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VIBRATIONAL ENERGY TRANSFER IN A DIFFUSION FLOW CYCLOPROPANE-D2--ETC(U)

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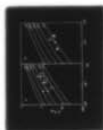


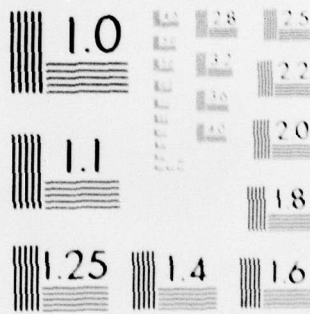
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Vibrational Energy Transfer in a Diffusion Flow Cyclopropane-d₂ System.

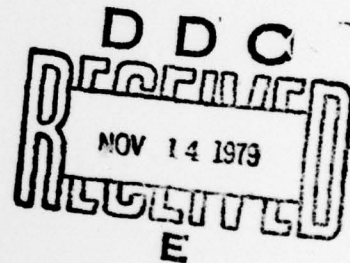
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Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane-d₂ System^a

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Abstract

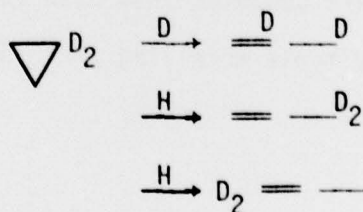
In a previous paper (ref. 2), the diffusion cloud technique was applied to the cyclo-C₃H₆ isomerization system. Vibrational energy transfer upon collision was measured. Relative reaction rates were measured and, by calibration from other work (ref. 3), were converted to absolute rate constants. In the present study, absolute rate constants for cyclopropane-d₂ were determined in a diffusion-flow system. The relative rates of the competitive isotopic isomerization channels were measured for two bath gases, N₂ and He, at two temperatures, 973K and 1073K. Values of the average energy down-jump size $\langle \Delta E \rangle$ were computed from both the absolute rates and the isotopic relative rates by suitable modelling (ref. 3).

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Introduction

The diffusion cloud technique¹ has been used by us to measure vibrational energy transfer for cyclopropane in an earlier study.² In that work, only relative rate constants could be determined and a calibration of rates derived from other work³ was used to find absolute values. In the work reported in this study, we have modified the diffusion cloud apparatus in order to make total collection of all of the sample that issues from the reactor. In this way, some rate measurements have been made under similar reaction conditions to those used in the previous study. This has permitted a direct test of the previously used calibration.

We have simultaneously extended the study to the measurement of competitive isotopic rates by use of the substrate 1,1-cyclopropane-d₂. Isotopic rate effects in this system have previously been studied in static and flow reactors.^{3,4} Due to the fast transport in the diffusion cloud apparatus, higher temperature effects can be studied. The unimolecular isomerization of 1,1-cyclopropane-d₂ proceeds as follows:



where the migrating atom is shown.

In the present note, absolute rates and comparative isotopic rates are reported for two bath gases, N₂ and He, at two temperatures, 973K and 1073K. Vibrational energy transfer amounts were computed from these measurements.

Experimental

Apparatus and Procedure. The diffusion cloud apparatus has been previously described.² Flow velocities in the reactor were varied between 8-45 cm sec⁻¹. The apparatus was modified slightly by inclusion of two liquid nitrogen-cooled traps, a large (50 mm diameter) glass trap followed by a stainless steel protective trap, between the diffusion chamber and the main Roots pump. In this way, all products and remaining reactant were trapped. The glass trap could be isolated by two 1-inch brass Veeco bellows valves, then warmed, and the product-reactant mixture transferred and collected through a separate side-line. It was analyzed by GC using a 500 ft 30% 3M AgNO₃/ethylene glycol-Chromosorb P column to separate the deuteropropene isomers and cyclopropane.

Treatment of Data. GC analysis of the reaction mixture yielded three peaks which corresponded to the three isomers of dideutero propylene (1,1-propylene-d₂, 3,3 propylene-d₂ and 2,3 propylene-d₂). The ratio of rate constants due to D-migration and H-migration was determined from the simple expression,

$$\frac{k(D)}{k(H)} = \frac{C(2,3\text{-propylene-d}_2)}{C(1,1\text{-propylene-d}_2) + C(3,3\text{-propylene-d}_2)}$$

where C is the experimentally determined product concentration.

The absolute rate constant for total reaction was calculated using a method described in detail by Mulcahy⁵ for flow reactors. By this method, one first calculates the rate constant assuming a flat velocity profile and no diffusion effects, according to the equation,

$$k_{app} = - \ln[C(\text{cyclopropane}) / (C(\text{cyclopropane}) + C(\text{propylene}))] / t_c$$

where C is the experimentally determined concentration and $C(\text{propylene})$ is the total concentrations of all three propylene isomers; t_c is the nominal contact time of the reactant in the reaction chamber. Corrections to k_{app} are then added to provide the true rate constant, where the correction is a function of the apparatus constants and molecular properties (diffusion coefficient) and may be determined from a graph that is presented by Mulcahy. The application of these corrections has been described in greater detail in ref. 4.

Results

Experiments were performed at two temperatures 973K and 1073K using two flowing bath gases, helium and nitrogen. Experimentally determined $k(D)/k(H)$ are shown in Fig. 1 as a plot against the specific collision rate ω . Experimentally determined total rate fall off constants are plotted in Fig. 2. The fall-off curves were computed with a step-ladder probability distribution model using a stochastic calculation.^{3,6} Model parameters for RRKM calculations are described in App. 1.

Absolute Rates. The absolute rates determined in this paper overlap those of ref. 1 at 973K. They are in general agreement with, but somewhat higher, than those determined by Kamaratos et al. Here, for nitrogen, the rate constant is 0.18 (or 0.24 sec^{-1}) with inclusion of a high value at 1 torr and 0.26 sec^{-1} at 2.2 torr, as compared with 0.13 sec^{-1} at 1 torr and 0.23 sec^{-1} at 2.1 torr, as measured earlier. For helium, the rate constant is 0.12 sec^{-1} at 0.8 torr and 0.22 sec^{-1} at 2.2 torr, as compared to the previous values 0.065 sec^{-1} at 1.0 torr and 0.14 sec^{-1} at 2.1 torr. The present results check the previously used calibration derived from another system³ within useful, although not high, precision.

Collisional Efficiency. The $k(D)/k(H)$ data (Fig. 1) give $\langle \Delta E \rangle_d$, the average energy down jump, to be about equal for helium and nitrogen. At 973K, $\langle E \rangle_d$ equals 600 cm^{-1} for both nitrogen and helium. At 1073 K, $\langle E \rangle_d$ for nitrogen is 550 cm^{-1} and for helium it is 650 cm^{-1} . The fall off data (k/k_∞) (Fig. 2), gives slightly different $\langle \Delta E \rangle_d$: at 973K, $\langle E \rangle_d$ for nitrogen is 550 cm^{-1} and $\langle E \rangle_d$ for helium is 400 cm^{-1} . At 1073K, $\langle E \rangle_d$ nitrogen is 300 cm^{-1} and for helium is 450 cm^{-1} . Thus, the values for nitrogen are in good concordance by the two methods, with the average values being $\langle \Delta E \rangle = 575 \text{ cm}^{-1}$ at 973K and 425 cm^{-1} at 1073K. The corresponding average values for helium are 500 cm^{-1} for He, at 973K, and 550 cm^{-1} , at 1073K. The value for helium is high, especially at 1073K, and simply reflects experimental error.

Discussion

In the previous diffusion cloud paper,² energy transfer was studied for a variety of gases. In that paper at 975K, $\langle E_d \rangle$ for nitrogen was $450 \pm 150 \text{ cm}^{-1}$ and $190 \pm 50 \text{ cm}^{-1}$ for helium. The nitrogen results here seem to agree very well. The helium results here are evidently somewhat too high. But, nonetheless, the data reveal that comparatively low collisional efficiencies are again obtained for these weak colliders in the present work.

Appendix I. Vibration Frequency Assignments and Related Calculation Parameters

Complex I (D-migration) frequencies (cm^{-1}): 3020(4), 2260(1), 1440(1), 1300(1), 1250(1), 1230(1), 1130(1), 970(1), 960(1), 890(1), 850(1), 820(1), 770(1), 750(1), 470(2), 450(1)

$$d = 4, (I^+/I)^{\frac{1}{2}} = 1.195, E_0 = 22450 \text{ cm}^{-1}.$$

Complex II (H-migration) frequencies (cm^{-1}): 3020(3), 2270(2), 1440(1), 1400(1), 1330(1), 1290(1), 1130(1), 1020(1), 970(1), 930(1), 850(2), 820(1), 780(1), 490(1), 470(1), 390(1)

$$d = 8, (I^+/I)^{\frac{1}{2}} = 1.195, E_0 = 22250 \text{ cm}^{-1}.$$

Molecule frequencies (cm^{-1}): 3100(1), 3080(1), 3040(1), 3020(1), 2330(1), 2210(1), 1480(1), 1350(1), 1180(1), 1130(1), 1110(1), 1100(1), 1070(1), 1030(1), 1020(1), 980(1), 850(1), 810(1), 760(1), 620(1), 590(1)

References

- a This work was supported by the Office of Naval Research
 - b NSF ERG fellow. Present address, Chemical Research and Development Dept., Halliburton Services, Duncan, Oklahoma.
 - c Department of Chemistry, Tougaloo College, Tougaloo, Miss. 39174
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Figure Captions

Fig. 1 Isotopic relative rate data $k(D)/k(H)$ vs ω : a) 973°K, b) 1073°K.
● N_2 , □ He. Solid curves are calculated on a step ladder model with $\langle \Delta E \rangle_d$ shown (cm^{-1}).

Fig. 2 Fall-off curves, k/k_∞ vs ω : a) 973°K, b) 1073°K
● N_2 , □ He. Curves are step ladder model with $\langle \Delta E \rangle_d$ in cm^{-1} .

