

## Photo-oxidation reactions of ethylene in supercritical CO<sub>2</sub>

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### Abstract

KrF excimer laser-induced reactions in the mixture of ethylene/O<sub>2</sub>/CO<sub>2</sub> under sub- and super-critical conditions were investigated. The main products were acetaldehyde and ethylene oxide. The total quantum yield decreased with the increase of mixture density, but the branching ratio between the two products were almost independent on the density. The branching ratio was found to be what is expected if the reactive species is O(<sup>3</sup>P). Any distinctive specific pressure effect has not been observed in the near-critical region. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Photo-oxidation; Ethylene; Supercritical CO<sub>2</sub>

### 1. Introduction

It was found in our previous research [1] that relatively large amounts of oxidized products were obtained when a mixture of ethane (C<sub>2</sub>H<sub>6</sub>)/O<sub>2</sub> was photolysed with KrF excimer laser light at 30–40°C at pressures close to the critical one, in spite of the fact that both C<sub>2</sub>H<sub>6</sub> and O<sub>2</sub> do not absorb the KrF excimer laser light at ordinary pressures. At that time, the mechanism of the 248 nm light absorption was not clear. Later, we studied the effect of pressurized foreign gases on the photo-absorption of O<sub>2</sub> in the 230–280 nm wavelength range [2]. The photo-absorption by O<sub>2</sub> in the mixtures with CO<sub>2</sub>, ethylene (C<sub>2</sub>H<sub>4</sub>) and several other gases was found to increase considerably with cross-sections proportional to the number density of the foreign gases. It was concluded that the mechanism of the absorption augmentation is the collision-induced relaxation of the selection rule for the dipole-forbidden Herzberg III system (A'<sup>3</sup>Δ<sub>g</sub>–X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>). In the neighborhood of critical point, light scattering also contributes to decrease the transmitted light intensity. This scattering, in some cases, might be useful in order to lengthen the effective absorption path length which is important for complete absorption of photon.

On the other hand, the supercritical CO<sub>2</sub> is a potential alternative solvent for various photochemical reactions, particularly for photo-initiated oxidation reactions, due to the non-flammability of CO<sub>2</sub>. Thus, we are studying photo-induced oxidation reactions of ternary mixtures of

hydrocarbon/O<sub>2</sub>/CO<sub>2</sub>. The present paper reports the case of C<sub>2</sub>H<sub>4</sub> in order to understand the behavior of typical olefins which are expected to trap some active species during the reaction.

### 2. Experimental

The experimental apparatus is shown in Fig. 1. The reaction cell consists of a stainless-steel cylinder (length, 31 mm; inner diameter, 16 mm) with quartz windows at both ends for light introduction. After evacuating the cell, C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> were introduced into the reactor to an individual fixed pressure (typically, C<sub>2</sub>H<sub>4</sub>, 11–20 atm; O<sub>2</sub>, 6–11 atm), followed by the addition of CO<sub>2</sub> up to the reaction pressure. The contents were mixed with a magnetic stirrer inside the cell for 5 min, and then a KrF (at 248 nm) excimer laser (Lambda Physik; Lextra 100) irradiated the mixture for a desired period (typically, 5–60 min at a 10 Hz repetition rate), with keeping the stirring of the contents all through the irradiation. The reaction cell was placed in a constant temperature bath at 308 K. After the irradiation of a desired period, the contents were expanded into a container at 1 atm for quantitative analysis by gas chromatography. The laser intensity coming through the reaction cell was monitored using a joule meter (Gentec, ED-500).

The PVT relation of the mixture was estimated using a modified BWR equation with appropriate parameters. Adopted *k<sub>ij</sub>* values are: 0.0370 for C<sub>2</sub>H<sub>4</sub>–O<sub>2</sub>, 0.0537 for C<sub>2</sub>H<sub>4</sub>–CO<sub>2</sub>, and 0.0018 for O<sub>2</sub>–CO<sub>2</sub> [3]. Because the relevant val-

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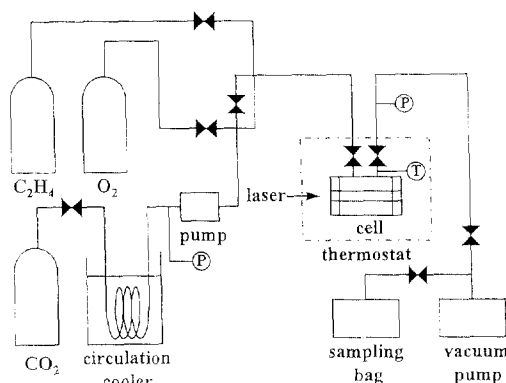


Fig. 1. Experimental apparatus. P: pressure gauge, T: thermocouple.

ues for  $O_2$  are not known, we employed the values of  $N_2$  in place of those of  $O_2$ . The mixture density was thus derived from the initial  $C_2H_4$  and  $O_2$  amounts and the total pressure.

In the present method of changing the pressure in order to investigate the pressure effect, the fraction of individual component is continuously changing, and then also, the critical point of the mixture. We estimated the critical temperature, pressure, and density for the mixture whose composition is the same as that of the experimental mixture under the given pressure using the above PVT relation. According to the estimation, in the typical experiments of 11 (or 20) atm  $C_2H_4$  and 6 atm  $O_2$  at 308 K, the experimental temperature (308 K) is always higher than the critical temperature of the mixture at any pressure studied. When the experimental pressure is higher than 73 atm (or 67 atm in the case of 20 atm  $C_2H_4$ ) with the corresponding mixture density of 5.1 (or 4.1) mol  $l^{-1}$ , it is higher than the critical pressure of the mixture, and thus, the experimental mixture can be regarded to be in the supercritical region. Below 73 (or 67) atm, the mixture can be regarded to be in the gas phase.

### 3. Results and discussion

#### 3.1. Products

Acetaldehyde ( $CH_3CHO$ ) and ethylene oxide ( $C_2H_4O$ ) were main products. CO was also detected. The main-product yields show linear dependence on the pulse energy as shown in Fig. 2, which indicates that the process is initiated by one-photon absorption.

Fig. 3 shows a typical time dependence of the three products under the conditions in the gas phase. On the other hand, an example in the supercritical region is shown in Fig. 4 (in this experiment, CO was not tried to measure). The yield of  $C_2H_4O$  increases linearly with time, which indicates that  $C_2H_4O$  does not react to any appreciable extent through secondary reactions or subsequent photolysis. On the contrary, the yield of  $CH_3CHO$  shows a tendency to become flat upon the continuation of the irradiation, and CO has a certain initial time delay. The concerted behavior of these products strongly suggests that the primarily produced  $CH_3CHO$  is photolysed

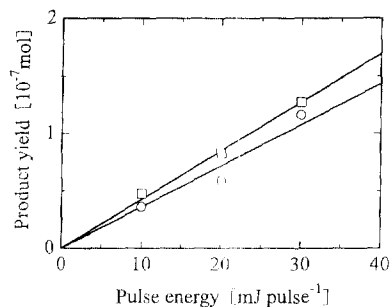


Fig. 2. The product yield as a function of laser pulse energy. Reaction conditions:  $C_2H_4$ , 11 atm;  $O_2$ , 6 atm; total pressure, 65.5 atm; temperature, 308 K; irradiation time, 10 min at 10 Hz.  $\square$ ,  $CH_3CHO$ ;  $\circ$ ,  $C_2H_4O$ .

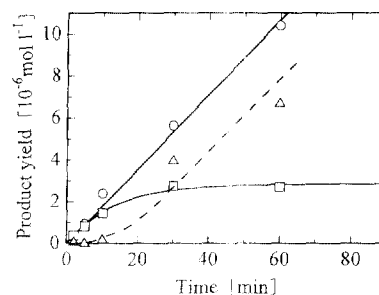


Fig. 3. The time dependence of the product yield (1). Reaction conditions:  $C_2H_4$ , 20 atm;  $O_2$ , 6 atm; total pressure, 65.5 atm; temperature, 308 K; laser pulse energy, 40 mJ pulse $^{-1}$ ; irradiation, at 10 Hz.  $\square$ ,  $CH_3CHO$ ;  $\circ$ ,  $C_2H_4O$ ;  $\triangle$ , CO.

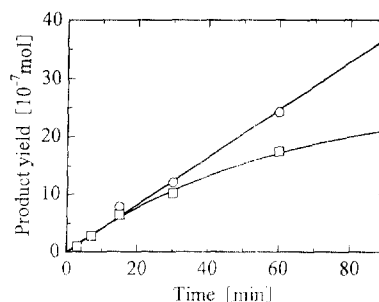
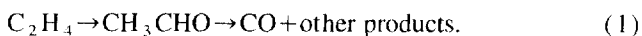


Fig. 4. The time dependence of the product yield (2). Reaction conditions:  $C_2H_4$ , 20 atm;  $O_2$ , 6 atm; total pressure, 88 atm; temperature, 308 K; laser pulse energy, 20 mJ pulse $^{-1}$ ; irradiation, at 10 Hz.  $\square$ ,  $CH_3CHO$ ;  $\circ$ ,  $C_2H_4O$ .

further upon the continuation of irradiation and CO is one of the main products, i.e.,



The other products may contain  $CH_4$ , whose quantitative analysis, however, was not performed.

By extrapolating the obtained fraction of  $CH_3CHO$  against the sum of  $CH_3CHO$  and  $C_2H_4O$ ,  $[CH_3CHO]/([CH_3CHO] + [C_2H_4O])$ , as a function of the irradiation time, the fraction at the beginning of the irradiation was determined. Eventually, it was 0.55 in the case shown in Fig. 3, and 0.56, in the case shown in Fig. 4. In most cases, the fraction obtained at the 5-min irradiation time (which was 0.50 in the former case, and 0.51, in the latter case) is only slightly smaller than the extrapolated values to time = 0.

Thus, the 5-min irradiation data will be used as representing the time = 0 values.

### 3.2. Product yield against the density

The total yield of  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  obtained at the 5-min irradiation time was plotted against the mixture density in Fig. 5. Three different sets of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  pressures at the 10 Hz irradiation with a small number of experiments at different repetition rates were carried out. In parallel, the intensity of the laser light coming through the reaction cell was measured, and the fraction of the light extinction,  $(I_0 - I)/I_0$ , was plotted in Fig. 6. The photo-absorption is considered to be mainly due to the partially allowed Herzberg III absorption due to  $\text{O}_2$  itself,  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  according to the previous research [2]. Thus, the contribution to the  $\text{O}_2$  absorption was calculated based on the total absorption cross-section,  $\sigma_{\text{total}}$ , from the density  $\rho(i)$  of individual component  $i$  according to the following equation,

$$\sigma_{\text{total}} = \sigma_0 + \sigma_1(\text{O}_2)\rho(\text{O}_2) + \sigma_1(\text{CO}_2)\rho(\text{CO}_2) + \sigma_1(\text{C}_2\text{H}_4)\rho(\text{C}_2\text{H}_4), \quad (2)$$

using the  $\sigma_0$  and individual  $\sigma_1(i)$  coefficients obtained in the previous research [2]. The contributions of individual components under the typical experiments with 11 atm  $\text{C}_2\text{H}_4$  and 6 atm  $\text{O}_2$  are drawn in Fig. 6. The contribution of the  $\sigma_0$  and  $\sigma_1(\text{O}_2)\rho(\text{O}_2)$  terms is negligibly small. The reason for the disagreement between the observed and estimated values in the lower density region may be found in the difficulty to measure the small absorption using the pulsed-laser joule meter. The fact that the observed fraction of the light extinction,  $(I_0 - I)/I_0$ , is 2–3 times larger than the estimated value in the higher density region is attributable to the augmented contribution of the light scattering in the mixtures under the near-critical region. This fact gave a certain difficulty to precisely estimate the number of absorbed photons in the reaction cell. However, for simplicity, we estimated the quantum yield of the sum of  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$ , assuming that the

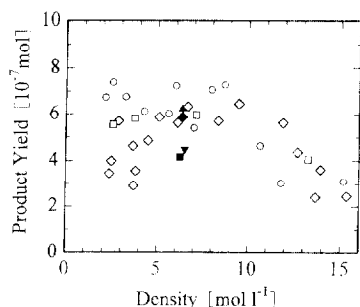


Fig. 5. The product ( $\text{CH}_3\text{CHO} + \text{C}_2\text{H}_4\text{O}$ ) yield dependence on the mixture density. Reaction conditions: temperature, 308 K; laser pulse energy, 20 mJ pulse $^{-1}$ .  $\circ$ ,  $\text{C}_2\text{H}_4$  20 atm +  $\text{O}_2$  6 atm, irradiation at 10 Hz, 5 min;  $\diamond$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm; irradiation at 10 Hz, 5 min;  $\square$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  11 atm, irradiation at 10 Hz, 5 min;  $\blacksquare$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 2 Hz, 25 min;  $\blacklozenge$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 5 Hz, 10 min;  $\blacktriangle$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 25 Hz, 2 min;  $\blacktriangledown$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 1 Hz, 50 min.

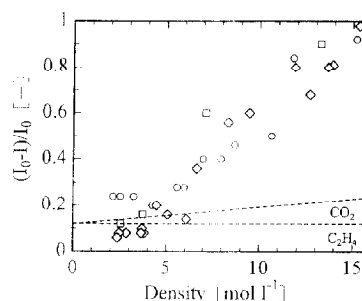


Fig. 6. The fraction of the extinction,  $(I_0 - I)/I_0$ , vs. the mixture density. Temperature, 308 K.  $\circ$ ,  $\text{C}_2\text{H}_4$  20 atm +  $\text{O}_2$  6 atm;  $\diamond$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm;  $\square$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  11 atm. The contribution of individual components to the photo-absorption by  $\text{O}_2$  is calculated using Eq. (2) in the text, and the result for the  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm mixtures is drawn using dashed lines.  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  contribute exclusively.

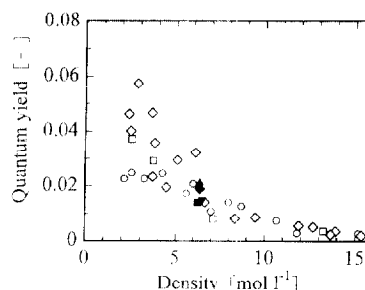


Fig. 7. Quantum yield dependence on the mixture density. Reaction conditions: temperature, 308 K; laser pulse energy, 20 mJ pulse $^{-1}$ ;  $\circ$ ,  $\text{C}_2\text{H}_4$  20 atm +  $\text{O}_2$  6 atm, irradiation at 10 Hz, 5 min;  $\diamond$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm; irradiation at 10 Hz, 5 min;  $\square$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  11 atm, irradiation at 10 Hz, 5 min;  $\blacksquare$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 2 Hz, 25 min;  $\blacklozenge$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 5 Hz, 10 min;  $\blacktriangle$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 25 Hz, 2 min;  $\blacktriangledown$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 1 Hz, 50 min.

observed decrease of the transmitted light finally corresponds to the real absorption, considering that even the scattered light is eventually absorbed inside the cell. The quantum yield estimated as above is shown in Fig. 7.

The quantum yield seems not to be strongly dependent on the absolute and relative amount of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$ , in particular, in the higher density region. The different repetition rate of the laser pulse does not result in any apparent difference in the quantum yield, provided that the total pulse number for the irradiation is kept constant. This indicates that the main reaction progress is completed before the next laser pulse comes; the smallest time interval employed was 40 ms (25 Hz).

The quantum yield is quite small; indeed it is ca. 0.01 at the mixture density of 10 mol l $^{-1}$ , which is much smaller than the case of photolysis of  $\text{C}_2\text{H}_6/\text{O}_2/\text{CO}_2$  mixtures to yield  $\text{CH}_3\text{CHO}$  and ethanol as the main products under the similar condition ( $\text{C}_2\text{H}_6 = 11$  atm,  $\text{O}_2 = 6$  atm, total density = 10 mol l $^{-1}$  at 308 K) of 0.05 [S. Koda et al., experimental results whose details will be published elsewhere.]. It is also interesting to note that the quantum yield has a tendency to decrease rapidly with the increase of the density. Fig. 8 shows the relationship between the quantum yield  $\phi$  and the total

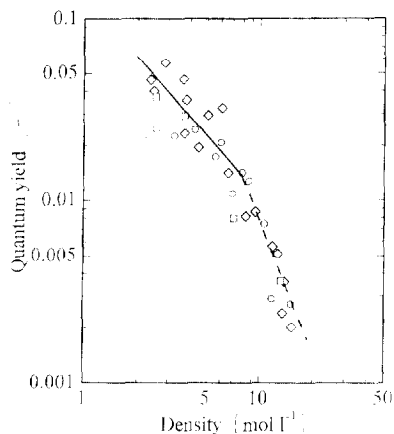


Fig. 8. Logarithmic plot of the quantum yield vs. the mixture density. The data are taken from Fig. 7. The meaning of the keys is the same. The bold line shows the relationship,  $\phi \propto \rho^{-1.0}$  and the dashed line,  $\phi \propto \rho^{-2.3}$ .

density  $\rho$ , using logarithmic scales. The dependency of  $\phi$  on  $\rho$  is approximately described by

$$\phi \sim \rho^{-1.0} \text{ in the region } \rho < 8 \text{ mol l}^{-1} \quad (3)$$

$$\sim \rho^{-2.3} \text{ in the region } \rho > 8 \text{ mol l}^{-1}. \quad (4)$$

### 3.3. Fraction of $\text{CH}_3\text{CHO}$ against the density

The fraction of  $\text{CH}_3\text{CHO}$  against the sum of  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  obtained at the 5-min irradiation time is plotted against the mixture density in Fig. 9. The fraction is almost independent of the change of the ratio of  $\text{C}_2\text{H}_4/\text{O}_2$ , and is not affected by the different laser-pulse repetition rate.

### 3.4. Reaction mechanism

The oxygen molecule does not directly dissociate when it absorbs the KrF excimer laser light at 248 nm, which is longer than 242.4 nm, the conventionally accepted threshold for the photo-dissociation of the ground electronic state  $\text{O}_2(\text{X}^3\Sigma_g^-)$

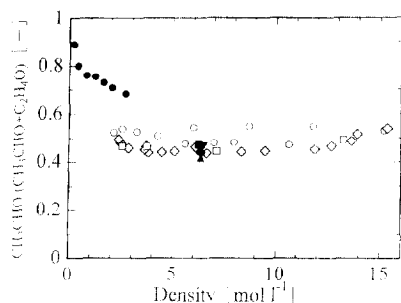
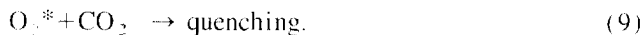


Fig. 9. The fraction,  $[\text{CH}_3\text{CHO}]/([\text{CH}_3\text{CHO}] + [\text{C}_2\text{H}_4\text{O}])$ , vs. the mixture density. Reaction conditions: temperature, 308 K; laser pulse energy, 20 mJ pulse $^{-1}$ ;  $\circ$ ,  $\text{C}_2\text{H}_4$  20 atm +  $\text{O}_2$  6 atm, irradiation at 10 Hz, 5 min;  $\diamond$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 10 Hz, 5 min;  $\square$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  11 atm, irradiation at 10 Hz, 5 min;  $\blacksquare$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 2 Hz, 25 min;  $\blacklozenge$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 5 Hz, 10 min;  $\blacktriangle$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 25 Hz, 2 min;  $\blacktriangledown$ ,  $\text{C}_2\text{H}_4$  11 atm +  $\text{O}_2$  6 atm, irradiation at 1 Hz, 50 min. The fraction for the reaction of  $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$  under the pressurized  $\text{N}_2$  [4] is also shown by  $\bullet$ .

[5]. We have already suggested that the initial excited species under the KrF excimer laser irradiation is  $\text{O}_2$  in its  $A'$  state due to the absorption augmentation. However, there is only a very poor bibliographical information concerning the reactivity of  $\text{O}_2(A'^3\Delta_u)$ .

Below, we will qualitatively discuss a possible reaction mechanism based on the results of the final product analysis. Whether a certain reaction proceeds or does not proceed between the nascent  $\text{O}_2(A'^3\Delta_u)$  and the foreign gas, principally  $\text{C}_2\text{H}_4$ , concertedly along with the photo-absorption is not known. We will, however, only take into consideration the isolated  $\text{O}_2(A'^3\Delta_u)$  (which will be described as  $\text{O}_2^*$  in below), whose plausible subsequent processes are:



The reaction (5) is certain to proceed, consulting the recent observation of  $\text{O}_3$  production at 248 nm irradiation [5–7] and subsequent discussions for the mechanism. It is argued that  $\text{O}_2(A'^3\Delta_u)$  easily converts to vibrationally excited  $\text{O}_2$  and that the vibrationally excited  $\text{O}_2$  can react with  $\text{O}_2$  to yield  $\text{O}(^3\text{P}) + \text{O}_3$ .

The product of the  $\text{O}(^3\text{P})$  reaction with  $\text{C}_2\text{H}_4$  at relatively high pressure and/or in liquid phase is established to be  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  [4,8]. Though some part of  $\text{O}_3$  produced via Eq. (5) may be dissociated through the subsequent laser pulses to yield  $\text{O}(^1\text{D})$  which is readily quenched in the dense  $\text{CO}_2$  to  $\text{O}(^3\text{P})$ , the remaining part of  $\text{O}_3$  might react directly with  $\text{C}_2\text{H}_4$  [9], whose products are not known in the present mixtures. Whether the chemical reaction between  $\text{O}_2(A'^3\Delta_u)$  and  $\text{C}_2\text{H}_4$  proceeds or not is also not known.

The similarity of the products between the  $\text{O}(^3\text{P})$  reaction and the present experiments is worthy to note. The fraction of  $\text{CH}_3\text{CHO}$  from the  $\text{O}(^3\text{P})$  reaction with  $\text{C}_2\text{H}_4$  measured under the pressurized  $\text{N}_2$  [4] is compared with that of the present experiments in Fig. 9. The fraction from the two reaction systems is quite similar, taking into account the tendency of the slight increase of the fraction from the time = 5 min value towards time = 0 as mentioned in Section 3.1. The other important observation that the total quantum yield is much smaller than the case of the  $\text{C}_2\text{H}_6/\text{O}_2/\text{CO}_2$  mixtures is considered to evidence that the important intermediates such as  $\text{O}(^3\text{P})$  are trapped by  $\text{C}_2\text{H}_4$ , so as not to induce any subsequent radical reactions. In the  $\text{C}_2\text{H}_6/\text{O}_2/\text{CO}_2$  mixtures,  $\text{O}(^3\text{P})$  is expected to abstract hydrogen atoms from  $\text{C}_2\text{H}_6$  and induces a certain radical chain reaction to result in higher quantum yields. Thus, we suspect that most of the observed  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  are produced via the reaction of  $\text{C}_2\text{H}_4$  with  $\text{O}(^3\text{P})$ . Unfortunately, we could not conclusively remark about the products from the other oxidants,  $\text{O}_2(A'^3\Delta_u)$  and  $\text{O}_3$ .

The main reaction route to yield  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  is the production of  $\text{O}(^3\text{P})$  via (5), and its subsequent reaction with  $\text{C}_2\text{H}_4$ . The quantum yield is expected to change inversely proportional to the concentration of  $\text{CO}_2$ , which is approximately obeyed by the relation (3), provided that the main quencher of  $\text{O}_2^*$  is  $\text{CO}_2$ . The more serious dependence at higher densities described by Eq. (4) may be attributed to greater diffusion limitation and/or stronger cage effect for some active species. Though any detailed mechanism cannot be identified, various cases are imagined. For example, the elongated lifetime of the reaction pair,  $\text{O}_2^* + \text{O}_2$ , in a certain cage may cause the change in the branching ratio between (5) and (6).

#### 4. Conclusions

The main products from the mixture of  $\text{C}_2\text{H}_4/\text{O}_2/\text{CO}_2$  irradiated by a KrF excimer laser are  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_4\text{O}$  under pressurized conditions. The primary absorption of the laser light produces  $\text{O}_2(A'^3\Delta_u)$ , while the ratio of the reaction products suggests the principal contribution of  $\text{O}(^3\text{P})$  as one of the real oxidants. Although the quantum yield shows

a tendency to decrease with the increase of the mixture density, any distinctive specific pressure effect has not been observed in the near-critical region.

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