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PHOTOEXCITATION AND PHOTODISSOCIATION LASERS. III. MECHANISMS OF CO LASER EMISSION FROM THE VACUUM UV PHOTODISSOCIATION OF CH_2CO–O_2 AND CH_2CO–SO_2 MIXTURES*

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CO laser emission was detected in the vacuum UV flash photolysis of CH_2CO. The emission is attributed to the initial photodissociation reaction

$CH_2CO + h\nu\ (\lambda \approx 175\ nm) \rightarrow CH_2^* + CO^\dagger$.

Addition of O_2 to the CH_2CO system caused a pronounced enhancement in the laser intensity. This effect is believed to be due to the removal of the CH_2 + CH_2CO reaction, which produces uninverted CO molecules. A greater laser output was obtained when SO_2 was used instead of O_2. In the O_2-added system, a total of 16 transitions ranging from $\Delta v(8\rightarrow7)$ to $(4\rightarrow3)$ were identified. Addition of SO_2 increased the total number of lines to 34, lasing in the range between $(11\rightarrow10)$ and $(4\rightarrow3)$. This enhancement is ascribed to the occurrence of the reaction

$O(^3P) + CH_2 \rightarrow CO^\dagger + 2H$.

In addition to these chemical effects, the effects of flash energy, inert gases and total pressures have been investigated.

1. Introduction

In the preceding paper, we discussed the results obtained from our CO laser emission study of the photodissociation of COS near 170 nm [1]. In this article, we report the results obtained from the photodissociation of ketene (CH_2CO) in the same spectral region.

The photodissociation of CH_2CO is known to generate CH_2 radicals. The production and disappearance of the CH_2 radical in the pure CH_2CO system occur via the following sequence:

$$CH_2CO + h\nu \xrightarrow{(1)} CH_2 + CO,$$

$$CH_2 + CH_2CO \xrightarrow{(2)} C_2H_4 + CO.$$

Since CO can be generated from both reactions, one would therefore expect a significant perturbation on the total CO emission if reaction (2) is chemically inhibited by addition of such reactive species as O_2 or the O atom to the CH_2CO system. The O + CH_2 reaction has been shown to be the principal laser pumping reaction in both SO_2–CH_2Br_2 and SO_2–C_2H_2 laser systems [3,4].

We have examined these effects as well as the effects of various inert gases, flash energy and total pressure on the overall CO laser outputs. These results are presented in this paper.

2. Experimental

The experimental setup is essentially the same as that described in the preceding paper [1].

All chemicals used in this work except CH_2CO were obtained from the Matheson Gas Products Company. CH_2CO was prepared by the pyrolysis of acetic

* The preliminary results of this work were first reported in the 8th ACS Middle Atlantic Regional Meeting, Washington, D.C., January, 1973.

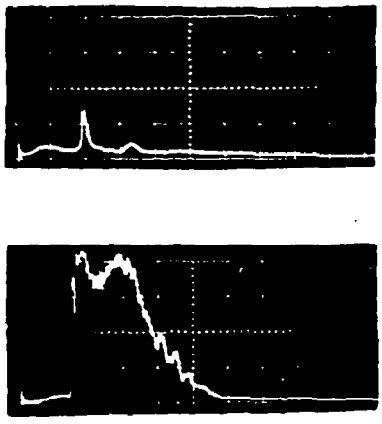

Fig. 1. Typical CO laser emission traces with or without added O_2. Time scale: 10 μs/div, flash energy 1.6 kJ, laser mixture: 20 torr 1:20/CH_2CO:SF_6. Upper trace: P_{O_2} = 0 torr, 2V/div. Lower trace: P_{O_2} = 4 torr, 10 V/div.

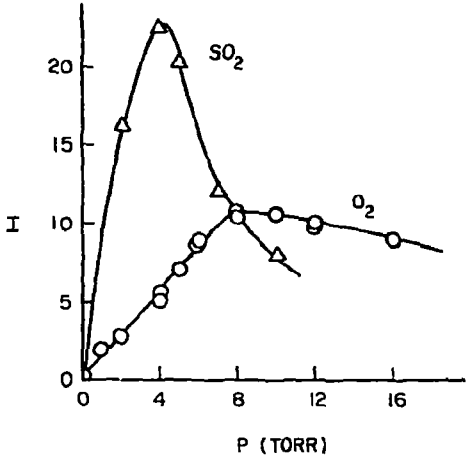

Fig. 2. Effects of O_2 and SO_2 on the total CO laser intensity.

anhydride ($CH_3COOCOCH_3$) at about 500°C in a 50 cm, 15 mm i.d. Pyrex flow tube. The anhydride was pumped continuously through the hot tube under vacuum. The products of decomposition were rapidly separated in a train of traps maintained at −22°C (CCl_4 slush), −78°C (dry ice-isopropanol slush) and −127°C (*n*-propanol slush) respectively. At the end of pyrolysis, the −127°C fraction was collected and distilled twice from −78°C to −127°C under constant evacuation to remove any traces of CH_3COOH and CO_2. The final −127°C fraction was then stored in a trap maintained at dry-ice temperature for prolonged use. It should be noted that ketene polymerizes slowly at room temperature at, particularly, high pressures; therefore, it cannot be stored in a bulb at room temperature.

3. Results and discussion

3.1. Effects of added O_2 and SO_2

Weak CO stimulated emission at 5 μm was detected when CH_2CO was flash-photolyzed in the vacuum UV above 165 nm, in the presence of an excess amount of a diluent (He, Ar or SF_6). A typical oscilloscope trace of the total laser emission taken from a 20 torr 1:20/CH_2CO:SF_6 mixture, flashed at 1.6 kJ, was shown in fig. 1 (the upper trace). Two weak laser peaks appear at about 19 and 30 μs after flash initiation. This weak emission, however, was found to be enhanced very pronouncedly by the addition of a small amount of O_2. The lower trace in fig. 1 shows the effect of 4 torr O_2 added to 20 torr 1:20/CH_2CO:SF_6 mixture on the total laser emission. The total energy was found to increase by several orders of magnitude. Similar, though even stronger, enhancement was observed when SO_2 was introduced into the CH_2CO–SF_6 mixture instead of O_2.

The peak power of CO emission as functions of the partial pressures of both O_2 and SO_2 are shown in fig. 2. The intensity of CO emission increases linearly with the pressure of O_2 below 8 torr; however, it starts to decline slowly as the pressure of O_2 increases further.

The addition of a small amount of SO_2 enhances the laser intensity very drastically. The intensity reaches its maximum value when 4 torr SO_2 is present, but it drops rather rapidly when more SO_2 is added. The chemical significance of these interesting findings will be fully discussed later.

3.2. Total pressure dependence

Fig. 3 shows the total pulse intensity observed from flashing a 1:6:20/CH_2CO:O_2:SF_6 and a 1:20/CH_2CO:O_2 mixture at various pressures; the flash energy was kept constant at 1.6 kJ. Apparently the SF_6-diluted mixture has a much higher output, due probably to its

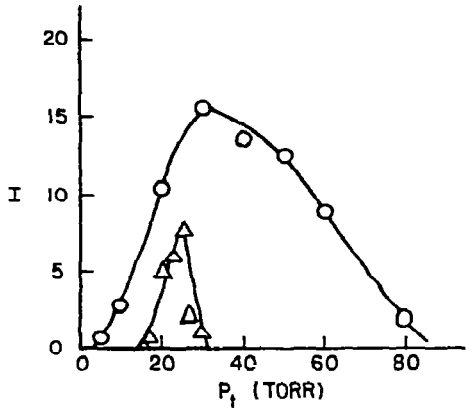

Fig. 3. Relative CO laser intensity as a function of total pressure. circle, 1:6:20/CH_2CO:O_2:SF_6 mixture; triangle, 1:20/CH_2CO:O_2 mixture. Flash energy = 1.6 kJ.

larger heat capacity and its slower $CO^{\dagger}$ relaxation rate than O_2. Because of these effects, the operational range of the SF_6-diluted mixture (5–90 torr) is much wider than that of the 1:20/CH_2CO:O_2 mixture (17–30 torr).

3.3. Effects of inert gases

Inert gas dilution was found to be essential for laser oscillation. Fig. 4 shows the effect of He, Ar and SF_6 on the total laser output from a 4 torr 1:8/CH_2CO:O_2 mixture, flashed at 1.4 kJ. No laser action was detected in the absence of these diluents. Both He and Ar have comparable efficiency, and at least 10 torr of each gas was required for laser oscillation. As was found in many other systems previously studied [1, 4–8], SF_6 was the most efficient diluent in enhancing the laser power. In several cases [4,6], SF_6 was found to be the only inert diluent that could promote laser oscillation. This enhancement is due to the lowering of rotational–translational temperature of the lasing species. The fact that inert gas dilution is indispensable in the present system indicates that CO formed in the initial photodissociation reaction is rotationally nd translationally hot.

3.4. Flash energy dependence

The dependence of the peak laser pulse intensity on flash energy (i.e., the total electrical input energy)

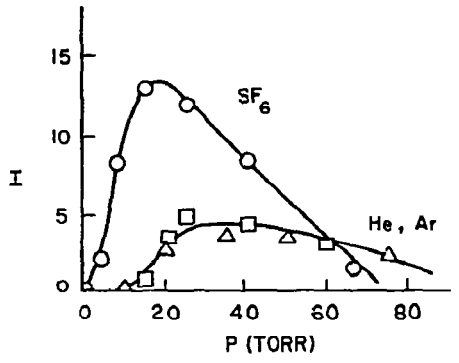

Fig. 4. Effects of inert gases on CO emission intensity.

is presented in fig. 5 for a 30 torr 1:6:20/CH_2CO:O_2:SF_6 mixture. The intensity of laser pulse varies linearly with flash energy within the scatter of our intensity measurements. This observation implies that the pumping mechanism is a single photon excitation process. The mechanism will be discussed later.

3.5. Identification of laser transitions

The emission from the 1:20/CH_2CO:SF_6 mixture was too weak to be resolved with the half-meter Minuteman Model 305 MI3 monochromator used in the present work. Instead, we examined the outputs from both 1:8:20/CH_2CO:O_2:SF_6 and 1:4:20/CH_2CO:SO_2:SF_6 mixtures. The observed transition, are given in table 1.

The CO emission from the O_2-added laser mixture ranges from $\Delta v(8\rightarrow7)$ to $(4\rightarrow3)$, whereas the emission from the 1:4:20/CH_2CO:SO_2:SF_6 mixture ranges from $\Delta v(11\rightarrow10)$ to $(4\rightarrow3)$ with the total laser lines increasing from 16 for the O_2–CH_2CO mixture to 34 for the SO_2–CH_2CO mixture. This significant change in the range of laser oscillation as well as the intensity of laser output (see fig. 2) can be ascribed essentially to chemical rather than physical effect, as was anticipated for reasons mentioned in the introduction.

3.6. Reaction mechanism

Ketene has been used photolytically as a convenient CH_2 radical source in the UV region [9]. There are two weak absorption bands above 200 nm; one extends from about 380 nm to nearly 240 nm with a

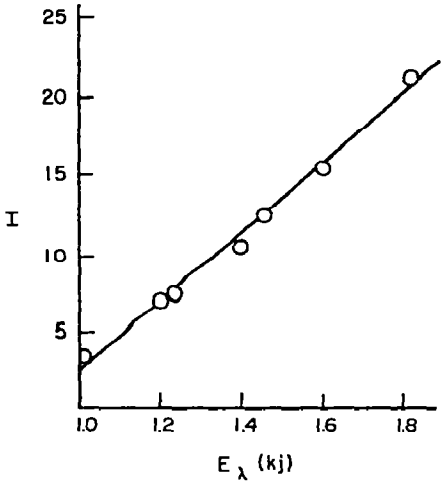

Fig. 5. Relative CO laser intensity as a function of flash energy. Laser mixture: 30 torr of 1:6:20/CH_2CO:O_2:SF_6.

broad maximum at 320 nm, the other more intense band starts near 240 nm and rises to a sharp maximum at about 213 nm [2]. The first band, which has been assigned as the $^1A_2 \leftarrow {}^1A_1$ transition and has the vibrational spacings of about 365 cm^{-1} as progression in the bending mode, consists of a number of diffuse peaks that are pressure-dependent. The transition corresponds to the forbidden $n \rightarrow \pi^*$ transition of aldehydes and ketones which is usually found between 340–250 nm. Most photochemical studies with CH_2CO have used light absorbed by this band [9].

The second band peaks at 213 nm, though much stronger, is still weak because it is related to the forbidden $^1B_2$ ($^1\Delta_u$) $\leftarrow {}^1A_1$ ($^1\Sigma_g^+$) transition. Four vibrational bands with an average spacings of about 1040 cm^{-1} have been observed [2].

Because of the weak absorption of the aforementioned two bands, in comparison with the strong absorption band below 185 nm [10,11], the photodissociation of CH_2CO probably results primarily from absorption in the spectral region 185–165 nm which is accessible to the present flash. The vacuum UV band is a strong continuum ($\epsilon_{max} \approx 3 \times 10^4$ ℓ/mole cm [11]); the high intensity of this absorption indicates that it is strongly allowed, due probably to the $^1B_2$ ($^1\Sigma_u^+$) $\leftarrow {}^1A_1$ ($^1\Sigma_g^+$) transition [2] (or the $\tilde{C}\ {}^1A_1 \leftarrow \tilde{X}\ {}^1A_1$ transition according to Herzberg [12]). This continuum is superimposed by a number of intense dis-

Table 1
Observed CO Laser Transitions in the O_2–CH_2CO and SO_2–CH_2CO Systems [a]

Transition		Relative intensity [b]	
		O_2	SO_2
11→10	P(16)		w
10→ 9	P(14)		m
	P(13)		m
9→ 8	P(16)		s
	P(15)		s
	P(14)		s
	P(13)		m
	P(12)		w
8→ 7	P(17)		s
	P(16)		w
	P(15)		m
	P(14)		s
	P(13)		w
	P(12)	m	w
7→ 6	P(17)		s
	P(16)		
	P(15)	s	s
	P(14)	s	s
	P(13)	w	w
	P(12)		
	P(11)	w	
6→ 5	P(17)	w	s
	P(16)	s	w
	P(15)	s	s
	P(14)	m	s
	P(13)	m	s
	P(12)	w	w
5→ 4	P(18)		m
	P(17)		s
	P(16)		w
	P(15)		m
	P(14)	m	m
	P(13)	m	s
	P(12)	m	w
4→ 3	P(15)		m
	P(14)		
	P(13)	w	w
	P(12)		
	P(11)	w	w

[a] The mixtures used in these experiments were O_2:CH_2CO:SF_6 = 8:1:20 and SO_2:CH_2CO:SF_6 = 4:1:20; p_t = 20 torr, E_λ = 1.6 kJ. The resolution was better than ±0.7 cm^{-1}.

[b] s = strong, m = medium and w = weak; no entry means the transition is absent.

crete Rydberg bands. The first Rydbergs begin at ~183 nm. In this region, the spectrum is similar to that of C_2H_4, which has an absorption continuum with maximum at 163 nm and first strong Rydberg at ~175 nm. The spectrum of CH_2CO is red-shifted from C_2H_4 by about 2600 cm^{-1} [2,10].

The products of the initial photodissociation reaction are CO and CH_2 :

$$CH_2CO + h\nu(\lambda \leqslant 185\ nm) \rightarrow CO^{\dagger} + CH_2^{*},$$

where the dagger and asterisk denote vibrational and electronic excitations, respectively. The extent of CO vibrational excitation has not been investigated before, and it is subject of the present study. The exact electronic state of the CH_2 radical formed in this spectral region is not known. At longer wavelengths ($\lambda \geqslant 195$ nm), the possible product states of the CH_2 radical formed in the dissociation of CH_2CO had been discussed by Basch [13] on the basis of a state energy correlation for the least motion paths. However, no direct reference was made with regard to the dissociation in the 170–185 nm region corresponding to the $\tilde{X}\ ^1A_1 \rightarrow \tilde{C}\ ^1A_1$ transition [12]. A similar correlation (cf. fig. 1 of ref. [13]) for the dissociation from the $\tilde{C}\ ^1A_1$ state would predict the production of $CO(X\ ^1\Sigma^+) + CH_2(\tilde{c}\ ^1A_1)$. In this case, the available energy, $\langle E \rangle$, for distribution into both products is only ~7 kcal/mole. Evidently, this is not enough to account for the observed CO laser emission ($V_{max} = 8$). The formations of $CH_2(\tilde{b}\ ^1B_2)$ and $CH_2(\tilde{a}\ ^1A_1)$, however, would increase $\langle E \rangle$ to 65 and 85 kcal/mole, respectively; these energies are sufficient to explain the observed CO emission. The above estimates were based on the value of $\Delta H_f^0(\tilde{a}\ ^1A_1\ CH_2) \approx 92$ kcal/mole, obtained from a number of chemical activation studies involving the CH_2-hydrocarbon insertion reactions [14]. The mechanism by which either state ($\tilde{a}\ ^1A_1$ or $\tilde{b}\ ^1B_2$) of the CH_2 radical may be produced from the dissociation of the $\tilde{C}\ ^1A_1$ CH_2CO molecule are by no means clear. We plan to measure the exact $CO^{\dagger}$ population in the photodissociation of CH_2CO at both 213 and 175 nm bands in order to determine the initial states of the CH_2 radical produced at both bands.

Since the rates of $CH_2 + CH_2CO$ and $CH_2 + CH_2$ are known to be fast [11], both reactions should also take place concurrently during a flash

$$CH_2 + CH_2CO \xrightarrow{(2)} \triangleright C = O^{\dagger} \rightarrow C_2H_4 + CO,$$

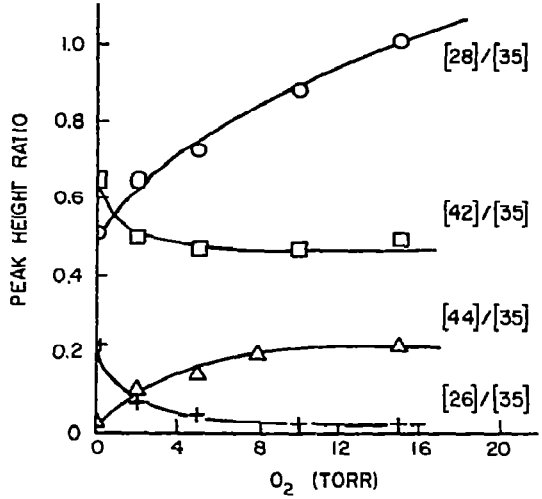

Fig. 6. The effect of O_2 on the relative yields of various flash products. Varying amounts of O_2 was added to 20 torr of 1:20/ CH_2CO:SF_6 mixture flashed at 1.6 kJ.

$$\Delta H_2^0 \approx -100\ kcal/mole,$$

$$CH_2 + CH_2 \xrightarrow{(3)} C_2H_4^{\dagger} \xrightarrow{(a)} C_2H_2 + H_2,$$

$$\xrightarrow[[M]]{(b)} C_2H_4.$$

The rapid occurrence of reaction (2), which is though considerably exothermic, is believed to be detrimental to laser action, judging by the extraordinary effect of O_2 on enhancing the laser power in this system. The energy of reaction (2) probably releases primarily into the more complex C_2H_4 molecule. A direct experimental evidence obtained from a population measurement of the CO formed in the decomposition of a chemically activated cyclopropanone indeed supported this conclusion [15]. Thus, the production of the vibrationally partially excited CO from reaction (2) can alternate significantly the population inversion created by the initial photodissociation reaction (1). The removal of such CO molecules by chemically arresting reaction (2) with O_2 [4]

$$CH_2 + O_2 \xrightarrow{(4)} \text{products},$$

therefore enhances the power of CO laser emission as was demonstrated by the results shown in figs. 1 and 2.

O_2 is known to be a more effective scavenger for the $^3B_2$ CH_2 radical than for the $^1A_1$ CH_2 radical. A plausible explanation has been given elsewhere [16].

The chemical effects of O_2 on the formation of major products: CO (*m/e* 28), CO_2 (*m/e* 44) and C_2H_2 (*m/e* 26) were examined mass-spectrometrically. The results are shown in fig. 6. The data were taken from the flash photolysis of a 20 torr 1:20/CH_2CO:SF_6 mixture in the presence of varying amounts of O_2. The flash energy was kept constant at 1.6 kJ. These measurements were made by internally standardizing the peak height of each mass with that of SF_6 using the *m/e* 35 (SF_2^{2+}) peak. In the absence of O_2, about 39% of CH_2CO was destroyed in a single flash at 1.6 kJ.

Addition of O_2 increases the yields of both CO and CO_2, in concordance with the proposed mechanism for the $CH_2 + O_2$ reaction [4]. The yield of C_2H_2, which is probably produced from reaction (3a), decreases rapidly as the pressure of O_2 increases. This is believed to be caused by the removal of the CH_2 radical via reaction (4). The decrease in CH_2CO (*m/e* 42) upon the addition of O_2 can be attributed to the occurrence of secondary reactions such as $H_2O + CH_2CO$, $HCOOH + CH_2CO$ and atom (or radical) + CH_2CO. H_2O, HCOOH and the reactive species like H, OH and HCO are believed to be the products of the $CH_2 + O_2$ reaction [4]. It should be mentioned that in our gas analysis, a liquid nitrogen trap was used to separate CO from C_2H_4 and CH_2CO to avoid the interference of the mass 28 measurement by both compounds.

Instead of removing the CH_2 radical chemically, it can be more productively utilized for generating additional excited CO via the following reaction

$$O(^3P) + CH_2 \xrightarrow{(5)} CO^\dagger + 2H, \qquad \Delta H_5^0 \approx -75 \text{ kcal/mole}.$$

This is achieved by adding SO_2 to the CH_2CO/SF_6 system as has been demonstrated by the results given in fig. 2. SO_2 has been shown to be a convenient photolytic $O(^3P)$-atom source [3]. The $O + CH_2$ reaction was previously proposed as the primary laser pumping process in both $SO_2 - C_2H_2$ and $SO_2 - CH_2Br_2$ flash-initiated laser systems [4]. The present results further support our previous conclusion with regard to the importance of reaction (5) for generating vibrationally excited CO. The presence of these $CO^\dagger$ molecules pushes the range of laser transitions upward to higher vibrational levels (cf., table 1).

4. Conclusion

Weak CO laser emission was detected in the flash-initiated CH_2CO–SF_6 mixture above 165 nm. In this case, the emission is attributed to the following reactions

$$CH_2CO + h\nu \xrightarrow{(1)} CO^\dagger + CH_2,$$

$$CH_2 + CH_2CO \xrightarrow{(2)} CO + C_2H_4.$$

The CO molecule formed in reaction (2) is believed to be uninverted and its presence results in the observed weak emission. Addition of O_2 to chemically removed the CH_2 radical, and thus arresting the occurrence of reaction (2), enhances the total laser energy by several orders of magnitude. An even greater laser output was obtained when SO_2 was used instead of O_2. The chemical effects of O_2 and SO_2 have been discussed. In the O_2-added system, a total of 16 transitions ranging from $\Delta v(8\rightarrow7)$ to $(4\rightarrow3)$ were identified. The emission was concluded to be due to reaction (1). Addition of SO_2 increased both intensity and the total number of oscillating lines (34 transitions from $11\rightarrow10$ to $4\rightarrow3$). This is ascribed to the occurrence of reaction (5),

$$O(^3P) + CH_2 \xrightarrow{(5)} CO^\dagger + 2H.$$

Acknowledgement

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