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Energy Disposal in the Photofragmentation of Ketene

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Abstract: Photofragment infrared fluorescence methods are used to study energy disposal to the carbon monoxide product of ketene photodissociation. We find that vibrationally excited CO is formed upon photolysis at 193 nm, but not at 249 or 308 nm. For 193-nm photolyses, the nascent CO vibrational energy distribution can be characterized by a temperature, $T_v = 3750$ K. Additionally, the nascent CO rotational energy distribution can be characterized by a temperature, $T_r = 6700$ K. This suggests that ketene undergoes dissociation by a nonlinear path following photoexcitation at 193 nm.

In a recent communication,[1] we outlined the application of a photofragment infrared fluorescence method for characterizing ro-vibrational energy disposal to the carbon monoxide product of ketene photodissociation. We discuss these experiments in some detail here and consider our results in terms of their mechanistic implications.

The photochemistry of ketene has been extensively studied, in many cases because it is a convenient way to generate methylene. The UV photodissociation of ketene can yield both $CH_2(\tilde{X}^3B_1)$ and $CH_2(\tilde{a}^1A_1)$ with a branching ratio determined by the available energy and the decay dynamics of the electronically excited reactant. Some spectroscopic and photochemical data on ketene have been summarized by Okabe.[2] Molecular beam and laser spectroscopic techniques have provided means to study the photodissociation dynamics of ketene and the electronic structure of the nascent products in the absence of collisional relaxation processes. For example, Lengel and Zare[3] have used laser flash photolysis in conjunction with laser-induced fluorescence detection in determining that $CH_2(\tilde{a}^1A_1)$ is formed on the photodissociation of ketene between 3400 and 2900 Å. Lee and co-workers[4] have studied the photofragmentation of molecular beams of ketene and found that methylene is formed exclusively in its $\tilde{X}^3B_1$ state on 351-nm photolysis and exclusively in its $\tilde{a}^1A_1$ state on 308-nm photolysis. Lin and co-workers[5] have used time-resolved CO laser absorption spectroscopy in determining the nascent vibrational distribution for CO formed by the 193-nm photodissociation of ketene. Such studies are beginning to provide a useful picture of the photofragmentation dynamics of ketene. Still, important questions remain. For example, the role of nonradiative relaxation processes prior to fragmentation has not been directly addressed. The nature of the potential surfaces over which dissociation occurs has not been conclusively established. In principle, such problems might be treated by theoretical methods. However, ab initio theoretical approaches for estimating the rates of radiationless transitions in polyatomics have not been developed to the point where quantitative predictive accuracy can be expected. A similar situation often arises with electronic structure calculations for electronically excited species. By studying polyatomic reactivity at an increasingly microscopic level, we can begin to develop useful points of comparison for new theoretical methods in dynamics.

One of the more promising techniques for studying the dynamics of photodissociation reactions is photofragment infrared (IR) fluorescence spectroscopy. Following the photoactivation of a reactant with a pulsed UV laser, IR emission from one or more product modes is monitored as a function of time and/or wavelength. In this way, information on energy disposal to the photofragments can be directly obtained. For example, energy partitioning among product vibrational modes following the UV photofragmentation of haloethylenes has been studied by McDonald and co-workers.[6] Leone and co-workers[7,8] have characterized the photodissociation dynamics of CH_3I, CH_2I_2, and $Hg(CH_3)_2$ by time-resolved IR fluorescence methods and have elucidated some aspects of the vibrational spectroscopy of the radical products. In our work on ketene, a simple time-resolved photofragment IR fluorescence method is used to characterize ro-vibrational energy disposal to the CO product as described below.

Experimental Section

The basic experimental procedure employed in our photofragment fluorescence studies has been discussed previously[1,9] and will be outlined only briefly here. Ketene, either neat or diluted in a buffer gas, is flowed through an aluminum cell. The cell is equipped with a pair of quartz windows through which a UV laser beam can be directed and, at 90°, a CaF_2 window for viewing IR emission. The UV laser employed here is a Lambda Physik EMG 101 rare gas halid excimer laser, which can provide ca. 15-ns pulses at 193 nm (ArF*), 249 nm (KrF*), or 308 nm (XeCl*). The laser repetition rate is normally maintained below 5 Hz. IR fluorescence is viewed with an InSb detector (50 mm², 7-μm cut-off) after passage through a 0.5-cm evacuable cold gas filter[10] (CGF) cell, a 4.7-μm-wide bandpass filter (1.0 μm, FWHM), and a 1-μm longpass filter. The detector output is preamplified and then averaged with a PARC 162/164 Boxcar Integrator. The detection system rise time is $\lesssim 1$ μs. Ketene is prepared by the pyrolysis of acetic anhydride[11] and is stored at 77 K prior to use, when it is flowed into the fluorescence cell from a 195 K bath. Pressure in the fluorescence cell is measured with calibrated thermocouple gauges, a dibutyl phthalate manometer, or a mercury manometer, while pressure in the CGF cell is measured with a Bourdon gauge.

Results

Irradiation of ketene at 193 nm results in intense IR fluorescence at 4.7 μm due to the CO product. A typical fluorescence decay curve is shown in Figure 1. The CO fluorescence intensity is found to vary linearly with UV laser intensity between 2 and 9 mJ/cm². This suggests that the observed CO is formed as the result of a single photon absorption process. Irradiation of up to 2 torr of ketene at 249 nm (25 mJ/cm²) or 308 nm (6 mJ/cm²) yields no detectable IR fluorescence. The IR fluorescence observed on photoexcitation at 193 nm can be viewed through a CGF cell containing several torr of ketene or ethylene with no effect on the observed fluorescence amplitude or decay time. If the fluorescence is viewed through a 3.3-μm bandpass filter, the signal is completely attenuated. These results indicate that none of the IR fluorescence detected in our experiments arises from ketene, ethylene, or the asymmetric stretching vibration of CH_2. We cannot, however, exclude the possibility that the CH_2 photoproduct is excited in

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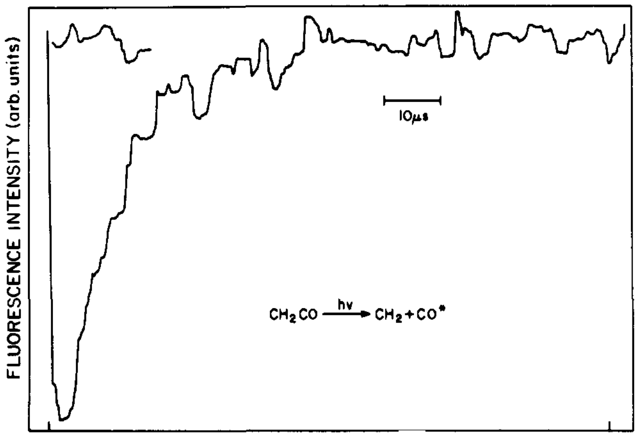

Figure 1. 4.7-μm fluorescence decay for CO formed by the irradiation of 0.34 torr of ketene at 193 nm (4 mJ/cm^2).

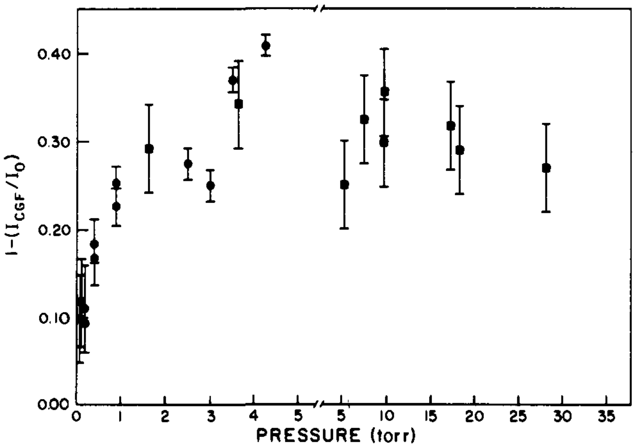

Figure 2. Attenuation of 4.7-μm fluorescence by a CGF containing 20 torr of CO as a function of total pressure: (●) pure ketene; (■) 0.16 torr ketene in argon.

its bending mode since the corresponding fluorescence would occur outside our detector's 7-μm cut-off and so would not produce a signal. Faint visible fluorescence can be observed following the photodissociation of ketene at 193 nm (ca. 4 mJ/cm^2). The emission was dispersed with a 0.6-m monochromator and found to correspond[12] to $CH(\tilde{X}^2\Pi \leftarrow \tilde{A}^2\Delta)$ fluorescence with a (0,0) transition near 4315 Å. No emission in the range 5000–7000 Å, corresponding to $CH_2(\tilde{a}^1A_1 \leftarrow \tilde{b}^1B_1)$ fluoresecence, was observed. This indicates that no $CH_2(\tilde{b}^1B_1)$ is formed upon the photolysis of ketene at 193 nm. Thus, photofragmentation yields $CH_2(\tilde{a}^1A_1)$, which may undergo subsequent UV multiphoton absorption to yield $CH(\tilde{A}^2\Delta)$.

The extent of vibrational excitation in the CO product formed via 193-nm photolysis can be estimated by CGF studies as described by Flynn and co-workers.[10] When relatively high sample pressures are employed in the fluorescence cell, e.g., for 0.16 torr of ketene in 20 torr of argon, introducing 20 torr of CO into the CGF cell attenuates the peak IR fluorescence intensity (i.e., that within the first 5 μs following the UV laser pulse) by ca. 32% relative to that observed through an evacuated CGF. When low pressures are employed, e.g., 0.1 torr of pure ketene, a filled CGF cell attenuates the resulting fluorescence intensity only to the extent of ca. 10% (see Figure 2).

Discussion

Although the photodissociation of ketene at 193 nm results in easily observed CO photofragment IR fluorescence, no fluorescence is observed following irradiation at 249 or 308 nm. On the basis of our detection sensitivity, the experimental conditions employed (e.g., ketene pressure, laser fluence, volume subtended by the detector field of view), and the absorption coefficient of ketene at each irradiation wavelength,[13] we can determine that following the photoexcitation of ketene at 249 nm <30% of the CO product fluoresces at 4.7 μm while in the case of 308-nm photoexcitation <6% of the CO product fluoresces at 4.7 μm. The upper limit for 249-nm excitation is rather high due to ketene's small absorption coefficient at this wavelength. For 308-nm excitation, note that almost all of the available energy must be partitioned to the CO product's vibrational mode to yield any fluorescence at 4.7 μm. Thus no CO fluorescence is anticipated following photoexcitation of ketene at 308 nm. Relevant data are summarized in Table I.

Table I. Summary of Observations on CO Photofragment Fluorescence Intensity vs. Ketene Excitation Wavelength

excitation wavelength, nm	absorption cross section,[a] cm^2	available energy,[b] kcal/mol	4.7-μm fluorescence obsd
193	5×10^{-19}	63	yes
249	2×10^{-21}	30	no
308	3×10^{-20}	8	no

[a] See ref 13. [b] Assuming the methylene product is formed exclusively in its $\tilde{a}\,^1A_1$ state.

The CGF studies described above provide a means for characterizing the CO photoproduct's vibrational distribution in terms of a temperature, T_v, assuming a Boltzmann distribution of product vibrational states and a 300 K rotational distribution.[10] CO rotational thermalization is accomplished in our experiments by using moderate pressures of argon. The data in Figure 2 indicate that for argon pressures ≳4 torr rotational relaxation is complete within our detection system rise time. Even for argon pressures of ca. 30 torr, no significant CO *vibrational* relaxation occurs during the 5 μs following the UV laser pulse. Thus for total sample pressures in the range 4–30 torr, we can compute T_v from the data in Figure 2. To do this, we express the CO fluorescence spectral distribution as a function of T_v as shown in eq 1, where $I_0(v,J')$

$$I_0(v,J') = I_0 D_v(T_v) D_r(T_v,T_r) A_v F_v(J',J'') \tag{1}$$

is the fluorescence intensity originating from the indicated ro-vibrational state, I_0 is the total fluorescence intensity, $D_v(T_v)$ is the Boltzmann distribution of vibrational states at temperature T_v, $D_r(T_v,T_r)$ is the corresponding Boltzmann rotational state distribution (here, we assume T_r = 300 K), A_v is the Einstein coefficient for spontaneous emission[14] from state v, and $F_v(J',J'')$ is the Herman–Wallis factor for the $(v,J' \rightarrow v-1,J'')$ transition.[15] The emission intensity transmitted through a CGF cell of length l, containing CO gas at 300 K and pressure p, is given by eq 2,

$$I_{CGF}(v,J') = I_0(v,J')10^{-kpl} \tag{2}$$

where k is the population weighted absorption coefficient for the indicated ro-vibrational transition. Values for k were determined by scaling low-resolution absorption coefficients[16] to an empirically determined[17] $P_{1,0}(9)$ high-resolution absorption coefficient at 300 K. In our experiments, we measure the ratio of fluorescence intensities transmitted through filled and evacuated CGF cells, i.e., I_{CGF}/I_0. This ratio can be calculated as a function of T_v from 1 and 2 as shown in eq 3. Thus, by fitting our experimentally

$$I_{CGF}/I_0 = \sum_v \sum_{J'} I_{CGF}(v,J') \Big/ \sum_v \sum_{J'} I_0(v,J') \tag{3}$$

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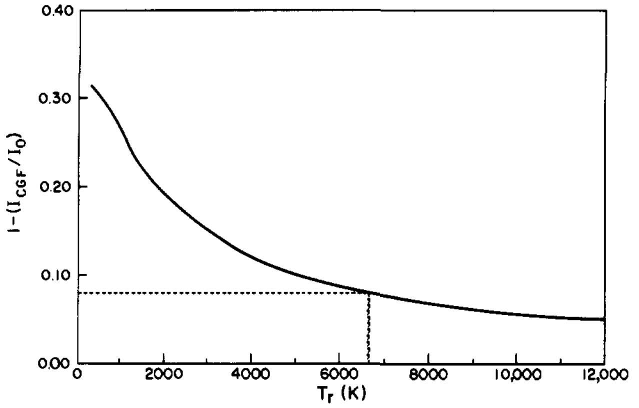


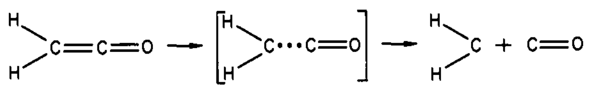
Figure 3. Calculated attenuation of 4.7-μm fluorescence by a CGF containing 20 torr of CO as function of the rotational temperature, T_r, of the emitting CO. A vibrational temperature of 3750 K is assumed for the emitting CO. A dashed line is drawn at the experimentally determined zero-pressure attenuation and the corresponding T_r (see text).

determined high-pressure I_{CGF}/I_0, 0.69, to that calculated from eq 3, we find[18] $T_v = 3750 \pm 400$ K. This is in good agreement with the results of Lin and co-workers[5] who find $T_v \simeq 4000$ K using a CO laser absorption method. This agreement, in conjunction with the CO vibrational relaxation time we observe via fluorescence decay ($p\tau \simeq 48$ torr μs for CO–argon collisions), provides strong evidence that the T_v determined here corresponds to the nascent CO vibrational population. We note that the method for approximating T_v described by Flynn and co-workers,[10] eq 4, where $h\nu$ is the CO(0 ← 1) vibrational quantum, gives a result in good agreement with the value obtained here.

$$I_{CGF}/I_0 = 1 - [1 - \exp(-h\nu/kT_v)]^2 \qquad (4)$$

In the CGF experiments described above, addition of room-temperature CO to the CGF cell attenuates the fluorescence intensity reaching the IR detector by selectively absorbing radiation due to transitions that terminate on thermally populated states of CO. Only the ground vibrational state is appreciably populated at 300 K. Since the CO photoproduct vibrational distribution characterized by $T_v = 3750$ K is unrelaxed even in our high-pressure experiments, it might be anticipated that reducing the sample pressure should result in essentially no change in the observed CGF attenuation of 4.7-μm fluorescence intensity if rotational excitation is absent. However, we find significantly *less* attenuation at low sample pressures; e.g., $I_{CGF}/I_0 \simeq 0.90$ at a total pressure of ca. 0.1 torr of ketene (see Figure 2). Thus, with decreasing sample pressure, a larger component of the observed ir fluorescence intensity must consist of transitions that terminate on CO states that are not populated at 300 K, i.e., highly excited rotational states. A linear extrapolation of the data indicates that in the limit of zero pressure, corresponding to a near-nascent CO rotational state distribution, $I_{CGF}/I_0 \simeq 0.92$. The CGF data thus demonstrate that CO formed via the photofragmentation of ketene at 193 nm is rotationally excited. The extent of this rotational excitation can be gauged by using the model for CGF attenuation experiments implicit in eq 1–3. If we assume the nascent CO rotational state distribution can be represented by a Boltzmann function, $D_r(T_v = 3750$ K, $T_r)$ in eq 1, then the rotational temperature, T_r, can be obtained by iteratively computing I_{CGF}/I_0 (eq 3) as a function of T_r until the simulated ratio agrees with that determined by extrapolating the data in Figure 2 to zero pressure. The results of such computations are illustrated in Figure 3, which indicates that the extrapolated CGF attenuation at zero pressure corresponds to $T_r \simeq 6700 \pm 1500$ K. We have assumed a Boltzmann rotational state distribution for CO in order to characterize the photoproduct population by a single parameter T_r. It is certainly possible that the nascent state distribution is non-Boltzmann with an average degree of excitation less than that indicated by $T_r = 6700$ K. Nevertheless, our data suggest that extensive rotational energy release is a dominant feature of the photofragmentation dynamics of ketene at 193 nm.

This result might be obtained if ketene undergoes dissociation from an excited state where the CCO bond angle is less than 180°. In fact, all of the excited singlet states accessible[19] via 193-nm photon absorption are "nonlinear" in this sense. However, fluorescence has never been reported from any of these excited states, an observation suggesting rapid nonradiative decay processes are operative. Additionally, the methylene photoproduct is formed only in its $\tilde{a}^1A_1$ state when ketene is irradiated[5] at 193 nm, and correlation diagrams[20] indicate that this product state can be readily accessed only from keetene's ground electronic state. These observations suggest that photoexcitation of ketene at 193 nm is followed by rapid internal conversion to its ground electronic state prior to fragmentation. Thus, dissociation occurs on the ground electronic state surface. Ab initio calculations of the potential surface for ketene fragmentation have been reported. Pendergast and Fink[20] found that linear (least-motion) and nonlinear decay channels, eq 5 and 6, respectively, have comparable energetic requirements so that either is feasible. Yamabe and Morokuma[21] report that nonlinear decay channels, eq 6, are preferred. Apparently, the computational studies available do not provide a sufficient basis for predicting which of the two types of fragmentation channels is operative. We note that in the case of the linear channel, eq 5, motion along the reaction coordinate correlates directly with product translational excitation. For fragmentation via a nonlinear channel, eq 6, motion along the reaction coordinate also correlates with product rotational excitation. Thus, eq 6 provides a means for efficiently coupling available energy to the products' rotational degrees of freedom that is not available in the case of eq 5. We conclude that the photofragmentation of ketene is a nonlinear process although, from our data, we cannot determine whether the CCO angle bends in or out of the molecular plane as the reaction occurs.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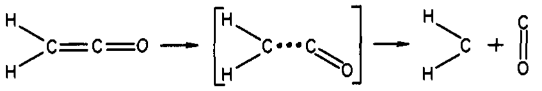
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Conclusions

Photofragment infrared fluorescence methods have been used to monitor rovibrational energy disposal to the carbon monoxide product formed upon the photolysis of ketene at 193 nm. We find that the nascent CO vibrational distribution can be characterized by a temperature $T_v = 3750$ K. Rotational excitation in the CO product can be characterized by a temperature $T_r = 6700$ K, assuming a Boltzmann distribution of CO rotational states. These results indicate that the photofragmentation of ketene at 193 nm proceeds via a nonlinear geometry.

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Registry No. Ketene, 463-51-4; carbon monoxide, 630-08-0.

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