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INFRARED LASER PHOTOCHEMISTRY: EVIDENCE FOR HETEROGENEOUS DECOMPOSITION *

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Gas samples of cyclopropane, propylene, and *trans*-1,2-dichloroethylene at pressures of 0.5 to 10 torr were exposed to the focussed output of a grating-tuned TEA CO_2 laser (0.7 J/pulse 300 ns fwhm, 1 pps) and the products were analyzed by gas chromatography and by infrared absorption measurements. Extensive decomposition occurs in the case of cyclopropane, propylene, and trans-dichloroethylene when the cell windows are not scrupulously clean or when the cell walls are close to the focal zone of the laser. Under these conditions, photolysis products appear even when the radiation is tuned far from resonance and the product composition and/or concentration differs from that obtained with cells having clean windows or having large volumes. In contrast, the photoisomerization of *trans*-1,2-dichloroethylene appears to be unaffected by cell conditions and to proceed only when the laser is tuned to the absorption features of the gas sample, although the formation of acetylene is cell-dependent.

1. Introduction

Since the first reports [1,2] that it is possible to achieve isotope separation by collisionless multiple absorption of infrared photons in which the molecule containing the desired isotope is selectively driven to dissociate, much attention has been given to devising theories and experiments to help elucidate this still poorly understood phenomenon. While initial efforts have concentrated on the practical aspects of isotope separation [3], there has been increasing recognition that irradiation by powerful infrared lasers may permit the synthesis of specific compounds [4]. A problem of fundamental importance to this emerging field of infrared photochemistry is to find the conditions under which it is possible to enhance one among several reaction pathways and to produce a product mix differing from thermal heating.

We report here on the photolysis of cyclopropane and propylene and on the *trans–cis* isomerization of 1,2-dichloroethylene under intense infrared laser irradiation. The most remarkable finding of this study is the ease with which gas samples can be decomposed by trace impurities on the windows of the gas cell or by the proximity of the cell walls to the focal zone. While such decomposition may permit the investigation of surface reactions, it also raises doubts that product formation in some previous experiments was a purely gas-phase process.

2. Experimental

A TEA CO_2 laser, tuned with a grating, produced up to 0.7 J per pulse at a repetition rate of 1 Hz and with a pulse duration of 300 ns fwhm. Its output was focussed by means of a BaF_2 lens (6 cm focal length) into the center of a pyrex cell equipped with NaCl windows held in position with greased O rings or by epoxy.

The gases, cyclopropane and propylene, were obtained from Matheson (99% stated purity) and were used without further distillation. The pressure in the reaction cell was between 0.5–10 torr. No buffer gases were introduced.

After irradiation, the gas samples were analyzed by

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gas chromatography (Beckman Model GC 45) with a flame ionization detector. The column used was 8 ft Poropak S (1/8") for the cyclopropane and propylene experiments, and 6 ft Carbowax 20M for the *trans*-dichloroethylene. In the latter case infrared absorption spectra were also taken with a JASCO model IRA-1 spectrophotometer before and after laser irradiation.

Two different pyrex cells were used to study the importance of cell conditions and cell cleanliness: a small cell, 0.7" i.d. 4" long; and a larger cell, 2.0" i.d. 5" long. In both cells, the IR radiation was carefully focussed into the center of the reaction vessel. Before each gas filling, the reaction cell is evacuated to less than 5 X 10^{-6} torr pressure.

3. Results

3.1. *Cyclopropane*

The infrared spectrum of cyclopropane is well known [5] and the thermal decomposition of cyclopropane has been well characterized [6]. These facts made this simple three-member ring compound attractive for study by infrared laser photolysis [7].

Preliminary experiments on cyclopropane (C_3H_6) contained in the small reaction cell gave products, such as CH_4, C_2H_2, C_2H_4, and propylene (CH_3CHCH_2), in very high yield after 100 laser shots or less. The dissociation process was not dependent on wavelength and occurred over the entire tuning range of the CO_2 laser.

Dissociation even resulted when the gas sample was exposed to the output of a Nd-YAG laser (1.06 μ, 300 mJ/pulse, ≈30 ns fwhm). Our first surmise was that under the very intense IR field molecular dissociation (break-up) preceded breakdown. However, further investigation showed that contamination of the entrance cell window, for example from grease, dust, or dirt, accounted for the product formation.

Upon careful cleaning of the cell windows, the yield of photolysis products was found to diminish in the small cell. The decrease was larger for the Nd-YAG laser than the CO_2 laser. We attribute this difference to the area of the cell window exposed, the diameter of the Nd-YAG laser being the smaller. To check this hypothesis, an adjustable iris was placed between the CO_2 laser and the reaction cell. As the CO_2 laser beam is stopped down, the amount of dissociation products formed is reduced. We conclude that cyclopropane is readily dissociated by direct heating of the cell window or walls in contact with it. Moreover, under such conditions the products formed are characteristic of thermal cracking.

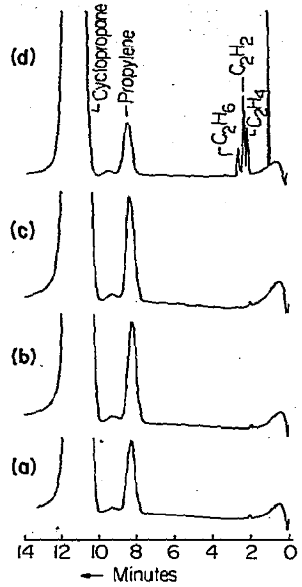

Fig. 1. Gas chromatograms from the photolysis of 3 torr cyclopropane by the P(38) line, 9.6 μ: (a) large cell before irradiation; (b) large cell after 1500 pulses; (c) large cell after 3000 pulses; (d) small cell after 1000 pulses. Propylene is present as an impurity in the cyclopropane [see (a)] but its concentration increases upon irradiation [see (b) and (c)] of the large cell. For irradiation of cyclopropane in the small cell [see (d)] additional decomposition products appear.

Experiments with the large cell (2" i.d.) showed no decomposition of cyclopropane except when we irradiated on the absorption feature (ν_{10} mode) of cyclopropane at 9.6 μ using the CO_2 P(38) line or at 9.552 μ using the CO_2 P(20) line. The only photolysis product of cyclopropane (3 torr) under irradiation at 1029 cm^{-1} is propylene (see fig. 1), corresponding to the opening of the ring. At a pressure of 10 torr of cyclopropane, other products appear but are of minor concentration compared to the propylene. These results are in contrast to those of Lesiecki and Guillory [7] who report that the major products are acetylene, propylene, methane, and ethylene, when cyclopropane is irradiated at 9.552 μ. Our results indicate that here unimolecular decomposition proceeds via a *specific* excitation by the laser. From this study we are unable to rule out that the above process is collisionless, but we suspect it occurs instead by rapid V–V pumping [8].

3.2. Propylene

Because propylene is the only product of the gas-phase decomposition of cyclopropane by intense infrared laser irradiation, we decided to study its behavior on exposure to the CO_2 laser in order to learn more about the difference between thermal and infrared-specific dissociation.

In the small reaction cell irradiation of propylene yielded the products CH_4, C_2H_2, C_2H_4, C_2H_6, and others which were found to be independent of laser wavelength, while in the large reaction cell the decomposition of propylene is wavelength-dependent and occurs only upon irradiation of the absorption feature at 10.6 μ by the CO_2 P(34) line. In contrast to cyclopropane, the propylene decomposition products are the *same* for both cells, but differ in their relative rate of production with cell conditions. In the large reaction cell the ratio between the C_2H_2, C_2H_4, and C_2H_6 product concentration is constant and does not depend on irradiation *time* (see fig. 2); however, in the small reaction cell this ratio is *not* constant (see fig. 3), indicating that further decomposition occurs. Presently we cannot distinguish for propylene whether photolysis proceeds via specific excitation or by thermal heating due to rapid V–T transfer [8]. The infrared photolysis of propylene has been studied previously by Braun and Tsang [9] who used a reaction cell with a 1 cm^3 volume. Their results are similar to those we found with our small cell, namely further decomposition of the products, but not our large cell. Additional evidence that the work of Braun and Tsang [9] involves heterogeneous decomposition is their finding that the introduction of inert buffer gases causes the product yield to reach a plateau.

3.3. Trans–cis isomerization of 1,2-dichloroethylene

Given that most previous studies of infrared photochemistry by the intense field of a CO_2 laser have em-

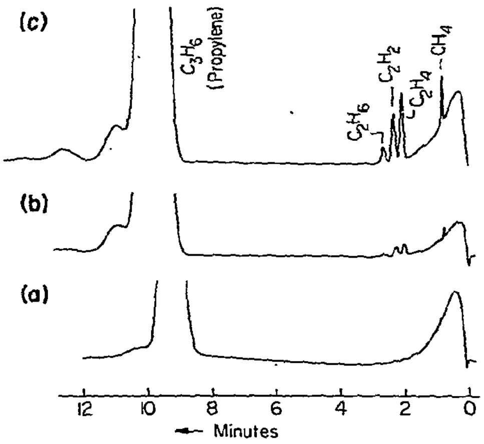

Fig. 2. GC traces of the reaction products from the photolysis of 0.7 torr propylene in the large cell by the P(34) line, 10.6 μ: (a) before irradiation; (b) after 200 pulses; and (c) after 1500 pulses.

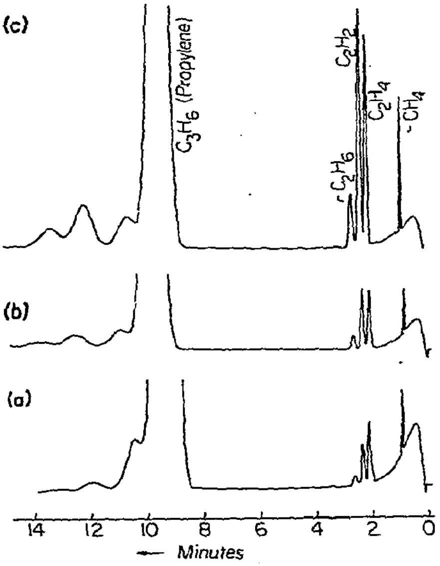

Fig. 3. GC traces of the reaction products from the photolysis of 0.7 torr propylene in the small cell: (a) after 200 pulses by the P(24) line, 9.6 μ, at which wavelength propylene does not absorb; (b) after 200 pulses by the P(34) line, 10.6 μ; and (c) after 750 pulses by the P(34) line, 10.6 μ.

ployed reaction vessels of about the same dimension as our small cell, and that the presence of a grease film on the salt windows under these circumstances is difficult to avoid, we have become troubled about the possibility that direct cell window heating or the production of ions from the cell window [10] is causing some of the remarkable observations reported. Of particular interest to us is the recent study by Ambartzumian et al. [11] on the trans–cis isomerization of $C_2H_2Cl_2$ molecules in the strong field of a TEA CO_2 laser. When the power density is above 0.5 GW/cm^2 they report that three processes occur: (1) transformation of *trans*-$C_2H_2Cl_2$ into *cis*-$C_2H_2Cl_2$; (2) molecular dissociation yielding C_2H_2 as an end product; and (3) production of electronically excited fragments, e.g. CH^* and C_2^*. Because the activation energy (55.3 kcal/mol) for trans–cis conversion [12] is lower than that of unimolecular decomposition [6] of cyclopropane (65.6 kcal/mol), we decided to investigate the role cell conditions might play in this process.

Trans-$C_2H_2Cl_2$ was irradiated at 10.6 μ by the P(30) line of the CO_2 laser. IR absorption spectra were recorded before and after irradiation, as shown in fig. 4. We find that isomerization to *cis*-$C_2H_2Cl_2$ occurs only upon irradiation at or near the *trans*-$C_2H_2Cl_2$ absorption feature (ν_6 mode) and *is not* dependent on the cell dimensions. Thus, we conclude that the photo-isomerization of *trans*-1,2-dichloroethylene does not involve heterogeneous isomerization.

Ambartzumian et al. [11] reported that after long exposure, both isomers of CHClCHCl decompose to give acetylene. However, we attribute these observations once again to heterogeneous decomposition. To prove this, we filled our large cell with *trans*-dichloroethylene (5 torr pressure) and exposed the sample to 10000 shots of the CO_2 P(30) line at 10.6 μ. Fig. 5 shows a GC trace of the sample, demonstrating that decomposition is minor compared to photo-isomerization.

So far, we have not investigated whether other processes observed by Ambartzumian et al. [11] are free from surface chemistry. Ambartzumian et al. report

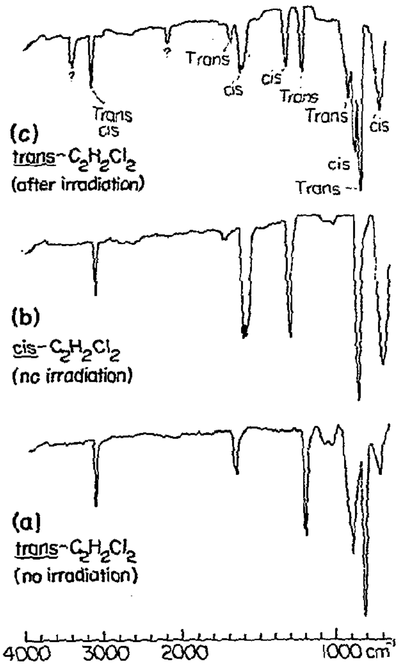

Fig. 4. Infrared absorption spectrum of (a) 10 torr of *trans*-$C_2H_2Cl_2$ before irradiation; (b) 10 torr of *cis*-$C_2H_2Cl_2$ before irradiation; and (c) 10 torr of *trans*-$C_2H_2Cl_2$ after 500 pulses by the P(34) line, 10.6 μ.

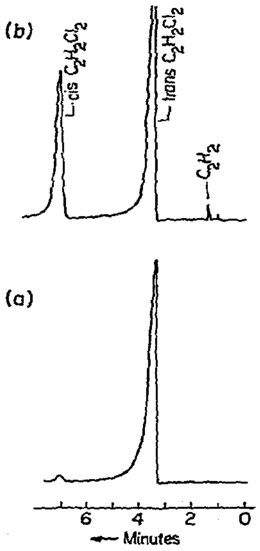

Fig. 5. GC trace of *trans*-dichloroethylene (5 torr) in the large cell (a) before irradiation and (b) after 10000 shots of the CO_2 P(30) line at 10.6 μ.

that for example the visible luminescence they observe remains practically constant as the CO_2 laser is tuned, suggesting to us the possibility that surface reactions are also involved here.

4. Concluding remarks

The proximity of cell walls to the focal volume and the cleanliness of cell windows has been shown to influence the decomposition of molecules irradiated by an intense CO_2 laser. These results serve as a warning that surface chemistry must be carefully excluded in multiple absorption of infrared photons if the results are to be interpreted solely in terms of isolated molecule or gas-phase phenomena.

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