The first order rate coefficient for the thermal decomposition of oxetane and oxetane-d$_2$ has been investigated at two temperatures as a function of pressure. Gas phase collisional relaxation results are obtained by using RRKM theory and various energy transfer probability models.

INTRODUCTION

In comparison with the vibrational energy transfer data on cyclopropane and cyclobutane systems, there is almost no similar quantitative information available on small cyclic molecules with heteroatoms. Oxetane is one of the representatives of the latter compounds. Oxetane and oxetane-d$_2$ were found [1,2] to decompose thermally into ethylene and formaldehyde in clean unimolecular processes with high-pressure...
rate coefficients of

\[ \log(k_\infty/s^{-1}) = (15.42 \pm 0.31) - (259.5 \pm 3.8) \text{kJ mol}^{-1}/2.303 \text{RT} \]  
(1)

and

\[ \log(k_\infty/s^{-1}) = (15.54 \pm 0.16) - (262.8 \pm 1.9) \text{kJ mol}^{-1}/2.303 \text{RT} \]  
(2)

for oxetane and oxetane-2,2-\text{d}_2, respectively. The pseudo first order decomposition rate coefficients were shown to be pressure-dependent below about 5 kPa [1,2], collisional energy transfer efficiencies were not determined.

EXPERIMENTAL

Materials and experimental details were given in previous publications [1,2]. Kinetic experiments were carried out in a cylindrical pyrex vessel of 450 cm$^3$ volume enclosed in an air thermostat and attached to a vacuum apparatus. The extent of decomposition as a function of time was determined by gas-liquid chromatographic analysis.

DESCRIPTION OF THE COLLISIONAL ENERGY TRANSFER PROCESS

The time evolution of the population at a given energy level in the molecule is described by the master equation [3]:

\[ \frac{dn_i}{dt} = Rf_i + \sum P_{ij} n_j - \omega n_i - k_i n_i \]  
(3)

where $n_i$ designates the population of energy level $i$, $Rf_i$ is the rate of external input into level $i$, $P_{ij}$ is the collisional transitional probability from $j$ to $i$, $k_i$ stands for the microscopic rate constant and $\omega$ is the collisional frequency.

In the case of our thermal decomposition reaction, steady-state conditions are valid, i.e. $dn_i/dt=0$ and $Rf_i=0$. The solu-