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# SOME SIMPLE UNIMOLECULAR TWO-CHANNEL DECOMPOSITIONS IN THERMAL, UV AND IR PHOTOCHEMICAL SYSTEMS*

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Molecules which undergo simple unimolecular decomposition photochemically or thermally by two (or more) channels are of interest from several points of view. In a thermal decomposition at high pressure in which the decomposing molecules come from a population at thermal equilibrium, the Arrhenius parameters furnish information about the nature and the thermochemistry of the decomposition channels of the vibrationally excited ground state. These data provide a standard calibration of the system under well-defined conditions, against which the decomposition under other conditions of excitation can be compared. A comparison of activation energies and frequency factors with theoretical calculations can distinguish between possible transition states and can sometimes determine whether or not two channels involve a common transition state or intermediate. If the same system that was studied under standard conditions is then examined at pressures and temperatures at which the decomposition becomes pressure dependent, the measurement of the ratio of two channels with different energy requirements can yield information about the depletion of the high energy tail of the Boltzmann distribution under these conditions [1].

Many photochemical decompositions in the UV region have been observed to proceed by more than a single path, and the ratio of quantum yields for these paths usually varies with wavelength. In cases where decomposition proceeds through radiationless transitions to the ground state, this may simply reflect the changing energy of the excited molecule; in other cases the variation may arise from the direct involvement of electronically excited singlet or triplet states in the decomposition. The measurement of the ratio of the quantum yields for the different channels as a function of wavelength, pressure and added quenching gases can give information about the electronic and vibrational excitation of the dissociating molecules.

In multiphoton IR photochemistry a suitable two-channel decomposition, calibrated by conventional pyrolysis measurements, offers a unique probe of the energy of the decomposing molecules. In high pressure collisionally equilibrated systems the two-channel system is simply an internal thermometer with the ratio of the two channels indicating the average effective temperature of the decomposition. At low pressures or in the selective decomposition of a minor component at higher pressures, individual molecules are pumped to energies above the dissociation threshold by the successive absorption of many photons. A two-channel decomposition in this case can probe very directly the average energy of the dissociating molecules, providing information about the relative efficiency of

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the pumping process, collisional deactivation and decomposition. Finally, the study of two-channel decompositions can play an obvious role in the search for the "holy grail" of the IR photochemist: "bond-selective" chemistry, in which, under a sufficiently high photon flux and collision-free conditions, vibrational excitation of a particular bond in a molecule leads to decomposition via a particular channel associated with that bond before internal energy equilibration can occur.

Three two-channel systems are discussed in the present paper: the decomposition of the three cyclobutane derivatives cyclobutanone, cyclobutanol and cyclobutane-*cis*-1,2-dicarboxylic acid anhydride (CBA). Each of these molecules decomposes thermally by a major process analogous to the decomposition of cyclobutane itself, yielding ethylene and the appropriate substituted ethylene, very probably through a biradical mechanism. In each case there is a second much less important decomposition channel with a different activation energy. Measurements of the thermal decomposition of each molecule have determined the relative frequency factors and energy requirements and serve to calibrate each two-channel system as a probe to explore the UV and IR photodissociation processes.

Both the thermal and the UV photochemical decomposition of cyclobutanone have been thoroughly studied in a number of laboratories and are well understood [1 - 6]. More recently, the IR-laser-induced decomposition has been studied in this laboratory [7] and elsewhere [8 - 10]. In all systems the two decomposition channels observed are

 $=O \rightarrow C_2H_4 + CH_2C{=}O$ (1)

and

 $=O \rightarrow + CO$ (2)

with rate constants for the thermal decomposition of $k_1 = 3.60 \times 10^{14} \times \exp(-52\,000/RT)\ s^{-1}$ and $k_2 = 2.34 \times 10^{14} \exp(-58\,000/RT)\ s^{-1}$ (with $RT$ in kilocalories per mole). It is not clear whether reaction (2) proceeds through the same biradical as reaction (1) or by a totally different path. Some discrepancies between the results of the IR multiphoton decomposition obtained in different laboratories are discussed and new data are presented.

We have recently investigated the thermal and photochemical (UV and IR) decomposition of cyclobutanol, the second system to be discussed. Primary decomposition channels in the thermal and IR systems are

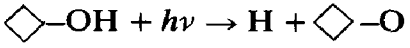
 $-OH \rightarrow C_2H_4 + C_2H_3OH$ (3)

and

 $-OH \rightarrow C_3H_7CH{=}O$ (4)

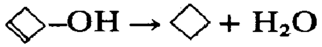
with rate constants for the thermal decomposition given by $k_3 = 2.14 \times 10^{14} \times \exp(-57\,300/RT)\ s^{-1}$ and $k_4 = 2.14 \times 10^{10} \exp(-50\,000/RT)\ s^{-1}$. Both channels are believed to proceed through the $\dot{C}H_2CH_2CH_2\dot{C}H{-}OH$ biradical which can either decompose with an activation energy of 7.3 kcal mol$^{-1}$ (reaction (3)) or isomerize to butyraldehyde through a six-membered cyclic transition state. The isomerization will be recognized by photochemists as the reverse of the Norrish type II decomposition of butyraldehyde which has been observed to yield both $C_2H_4 + C_2H_3OH$ and cyclobutanol [11].

The IR photodecomposition of cyclobutanol was also studied, using both a $CO_2$ laser (which excites a methylene bending vibration) and an HF laser (which excites the O–H stretching vibration); little significant difference was observed between the two methods. The dependences on fluence and pressure were compatible with the energetics of the two channels established in the thermal decomposition. The UV photolysis, however, proceeds almost entirely by a third channel



(5)

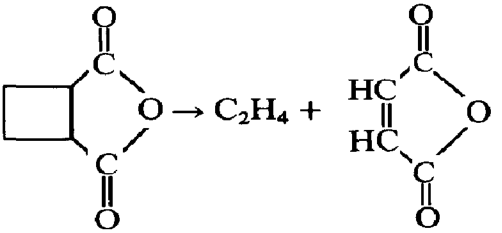
typical of the OH chromophore. The molecular dehydration reaction



(6)

which is observed in the thermal decomposition of some alcohols is of very minor importance (very much less than 1%) in all these systems and probably has a rather high activation energy.

The third molecule we studied, CBA, decomposed thermally almost entirely by breaking the cyclobutane ring:



(7)

The first-order rate constant $k_7 = 1.14 \times 10^{14} \exp(-55\ 100/RT)\ \mathrm{s}^{-1}$. A minor second channel was observed

$$\mathrm{CBA} \rightarrow CO_2 + CO + \text{1,3-butadiene} \tag{8}$$

with $k_8 = 8.40 \times 10^{14} \exp(-67\ 000/RT)\ \mathrm{s}^{-1}$, amounting to about 0.1% of reaction (7) at 430 °C. Reaction (8) may yield cyclobutene initially, which is unstable at the temperature of the pyrolysis, and probably proceeds through a concerted mechanism as recently observed in the decomposition of maleic anhydride [12].

The UV photolysis of CBA was studied at 125 °C at wavelengths from 200 to 300 nm. Reactions (7) and (8) were both observed, together with a third channel

$$\mathrm{CBA} \rightarrow CO_2 + CO + \text{cyclobutene} \tag{9}$$

Both butadiene and cyclobutene appear to be the primary products, and reactions (8) and (9) are much more important than in the thermal decomposition, with quantum yields comparable with that of reaction (7). The relative yields of the three channels vary in a rather complicated way with wavelength, pressure and conversion, and a mechanism accounting for this behaviour is presented. Decomposition of CBA by IR radiation from a pulsed $CO_2$ laser is also discussed.

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