$CH_2(^1A_1)$ FROM CH_2N_2 PHOTOLYSES AT 4358 AND 3660 Å. VIBRATIONAL ENERGY DISTRIBUTIONS UPON REACTION WITH CYCLOBUTANE

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Approximate vibrational energy distributions for $CH_2^*(^1A_1)$ from diazomethane photolyses at 4358 and 3660 Å have been determined to be reasonably broad. These distributions apply to $CH_2^*(^1A_1)$ at the time of reaction with cyclobutane and were deduced from the internal energy distribution of the formed chemically activated methylcyclobutane. An apparent anomaly in the pressure dependence of the decompositions of $CH_2(^1A_1)$ generated chemically activated molecules is explained. The anomaly pertains to the relative behavior of systems utilizing ketene and diazomethane photolyses as $CH_2(^1A_1)$ sources. The explanation offered is that the vibrational energy distributions for $CH_2^*(^1A_1)$ are narrow for ketene photolyses at 3340 or 3130 Å and broad for diazomethane photolyses at 4358 or 3660 Å.

1. Introduction

The step sizes for multistep collisional deactivation of highly vibrationally excited species by various molecules have been a subject of intense investigation for several years. An important source of highly vibrationally excited molecules has been chemical activation by the insertion and addition reactions of $CH_2(^1A_1)$. When ketene photolysis at 3130 and 3340 Å is the $CH_2(^1A_1)$ source a smaller step size for a given bath molecule–chemically activated molecule system has been observed than when diazomethane photolysis at 3660 and 4358 Å is the $CH_2(^1A_1)$ source [1,2]. This is an apparent anomaly since ketene photolyses at 3130 and 3340 Å produce lower energy $CH_2(^1A_1)$ than diazomethane photolyses at 3660 and 4358 Å [1,2].

In this communication we report an interpretation of some preliminary experiments, for the $CH_2(^1A_1)$ + □ chemical activation system, that appears to resolve this anomaly.

2. Experimental

2.1. Materials

Diazomethane (DM) was prepared in vacuo by the action of sodium hydroxide in 1,4-butanediol on N-methyl-N-nitroso-*p*-toluenesulfonamide (Matheson, Coleman and Bell). The fraction condensed at 77 K was transferred to a dibutylphthalate solution and stored at 77 K for subsequent use.

Cyclobutane (CB) was prepared in vacuo by the 2537 Å photolysis of cyclopentanone (PRC, Incorporated). The fraction distilled from 195 K to 77 K was purified via multiple pass glpc. The final fraction collected was verified by mass spectrometric comparison to authentic cyclobutane.

Oxygen was obtained by passing commercial Airco material through a 195 K trap prior to storage for future use.

2.2. Experiments

Mixtures of CB/DM/O_2 in the ratio of 10 : 1 : 1 were prepared on a standard high vacuum system featuring greaseless stopcocks in the reactant measuring selection. Various total amounts of reactants and various reactor volumes were used to obtain reaction pressures ranging from 5 torr to 2 atmospheres. Reaction mixtures were photolyzed at 4358 and 3660 Å. The wavelengths were isolated by a 0.25 m Jarrell–Ash monochromator (model 82-140) following a high pressure mercury arc source (Osram HBO 500 W). Photolysis times were inversely proportional to reaction pressure, ranging from six to twenty-four hours.

2.3. Analysis

Following photolysis, the portion of the reaction mixtures condensible at 77 K was subjected to two passes through a 3/16" i.d. × 23' polyethylene column consisting of 30% dibutylphthalate/dinonylphthalate (85 : 15) on 60/100 Chromosorb at ca. 25°C. The first pass permitted removal of approximately 95% of the unreacted cyclobutane. The ratio of the products of retention time and peak height of methylcyclobutane and propene was determined from the second peaks and related to moles by comparison to the ratio determined in the same fashion for authentic mixtures of methylcyclobutane and propene of known composition.

2.4. Notes

Dark reactions duplicating various experiments were performed. No reactions of interest were observed.

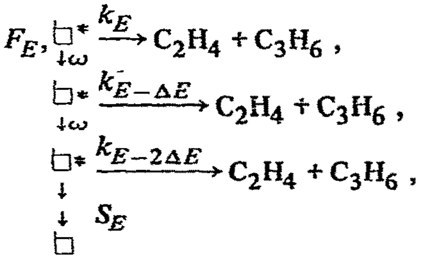
Reactors were of pyrex equipped with greaseless stopcocks. Large reactors were of conical construction with a flat pyrex window at the small end. This permitted optimal use of the narrow beam exiting the monochromator and its subsequent divergence.

3. Results

The following reaction scheme adequately describes the formation of propylene and methylcyclobutane and their pressure dependence in this system.

$$CH_2N_2 + h\nu \to CH_2^*(^1A_1) + N_2 \,, \tag{1}$$

$$g_v, CH_2^*(^1A_1) + □ \to ⊡^*, F_E \,, \tag{2}$$



$$F_E, ⊡^* \xrightarrow{k_E} C_2H_4 + C_3H_6 \,,$$
$$\downarrow \omega$$
$$⊡^* \xrightarrow{k_{E-\Delta E}} C_2H_4 + C_3H_6 \,,$$
$$\downarrow \omega$$
$$⊡^* \xrightarrow{k_{E-2\Delta E}} C_2H_4 + C_3H_6 \,,$$
$$\downarrow$$
$$\downarrow S_E$$
$$⊡$$

where * represents vibrational excitation; g_v is the population of the vth vibrational energy level of $CH_2^*(^1A_1)$, it is assumed that $CH_2^*(^1A_1)$ is translationally and rotationally thermalized [7]; F_E is the vibrational–internal rotational energy level population at E for ⊡*; ω is the gas kinetic theory collision frequency of ⊡* with □; k_E is the specific decomposition rate of ⊡* at the energy, E; ΔE is the average energy removed from ⊡* by a collision with □; and S_E is the fraction of ⊡* formed at E that is eventually collisionally stabilized below E_0, the critical energy for decomposition.

A mathematical analysis of the above scheme leads to the equations

$$S_E = \prod_{n=0}^{L} \omega/(k_{E-n\Delta E} + \omega) \,, \tag{3}$$

where $L = (E-E_0)/\Delta E + X, 0 \leqslant X < 1$ and takes the value necessary to make L an integer.

$$S = \sum_{E=E_{\min}}^{\infty} F_E S_E, \quad D = 1-S \,. \tag{4}$$

Defining the apparent rate constant for ⊡* decomposition as

$$k_a = D/S = (C_3H_6)/(⊡) \tag{5}$$

and plotting the data as $k_a/k_a(S/D > 2)$ versus log S/D gives fig. 1. The value of k_a for $S/D > 2$ is essentially

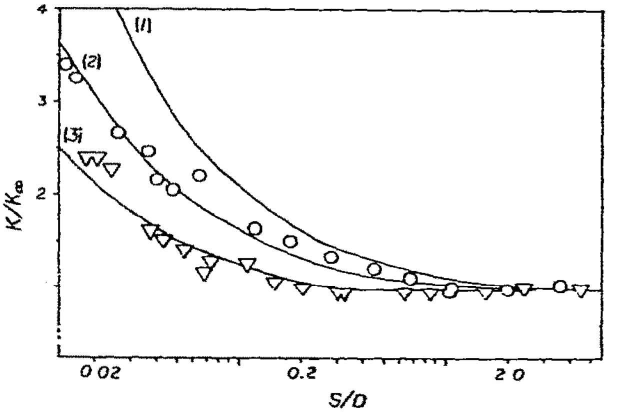


Fig. 1. Plot of k_a/k_a ($S/D > 2$) versus log S/D; ○, diazomethane/cyclobutane/oxygen 4358 Å photolysis data; △, diazomethane/cyclobutane/oxygen 3660 Å photolysis data. Curve (1), theoretical curve that fits existing ketene/cyclobutane/oxygen 3340 Å photolysis data; curve (2), theoretical curve for 4358 Å diazomethane results; curve (3), theoretical curve for 3660 Å diazomethane results.

constant for a particular system and plotting the ratio $k_a/k_a(S/D > 2)$ has the advantage that any uncertainties in collision cross sections and activated complex model cancel out. Curve (1) in fig. 1 is a "best fit" theoretical curve [calculated by us from eqs. (3) – (5)] for the available results on ketene photolyses at 3340 Å in the presence of cyclobutane and oxygen [1,3]. The k_E values used in our calculations are those given by activated complex Model II of ref. [1]. The k_E values for the other models in ref. [1] give essentially the same curves. The F_E values used for curve (1) are simply those calculated from f_E, the energy level populations of □* due to the thermal energy distribution [4], since $CH_2(^1A_1)$ produced by ketene photolysis at 3340 Å has been shown to be essentially thermalized [1,5]. The value of E_{min} = 105.6 kcal/mole for this system was deduced from the 0 K exothermicity of reaction (2) utilizing ΔH^0_{f0} values of 99.0 [5], 12.3 [1], and 6.7 [1] kcal/mole for $CH_2(^1A_1)$, □, and □, respectively, and adding 1 kcal/mole activation energy for reaction (2). Using a value of $\Delta E = 6$ kcal/mole we calculate a theoretical curve, curve (1), that satisfactorily fits the available data for ketene photolysis at 3340 Å. We find this value is uncertain by about 2 kcal/mole primarily due to a rather large scatter in the available data.

Curves (2) and (3) of fig. 1 were calculated from eqs. (3), (4) and (5) using exactly the same input information as for curve (1) except the sets of F_E values were adjusted so as to fit our diazomethane data. The sets of F_E values are related to sets of g_v and f_E values by the equation

$$F_E = \sum_{v=0}^{n} g_v f_{E-4V} , \qquad (6)$$

where $n = (E - E_{min})/4 - \epsilon$; $0 < \epsilon < 1$ and takes the value necessary for n to be an integer.

In eq. (6) all energies are in kcal/mole units and 4 kcal/mole is taken as a close approximation to the vibrational energy level spacing of $CH_2(^1A_1)$ [6]. Sets of g_v values that fit our 4358 Å [curve (2)] and 3660 Å [curve (3)] diazomethane photolyses data are depicted in fig. 2. It is seen that the vibrational energy distributions for $CH_2^*(^1A_1)$ from diazomethane photolyses are quite broad and, reasonably, become broader as the photon energy increases. The distributions in fig. 2 may not be unique with respect to exact shapes but a further discussion of the shapes must await more reliable and more complete sets of data, especially for ketene photolyses at 3340 Å. Once this is accomplished, studies designed to relate the vibrational energy distributions of the *reacting* $CH_2^*(^1A_1)$ to the vibrational energy distributions of the *initially formed* $CH_2^*(^1A_1)$ will be in order.

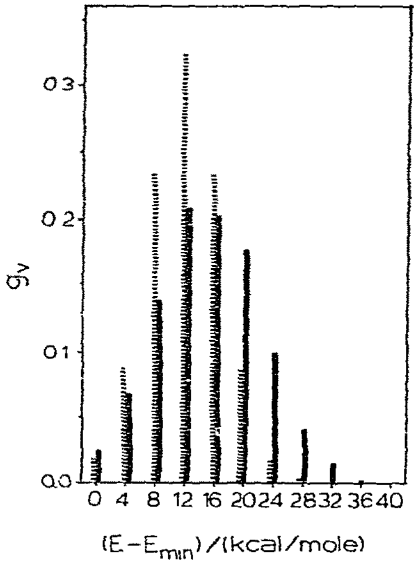


Fig. 2. Vibrational energy level populations for *reacting* $CH_2^*(^1A_1)$ from diazomethane photolyses; – – –, 4358 Å; ——, 3660 Å.

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