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INTRAMOLECULAR ENERGY PARTITIONING IN MULTIPHOTON EXCITATION BY ISOTOPIC BRANCHING*

SIDNEY W. BENSON, PETER PAPAGIANNAKOPOULOS and KEN KOSNIK

Hydrocarbon Research Institute, and Department of Chemistry, University of Southern California, Los Angeles, CA 90007 (U.S.A.)

Summary

The IR multiphoton dissociation of CH_2DCH_2Cl was studied by observing the yields and the branching ratio R = [HCl]/[DCl] of the two unimolecular reaction channels. The yields and R were examined as a function of beam energy, beam geometry, excitation wavelength, irradiation time and the pressure of various added inert gases. It was found that R initially decreased with increasing inert gas pressure in the range 0 - 5 Torr and finally reached a plateau at higher pressures; the plateau corresponded to internal energies E^* up to 120 kcal mol^{-1} (about 40 photons) and lifetimes of about 10^{-1} - 10^{-11} s. The effects of various added inert gases, changes in excitation wavelength and the inert gas pressure were incompatible with a Boltzmann population but quantitatively compatible with a Rice–Ramsperger–Kassel–Marcus transition state model.

1. Introduction

Multiphoton dissociation (MPD) of polyatomic molecules in intense IR beams has been an actively expanding research area during the past decade [1]. By now the main features of the process seem to have been recognized and recent researchers have been concerned with constructing a quantitative model for the overall process. One of the important pieces of information needed for such a model is the time scale for the observed events. The study of molecules with two or more competing channels for reaction can in principle provide a "chemical clock" in such studies where the absolute rates of the individual channels are known independently. We have recently made use of isotopically labelled 2-deutero ethyl chloride (CH_2DCH_2Cl) to provide such a time scale [2] and in the present paper we report some results from our most recent measurements on this system.

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2. The chemical time scale

Chemical unimolecular rate constants which can be represented by a simple Arrhenius expression $k = A \exp(-E/RT)$ are equilibrium rate constants in the sense that the decomposing molecules form a population in Boltzmann equilibrium with the unreacted molecules [3]. The activation energy E is the difference in mean energy of this population from the unreacted molecules and the A factor can be related to the difference in mean entropy. Transition state theory which has been very successful in describing chemical rate constants in molecular terms permits us to assign (from experimental data) a geometry and spectroscopy to the transition state [4]. The transition state is conceived as a dynamic structure at the potential energy maximum for the reaction. It is a point of "no return" in the dynamic trajectory of the reaction. The theory of unimolecular reactions (Rice–Ramsperger–Kassel–Marcus (RRKM)) then permits us to assign a function $k(E)$ which represents the unimolecular rate constant for a set of molecules of internal energy E. The natural lifetime of such molecules is simply $\tau_E = 1/k(E)$. Conversely, if we have measured A and E for a unimolecular reaction then we can specify for each energy class in the reacting population its mean lifetime τ_E.

In the usual MPD experiment where only one channel exists there is no way of establishing a time scale for the decomposition event. When two channels exist that differ in their activation energies, their branching ratio is very sensitive to the mean energy of the population of decomposing molecules. Thermal studies can provide A factors and activation energies for each of the channels and RRKM theory can then allow us to develop $k(E)$ functions for each channel so that in an MPD experiment we can, from an observation of the branching ratio, assign a mean energy content and a mean time to the decomposition event.

In our previous work with CH_2DCH_2Cl [2] we observed a branching ratio $[HCl]/[DCl] = 2.65 \pm 0.1$ which we interpreted as corresponding to a mean internal energy content of 88 ± 6 kcal mol^{-1} for a reaction whose activation energy to give HCl was 56 kcal mol^{-1}. From RRKM theory this energy yields a mean lifetime of $10^{-9.0 \pm 0.5}$ s for the decomposition and further implies that the last photon was absorbed in this time span. Since 88 kcal mol^{-1} corresponds to about 30 photons (CO_2 laser), this suggests that the entire pumping process might take of the order of only 30 ns. This provided an interest in exploring the effect of buffer gases which was the goal of the present investigation.

3. Experimental details

We used a Tachisto triethylamine–CO_2 laser (215G) line tunable over the CO_2 spectra with an energy of 1 - 2 J pulse^{-1} and very reproducible from pulse to pulse (4%). Each pulse consisted of a very sharp spike (70 ns full width at half-maximum) followed by a weaker tail of about 1.6 μs with about half the energy in the sharp spike.

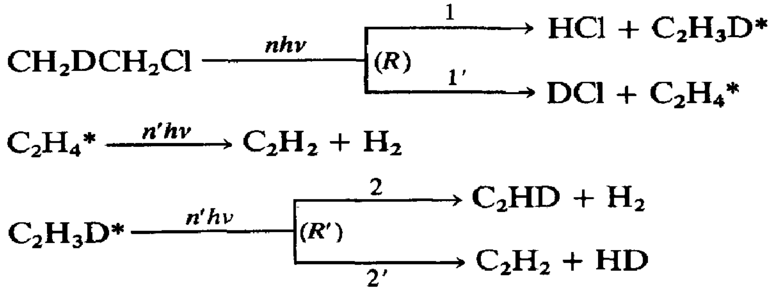
Experiments were done with focused beams (14.8 and 22.5 cm focal length lenses) and collimated beams (lens, f = 200 cm). Polyethylene sheets were used for attenuation.

A UTI (model 100C) quadrupole spectrometer was used for the analysis of products which included undecomposed CH_2DCH_2Cl, C_2H_4, C_2H_3D, C_2H_2, C_2HD and $C_2H_2F_2$, the $C_2H_2F_2$ being used as an internal standard. Suitable standards were used for calibration before and after each run and analysis.

In a typical experiment samples consisted of 50 mTorr of CH_2DCH_2Cl, 20 mTorr of $C_2H_2F_2$, 100 mTorr of xenon (standard) and the buffer gases neon, helium or CF_4 (0 - 30 Torr). Pressures were measured with a calibrated transducer. Typical amounts of dissociation were 18% in 1200 pulses with the P(10) line and about 10% with the R(16) line. $C_2H_2F_2$ gave 28% and 45% dissociations under the same conditions. The repetition rate was $\frac{1}{3}$ Hz. Thermal studies of the decomposition were also made [5].

4. Results

CH_2DCH_2Cl can undergo what appears to be two consecutive decomposition reactions in the single-pulse experiments:



In consequence we found both labelled and unlabelled acetylenes (C_2H_2 and C_2HD) in our final products. The branching ratio for the first step R must then be corrected for the secondary decomposition and possible branching of C_2H_3D measured as R'. In interpreting these data we must make the assumption that the MPDs of C_2H_4 and C_2H_3D have the same cross sections. However, the amount of secondary dissociation is only about 10% of the ethylenes produced. With $R = ([HCl]/[DCl])_{\text{corrected}}$ and $R' = ([H_2]/[HD])_{\text{corrected}}$ the results in the absence of buffer gas are shown in Table 1. To a first approximation both R and R' appear to be insensitive to the focal conditions used or to the wavelength (P(10) or R(16)). However, R' may be slightly smaller for P(10) than for R(16). Variations in the fluence seem to play no role in agreement with our earlier results.

The dissociation yields α, β and γ per pulse for CH_2DCH_2Cl, C_2H_4 and $C_2H_2F_2$ respectively were examined as a function of number of pulses, geometry, energy or/and power density of the beam and excitation laser line; the results are presented in Table 2.

TABLE 1

Multiphoton dissociation of CH_2DCH_2Cl by a pulsed CO_2 laser

Run	*Number of pulses*	*E* (J pulse^{-1})	*f* (mm)	*Line*	*R*[a]	*R'*[b]
7	1200	1.77	148	P(10)	2.76 ± 0.07	1.58 ± 0.06
5	1200	2.04	148	R(16)	2.63 ± 0.12	1.77 ± 0.10
7	2400	1.32	148	P(10)	2.52 ± 0.03	1.51 ± 0.13
5	2400	1.86	225	P(10)	2.69 ± 0.04	1.56 ± 0.06
3	3420	1.81	148	P(10)	2.79 ± 0.02	1.43 ± 0.08
3	2400	1.53	127	P(10)	2.76 ± 0.12	1.51 ± 0.04
3	2400	1.53	127	P(10)	2.72	1.52
3	2430	2.08	127	R(16)	2.60	1.73
3	3360	2.08	127	R(16)	2.67	1.59

[a] $R = [C_2H_3D]/[C_2H_4]$, corrected for secondary decomposition.

[b] $R' = [C_2HD]/[C_2H_2]$ from C_2H_3D, corrected for branching and primary decomposition.

TABLE 2

Multiphoton dissociation yields α, β and γ per pulse for CH_2DCH_2Cl, C_2H_4 and $C_2H_2F_2$ respectively observed with a CO_2 laser

Run	*Number of pulses*	*f* (mm)	E_0 (J)	I_0 (MW cm^{-2})	α (× 10^4)	β (× 10^4)	γ (× 10^4)
P(10) line							
7	2400	148	1.32	2.97 ± 0.11	0.79 ± 0.06	1.04	0.24
3	2400	127	1.53	3.44 ± 0.13	0.86 ± 0.05	0.73	1.67
3	2400	127	1.53	3.44 ± 0.13	0.92 ± 0.11	0.74	1.80
7	1200	148	1.77	3.98 ± 0.15	1.20 ± 0.11	1.93	2.77
3	3420	148	1.81	4.07 ± 0.15	1.17 ± 0.13	0.51	1.17
5	2400	225	1.86	4.18 ± 0.16	1.10 ± 0.10	0.88	1.75
R(16) line							
5	1200	148	2.04	4.59 ± 0.17	0.65 ± 0.12	2.14	4.61
3	2430	127	2.08	4.68 ± 0.17	0.28 ± 0.11	0.76	1.17
3	3360	127	2.08	4.68 ± 0.17	0.36 ± 0.06	0.66	—

The dissociation yield per pulse for CH_2DCH_2Cl was sensitive to small changes in the beam energy and was found to increase linearly with $E^{1.5}$ for the P(10) line (Fig. 1). This 1.5 power dependence of the dissociation yield on the beam energy in a focused geometry has been observed previously by others [6]. The dissociation yield of CH_2DCH_2Cl was also independent of the geometry (f = 12.7 cm, f = 14.8 cm and f = 22.5 cm) and its values lie along the previously obtained line of rate *versus* $E^{1.5}$ (Fig. 1). It changed with excitation line and its value was two to three times higher for the P(10) line than for the R(16) line.

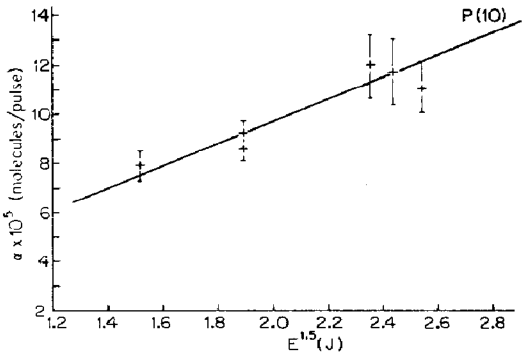


Fig. 1. Dissociation yield a per pulse for CH_2DCH_2Cl *vs.* laser energy E (P(10) excitation line).

The dissociation yields per pulse for C_2H_4 and $C_2H_2F_2$ were also found to increase with beam energy, but the experimental error was large owing to the low concentration of both molecules. The rates were also independent of geometry and excitation line.

5. Pressure dependence of R and R'

The branching ratios R and R' were examined as a function of pressure for three buffer gases (helium, neon and CF_4) added to the reaction sample. The graphs of branching ratio R *versus* pressure in the pressure region 0 - 35 Torr for the same number of pulses, same geometry, same excitation line P(10) and a constant power density $I_0 \approx 4$ MW cm^{-2} but for the three buffer gases neon, helium and CF_4 are presented in Fig. 2. The branching ratio R has the same behavior in all three cases; the ratio decreases with increasing pressure in the range from 0 to 5 Torr and reaches a plateau for pressures higher than 5 Torr. The initial decrease in R is steeper with CF_4 than with neon and helium.

The graphs of branching ratio R' *versus* pressure in the pressure region 0 - 35 Torr for the same number of pulses, same geometry, same excitation line P(10) and a constant power density $I_0 \approx 4$ MW cm^{-2} but for the three buffer gases neon, helium and CF_4 are presented in Fig. 3. R' decreases linearly with increasing pressure for all three buffer gases.

The dissociation yields y for CH_2DCH_2Cl, C_2H_3D and $C_2H_2F_2$ behave differently as a function of pressure. Typical behavior is shown in Fig. 4. For CH_2DCH_2Cl there is a small increase to a maximum between 3 and 5 Torr of buffer gas which amounts to a value for y of about 30%. This is followed by a slow asymptotic decrease to about half the maximum value at 33 Torr. The behaviors with the three gases helium, neon and CF_4 were similar. In contrast the yield from C_2H_3D dissociation increased asymptotically to a value about three times greater than its initial value. The yield from $C_2H_2F_2$ showed no initial rise but only a slow asymptotic decrease similarly to CH_2DCH_2Cl.

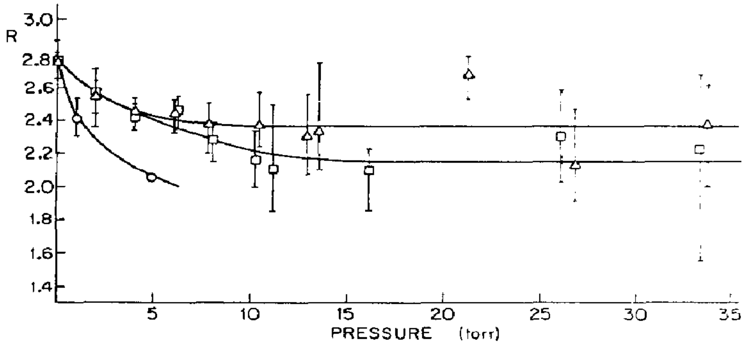


Fig. 2. Branching ratio R as a function of buffer gas pressure: □, helium; △, neon; ○, CF_4.

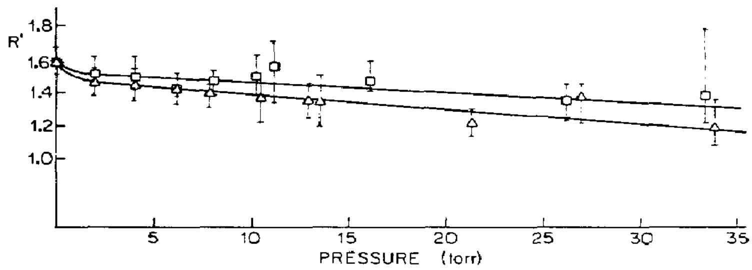


Fig. 3. Branching ratio R' for C_2H_3D as a function of buffer gas pressure: □, helium; △, neon.

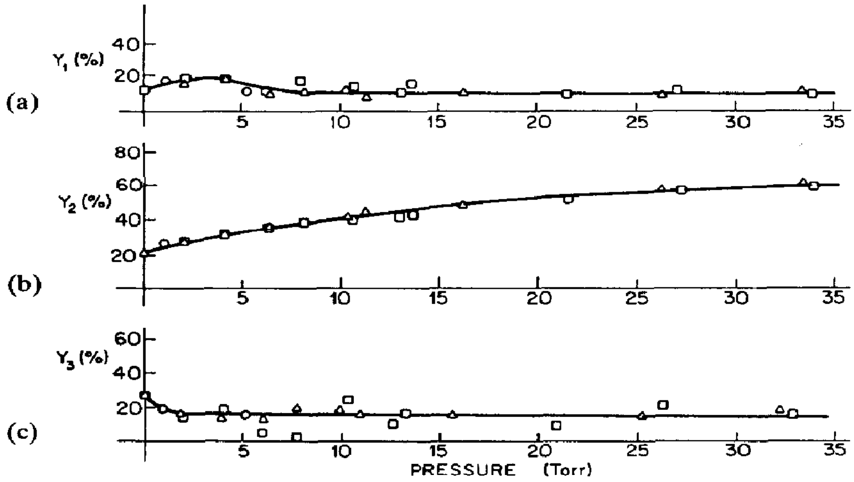


Fig. 4. Dissociation yields (1200 pulses) for (a) CH_2DCH_2Cl (y_1), (b) C_2H_4 (y_2) and (c) $C_2H_2F_2$ (y_3) with buffer gases neon (□), helium (△) and CF_4 (○).

6. Discussion

The most surprising aspect of these results is the increase in *R* with increasing pressure, suggesting that collisions are driving the system to higher mean energies. Although the data are unequivocal, the finding appears to be contrary to expectations. We believe that the explanation lies in the bimodal character of the laser pulse. The intensity in the initial sharp spike is about 10 - 15 times greater than in the long tail. In consequence, pumping rates will be at least 10 - 15 times faster during the spike. Since the mean energy of the molecules is fixed by the competition between pumping by the laser beam and both dissociation and collisional de-excitation, an increased pumping rate will lead to higher energies before dissociation. De-excitation can only be important if it is fast enough to compete with pumping and dissociation.

From our thermal experiments on the branching ratio, using RRKM theory, we can make a curve showing *R* as a function of mean internal energy E^*. For the results obtained this leads to an energy at the 30 Torr plateau level of about 120 kcal mol^{-1} (Fig. 5) and this is consistent with a mean decomposition time of 3×10^{-11} s. To compete with such a process would require pressures of about 10 atm. Pressures in the range 1 - 30 Torr correspond to collision times of the order of 300 - 10 ns, which corresponds quite well to the time scale of the tail in the pulse and the plateau behavior which is found essentially above 3 Torr. In

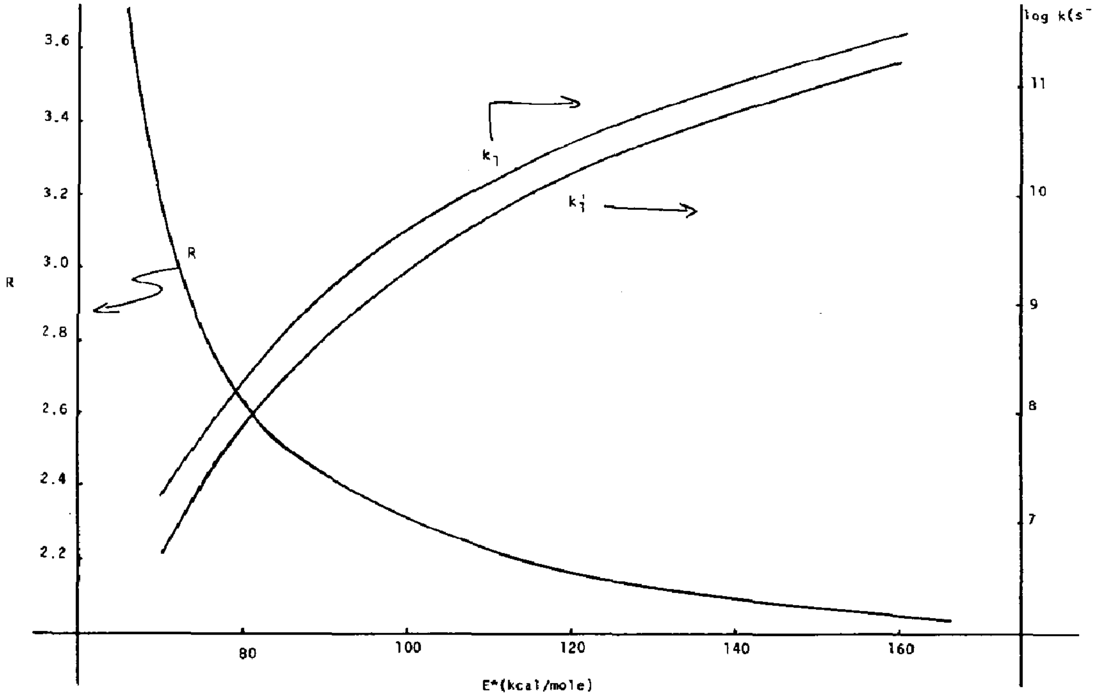


Fig. 5. Plots of R *vs.* E^* (left-hand ordinate), and $k_1(E)$ *vs.* E^* and $k_1'(E)$ *vs.* E^* (right-hand ordinate).

support of this interpretation is the observation that the total dissociation yield per pulse decreased by a factor of about 2 from its peak value at 3 Torr.

If we assume for the moment that this interpretation is correct, then we can conclude that the value $R = 2.7 \pm 0.1$ observed at 50 - 100 mTorr with no added buffer gas must represent an average result arising from the essentially independent photolysis produced by the peak and by the tail. Assigning about 50% of the dissociation yield to each of these processes then leads to $R_p = 3.2 \pm 0.1$ for the tail. This in turn corresponds to mean energies of 115 ± 15 kcal mol^{-1} for the peak and 70 ± 2 kcal mol^{-1} for the tail. The difference in energy spread arises from the changing curvature of the RRKM plot of R *versus* E^* (Fig. 5). These two energy ranges in turn correspond to time scales of about $10^{-10.5}$ s for the molecules in the peak and 10^{-7} s in the tail.

These peak values are the shortest lifetimes reported so far while the values for the tail are in the range reported by most investigators for a variety of molecules. They imply further that in the peak the decomposing molecule is absorbing photons at a rate of about $10^{10.5}$ s^{-1}. This implies a cross section of about $10^{-17.5}$ cm^2 for $(CH_2DCH_2Cl)^*$. Our measured values of the cross sections for CH_2DCH_2Cl at 300 K at the wavelengths used are in the region $10^{-19.5}$ cm^2, about a hundredfold smaller. Some of this apparent discrepancy can be accounted for by assuming an effective reactive volume that is smaller than that estimated by us for the focused beams, but a larger discrepancy would still remain, implying an appreciably higher cross section for the excited molecules.

Acknowledgment

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