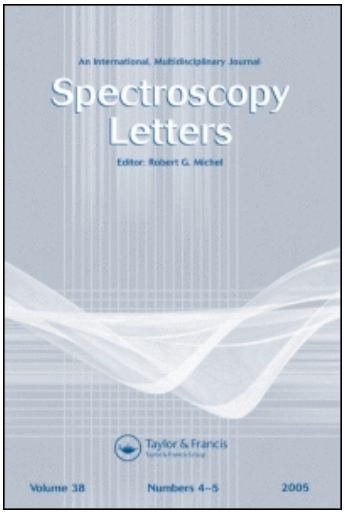

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ETHYLENE-OXYGEN REACTIONS INDUCED BY EXPOSURES TO A CONTINUOUS CO_2 LASER

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ABSTRACT

The reactions of ethylene induced by irradiation with a relatively low power, continuous CO_2 laser were studied. Ethylene and ethylene oxygen mixtures were irradiated using a laser beam of power (a) 25 watts and (b) 40 watts. Ethylene irradiated with a 25 watts laser produced propylene as the major product in a slow reaction. An 80:100 ethylene-oxygen mixture with a laser power of 25 watts produced a faster reaction, with acetaldehyde, 1,3-butadiene and benzene as major products. Both ethylene and an 80:20 ethylene:oxygen mixture produced methane propylene and 1,3-butadiene as major products when irradiated with 40 watts of laser power.

The reaction was found to result from a direct laser radiation-ethylene interaction and was not due to thermal effects. A study was undertaken to determine the reaction intermediates of these systems. The products suggested the formation of ethylene diradical at 25 watts and triplet methylene at 40 watts. These results were surprising since the energy available from a photon with 10.6 $\mu\lambda$ was insufficient to generate such radicals directly.

INTRODUCTION

Studies have been made of infrared fluorescence generated by molecular species irradiated with a CO_2 laser. During the course of these studies, unexpected chemical reactions were observed. In the first instance, copious quantities of paraformaldehyde were generated when ethylene-air mixtures were irradiated.[1] Reactions induced in irradiation of gases with an infrared laser have been reported elsewhere,[2,3,4] but all such studies employed very high power lasers and/or focused lasers. This study was conducted with a relatively low/power, continuous, unfocused CO_2 laser.

Products from the irradiation of ethylene and ethylene oxygen mixtures were characterized. Propylene was the major product of ethylene irradiated at 25 watts of power, while methane, propylene and 1,3-butadiene were produced with 40 watts of laser power. Adding oxygen to the system in both cases resulted in the production of acetaldehyde as well as increasing the yield of the other product. The reactions were apparently due to a laser beam-ethylene interaction and not to thermal effects or a laser beam-oxygen interaction. Several trapping studies were undertaken to identify intermediates of the reactions. Evidence indicated that ethylene was cleaved to triplet methylene when a laser power of 40 watts was used. This is quite unexpected because the energy available from a photon of wavelength 10.6 μ is insufficient to cleave ethylene. Multiple photon interacts are indicated but the precise mechanism is not clearly understood.

EXPERIMENTAL

Chemicals

Ethylene, propylene and oxygen were procured from Matheson Gas Products and used without further purification. Lecture bottles of

propane, anhydrous sulfur dioxide and 1,3-butadiene were also obtained from Matheson Gas Products. Reagent grade chloroform was supplied by Mallinckrodt Chemical Works. Impurities detected in ethylene were 0.1% propylene and a lesser amount of 1-butene. Propylene at 100 ppm was the only impurity detected in butadiene.

Equipment

1. Laser. The laser employed was a Perkin-Elmer Model 6200 CO_2 Molecular laser. It produced up to 40 watts of continuous power at 10.6 μ in a beam of 1 cm diameter.

2. Gas Chromatograph-Mass Spectrometer. Analyses were conducted on a combination Perkin-Elmer 990 gas chromatograph interfaced through a Bieman-Watson separator to a Perkin Elmer-Hitachi RMS-4 mass spectrometer. Columns employed for gas separations were 8' and 20' 1/8-inch aluminum with Porapak S packing.

3. Reaction Cell. Reactions were conducted in 1" diameter Pyrex cells of 6" length. Laser beam access was provided by Irtran 2 windows.

Experimental Procedure

The reaction cell was filled with the desired gas mixture by flushing the cell for about 10 minutes, stopping flow and then sealing the cell. The reactions were conducted as batch processes. Analysis of the products was performed qualitatively by GC-MS techniques and quantitatively using the gas chromatograph's flame ionization detector. Calibration of the flame response was as gaseous volume of the components at ambient conditions.

Several studies were conducted aimed at identification of reaction intermediates. These studies were performed under conditions similar to those described above. Irradiated mixtures contained

ethylene and a trapping species which was present in large abundance in an effort to eliminate secondary reactions. To check for inertness, neat samples of the chosen trapping species were subjected to laser irradiation. All compounds employed as traps were inert to the laser conditions employed in subsequent ethylene reaction studies.

RESULTS

Irradiated Mixtures

Studies were conducted at two separated laser conditions; laser powers of (1) 25 watts, referred to as low power, and (2) 40 watts, high power. Samples of (a) ethylene and (b and c) two ethylene-oxygen mixtures were irradiated. The mixtures chosen were (b) 80:20 ethylene:oxygen (outside the flammability limits) and (c) 50:50 ethylene:oxygen (within the flammability limits).

Reactions Initiated by Low Power Laser Beam (25 watts)

The products from these systems were previously reported,[1] although further research has extended this information. Table I lists the products of ethylene and 80:20 ethylene:oxygen systems. The major product from the reaction without oxygen was propylene, while acetaldehyde, 1,3-butadiene and benzene were formed in the presence of oxygen. The high oxygen mixture (50:50) produced very different products. Under these conditions, the only observed products were formaldehyde and water, produced by a rapid reaction. At times, a surface polymerization of the formaldehyde to paraformaldehyde was observed.

Reactions Initiated by High Power Laser Beam (40 watts)

The reactions of ethylene at higher laser beam power were much more rapid, and less dependent upon oxygen concentration. The yield of products are summarized in Table II. Propylene, methane, and

TABLE I

Products from Ethylene and Ethylene-Oxygen Irradiated at 25 Watts Laser Power

Product	Yield	
	Ethylene[a]	80:20 Ethylene:Oxygen[b]
Propylene	2.0	1.0
Acetaldehyde	-	7.1
1-Butene	-	0.3
1,3-Butadiene	0.3	5.2
Benzene	0.1	2.5
Total Conversion	2.5%	25%

(a) 15 minute irradiation.

(b) 20 minute irradiation.

1,3-butadiene were the major products in the system without oxygen. The major change occurring with addition of oxygen was an increase in the yield of methane. Products from the equal mixture of ethylene and oxygen are not reported as the system exploded.

Possible Laser Interaction Processes with Oxygen

The product yields showed a reaction dependence upon oxygen. This observation led to the consideration of a direct laser radiation-oxygen interaction producing an excited oxygen species. No evidence was found for either ozone or singlet oxygen being produced directly from oxygen by the influence of the laser beam.[1] However, it should be noted that under the experimental conditions employed, the absence of singlet oxygen was not firmly established. The detection of ozone was attempted by passing oxygen irradiated with the laser into a scrubbing vessel

TABLE II

Products from Ethylene and Ethylene-Oxygen Irradiated at 40 Watts of Laser Power

Product	Yield	
	Ethylene[a]	80:20 Ethylene:Oxygen[b]
Methane	7.4	18
Ethane	3.2	3.2
Propylene	12.0	10
Acetaldehyde	-	1.6
1-Butene	-	1.4
1,3-Butadiene	5.8	5.1
Cyclopentene	0.4	0.5
Benzene	0.9	2.0
	30%	42%

(a) 10 minute irradiation period.

(b) 5 minute irradiation period.

containing eugenol. The procedure would have detected 0.2 μg of ozone.

Effect of Heat

Another possible energy source was the heating effect associated with absorption of laser radiation by the entrance Irtran window and the gases. The temperature of the reacting gases, measured just outside the beam near the entrance point of the laser beam, was 110°C when using 25 watts laser power and 140°C when using 40 watts of laser power. Comparative thermal reactions were conducted at 250°C for periods up to three hours without evidence of reaction.[1] By elimi-

nation the reaction must be initiated by direct laser beam-ethylene interaction. A study was conducted to determine the type of reaction occurring and the reactive species initially produced from the interaction.

STUDY OF REACTION INTERMEDIATES

Lower Laser Beam Power

Gas phase reactions are expected to proceed via non-ionic processes, either through radical intermediates, or by processes involving no intermediates. Attempts were made to trap radical intermediates using propylene and chloroform. A 5:1 propylene-ethylene system, irradiated at 25 watts for 30 minutes, gave no detectable products. A 35:65 chloroform:ethylene system subjected to similar conditions produced very minor products (less than 1% yield). These were identified as dichloroethylene and 1,1,1-trichloropropane. Characterization of these minor products was not complete because of the minor quantities of species present.

The yield of radical-related products in this latter study was insufficient to explain the products observed in the previous reactions. The rather low, but still detectable yield of radical-related products lead to the consideration of a reaction proceeding via a diradical intermediate rather than a radical intermediate or no intermediate.

1,3-Butadiene was utilized as a possible trap for a diradical species. An 80:20 butadiene:ethylene mixture yielded a small amount of cyclohexane (0.3% in 30 minutes), the expected product from the reaction of butadiene with the ethylene diradical. It was realized that the Diels-Alder reaction of ethylene and butadiene is thermally allowed and conceivably the cyclohexane might result from this process rather than from laser irradiation. As a control, a similar mixture was heated to

thermal levels comparable to that occurring in the laser induced reaction studies. Cyclohexene did occur as a product, but at a much lower yield than detected in the laser induced reactions.

Interactions Induced Using High Laser Beam Power (40 watts)

Similar studies were conducted for the higher energy laser reaction. A 35:65 chloroform:ethylene mixture irradiated at 40 watts produced numerous products in high yield (20% conversion in less than 10 second irradiation) with major chlorinated products being chloromethane and chloroethane. A more complete listing of products appears in Table III.

This evidence indicated that this reaction is free radical in nature, and the presence of methane as a product lead to consideration of methylene intermediates. Methylene exists in two electronic states, singlet and triplet, of which the triplet state is reported to be the most stable.[5] 1,3-Butadiene reacts readily with triplet methylene

TABLE III

High Laser Power Irradiation of 35:65 Chloroform:Ethylene Mixture

Product	Yield
Methane	7.4
Acetylene	6.7
Chloromethane	1.3
Chloroethylene	0.4
Chloroethane	2.0
Dichloromethane and dichloroethylene	0.7
Benzene	0.9
Conversion	19%

producing cyclopentene via a 1,4-radical addition.[6] An 80:20 butadiene:ethylene mixture irradiated at 40 watts for 10 minutes produced (compared to ethylene concentration) 0.2% cyclopentadiene and 2.5% cyclopentene, in addition to 0.5% methane and 6% propylene. It should be noted that the yield of propylene was not as drastically reduced as was the yield of methane by addition of butadiene.

Singlet methylene characteristic alloy goes through addition reactions with double bonds and insertion into single bonds. An 80:20 ethylene:propane system was irradiated to provide a system for observing the latter reaction. Methylene insertion should produce butane and isobutane, neither of which were seen in significant yield. The former reaction (addition to double bonds) should produce cyclopropane in ethylene reactions. This species was not observed among the reaction products. A more sensitive test was conducted on the reaction mixture, using the GC-MS with the mass spectrometer as a specific detector for the ion with an m/e of 42. The retention time of cyclopropane on the gas chromatogram was such that no interference from propylene would occur. The data showed that no evidence of cyclopropane was formed.

CONCLUSIONS

The reactions observed when ethylene systems were exposed to the radiation from a CO_2 laser were due to a direct interaction between the radiation and ethylene molecules. The products have been characterized and the reaction, at least at 40 watts, was rapid.

The most interesting aspect of the reaction is that it occurs at all. The energy of photons with a wavelength of 10.6 μ is very low compared to the energy required to break any ethylene bond. It was unexpected that absorption of these photons would be sufficient to break a bond and thus cause a reaction. Studies of the reaction at

25 watts produced evidence, although inconclusive, that an ethylene diradical species might be the intermediate produced by absorption of the laser radiation.

Using high laser power, results indicated that at least part of the reaction proceded via a free radical mechanism, and it appeared that triplet carbene was the initially formed free radical. The latter reaction involved breaking of the carbon-carbon double bond, which would require 146 kcal of energy, equivalent to 52 photons[1] with wavelength 10.6 μ.

Further studies are underway in an effort to understand more fully the mechanism of the reaction, and to see if laser-induced reactions are more widely possible.

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