# THE REACTIONS AND EMISSION SPECTRA OF PROPYLENE IN ELECTRODELESS DISCHARGE

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# THE REACTIONS AND EMISSION SPECTRA OF PROPYLENE IN ELECTRODELESS DISCHARGE

THESIS

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For the Degree of

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By

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# PREFACE

The work described in this thesis constitutes only one part of the research done in fulfillment of the requirements for the degree of Master of Science. The second part may be found in the thesis entitled,"The Mercury-Sensitized Photochemical Reactions of Isopropyl Alcohol," May, 1959.

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# CHAPTER I

## INTRODUCTION

Tubes filled with gases at satisfactory pressures fluoresce in the presence of radio frequency energy (3, p. 192). Such fluorescent tubes have been used to probe fields of radio frequency oscillation and their emission spectra have been recorded and studied. Ions with multiple charges also exist in the gases of these tubes.

In 1941 Oliver (5) observed the fluorescence of an isobutane-isobutene gaseous mix flowing to a pump through a glass tube which was wrapped by the spiral antenna of a seven-megacycle transmitter. A white deposit was observed at a bend in the tubing on the pump side of the fluorescing section of the gas (5, p. 8). The work was not continued at that time as the chief research interest was the mercury-sensitized photochemical reactions of hydrocarbons.

In 1957 Blacknall (1) studied the fluorescence and reaction products of propylene in the presence of seven-megacycle radiation. The oscillator employed by Blacknall was an ARC-5/T-22 surplus transmitter of range 7.00 to 9.10 megacycles, operating at 7.00 megacycles. Blacknall observed a drop in pressure and the formation of brown deposit in the region of the coil. No analysis of this product was reported by Blacknall.

The following article was listed in the January, 1959, <u>Chemical Abstracts</u>:

> The discharge took place in a quartz tube at a frequency of six megacycles. In stationary $CH_4$, the lines CH 4315 and 3890Å, of $H_2$, H, and Hg and the bands of CO, CH, and OH were observed. The ratio of H/CH decreases with pressure and with the amount of impurities (city gas).
>
> Discharge in MeOH shows bands and lines of CH, OH, CO, $H_2$, H, $C_{11}$, and $C_1$; EtOH, BuOH, and isoamyl alc. show the same lines. In stationary gas intensity ratios of lines depend on the pressure. It can be shown by expts. in constantly evacuated tubes that $OH^*$ is a product of primary reaction (such as $e + MeOH \rightarrow OH^* + Me + e$) and that CO, H, and O are products of secondary reactions (4, pp. 753-6).

Other reactions induced by radio frequency oscillations have been reported. Seigi Nio and Noshiro Sasaki reported the taste and aroma of tobacco leaves were improved after treatment with 30, 50 and 100 megacycles radiation for ten, twenty, and thirty hours (6).

Saito Fujio reported an improvement in the color, flavor, and storage qualities of meat cured with exposure to fifty megacycles radiation over that of conventional methods.

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# CHAPTER II

## APPARATUS

The original system employed by Blacknall (1) is shown in Figure 1. A vertical section of twenty millimeter tubing wrapped with the radio antenna, a freeze-out trap, and a five-liter flask made up the system. Thermometers were positioned in the horizontal sections above and below the antenna. Pressure was measured by a vertical open end mercurical manometer.

TABLE I

LEGEND FOR FIGURE 1

| Number | Apparatus |
|---|---|
| 1 | Stopcock |
| 2 | Five-Liter Flask |
| 3 | Thermometer |
| 4 | Antenna Coil |
| 5 | Thermometer |
| 6 | Freeze-out Trap |
| 7 | Manometer |

The improved system used in this work is shown in Figure 2. The freeze-out trap was made an integral part

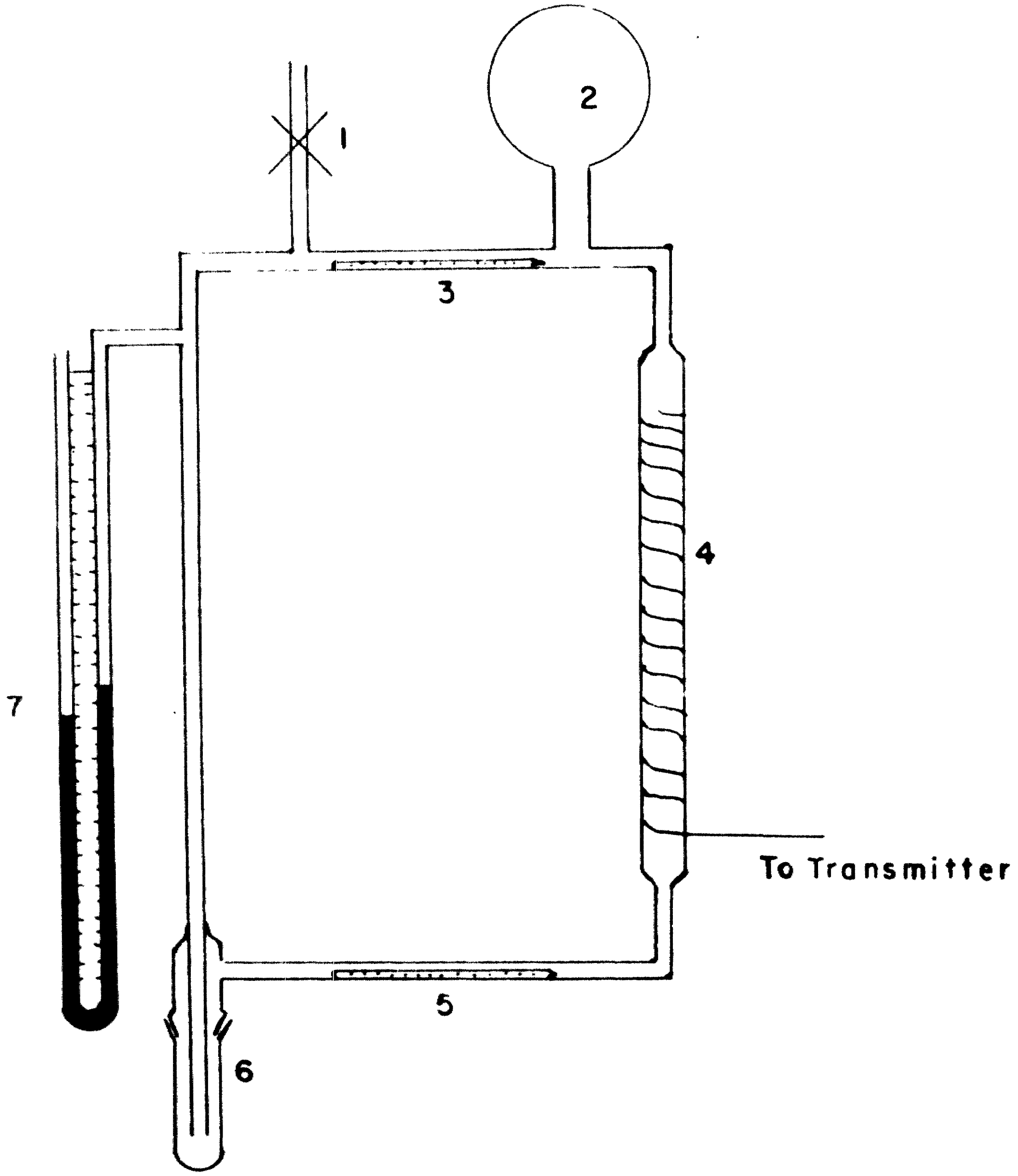

Fig. 1--Original apparatus

of the reaction chamber, and the heating coil condenser system was added to give thermal circulation of the propylene. The inclined manometer was installed to give more accurate pressure data and was covered with a layer of "octoil" to keep the system as free from mercury vapor as possible.

TABLE II

LEGEND FOR FIGURE 2

| Number | Apparatus |
|---|---|
| 1 | Antenna Well |
| 2 | Reaction Vessel |
| 3 | Heating Coil |
| 4 | Condenser |
| 5 | Manometer |
| 6 | Dewar for Freeze-out Trap |

The antenna used was made of number 12 B and S bare copper wire wrapped in a fifteen millimeter by thirty-five centimeter coil. The emission spectral data were obtained by using a 1.5 meter ARL grating spectrograph. The source was a twenty-five millimeter by sixty centimeter vycor vessel wrapped with a twelve-turn antenna, twenty-five centimeters long, connected to the antenna post of the transmitter.

The radio frequency source was the same as Blacknall's(1), an ARC-5/T-22 surplus transmitter, 7.00 to 9.10 megacycles

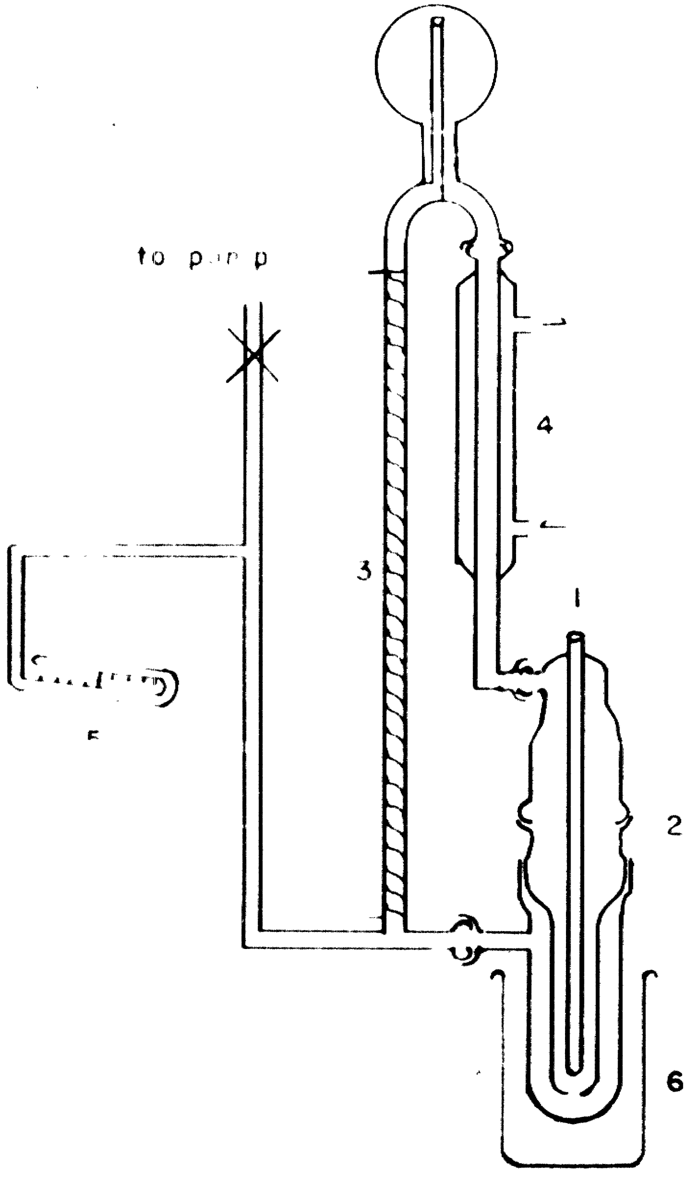

Fig. 2--Improved apparatus

range. A variable capacitor between the antenna post and ground served with the variable inductor in the transmitter to tune the antenna to the transmitter for maximum power transfer.

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# CHAPTER III

## RESULTS

Table III gives the results of Blacknall's (1) work. In runs one and two no corona was observed and no pressure change was observed.

TABLE III

DATA FROM ORIGINAL SYSTEM

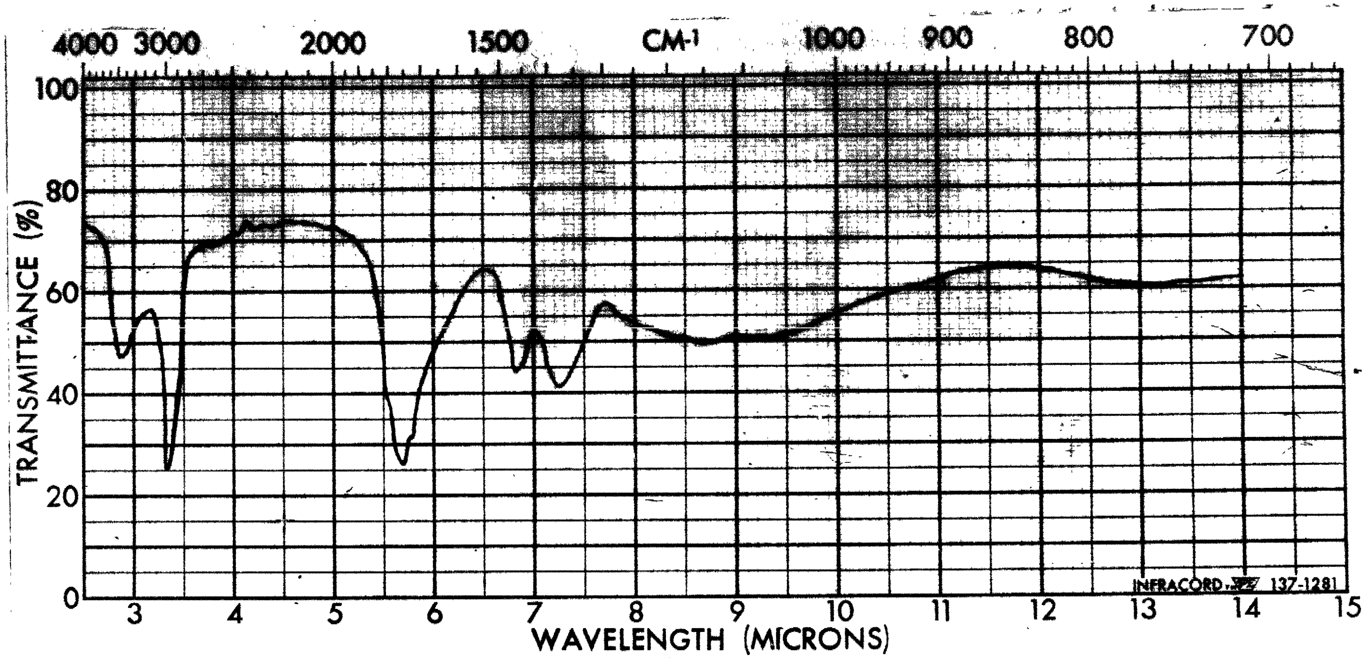
| Run | Pressure | ΔP | Temperature of Thermometers | Reaction Time | Corona | Products |
|---|---|---|---|---|---|---|
| 1 | 16mm | 0 | no change | 3.0hr | none | none observed |
| 2 | 1atm | 0 | no change | 10.0 | none | none observed |
| 3 | 3mm | ... | ..... | 2.0 | present | brown deposit in tube |
| 4 | 9mm | -2 | upper-55°C<br>lower-110°C | 6.5 | present | amber deposit near corona |

The reactions occurring in runs three and four were summarized by Blacknall as follows:

> In run three a pressure drop occurred and some products observed. A corona was developed and the reaction carried on for two hours.
>
> In run four no change of temperature was observed for the first three and one-half hours. Though full current was applied to the plates of the output tubes, there was no corona visible. The tuning of the coil was then adjusted to give a corona which at this time was very weak, being visible only in a darkened room. The upper and lower thermometers up to this time were recording room temperatures, 25°C. Five minutes after the corona was developed, the temperatures were 28.5°C and 29.5°C respectively. Six and one-half hours later the temperatures were 55°C and 110°C respectively, and the pressure in the system had fallen 2mm. The corona was definite, and it extended some 6cm from the ends of the coil. A deposit was observed on the walls of the vessel in the area of the corona which upon later examination proved to be a solid (1, p. 3).

Blacknall did not analyze the products from these runs. They were analyzed at a later date by the author, and the infrared spectrogram is shown in Figure 3. Absorption peaks were found at 2.92µ, 3.46µ, 5.85µ, 6.85µ, and 7.2µ. A characteristic peak at 5.85µ indicated the presence of a carbonyl group in the brown product. This was disconcerting as no carbonyl group is to be expected from the polymerization of propylene. There were no absorption peaks above 7.2µ.

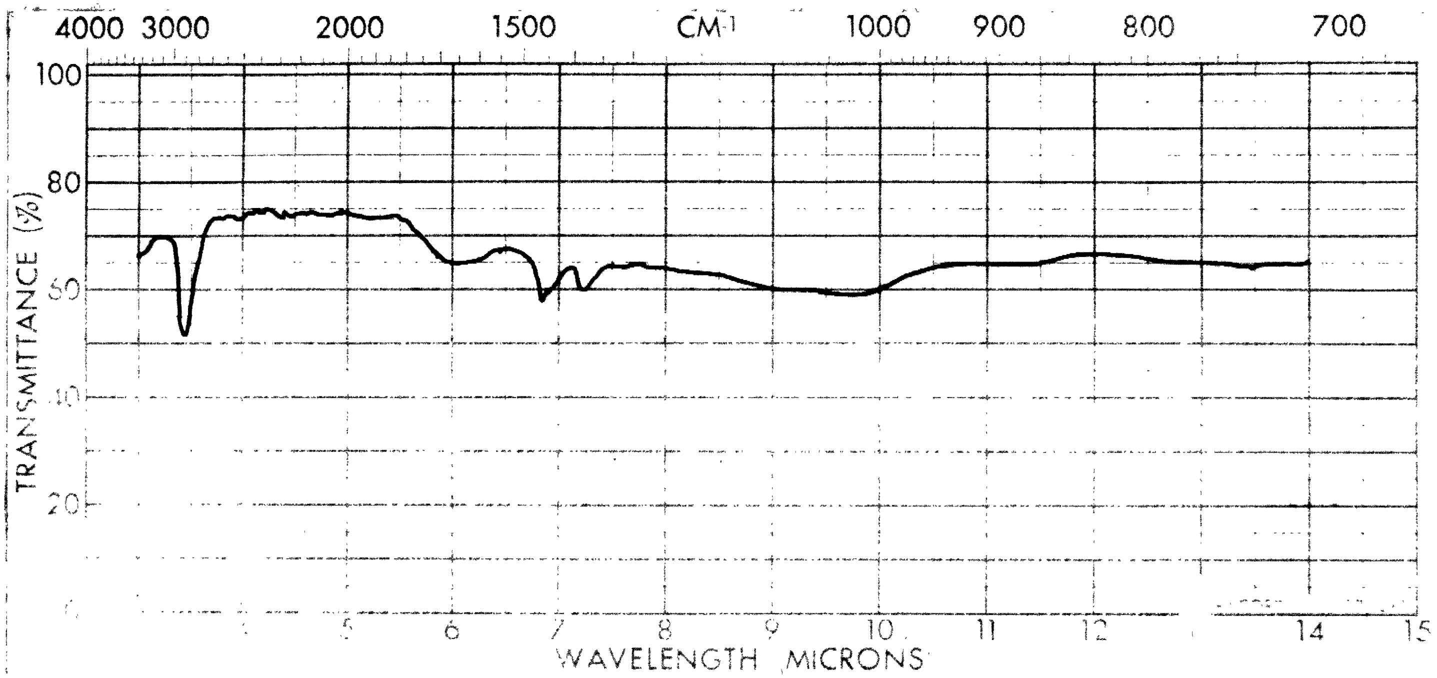
Investigation was continued at 8.87 megacycles, initial pressures ranging downward from 1.6 to 0.7 millimeters mercury, and the corona temperatures from 57°C to 44°C. Mercury present in the corona region gave rise to the line spectrum of mercury and was observed by the use



| | | | |
|---|---|---|---|
| SPECTRUM NO. | ORIGIN Propylene | LEGEND | REMARKS |
| SAMPLE light brown | 700 Mc. | 1. | concentration |
| solid Blacknall | PURITY | 2. | 1.0mg./360mg. |
| | PHASE Solid KBr | DATE | |
| | THICKNESS | OPERATOR J.J.S. | |

SPECTRUM NO.
SAMPLE

Fig. 3--Spectrum of light brown solid: Blacknall



| | | | | |
|---|---|---|---|---|
| NO. | ORIGIN Propylene | LEGEND | REMARKS | SPECTRUM NO.<br>SAMPLE |
| light brown | 8.87 Mc. | 1 | | |
| solid | PURITY | 2. | | |
| | PHASE Solid KBr | DATE | | |
| | THICKNESS 0.3/109 | OPERATOR J.J.S. | | |

Fig. 4--Spectrum of light brown solid

of a hand spectroscope. After a forty-six minute run, the product at the central section of the coil was dark brown; the spiral brown rings were coincident with the copper wire of the antenna spiral. There was a white product deposited as a spiral interlaced with the spiral of dark brown material. White deposits also were formed as far as ten centimeters from the corona region. An infrared spectrogram of the white material was made and the carbonyl peak at 5.8μ was observed.

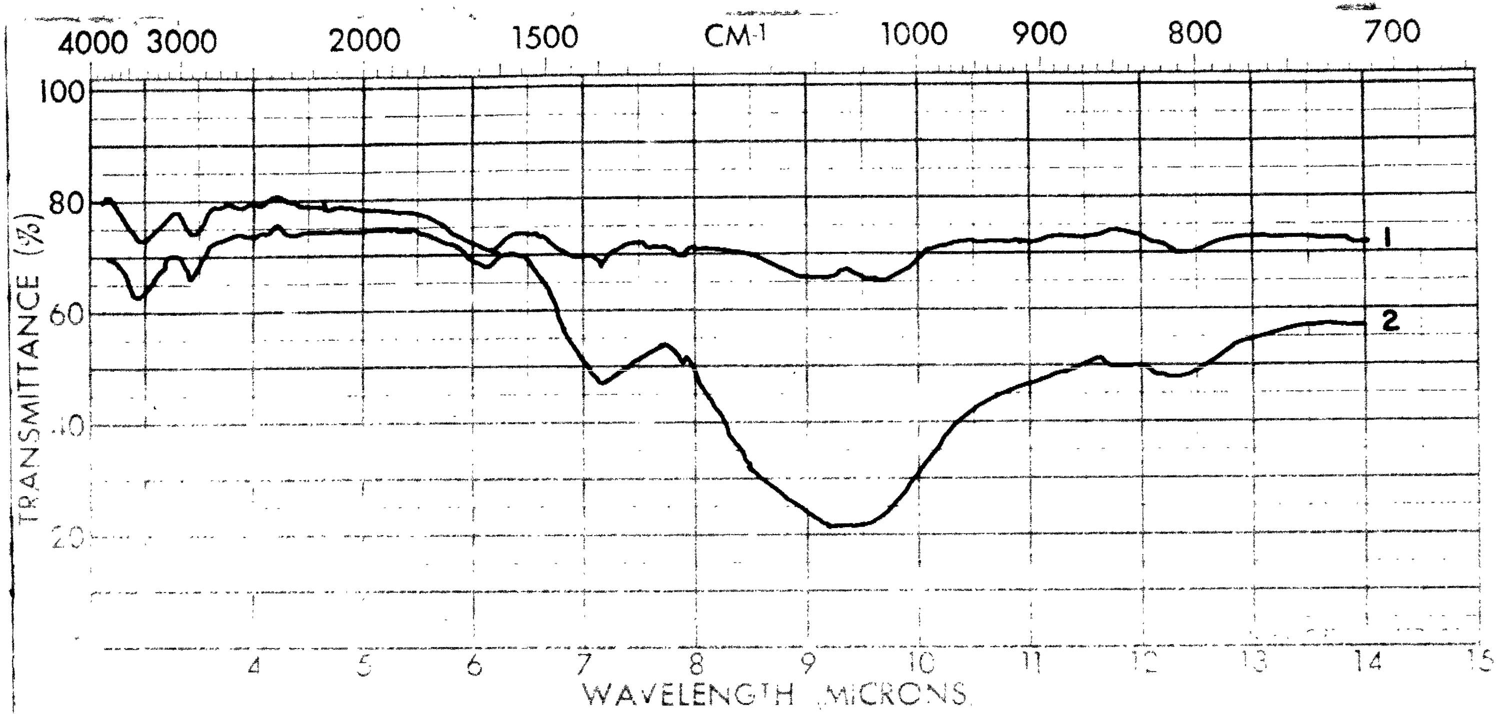
A spectrogram of the light brown material was made and is shown in Figure 4. There are absorption peaks at 2.9μ, 3.4μ, 6.85μ, and 7.25μ. It is noted that this light brown substance checks the peaks for Blacknall's brown deposit except that the 5.85μ sharp peak for the carbonyl group is not present.

The apparatus was rebuilt as shown in Figure 2. The flow of propylene was promoted by temperature difference. The manometer was inclined with a slope of 0.1 and overlaid with octoil, octyl sebacate, in an effort to keep mercury vapor out of the corona region. No mercury spectrum was obtained visually in the corona. Mercury lines were not present in the emission spectra taken on the ARL-1.5 meter grating spectrograph. The run was started with an initial propylene pressure of 1.46 millimeters. A light brown substance was formed in the corona region and a white deposit was formed in the freeze-out trap. After sixteen hours of irradiation the pressure had fallen to 0.27 millimeters.

Infrared spectrograms were made of the brown deposit from the corona region and of the white deposit of the freeze-out trap region and are given in Figure 5. The upper spectrogram in Figure 5, identified as number one, is 1.0 milligrams of the white solid in 333 milligrams of potassium bromide. Absorption peaks occurred at 2.95μ, 3.4μ, 7.25μ, 9.4μ(weak), and 12.5μ. These peaks check with the peaks of Blacknall's brown substance given in Figure 3. The carbonyl peak at 5.85μ is missing. The lower spectrogram, number two in Figure 5, is 0.8 milligrams of the brown substance in 360 milligrams of potassium bromide. Absorption peaks are noted at 2.9μ, 3.4μ, 6.1μ, 7.2μ, 9.4μ, and 12.5μ(weak).

The cryoscopic method for molecular weight determination using camphor gave a molecular weight of 962 and the substance had a melting point range of 140-154°C. The nature of the solubility was not determined due to the small amount of product.

Emission spectra of the corona of propylene at 1.5 millimeters pressure under excitation from the antenna of the 8.87 megacycle transmitter were made using the ARL-1.5 meter grating spectrograph. Exposure times of



| | | | |
|---|---|---|---|
| SPECTRUM NO. | ORIGIN | LEGEND | REMARKS |
| SAMPLE 1 white | propylene 8.87 Mc. | 1. | concentration |
| | PURITY | 2. | 1 1.0mg./333mg. |
| 2~light brown | PHASE solid KBr | DATE | 2 0.8mg./360mg. |
| | THICKNESS | OPERATOR J.J.S. | |

SPECTRUM NO.
SAMPLE

Fig. 5--Spectra comparison of products

ten hours in one case and thirty hours in another were necessary for obtaining the spectra in the visible region. Six hours exposure time was employed in the ultraviolet region. A glass envelope was used for the propylene exposures. The ultraviolet was cut off at 2800Å as a result. This was later corrected by the use of a vycor envelope.

Similarly, hydrogen gas was charged in the vycor tube at a pressure of about 1.5 millimeters. The fluorescent emission spectra of hydrogen excited in the field of the antenna of the 8.87 megacycle transmitter were photographed in both the visible and ultraviolet regions. The reference spectra of mercury were made for comparison and calibration purposes. The simulated scheme for comparison of hydrogen and propylene is shown in Figure 6 for the visible and in Figure 7 for the ultraviolet. The lines shown in the left-hand column are for the positions of spectral lines or spectral band heads for propylene. The central column is for the hydrogen spectrum and the mercury reference spectrum is on the right. Six points of coincidence of the propylene and hydrogen are noted for the visible region.

Figure 7 gives the emission spectrum for the ultraviolet region in the same manner as Figure 6 did of the visible region. Again there are six points of agreement for the lines or band heads.

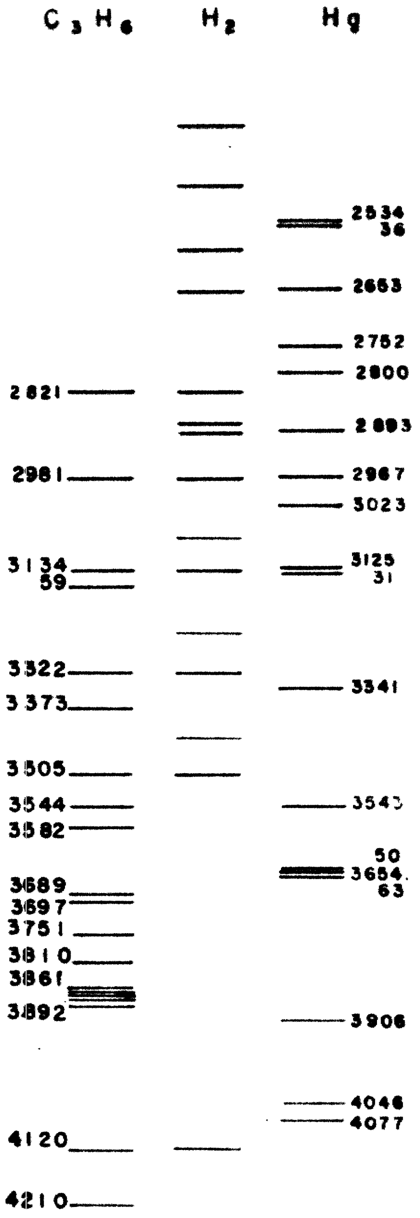


Fig. 6--Ultraviolet emission spectra of propylene, hydrogen, and mercury

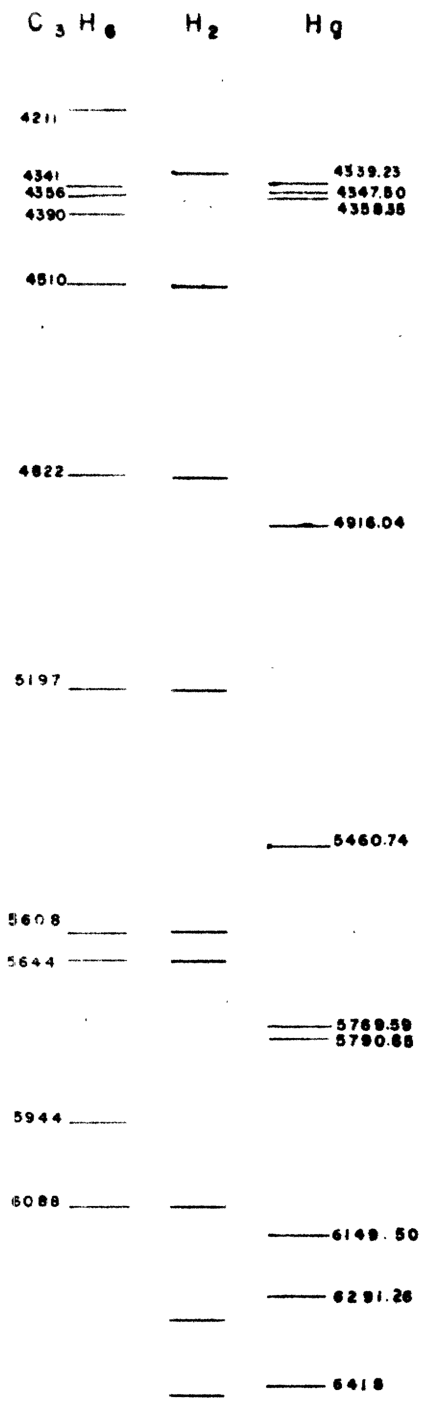


Fig. 7--Visible emission spectra of propylene, hydrogen, and mercury

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# CHAPTER IV

## DISCUSSION OF RESULTS

The infrared spectrogram absorption peaks could indicate the following types of groups in the solid deposits. Alkenes give a wide band at 9.4μ; however, aromatics also have absorption in this region. The 7.2μ peaks are shown by alkenes, 3.4μ peaks by hydrocarbons, and 2.9μ peaks by alcohols and other OH-containing groups. As noted previously, 5.85μ is characteristic of the carbonyl group. No attempt was made to give a structural or empirical formula for the substances obtained.

The emission spectra of propylene and hydrogen were compared with published spectra found in the book, Identification of Molecular Spectra, by Pearse and Gaydon (1). A striking resemblance of the propylene bands and CO bands was apparent. Agreement of band heads at 6088Å, 5608Å, 5197Å, 4830Å, and 4510Å in the visible and six checks for band heads in the ultraviolet at 2821Å, 2981Å, 3134Å, 3159Å (line), 3322Å, and 3373Å leaves no doubt that CO was the emission spectra of propylene and hydrogen. It appears that the check bands between the propylene and hydrogen spectra shown in Figure 6 and 7 are all bands of CO.

The propylene emission spectrum did notshow a band at 4315Å which would characterize CH. However, lines in the 4211Å region did indicate CH as well as the band structure at 3890Å and 3872Å. The latter band from the ethylene flame did not appear in the emission spectrum of propylene.

The source of CO in the spectra of both propylene and hydrogen was probably due to "trash" on the walls of the discharge tubes and a slight impurity of carbon dioxide in the propylene used. An attempt was made to remove the "trash" or adsorbed oxygen containing compounds from the walls of the emission tube by baking it under a vacuum. The impure (probably carbon dioxide) 99.7 per cent propylene was replaced with 99.9 per cent propylene contaminated only with propane. However, the emission spectra obtained in this manner still had the CO lines and band heads. The origin of these band heads and lines has not yet been determined.

The position of the band heads and lines in the spectrum was not changed by a shift in the frequency of the oscillator from 7.0 megacycles to 9.1 megacycles.

The product obtained melted, as was previously stated, at 140-154°C and was brittle. This strongly indicates that the polymer was isotactic-polypropylene. The prefix used was suggested by Natta in an article which has been listed in *Chemical Abstracts* as follows:

> Linear polymeric hydrocarbons were obtained by polymerization of $\alpha$-olefins and their properties were studied. Their high melting points (about 155°C) and degrees of crystallinity, low solubilities, and mechanical properties were ascribed to a structure regularity resulting from a long series of asymmetric C atoms all having the same steric configuration. The name "isotactical" was suggested for this type of order in linear macromols (2).

Further work is necessary to verify the identification of the products.

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