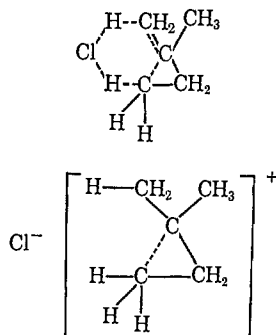Maccoll, et al.,[3] for the hydrogen halide catalyzed dehydration of alcohols,[6] for the hydrogen bromide catalyzed isomerization of but-1-ene,[11] and for the pyrolysis of 1-chloro-cis-but-2-ene.[17] Transition states of this type may be quasi-heterolytic[3] as represented by II in the case of the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

(17) P. G. Rodgers, Ph.D. Thesis, University of London, 1966.
(18) B. S. Rabinovitch, F. W. Schlag, and K. B. Wiberg, J. Chem. Phys., 28, 504 (1958); B. S. Rabinovitch and F. W. Schlag, J. Amer. Chem. Soc., 82, 5996 (1960).
(19) J. P. Chesick, ibid., 82, 3277 (1960).

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.

(20) D. H. R. Barton and K. E. Howlett, J. Chem. Soc., 155 (1949).

Shock Tube cis–trans Isomerization Studies

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Contribution from the Department of Chemistry, State University College, Cortland, New York 13045. Received June 11, 1969

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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(2) G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc., 56, 638 (1934).
(3) G. B. Kistiakowsky and W. R. Smith, ibid., 58, 766 (1936).

(4) W. F. Anderson, J. A. Bell, J. M. Diamond, and K. R. Wilson, ibid., 80, 2384 (1958).
(5) B. S. Rabinowitch and K. W. Michel, ibid., 81, 5065 (1959).
(6) R. B. Cundall and T. F. Palmer, Trans. Faraday Soc., 57, 1936 (1961).
(7) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., J. Chem. Phys., 38, 2056 (1963).

rates allowed determination of reasonable Arrhenius parameters.

$$k_{cis}{}^{\infty} = 3.5 \times 10^{14} \exp(-65,000/RT)$$

There are additional theoretical interests in these isomerizations. Lin and Laidler[8] considered the effect of back-reaction of activated, newly isomerized molecules on the apparent collision efficiency. They also observed a correlation[9] between the activation energy for isomerization and heat of hydrogenation of the corresponding double bond, and between the heats and entropies of activation.

Shock tube experiments have the attractive feature of assuring a completely homogeneous gas-phase reaction. This feature is especially important in view of the difficulties already cited which are encountered using conventional techniques for isomerization studies. *cis–trans* interconversions appear to be excellently suited for investigation by the relative rate method developed by Tsang[10] which leads to low experimental scatter in the rate data.

Experimental Section

The single-pulse shock tube[10] was constructed of heavy walled 0.75-in. i.d. Pyrex tubing. It is believed to be the smallest shock tube reported in the literature. The test section was 112 cm in length and the driver length, which was adjustable, was set at 45 cm for proper tuning in the pressure range of this study. The test and driver sections were attached by brass flanges (epoxyed to the glass) to an Al block. Also entering the block at right angles to the shock tube were the sample inlet and the connection to a 15.8-l. stainless steel dump tank. The dump tank was located 5 cm downstream from the diaphragm. The sample inlet and dump tank could be isolated from the tube with Worcester ball valves, and the dump tank could also be independently evacuated and filled from its other end. O rings were used at all joints, with the diaphragm held between one O ring in the Al block and another in the brass flange of the driver. The shock tube terminated in a brass end block which had a BaTiO₃ crystal mounted in the end wall for pressure trace monitoring. A 2-mm hole in the side of the end block led to a small valve and a standard taper joint by means of which 10-cc glass sample bulbs could be attached. The shock tube was evacuated to less than 1 μ with a conventional glass vacuum system and a Hg diffusion pump. The leak rate was considerably less than 1 μ/min for the entire system.

Platinum heat-transfer gauges were painted on the inside of the tube and leads of silver paint were extended around the end of the glass and under the brass flange. The gauges and leads were "fired" onto the glass in an annealing oven.

Output from the film gauges was amplified and superposed on a raster executed by one beam of a Tektronix 565 oscilloscope. The signal from the pressure crystal was displayed by the other beam and was also fed into the raster. Ten-microsecond time marks generated by a small crystal oscillator allowed accurate determination of the time between gauge signals. (Schematics of the raster mechanism, all amplifiers, and the oscillator are available upon request.) Determination of shock speeds was not essential since use of the relative rate method eliminated the need for estimating temperature. However, the calculated shock temperatures served as a useful check on the proper operation of the system.

Materials. Fisher certified *t*-butyl alcohol was recrystallized numerous times before use. The *cis*- and *trans*-2-butene were Phillips research grade; the former contained 0.08% of the *trans* isomer. *cis*- and *trans*-difluoroethylene were supplied by Penninsular Chemresearch. They contained 0.39 and 0.20% of the other isomer, respectively. The isobutylene for vpc calibration purposes was supplied by Air Products. The argon was Linde High Purity grade, as was the He used for the driver gas.
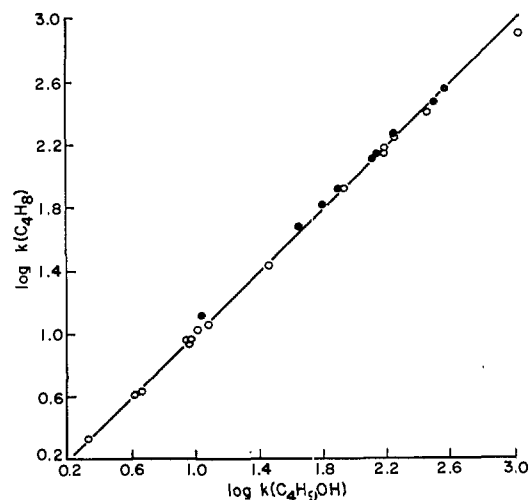
(8) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 94 (1968).
(9) M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **46**, 973 (1968).
(10) W. Tsang, *J. Chem. Phys.*, **40**, 1171 (1964); **41**, 2487 (1964); **42**, 1805 (1965); **43**, 353 (1965); **44**, 4283 (1966).

Figure 1. Plot of log $k(cis \rightarrow trans)$ for 2-butene vs. log k for *t*-butyl alcohol dehydration: O, 1% of each reactant; ●, 0.1% of each reactant.

Analysis. All analyses were performed with a Hewlett–Packard 5750 gas chromatograph using a flame ionization detector. All the products could be separated by a 0.25 in. × 6 ft AgNO₃-saturated ethylene glycol column in a series with a ¹/₈ in. × 12 ft 10% UCW98 column. The Argon carrier gas flow rate was 40 ml/min.

Ten-cubic centimeter samples extracted from the shock tube at 100–300 Torr were compressed to 1 atm by a Hg transfer system, and samples of 0.1–0.5 cc were injected with a gas syringe into the chromatograph. Amounts as small as 10⁻¹⁰ mole could be detected. The analysis was based on peak height measurements. The calibration was frequently checked against carefully prepared standard samples. Each sample was analyzed three or four times and the results were averaged.

Shock Experiments. Reagent mixtures were prepared manometrically, and subsequently were diluted with argon. Concentrations of reactants varied from 2 to 0.02%. Initial total pressures in the test section ranged from 100 to 200 Torr. The diaphragms were made of 0.5 mil Mylar and these ruptured consistently at about 48 psig. The density ratio of the shocked to the unshocked gas was in the range 4.2–5.2, and the temperatures were 1040–1350°K. Residence times in the reflected shock were 220–300 μsec. Ten-cubic centimeter samples for analysis were withdrawn immediately after the shock.

Calculations. Rate constants for the unimolecular *t*-butyl alcohol dehydration were evaluated using the integrated rate expression for a first-order nonreversible reaction. Rate constants for both *cis–trans* isomerizations were obtained through use of the integrated equation for a reversible first-order process. Equilibrium constants used for the *cis* → *trans* reactions were[11,12] $K(C_4H_8) = 2.37$ and $K(C_2H_2F_2) = 0.66$.

Results

2-Butene Isomerization. Two sets of shocks were run with mixtures of *t*-butyl alcohol and *cis*-2-butene; they were 1–1% and 0.1–0.1% of the reactants in argon. The calculated rate constants are shown in a relative rate plot (see Figure 1). On such a plot of log k_y vs. log k_x, the slope is, assuming $k = Ae^{-E_a/RT}$

$$m = \frac{\Delta Y}{\Delta X} = \frac{\log k_{y_2} - \log k_{y_1}}{\log k_{x_2} - \log k_{x_1}} =$$

$$\frac{\dfrac{-E_{a_y}}{2.3R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)}{\dfrac{-E_{a_z}}{2.3R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = \frac{E_{a_y}}{E_{a_z}} \quad (1)$$

(11) R. E. Duff and S. H. Bauer, *ibid.*, **36**, 1754 (1962).
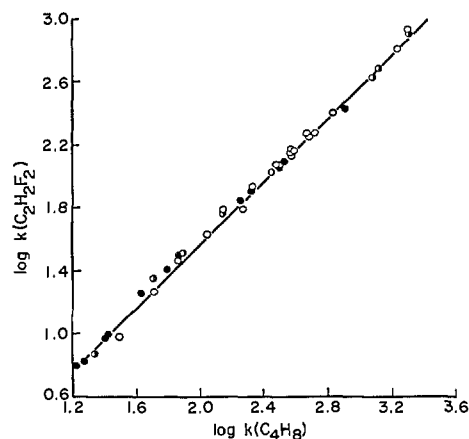(12) N. C. Craig and E. A. Entemann, *J. Am. Chem. Soc.*, **83**, 3047 (1961).

Figure 2. Plot of log $k(cis \rightarrow trans)$ for $C_2H_2F_2$ vs. log $k(cis \rightarrow trans)$ for 2-butene: ●, 1–2%; ◑, 0.1–0.2%; ○, 0.02–0.02% of C_4H_8 and $C_2H_2F_2$, respectively.

If the equation of the linear plots is $y = mx + b$, then

$$b = y - mx = \log A_y - (E_{a_y}/2.3RT) -$$
$$m[\log A_x - (E_{a_x}/2.3RT)] =$$
$$\log A_y - m \log A_x \quad (2)$$

Thus if E_{a_x} and A_x are known, the measured values of m and b give E_{a_y} and A_y. The slope of Figure 1 is 1.00 and the y intercept is 0.02. The value for t-butyl alcohol dehydration of $k = 10^{13.40}e^{-61,600/RT}$ sec^{-1} was taken from Tsang.[13] On this basis one finds, for cis-2-butene isomerization, $k = 10^{13.38}e^{-61,600/RT}$ sec^{-1}. The data are sufficiently precise to determine the slope to ±0.02 and, therefore, E_a to ±1.2 kcal. This then determines log A to within ±0.2.

Reflected shock temperatures for these experiments can be found from the measured 2-butene rate constants; the range is 1040–1325°K. These temperatures are slightly higher than those in the previous single pulse shock tube investigation of 2-butene isomerization,[7] but since the residence times with the 0.75-in. tube are significantly shorter than those measured with the 1-in. tube,[7] per cent conversions are comparable. Rate constants found in this investigation fall on the lower boundary of the log k vs. $1/T$ points presented by Lifshitz, Bauer, and Resler,[7] but show considerably less scatter.

The density ratio of reflected shock gas to unshocked gas is about 5. Thus, one finds the total pressure in the shock tube under reaction conditions to be 2000–2500 Torr. Even with a low collision efficiency for argon, all the reactions studied took place well within the high-pressure unimolecular region.

Difluoroethylene Isomerization. Both the $cis \rightarrow trans$ and $trans \rightarrow cis$ isomerization rates of 1,2-difluoroethylene were measured relative to that for $cis \rightarrow trans$ isomerization of 2-butene (see Figures 2 and 3). The cis-$trans$ mixtures investigated were 1–2, 0.1–0.2, and 0.02–0.02% C_4H_8 and $C_2H_2F_2$, respectively, while $trans \rightarrow cis$ mixtures used were 1–1, 0.1–0.1, and 0.04–0.04%. On the basis of the value cited above for 2-butene isomerization, one finds for $C_2H_2F_2$, $k(cis \rightarrow trans) = 10^{13.17} \cdot e^{-62,800/RT}$ sec^{-1} and $k(trans \rightarrow cis) = 10^{12.93}e^{-60,100/RT}$ sec^{-1}. Error limits for A and E_a in both sets are the
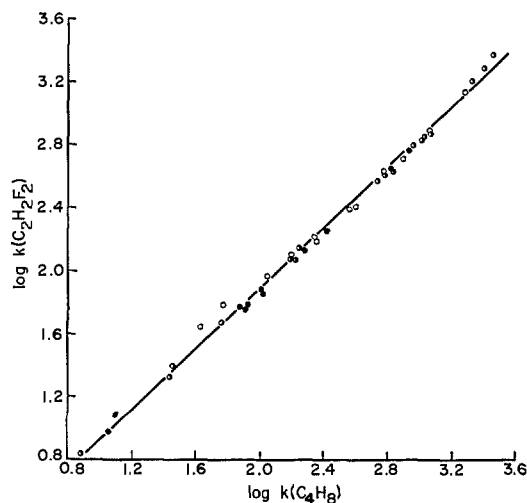
(13) W. Tsang, *J. Chem. Phys.*, **40**, 1498 (1964).

Figure 3. Plot of log $k(trans \rightarrow cis)$ for $C_2H_2F_2$ vs. log $k(cis \rightarrow trans)$ for 2-butene: ●, 1% of each reactant; ◑, 0.1% of each reactant; ○, 0.04% of each reactant.

same as were given for 2-butene. The rate constants listed graphically represent between 0.2 and 20% conversion, with most runs under 10% conversion. The lower limit was set by the analytical sensitivity, while at conversions above about 25% significant amounts of side products appeared. Below 20% conversion a mass balance was obtained and the amount of side products was negligible. The data were not edited, other than by per cent conversion. All shock experiments in each of the sets are incorporated in the figures.

Discussion

The accuracy of rate constants determined by relative methods is obviously no better than that of the constant which is used as reference. Tsang[13] estimates a maximum error of 7% in E_a for t-butyl alcohol dehydration. However, his value is supported by the excellent agreement between E_a determined in this study for 2-butene isomerization and the most reliable results in the literature;[5,6] the present value of 61.6 kcal is about 1.5% lower. The A coefficient ($10^{13.38}$) is smaller by a factor of 3 or 4 than was found in the conventional studies, but with $E_a = 61.6$ kcal, values for log A of 12.81 and 13.76 can be calculated from the low T investigations, and the present result is bracketed by these. An activation energy of 61.6 kcal fits almost perfectly on Lin and Laidler's plot[9] of E_a vs. $\Delta H°$ (hydrogenation), while the A factor of $10^{13.38}$ allows a reasonable fit on the $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$ plot. Thus it is reasonable to use the Arrhenius parameters found for the 2-butene isomerization as a basis for 1,2-difluoroethylene. The 2-butene is preferable to t-butyl alcohol as a reference since water formed by the dehydration might react with the fluorinated compounds at elevated temperatures. The ratio of forward to reverse rate constants for $C_2H_2F_2$ isomerization gives log $K = 0.19–589/T$ for 1040–1325°K. This value compares reasonably well with Craig and Entemann's[12] result of log $K = 0.03–202.8/T$ for the range 477–762°K. From the experimental activation energies one finds $\Delta H°_{1200} = 2.7$ kcal, which compares well, within the accuracy cited for the kinetics experiments, with 0.93 kcal found in the equilibrium study.[12] The frequency factors for forward and reverse reactions are almost equal, within experimental error; hence the

equilibrium constant is essentially an enthalpy effect, with *cis* being the thermodynamically more stable, in agreement with Craig and Entmann's findings. The heat of hydrogenation for $C_2H_2F_2$ is not known, but could be established from the experimental activation energies and Lin and Laidler's correlation[6] that $E_a \sim 2(-\Delta H°hyd)$.

A recent study of propylene-1-d_1 isomerization[14] gave $k(cis \rightarrow trans) = 10^{13.16}e^{-61,300/RT}$ sec^{-1}. An A factor of 10^{13} has been estimated[15] for $C_2H_2D_2$ isomerization. Hence the value of $10^{13.17}$ for $cis \rightarrow trans$ isomerization of $C_2H_2F_2$ is quite reasonable.

An interesting kinetic system for comparison is N_2F_2, for which a shock tube isomerization study[16] led to a *cis–trans* rate constant of $10^{14} \exp(-32,000/RT)$ sec^{-1}. Although this value was based on just five data points and the activation energy value is not well established, isomerization involving a linear transition state is possible for N_2F_2; and this might well allow a lower energy process than is possible with the twisted transition state which operates in carbon double bond systems.

Schlag and Kaiser[17] have measured *trans–cis* isomerization rates in perfluorobutene-2 and found a unimolecular constant of $k = 10^{13.53}e^{-56,400/RT}$ sec^{-1} over a range of 705–750°K. They explain the lower activation energy, relative to 2-butene, as due to destabilization of the π system caused by inductive effects of the adjacent F atoms. It is surprising, then, that difluoro-ethylene has essentially the same activation energy for isomerization as has 2-butene. Examination of perfluoro-2-butene by the shock tube relative rate method thus appears justified, since results in the same temperature range which are obtained by use of the same experimental techniques should be readily comparable.

Flowers and Jonathan[14] have called attention to the small amount of reliable data on geometrical isomerization, and the authors of the references cited above discuss the difficulty of separating the homogeneous isomerization reaction from significant contributing heterogeneous or bimolecular processes. The shock tube technique has been shown in this study to allow rather direct and uncomplicated access to the unimolecular high-pressure regime. Relative rate measurements eliminate much of the usual scatter in the experimental data (mostly the scatter is due to imprecise reflected shock temperature) and also simplify requirements for, and thus construction of, the shock tube. The instrument described in this paper was built entirely by the authors, using only a scantily equipped machine shop, at a total cost of under $1500, excluding oscilloscope and chromatograph. This sort of instrument and study could easily be adapted to advanced undergraduate laboratory work.

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Catalytic Recombination of Oxygen Atoms on Metal Surfaces in the 10⁻⁴–10⁻⁶ Torr Pressure Range

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Abstract: Reaction kinetic studies were made at 10⁻⁴–10⁻⁶ Torr total pressure on the recombination of oxygen atoms on metal surfaces. A flow system using an auxilliary reaction system at 0.1–1 Torr was used as an oxygen atom source with 10–20% oxygen mixed with argon. The ratio of O/O_2 varied from 2 to 1/2. Initially, ozone production over a long period of time was assumed equivalent to the O atoms surviving the reaction chamber. Chemiluminescence was observed and used as a measure of oxygen atoms. A technique was developed for rapid determination of recombination efficiencies (γ) for O atoms on various metal surfaces. Results for a variety of test specimens are presented. The sensitivity for O-atom detection for these methods is limited to a partial pressure of O atoms of 10⁻⁸ Torr.

Numerous investigators have performed experiments to detect and measure the heterogenous atom recombination on surfaces. Although the experimental procedures employed varied widely in detail, they may be classified according to the method by which the gaseous atom density was estimated. Direct measurements of atom density have been made using the Wrede–Harteck gauge,[1–4] the reduction of molybdenum trioxide by gaseous hydrogen atoms,[5] and more recently paramagnetic resonance.[6–9] Indirect methods of es-

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