropane, from infrared spectra via the matrix isolation technique. Although structures have not been deduced from these spectra, the shifts in certain frequencies suggest an interaction

(17) See, for example: Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972; pp 185-93.

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

(19) Ross, R. A.; Stimson, V. R. *J. Chem. Soc.* **1962**, 1602.

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

(21) Buxton, L. W.; Aldrich, P. D.; Shea, J. A.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75* (2681).

(22) Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1486.

(23) Truscott, C. E.; Ault, B. S. "Matrix Isolation Investigation of the Catalytic Isomerization of Cyclopropane by the Hydrogen Halides"; presented at the 186th National Meeting of the American Chemical Society, Washington, DC, 1983; Physical Chemistry Paper No. 42; *J. Phys. Chem.*, in press.

consistent with that deduced from the microwave data.

While there is clear-cut evidence for the formation of halogen acid dimers with cyclopropane at room temperature and below, it cannot yet be concluded that the formation of dimers of the type characterized is associated with the mechanism of catalysis at higher temperatures. Circumstantial evidence might be provided by searching for similar acid complexation with cyclobutane, cyclopentene, and cyclohexene. If adducts do not form with these molecules, this would lend weight to the supposition that the CP-HX dimers facilitate the isomerization. Conversely, the existence of similar adducts with molecules not subject to acid catalysis would suggest that the CP-HX structures are not related to the mechanism of catalysis. Thus, microwave and infrared spectroscopic studies of other reactant-HX systems should prove informative.

Another interesting mechanistic question is raised by the present study. Evidence is strong, though not conclusive, that the uncatalyzed cyclopropane isomerization occurs via formation of a diradical species, as mentioned above.^{17,18} Cyclopentene dehydrogenation seems to be the best understood of the four reactions under present consideration. The symmetry-allowed, concerted 3,5 elimination dominates at low temperatures,²⁴ and symmetry-disallowed (if concerted) 3,4 elimination becomes competitive at higher temperatures.²⁵ In contrast, the mechanisms of cy-

clobutane and cyclohexene decompositions are less well understood. For cyclobutane, the bulk of experiments and calculations seem to favor a diradical mechanism over either a symmetry-disallowed concerted fragmentation or a symmetry-allowed concerted fragmentation from an excited state.²⁶ With cyclohexene, arguments seem predominantly to favor the concerted reverse Diels-Alder mechanism over the diradical path.²⁷

If cyclopentene and cyclohexene decompositions are concerted processes and cyclopropane isomerization proceeds via a diradical, then the absence of acid catalysis in the former two reactions may not be surprising. However, if cyclobutane decomposition is also a diradical process, then the total absence of the catalytic effect seems puzzling; it will be even more so if it is subsequently found that the CP-HX dimers characterized are important in the mechanism of catalyses and that cyclobutane forms similar complexes with Lewis acids.

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Registry No. BCl₃, 10294-34-5; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentene, 142-29-0; cyclohexene, 110-83-8.

(24) (a) Baldwin, J. E. *Tetrahedron Lett.* **1966**, 2953. (b) Anet, F. A. L.; Leyendecker, F. J. *Am. Chem. Soc.* **1973**, *95*, 156.

(25) Lewis, D. K.; Greaney, M. A.; Sibert, E. L. *J. Phys. Chem.* **1981**, *85*, 1783.

(26) Reference 17, pp 247-9.

(27) Moore, J. W.; Pearson, R. W. "Kinetics and Mechanism"; Wiley-Interscience: New York, 1981; pp 211-2.

Thorough Study of Bromide Control in Bromate Oscillators. 1. The Effect of Bromo-Complex-Forming Metal Ions

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Bromo-complex-forming metal ions (Tl³⁺, Hg²⁺) affect the function of bromate oscillators considerably. Already at a few times 10⁻⁵ M metal ion concentration the period of chemical oscillation is doubled or tripled, and at 10⁻⁴ M chemical oscillation is completely quenched. The phenomenon was explained in terms of the bromide-buffer property of the thallium(III)-containing system. Above 10⁻³ M Tl(III) concentration high-frequency oscillations appear which are prolonged the higher the bromate concentration of the reacting BZ system. A detailed study was performed on dynamic bromide concentration conditions prevailing in the oscillatory systems. The accumulation of bromide could be followed when Tl(III) was present and the rate of the overall chemical reaction calculated. A method was developed to measure the amount of bromide formed in a single oscillatory step. This value depends on the chemical composition of the reacting system usually lying between 10⁻⁴ and 10⁻⁵ M.

Introduction

Of the chemical oscillators most experimental data are available on bromate oscillators. So far the cerium(III), bromate, malonic acid, and sulfuric acid reacting system—the Belousov-Zhabotinsky (BZ) reaction—has been investigated most thoroughly and the detailed mechanism of the BZ reaction has been elucidated on the basis of kinetic measurements on this system.¹

An important characteristic of the chemical mechanism suggested for the BZ system is that a key role is attributed to bromide ion, an intermediate of the reaction. In one of his early publications Zhabotinsky has already pointed to the significant role of bromide since he had found that the oxidation of cerium(III) with bromate—an essential composite reaction of the BZ reacting system—is an autocatalytic process and can be inhibited by

bromide.² Zhabotinsky assumed that in a system also containing malonic acid the bromide ion concentration varied in time periodically between two extreme values, but at that time he could not prove his assumption experimentally.³ This assumption prompted Noyes, Field, and one of the authors of the present publication (E.K.) to deal with this issue early during their investigations on the BZ reaction. A bromide-selective electrode immersed into a reacting BZ system showed that temporal periodic change of the bromide concentration, and the very characteristic $p[\text{Br}^-]$ vs. time traces contributed considerably to the elaboration of a chemical mechanism, nowadays referred to as the FKN mechanism.¹

Both in the catalyzed bromate oscillators, according to the FKN mechanism, and in the uncatalyzed bromate oscillators, according

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