

THE DECOMPOSITION OF C₂H₅OH VAPOUR BY IR RADIATION FROM A PULSED CO₂ LASER[†]

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(Received July 7, 1981; in revised form August 4, 1981)

Summary

The decomposition of C₂H₅OH vapour by IR radiation from a pulsed CO₂ transversely excited atmospheric pressure laser was studied briefly at pressures from 0.1 to 2.5 Torr. The major products analysed were H₂ and C₂H₄, and the minor products included CH₄, C₂H₆, C₃H₆ and C₃H₈. The H₂:C₂H₄ ratio increased from a limiting value of 0.07 at low pressure to about 0.5 at 2.5 Torr. The results are compared with those of an earlier study on the same compound using an HF laser; the differences can be explained largely by the higher fluence of the CO₂ laser beam.

1. Introduction

The decomposition of C₂H₅OH vapour by IR radiation from a pulsed HF laser was described in a recent publication from this laboratory [1]. In this paper a brief study of the same decomposition induced by 9.6 μm radiation from a pulsed CO₂ laser is reported. In the previous study the 2.744 μm radiation was found to be absorbed in the O—H stretching vibration of the C₂H₅OH molecule; the CO₂ laser radiation, with quanta less than one-third of this energy, is absorbed in a CH₂ rocking mode [2], and it is of interest to determine whether these differences are reflected in the decomposition.

2. Experimental details

C₂H₅OH vapour was irradiated in a cylindrical Pyrex vessel about 10 cm long and 5 cm in diameter fitted with plane NaCl windows cemented

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to each end. A Lumonics model 203 pulsed line-tunable CO₂ transversely excited atmospheric pressure laser was used for the irradiation. The beam was focused within the reaction vessel by an NaCl lens of focal length 5 cm mounted immediately before the front window. The laser was operated at 36 pulses min⁻¹ with an He:CO₂:N₂ mix of 10:3:1.1, and at a wavelength of 9.520 μm or 9.733 μm with an average energy of 6.2 J pulse⁻¹ or 4.2 J pulse⁻¹ respectively. These wavelengths lie on the shoulders of two absorption bands at 9.42 and 9.68 μm which have been assigned to CH₃ rocking modes in the C₂H₅OH molecule [2]. No important differences were observed between the results at these two wavelengths; the data reported below were obtained at 9.520 μm. The preparation and handling of the C₂H₅OH vapour and the analysis of the products was essentially the same as described previously [1]. The pressure of the C₂H₅OH vapour was limited to about 2.5 Torr by the onset of electrical breakdown in the focused laser beam which was avoided in all the experiments reported.

3. Results and discussion

The main products of the decomposition detected and measured were C₂H₄ and H₂, as in the previous study. The minor products were CH₄, C₂H₆, C₃H₆ and C₃H₈, with yields at 1 Torr pressure of about 4%, 8%, 1% and 3% respectively of that of C₂H₄. The yields per pulse were independent of the number of pulses for all products, indicating that these were primary in the sense that they did not arise from secondary decomposition of products accumulated from a series of pulses.

In the previous study three primary processes were suggested:



Thus H₂ and C₂H₄ were believed to arise directly from simple unimolecular decompositions, while CH₄ and the other hydrocarbon products were believed to be formed in free-radical reactions following reaction (3). To test these hypotheses in the present system, a series of experiments was made with C₂H₅OH at a pressure of 1 Torr and the addition of various pressures (0.2 - 2 Torr) of O₂. The yields of C₂H₄ were almost unaffected, confirming the unimolecular formation of this product. H₂ could not easily be measured in these experiments, but the lack of effect of accumulating C₂H₄ on its yield, noted earlier, strongly supports its formation by reaction (1) rather than through reactions of hydrogen atoms. Surprisingly, CH₄ was also unaffected by added O₂, although all other hydrocarbons were strongly suppressed as would be expected if they were formed in free-radical reactions. This points to another unimolecular primary decomposition



as the probable source of CH_4 .

Figures 1 and 2 show yields of C_2H_4 and H_2 respectively *versus* the pressure of $\text{C}_2\text{H}_5\text{OH}$, together with data from the HF laser experiments for comparison. The yields from both systems are presented as molecules per incident photon per torr, which if the radiation absorbed were proportional to pressure (probably approximately true) would be proportional to the quantum yields. The yields of the minor hydrocarbon products followed approximately the same trend as that of H_2 .

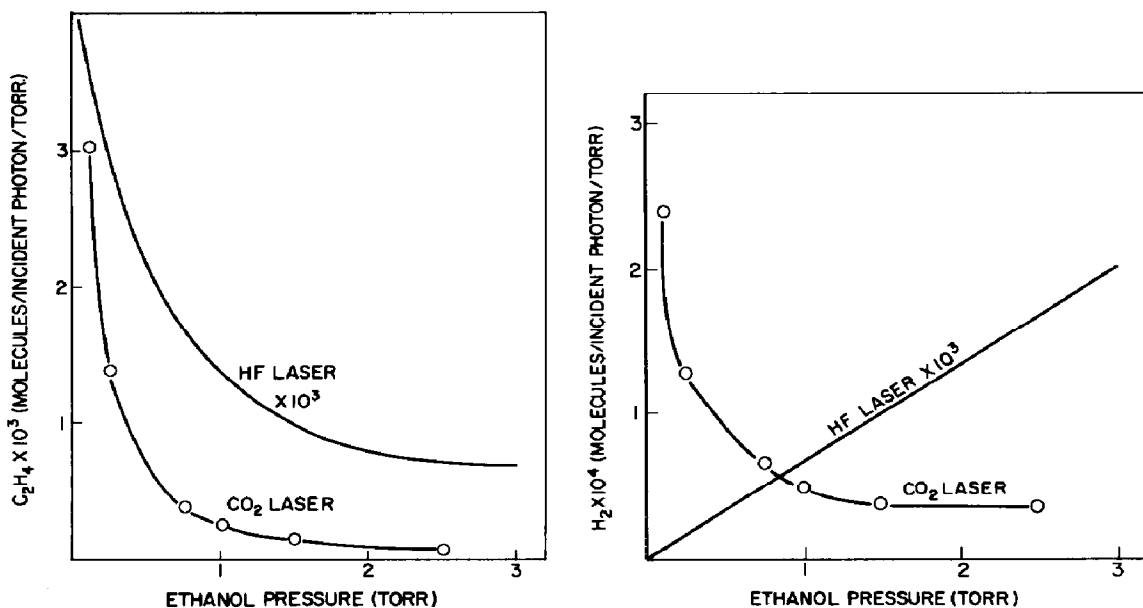


Fig. 1. Yield of C_2H_4 vs. pressure of $\text{C}_2\text{H}_5\text{OH}$. The HF laser data are from ref. 1.

Fig. 2. Yield of H_2 vs. pressure of $\text{C}_2\text{H}_5\text{OH}$. The HF laser data are from ref. 1.

The yields per incident photon of all products in the present study are several orders of magnitude larger than those observed with the HF laser (in Figs. 1 and 2 the HF data have been multiplied by 1000). The difference in terms of the incident energy is even larger as the photon energy from the HF laser was about 3.5 times larger than that from the CO_2 laser. Gross differences in absorption efficiency are not expected, and the large difference in yields is probably due to the large difference in the pulse energy, and thence in the fluence, between the two systems (about 6 J in the present experiments and 0.16 J in the earlier ones). The observed differences in yields are compatible with the well-established strong dependence on fluence found in multiphoton decompositions.

The variation in the yields of C_2H_4 with pressure was similar in the two systems, increasing sharply at low pressure (Fig. 1). The variation in the H_2 yield with pressure found with the CO_2 laser differed markedly from that

found with the HF laser (Fig. 2). This difference is put in better perspective in Fig. 3 where the $\text{H}_2:\text{C}_2\text{H}_4$ ratio is plotted against the $\text{C}_2\text{H}_5\text{OH}$ pressure.

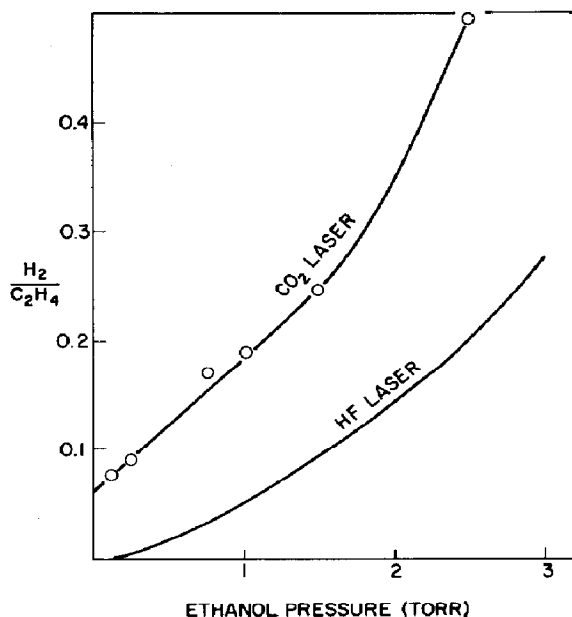


Fig. 3. $\text{H}_2:\text{C}_2\text{H}_4$ ratio vs. pressure of $\text{C}_2\text{H}_5\text{OH}$. The HF laser data are from ref. 1.

The ratio shows a similar upward trend with increasing pressure in both systems, but whereas it goes to zero at low pressure with the HF laser it approaches a value of about 0.07 in the present experiments. In the previous work it was concluded that at high pressure both H_2 and C_2H_4 were produced in a ratio of about 1.6:1 in what was essentially a thermal decomposition but that in the limiting low pressure collision-free multiphoton decomposition C_2H_4 was the only product. The trend is the same in the present work, except that H_2 appears to be a product even in the low pressure limit to the extent of about 7% of the C_2H_4 .

The present brief study confirms that the product ratios in the low pressure collision-free limit are substantially different from those of the "thermal" decomposition observed at higher pressures. Because this is one of the few examples of such behaviour where the processes involved appear to be simple unimolecular reactions, further more extensive studies of the system appear to be warranted.

References

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