traps on the injected charges. From the point at which charges begin to be injected at the barrier, the measured accumulated charge at applied V is calculated with

$$Q_{\rm i} = Q_{\rm ith} - Q_{\rm id} \tag{17}$$

 $\theta = 0.44$  and  $V_{\text{onset}} = 0.4$  V were used for  $Q_{id}$  in calculating the broken line curve of Figure 2.  $C_i$  is obtained by using eq 1. Usually,<sup>2</sup>  $\theta \approx 10^{-7}$  which is much smaller than the value reported here. However, the thickness of the region where electrons are injected through SAIPc extends only a few tens of angstroms from the CdS/SAIPc interface compared to the sample thickness of  $\sim 1$  mm ordinarily used in SCLC measurements. It is worthwhile also to notice that the experimental  $V_{\text{onset}}$  of  $\sim 0.4$  V corresponds reasonably well to the voltage at which charge injection should begin as expected from the position of the Fermi level in Figure 6. This indirectly confirms the validity of the model used to determine  $E_t$  from the  $Q_i$  vs. time experiments.

## Conclusion

The capacitance discharge technique can be used to determine

the barrier parameters  $V_0$ ,  $w_0$ , and N of the CdS/SAIPc junction. The p-type semiconducting character of SAIPc is due to "doping" by photogenerated electrons; the subsequent behavior of SAIPc in the dark is related to the energy  $E_t$  at which the electrons are trapped above the valence band during light exposure. As the SAIPc regains its equilibrium trap occupancy in the dark (after illumination), it is possible to monitor the electron detrapping rate with capacitance discharge measurements (at  $V << V_0$ ) vs. time. With this method, an energy of ~0.55 eV for  $E_t$  has been deduced, as well as the existence of a Gaussian distribution of valence and conduction band levels about  $E_v$  and  $E_c$ . The traps at  $E_t$  can be assumed to be of chemical origin but further investigation is needed to identify their exact nature.

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# Kinetic Studies of the Continuous Wave Laser-Induced Cyclization of Hexafluoro-1,3-butadiene

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Kinetics of the isomerization of hexafluoro-1,3-butadiene have been studied in the past by standard pyrolysis and by shock tubes, with conflicting results. The present study indicates that the pyrolysis results are correct and also indicates that vibrational-translational energy in hexafluoro-1,3-butadiene occurs through a vibrational mode that is nearly harmonic.

### Introduction

Conflicting reports have been published for the kinetics of the isomerization of hexafluoro-1,3-butadiene (HFB) to hexafluoro-cyclobutene (HFCB).



Schlag and Peatman,<sup>1</sup> using conventional pyrolytic techniques and temperatures of 465–540 K, obtained the rate constant expression

$$\log k = 12.03 - 35.38/2.303RT \tag{1}$$

where the gas constant R is in kcal/mol, while Lifschitz and Kahana,<sup>2</sup> using a shock tube and temperatures of 630-725 K, obtained

$$\log k = 14.5 - 42.0/2.303RT \tag{2}$$

The pyrolytic experiments used HFB at pressures of 1-20 torr while the stock tube contained HFB diluted in argon at total pressures of 100-400 torr. Schlag and Peatman seasoned the reactor vessel with various gases to eliminate the possibility of wall or inhomogeneous reaction effects and also reported that the reverse reaction was negligible under their conditions, i.e., the cyclic isomer is more stable. Both studies were carefully conducted and no side products were observed in either case. To resolve the discrepancy, we report here a study of the cyclization of HFB induced by a continuous wave (cw)  $CO_2$  laser operating at the frequency 965 cm<sup>-1</sup>, in near-resonance with the 969 cm<sup>-1</sup> absorption band of HFB. Initial HFB pressures of 2.5–10 torr were used, as well as 2.5 torr of HFB diluted in 97.5 torr of argon or nitrogen, and temperatures of 520–760 K were produced. Thus the present work includes the range of conditions of both the earlier studies.

Techniques for determining rate constants and translational temperatures in cw laser-induced reactions have been established in recent years.<sup>3-6</sup> The reaction occurs predominantly in the laser beam volume, far from the container walls, and inhomogeneous effects are negligible. Unlike standard pyrolysis or shock tubes, an infrared laser feeds power directly into the manifold of molecular vibrational levels, and extremely rapid transfer processes typically produce vibrational equilibrium at a vibrational temperature  $T_{v}$ . At pressures  $\leq 100$  torr, the molecular collision rate is generally insufficient to equilibrate  $T_{v}$  with the translational temperature T, and this effect provides a tool for the study of

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Figure 1. Laser-induced rate constant k vs. reciprocal translational temperature 1/T for HFB at 2.5, 5, and 10 torr and for 2.5 torr of HFB in 97.5 torr of argon or nitrogen.

vibrational-translational (VT) transfer rates.<sup>5,6</sup> Regardless of pressure, Arrhenius plots of the laser-induced rate constant k vs. 1/T are found to have slopes which correctly give the activation energy, but because of the difference between T and  $T_v$  the plots lie above those obtained from pyrolysis, i.e., the rate constants are larger than thermal values and total thermalization is achieved only in the high-pressure limit.<sup>3,5,6</sup>

In the present investigation of the isomerization of HFB, the activation energy obtained is an excellent agreement with the value given in relation 1, and the additions of 97.5 torr of argon or nitrogen give Arrhenius plots approaching (1) as the limiting case of total thermalization. Thus the present results indicate that Schlag and Peatman's rate constant expression is correct and the one given by Lifschitz and Kahana is incorrect. The results also indicate that VT energy transfer in HFB occurs through a low-lying vibrational mode that is nearly harmonic, in contrast to the anharmonicity evidenced by other compounds studied to data.<sup>5,6</sup>

#### **Experimental Section**

The experimental arrangement and procedures used have been described elsewhere,<sup>3-6</sup> and only details specific to the present work are given here. Laser beam powers of 1.2–15 W were used and reaction rates were measured in real time with an infrared spectrophotometer by observing the growth of the 1416-cm<sup>-1</sup> absorption band of the HFCB isomer during laser irradiation. Translational temperatures T were determined with a He–Ne laser beam in an interferometric configuration,<sup>4,5</sup> and the thermal conductivity parameters obtained for pure HFB were  $\kappa_r = 1.55 \times 10^{-4} \text{ W/(cm K)}$  and m = 2.3, where the temperature-dependent thermal conductivity is given by the empirical relation  $\kappa = \kappa_r \cdot (T/300)^m$ . The corresponding parameters for argon and nitrogen were deduced from tabulated data for those gases.<sup>7</sup> The HFB was purchased from PCR Research Chemicals, Inc., and was degassed before use.

#### **Results and Discussion**

Arrhenius plots of the laser-induced rate constant vs. the reciprocal of translational temperature are shown in Figure 1, which also includes the plots representing the results of the pyrolytic and shock tubes studies for comparison. The average activation energy value for all the laser experiments is 35.44 kcal/mol, in excellent agreement with Schlag and Peatman's value of 35.38 kcal/mol. Thus, the results of the shock tube experiment<sup>2</sup> are probably incorrect.





The laser-induced rate constants for pure HFB are larger than thermal values because of the difference between translational and vibrational temperature. As shown in the figure, the addition of 97.5 torr of argon or nitrogen to 2.5 torr of HFB nearly thermalizes the system, with nitrogen being somewhat more effective than argon in promoting VT equilibration. The vibrational temperature  $T_v$  satisfies the Arrhenius expression for the laserinduced rate constant

$$\log k = \log A - E/2.303 RT_{\rm v}$$
(3)

and under total thermalization  $(T_v = T)$  the thermal rate constant  $k_t$  is given by

$$\log k_{\rm t} = \log A - E/2.303RT$$

From the ratio of laser-induced to thermal rate constant, i.e., the difference between the expressions above, one obtains the quantity  $1/T - 1/T_v$ , which is a useful measure of the departure from thermal equilibrium for these systems.<sup>5,6</sup> Figure 2 shows the dependence of  $1/T - 1/T_v$  on HFB pressure at a constant translational temperature of 600 K. At constant T, the molecular collision rate is determined by pressure alone, and an increase in HFB pressure produces a higher VT deactivation rate which diminishes the difference  $1/T - 1/T_v$ .

The solid curve in Figure 2 has been calculated according to a model described elsewhere<sup>6</sup> for the net VT deactivation rate through the lowest-lying vibrational mode. Available spectroscopic data<sup>8</sup> indicate that the lowest mode in HFB is the torsional fundamental at 94 cm<sup>-1</sup>. Other parameters used in the model to obtain the fit shown in the figure are  $z_{01} = 42$  and  $\delta = 0.015$ ; here,  $z_{01}$  is the average number of collisions required to produce one VT transition from the first excited to ground state of the 94-cm<sup>-1</sup> mode, and the anharmonicity factor  $\delta$  is the fractional decrease in the separation between successive vibrational levels of the mode. The dashed curve in Figure 2 shows the results of a calculation for a perfectly harmonic mode with  $\delta = 0$ .

Apparently, the anharmonicity in HFB is significantly smaller than in other compounds studied to date.<sup>6</sup> In perfluorocyclobutane, for example, where  $\delta = 0.08$ , the quantity  $1/T - 1/T_v$  saturates with decreasing pressure, instead of continuing to increase as in the present case. A possible explanation may be found in a comparison of the structures of these molecules: c-C<sub>4</sub>F<sub>8</sub> has a bent-ring structure with a low inversion barrier associated with the lowest-lying ring-puckering vibrational mode, while HFB has a nonplanar, cisoid form with a dihedral angle of 47° and a high barrier separating the torsional forms.<sup>9</sup> On this basis, the vibrational potential for HFB is expected to be more harmonic, although a more convincing explanation would require a deeper study of the two molecules.

Registry No. Hexafluoro-1,3-butadiene, 685-63-2.

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