INFRARED SPECTROSCOPY APPLIED TO THE STUDY OF THE AUTOXIDATION OF DI-ISO-BUTYL KETONE

by

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INTRODUCTION

The Infrared Spectrum

The infrared spectrum is a portion of the complete electromagnetic spectrum. The complete electromagnetic spectrum includes: radio waves, infrared, visible light, ultraviolet, x-rays, gamma rays, secondary cosmic, and primary cosmic rays. These types of radiation are harmonious in that they all obey the fundamental law $\lambda\text{-}\nu = c$ where c is the maximum possible velocity being 3×10^{10} centimeters per second, λ is the wavelength in centimeters, and ν is the frequency in cycles per second. They have three basic differences; namely, each comes from a different source, they have characteristic energies, and they dissipate their energy in different ways.

That part of the electromagnetic spectrum which is defined as the infrared region has its origin in the radiation given off by molecules held together by inter-atomic or intra-molecular forces when they are in an induced excited state. The energies of infrared photons are of the order of magnitude of the differences of those molecular energy levels which are due to intra-molecular forces or due to rotation of the molecule as a whole. The absorption of the infrared radiation is a reversal of the emmision process as it is stated above. The wavelengths absorbed, which depend on the molecular energies, lie between 2 and 100 microns where a micron is defined as 10^{-4} centimeters; in actual practice only that radiation lying between 2 and 20 microns is used for infrared analysis since this region includes frequencies due to changes in the vibrations which involve inter-atomic bonds.

Absorption Theory

In a molecule the atoms are bonded together by forces which are elastic in nature and thus the atoms are in continous vibration. The frequencies of these vibrations are of the same order of magnitude as that of infrared radiation; therefore, one might suspect that the presence of a chemical bond in infrared radiation could result in the absorption of a photon with a consequent increase in the energy level of the molecule. This consideration has been confirmed by close correlation of experimental and theoretical data, for example, see Herzberg (1). These vibrational frequencies can be predicted theoretically from the structure of simple molecules but the complexity of the mathematical solution increases tremendously when the number of atoms per molecule increases by just a few. Fortunately the vibrational frequencies of bonds such as C-C, C-O, and C=O, and C-H are not changed to any great extent when they are contained in different molecules. As a very rough approximation Herzberg (2) shows that one can treat a complex molecule containing such a group as a diatomic molecule of the type R-X where X represents the O, H, S, etc. atom and R the remainder of the molecule. The frequency ν of vibration of such an approximate molecule would be given by $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ where k is the force constant for the bond and μ the reduced mass. It develops that k is determined principally by the nature of the R-X bond and only slightly by the nature of R. Similarly μ is almost equal to the mass of X and is only slightly affected by the mass of R. Actually the surroundings of the R-X group do have some affect on the frequency so that changes in R may produce a

slight shift in the characteristic frequencies of such bonds (Fig. 1). These characteristic frequencies have been experimentally determined and are listed in many places for example by Randall, Fuson, Fowler, and Dangl (3).

By placing a compound in a path of infrared radiation and noting the frequencies of the radiation which are absorbed one can identify certain atomic groups contained in the compound. Therefore it is seen that infrared spectroscopy can be very valuable for the qualitative analysis of organic compounds.

The amount of radiation which is absorbed by any medium is given by "Lamberts Law." This law states that the rate of decrease of intensity with thickness of absorbing material is directly proportional to the intensity of the light at any point; or;

$$-\frac{dI}{dL} = kI$$

where I is the transmitted intensity at the thickness L. Since at L = 0 the original intensity is I_o, the intensity I at any point L=L can be found by integrating between the limits I and I_o, and 0 and L. This solution yields:

$$\ln\left(\frac{I}{I_o}\right) = -kL$$

or:

$$\ln\left(\frac{I_o}{I}\right) = kL$$

where k is defined as the extinction coefficient and is a function of the wave length. It can be seen that the radiation is absorbed exponentially with the thickness L. For absorbing solutions the decrease in intensity is also proportional to the concentration. Thus "Beers Law" is:

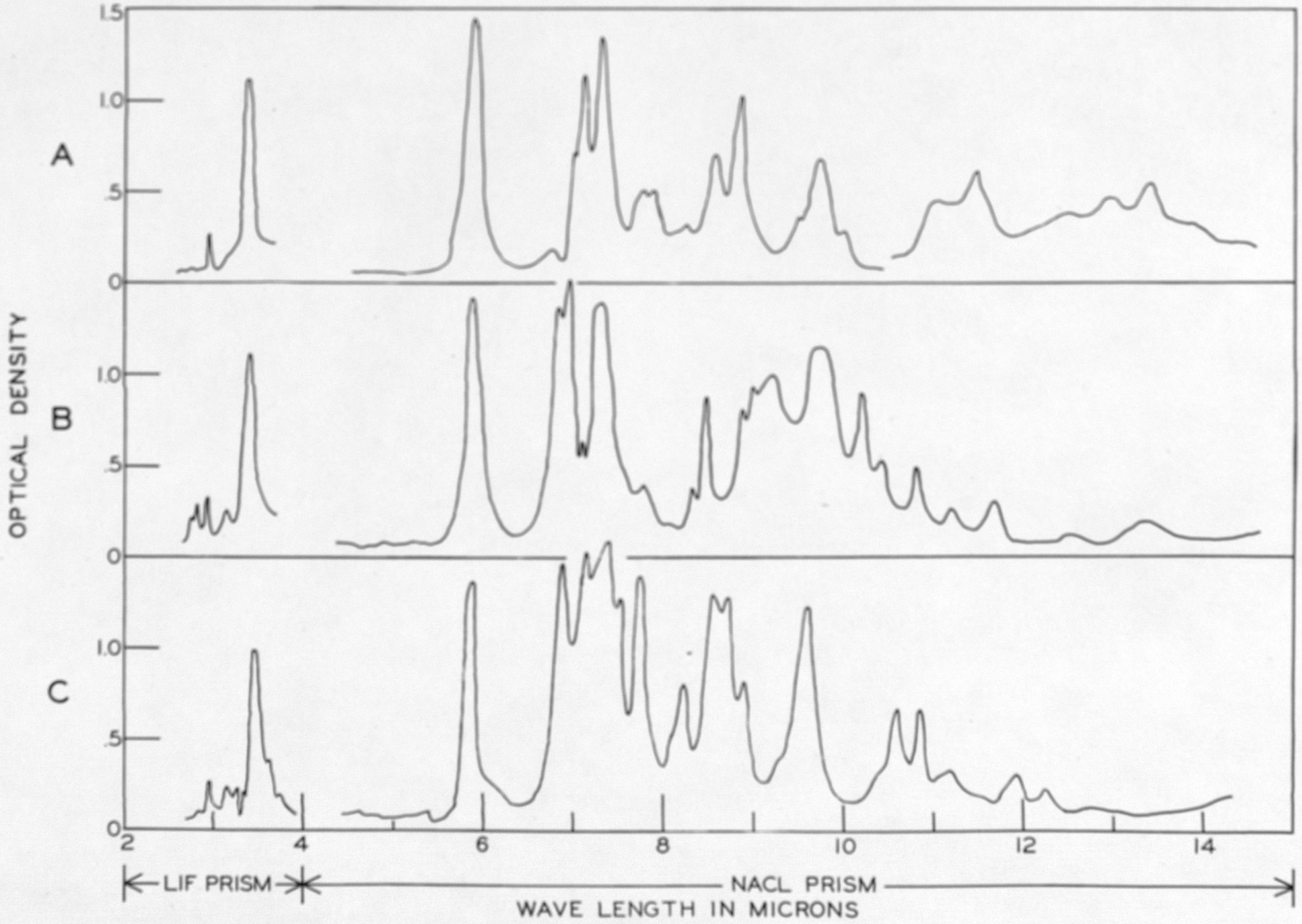


Fig. 1 INFRARED SPECTRA OF SYMMETRICAL KETONES

A DI-N-PROPYL KETONE .10MM CELL 2 TO 4 AND 10.5 TO 15 MICRONS, .05MM CELL 4 TO 10.5 MICRONS

B DI-ISO-PROPYL KETONE .10MM CELL FOR COMPLETE SPECTRUM

C DI-ISO-BUTYL KETONE .10MM CELL FOR COMPLETE SPECTRUM

$$\ln \left(\frac{I_o}{I}\right) = \epsilon cL$$

where ϵ is called the molar absorption coefficient and c is the concentration of the solution. This relationship has been shown to hold reasonably well in the infrared region. The expression $\ln (I_o/I)$ is called the optical density (OD), and it has been shown by Barnes, Gore, Kiddell, and Williams (4), that the total optical density of the mixture is equal to the sum of the optical densities which each component would produce if acting alone. Thus:

$$OD_t = \epsilon_1 c_1 l + \epsilon_2 c_2 l + \ldots + \epsilon_n c_n l$$

By using the above relationship when there are several compounds contained in a mixture one can tell the relative proportions of the compounds. Thus it is seen that infrared spectroscopy can be used both qualitatively and quantitatively in the identification of organic compounds.

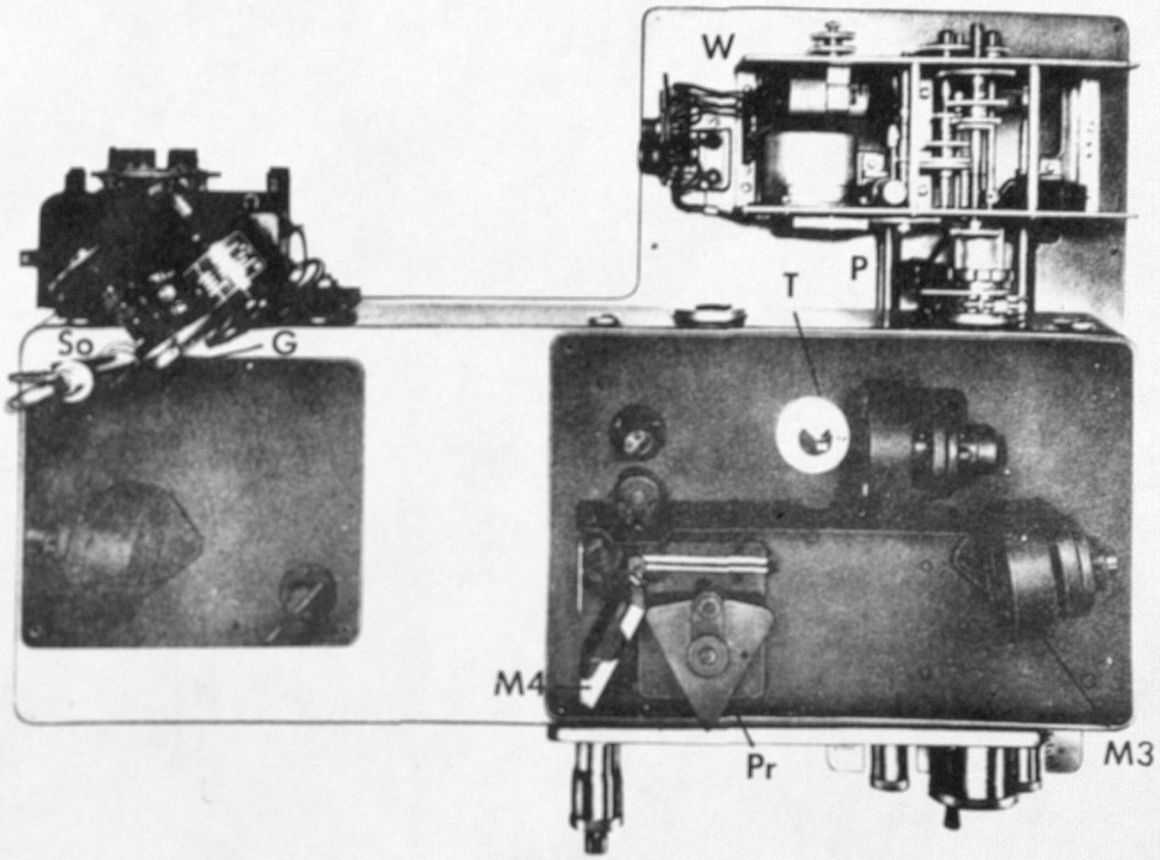
The Perkin Elmer Model 12-B Spectrometer

In order to obtain the desired data for the identification of an organic compound a device is needed to obtain the absorption spectrum of the compound and a spectrum without the compound with which to compare it. Thus one needs an infrared spectrometer the essential parts of which are: an infrared source, the optics necessary for passing the radiation through the sample and dispersing it and a means to record the amount of radiation which is transmitted.

This is accomplished quite well by the Perkin-Elmer Model 12-B Spectrometer. As a source a carborundum rod which is electrically heated and surrounded by a water cooled jacket is used.

It is heated to a temperature of 1000° C. by passing through it a current of 5 to 6 amperes at 40 to 50 volts.

The optical path of the instrument is shown in Fig. 2. The radiation beam from the source is focused through the sample cell, which is placed on the housing containing the prism etc., onto the entrance slit, S_1; then collimated by the off-axis parabolic mirror, M_3; dispersed by the prism, P_r; reflected by the Littrow mirror, M_4; again dispersed by the prism and eventually brought to a focus on the exit slit, S_2. The exit slit passes only rays of a narrow frequency band, after which the rays are focused onto a vacuum thermocouple. Since aluminum surfaces are quite permanent and are highly reflective in the infrared region, front surface aluminized mirrors are used for all the optical parts except the prism and the housing windows. The windows and the prism are made of sodium chloride because wave lengths transmitted by sodium chloride (2.5 - 15 microns) include most of the fundamental absorption bands which may be assigned to characteristic atomic groups in the molecule. Since a lithium flouride prism has better resolving power in the 2 to 6 micron region it is frequently used for quantitative analysis in this region. The two slits are jointly controlled by a slit micrometer, reading in thousandths of a mm from 0 to 2 mm. Wave length selection is obtained by rotation of the Littrow mirror M_4 which is controlled by the wavelength micrometer. The calibration of the drum of the wave-length micrometer is arbitrary and reads directly in hundredths from o to 20; therefore, a set of calibration tables is necessary to convert from readings on the wave length micrometer to wave length in microns. For the instrument used these cali-



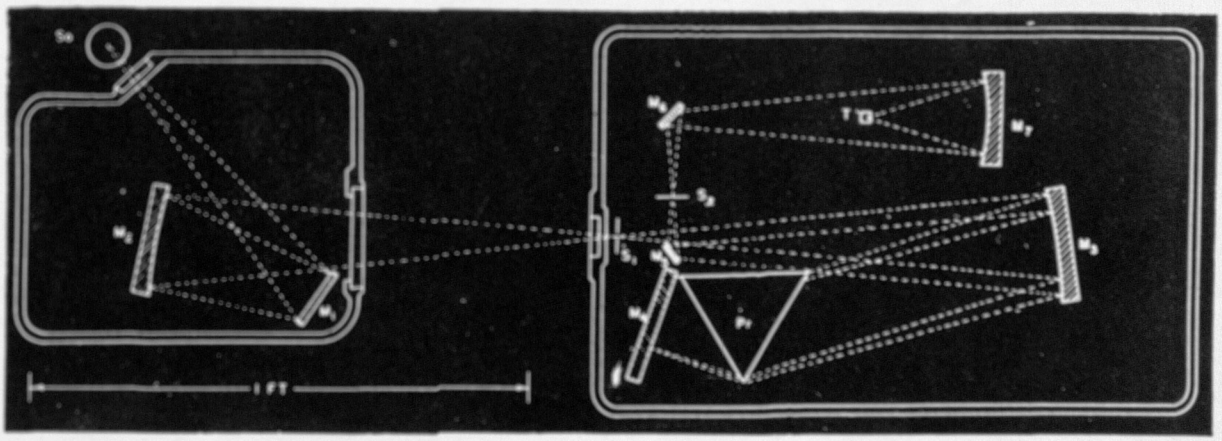


Fig. 2 The optics of the Perkin-Elmer model 12-B spectrometer

bration tables were first calculated by Collins (5), Moore (6), and Newkirk (7) and were recently corrected following the method outlined by Plyler (8). The amplification of the EMF set up in the thermocouple is accomplished by means of a linear DC amplifier and the amplified signal is fed into a Leeds and Northrup Speedomax Recorder. The deflection of the recorder pen is a linear function of the intensity of the radiation incident upon the thermocouple. There is a potentiometer between the amplifier signal and the recorder; it will be discussed in more detail later.

STATEMENT OF PROBLEM

Ketones are compounds containing the carbonyl group and having the type formula:

$$R - \overset{\overset{O}{\|}}{C} - R'$$

The R and R' can be the same or different alkyl radicals, thus permitting the exsistence of both symmetrical and mixed ketones. Only simple ketones were under consideration in this research project. In general ketones are used as solvents; therefore from the industrial point of view their rate of oxidation and the resultant products are of great importance for determining the stability of a solution which contains a ketone as a solvent. From the scientific point of view the oxidation of ketones is quite unique, as the process involves the formation of an intermediate product which readily breaks down into the final products (9). This type of reaction is known as autoxidation. The intermediate product is presumably a hydroperoxide (R-O-O-H) which further oxidizes to yield a heterogeneous mixture of different compounds including peroxides, alcohols, ketones, aldehydes, acids, etc. (9).

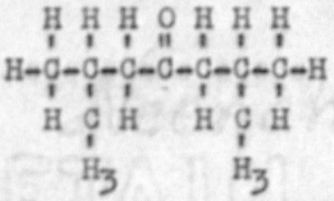
As would be expected these end products are a function of the particular ketone under consideration. The influence these end products have on the course of oxidation has been little studied. Thus the purpose of this investigation was to analyze as completely as possible the reaction which takes place when a ketone is exposed to molecular oxygen.

The problem as stated above appears to be of a purely chemical nature. Although this is true several factors appear which make chemical analysis extremely difficult; namely, 1) The identification of the compounds necessitates changing them chemically. 2) The time required for chemical analysis is in excess of ½ hour. 3) The amount of sample required is large (about 10cc). 4) It is impossible to distinguish between compounds which have the same chemical properties. Infrared spectroscopy offers a partial solution to these hindrances since compounds when identified through absorption curves are not changed chemically; a spectrum of sufficient length for identification takes only 15 minutes to run. The amount of sample necessary to make an absorption curve is very small (less than 1cc), and it is possible to distinguish between chemically akin compounds providing they have different optical properties due to differences in geometrical structure.

In the investigation not only was the complexity of the autoxidation of ketones studied, but also the applicability of infrared spectroscopy to the problem of oxidation. If this application of infrared spectroscopy could be shown to be useful the techniques learned would be of great value to future investigators of organic oxidation processes.

The ketones which have been studied during the course of

this investigation are: acetophenone (10, 11, 12), propiophenone (10, 11, 12), isobutyrophenone (10, 11, 12), di-n-propyl ketone (10, 11), di-iso-propl ketone (9, 10, 11, 12) and di-iso-butyl ketone (13). This thesis is limited to infrared studies of the autoxidation of di-iso-butyl ketone the structure of which is:



EXPERIMENTAL PROCEDURE

Chemical

Oxidation of the ketones was carried out by Yao Hsuing under the supervision of the Department of Chemistry. It was done in a four foot column made of three coaxial pyrex tubes the outer most of which served as an adibatic insulator (Fig. 3). The column was heated by a chromel ribbon which ws wound around the second tube. The operating temperature was regulated by means of a mercury filled tube which was inserted in the oxidation chamber. The leads from the mercury tube lead to the thermostat (Fig. 4). The high output variac was set to produce a temperature slightly above the desired temperature. When the temperature rose above the desired temperature the mercury in the tube expanded and tripped the control relay which turned off the high output variac and turned on the low output variac. When the chamber had cooled below the desired temperature the mercury contracted and the reverse of the above was enacted. This apparatus kept the temperature within 1° C. of the desired temperature. To insure against the possibility

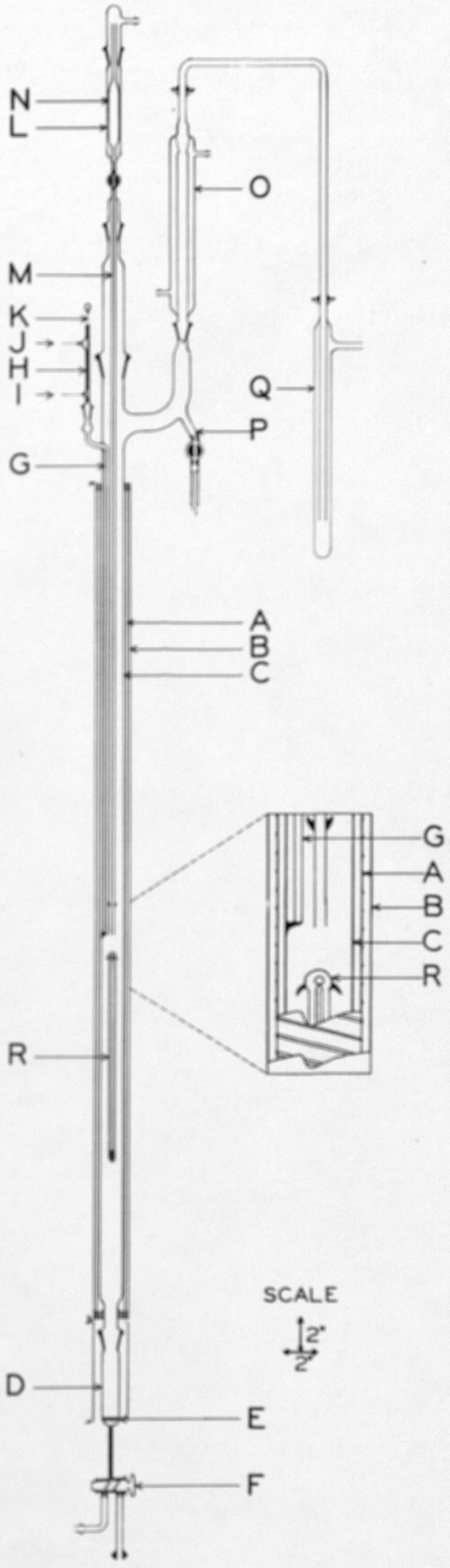


Fig. 3 OXIDATION APPARATUS

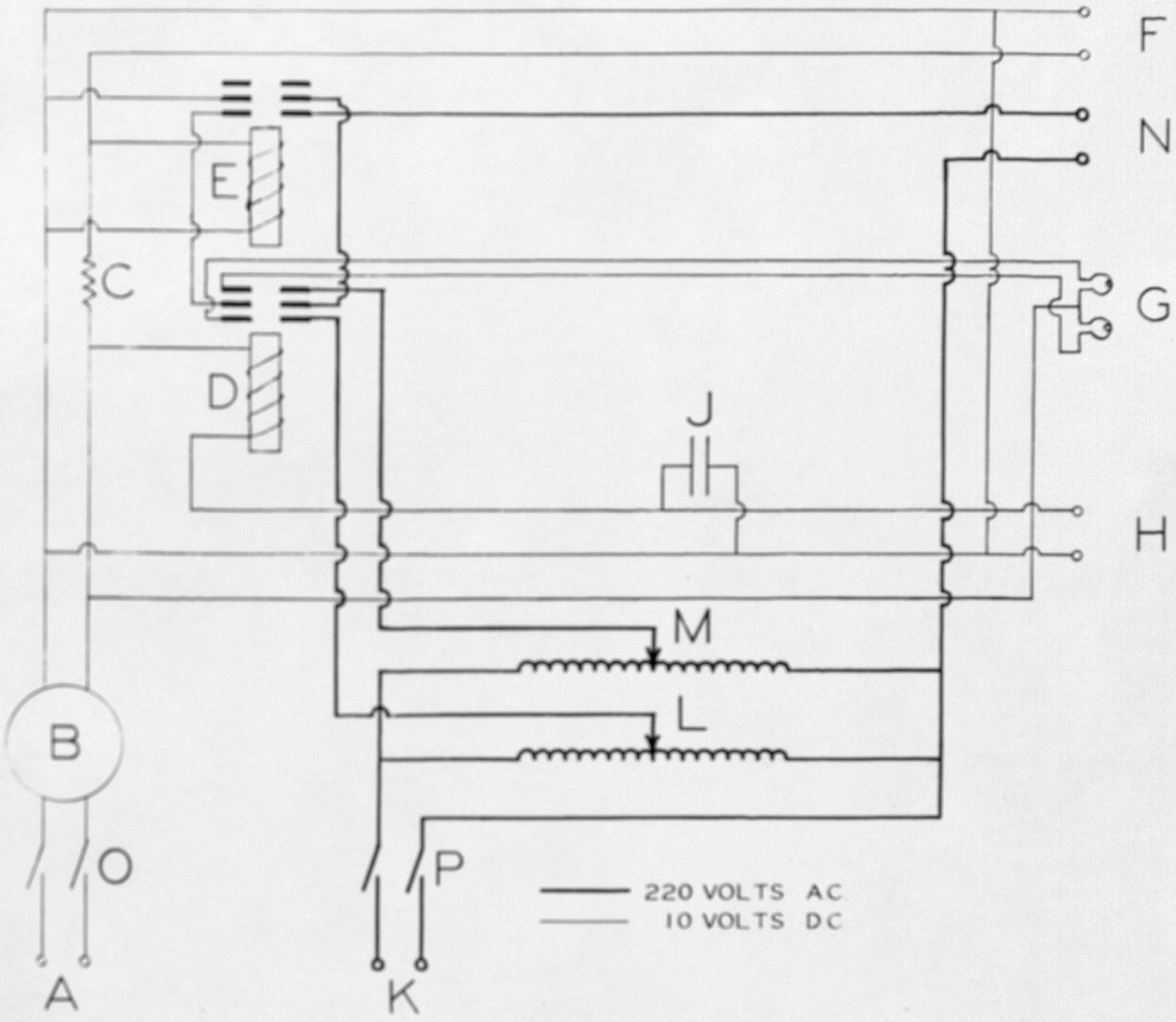


Fig. 4 HEATER CONTROL UNIT

of the column overheating a safety relay was put into the circuit which interupted the heating potential if either the DC voltage to operate the relay was cut off or the temperature in the tube rose to dangerous heights. This type of control allowed oxidation to be continued safely for long periods without an operator.

The inner tube was filled with ketone and molecular oxygen was bubbled through it. Provision was made for the withdrawal of samples from the column at any time during the oxidation process and samples were withdrawn as often as possible. The time required for chemical analysis was about one half hour. Calculations of the concentration of the acids and hydroperoxide/peroxide were made by titration in units of millimoles per gram for each sample withdrawn. At the end of each run the column was drained and a complete chemical analysis was made of the contents.

Infrared

The resolution necessary for infrared analysis was obtained by using a sodium chloride prism from 2.5 to 15 microns. It was found that most of the necessary data for the computation of concentrations of acid and hydroperoxide could be obtained in the 2.5 to the 4.0 micron region and since a lithium fluoride prism gives greater dispersion in this region than sodium chloride it was used for two runs. Three runs were made using the sodium chloride prism for further analysis and for the assignment of absorption bands observed in the spectra.

In the analysis of the spectra of the oxidized samples of di-<u>iso</u>-butyl ketone it was assumed that the initial concentration of the end products was zero. This assumption was justified in

that chemically pure ketone was distilled twice before the oxidation was initiated and all possible precautions were made to insure against contamination of the ketone and the oxidizing chamber. Any observed change in the spectrum of the samples during oxidation was then necessarily due to one or several of the resultant products (Fig.5).

In order to obtain the spectra of each sample, following the withdrawal from the oxidation column, it was placed in a sample cell, which was made of two optically flat sodium chloride plates separated by a .05 mm aluminum spacer. The ketone due to its low surface tension, had a tendancy to run out of the cell during the time necessary to run a spectrum. To prevent this undesirable occurance a permanent cell was constructed, a hypodermic needle was put into the cell and secured with a mixture of beeswax and rosin which was unaffected by the dissolving action of ketones. This was advantageous in three ways; namely, it solved the above problem, it was no longer necessary to clean the cell by hand as this could now be accomplished by flushing the cell with acetone and then removing the latter with a vacuum pump, and thirdly the thickness of the cell was constant and could be determined by use of interference patterns (14).

The filled cell was placed in the spectrometer and the spectrum was run over the desired range giving a curve of intensity versus wave length. The spectrum was then run over the same range with no cell in the radiation path thus obtaining a curve of incident intensity (I_o) versus wave length. Both spectra were recorded on the same chart with the same micrometer readings of each in the same position on the chart. The optical density at

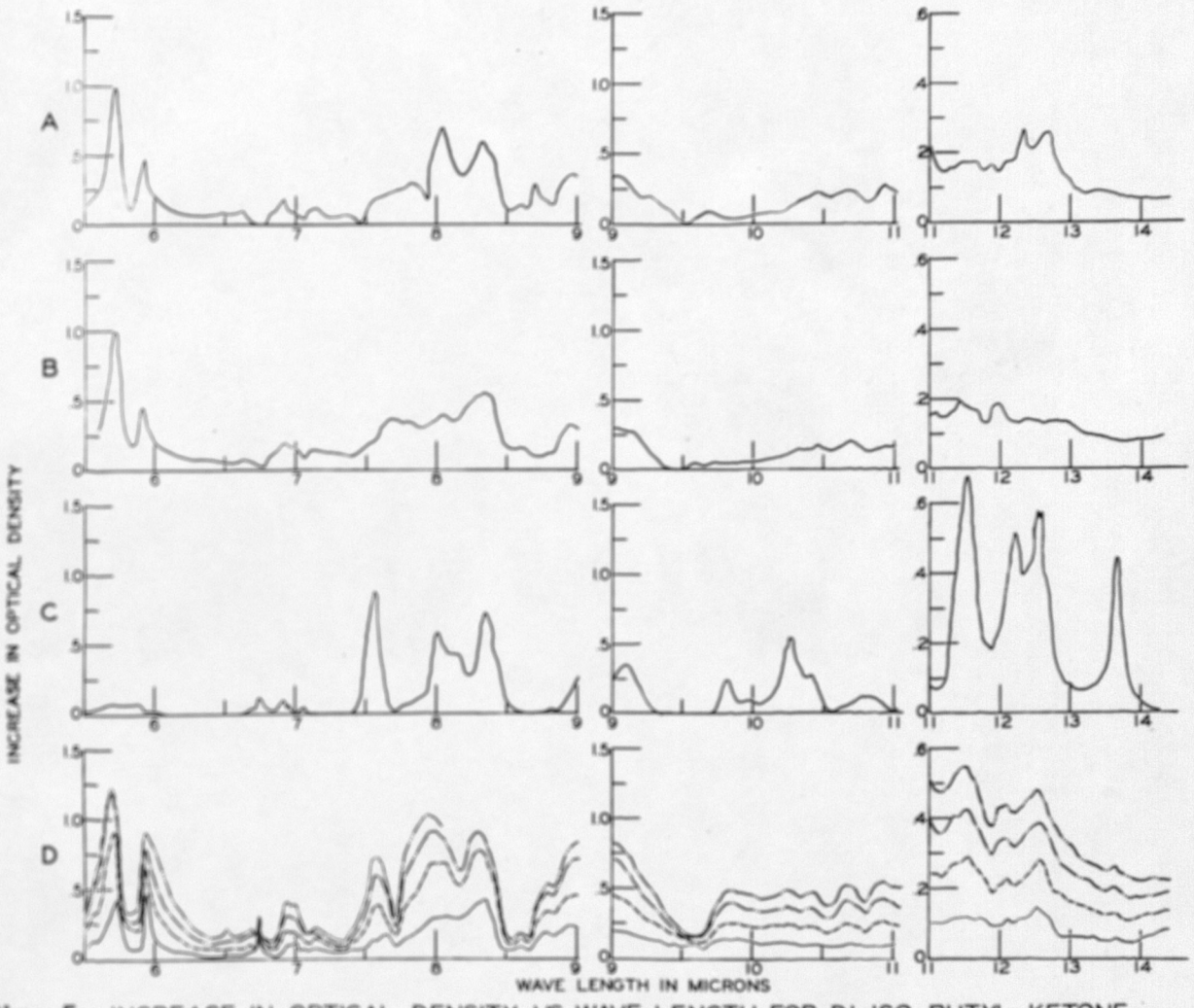


Fig. 5 INCREASE IN OPTICAL DENSITY VS. WAVE LENGTH FOR DI-ISO-BUTYL KETONE

A DI-ISO-BUTYL KETONE SOLUTION ISO-BUTYRIC ACID, .10MM CELL FOR COMPLETE SPECTRUM

B DI-ISO-BUTYL KETONE SOLUTION ISO-VALERIC ACID, .10MM CELL FOR COMPLETE SPECTRUM

C DI-ISO-BUTYL KETONE SOLUTION PEROXIDE, .10 MM CELL 5.5 TO 11.0 MICRONS, .20MM CELL 11.0 TO 14.5 MICRONS

D DI-ISO-BUTYL KETONE OXIDIZED AT 130°C, .10MM CELL FOR COMPLETE SPECTRUM,
OXIDIZED: ——— 2 HOURS, - - - - - 5 HOURS, — — — 9 HOURS, — · — · — 14.5 HOURS

NACL PRISM

each wave length was calculated from the recorded spectra by means of a simple instrument that can be read directly in optical density when settings are made on the two curves recorded on the chart. The total error in optical density measured in this way is less than two percent. The mechanical drive to the Littrow mirror had a slight amount of slack action, this resulted in a shift of the spectrum with respect to the micrometer reading. To overcome this it was necessary to use the first chart of the spectra as a standard for calculation of wave lengths. Wave lengths of other spectra obtained in the same series were computed by comparison with the first chart.

During the course of a run the optical density got so large, that is the samples got so black, that it was impossible to read the optical density with any accuracy. To overcome this difficulty a potentiometer having a tap switch was inserted between the amplifier and the recorder (Fig. 6). The precision resistors in the potentiometer were so chosen as to give a one-third drop of the next higher voltage and there were five individual drops. When calculating the optical density of a spectrum in which the divider was used, it was only necessary to add a predetermined constant to the observed optical density depending upon the fraction at which the divider was set for the background curve and for the sample curve. Since the intensity of radiation is not linear with wave length it is necessary to have a device to change the amount of radiation incident on the thermocouple. This is done by means of a slit and the adjustment of the slit required a considerable amount of time. The potentimeter reduced the number of slit settings necessary and thereby shortened the amount of time necessary for running a spectrum.

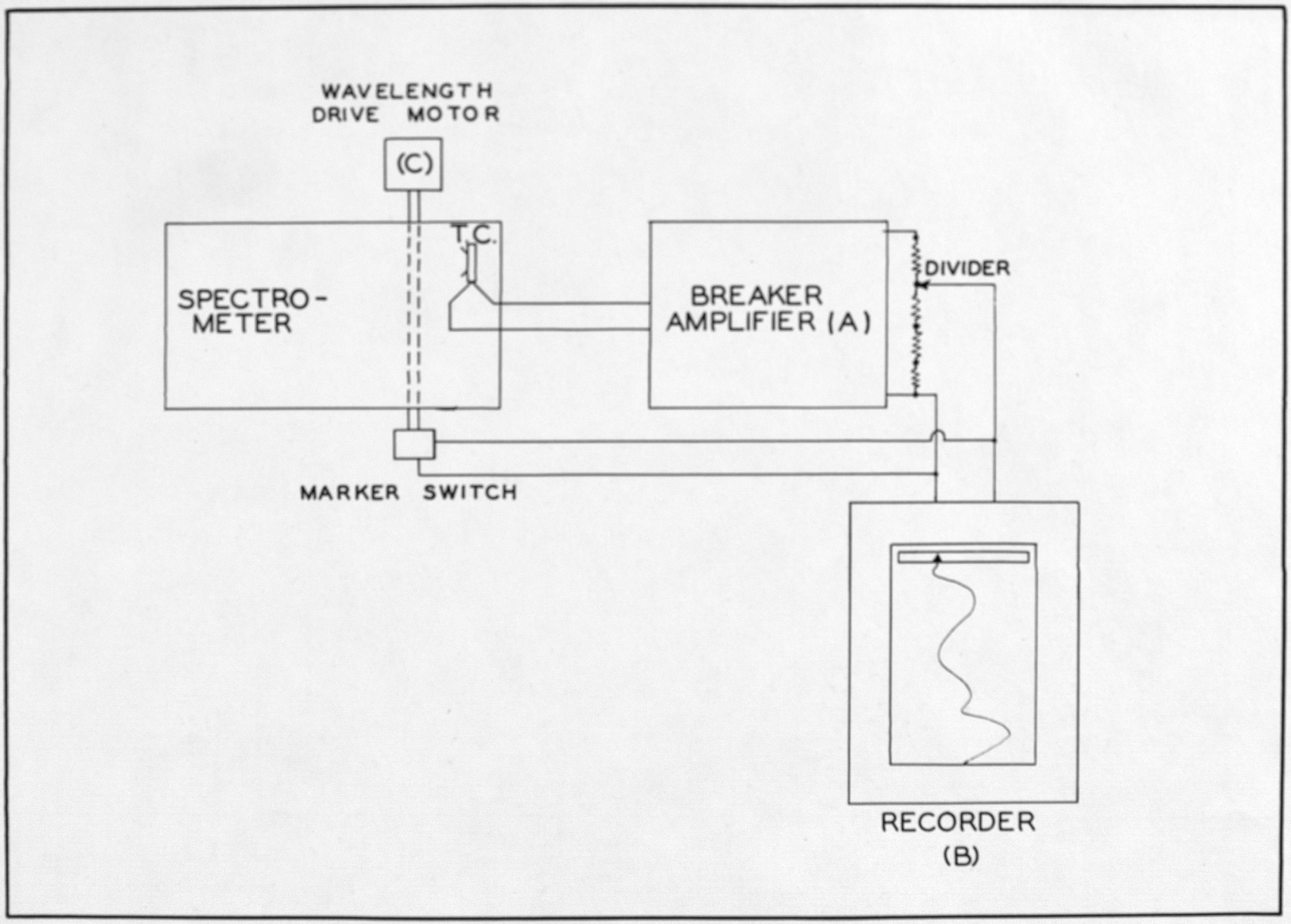


Fig. 6 A block diagram of the dividing potentiometer

RESULTS AND DISCUSSION

In order to assign the bands observed in the spectra due to functional groups it was necessary to take the complete spectrum of each end product in a solution of Di-iso-butyl ketone. These spectra are shown in Fig. 5. A comparison of the relative absorption in each portion of the spectra lead to the tentative assignments listed in Table I for each end product. More will be said of the peroxide appearing in this Table but for simplicity assume that it does not exist during the course of oxidation. This and other assumptions will be clarified later.

In order to make a quantitative analysis it was decided to use the highly dispersive lithium fluoride prism in a region which contained characteristic absorption from each product. The region chosen was 2.5 to 3.4 microns. The spectra in this region for several oxidation times are shown in Fig. 7. In Fig. 8 curves are given for two wave lengths of optical density versus time for three different oxidation runs at different temperatures.

The spectra from 2.5 to 3.4 microns were read at thirteen different wave lengths since the wave lengths were in the center of the characteristic absorption bands. Five of these wave lengths, between 2.5 and 2.8 microns, were found to give incoherent results probably caused by water produced in the reaction. It has been found by Nielsen (15), that the spectrum of water is very complex. These data were discarded since a large part of the water was evaporated off during the oxidation reaction.

This left eight wave lengths for analysis, five of which in the 3.0 to 3.3 micron region, were due principally to the two acids

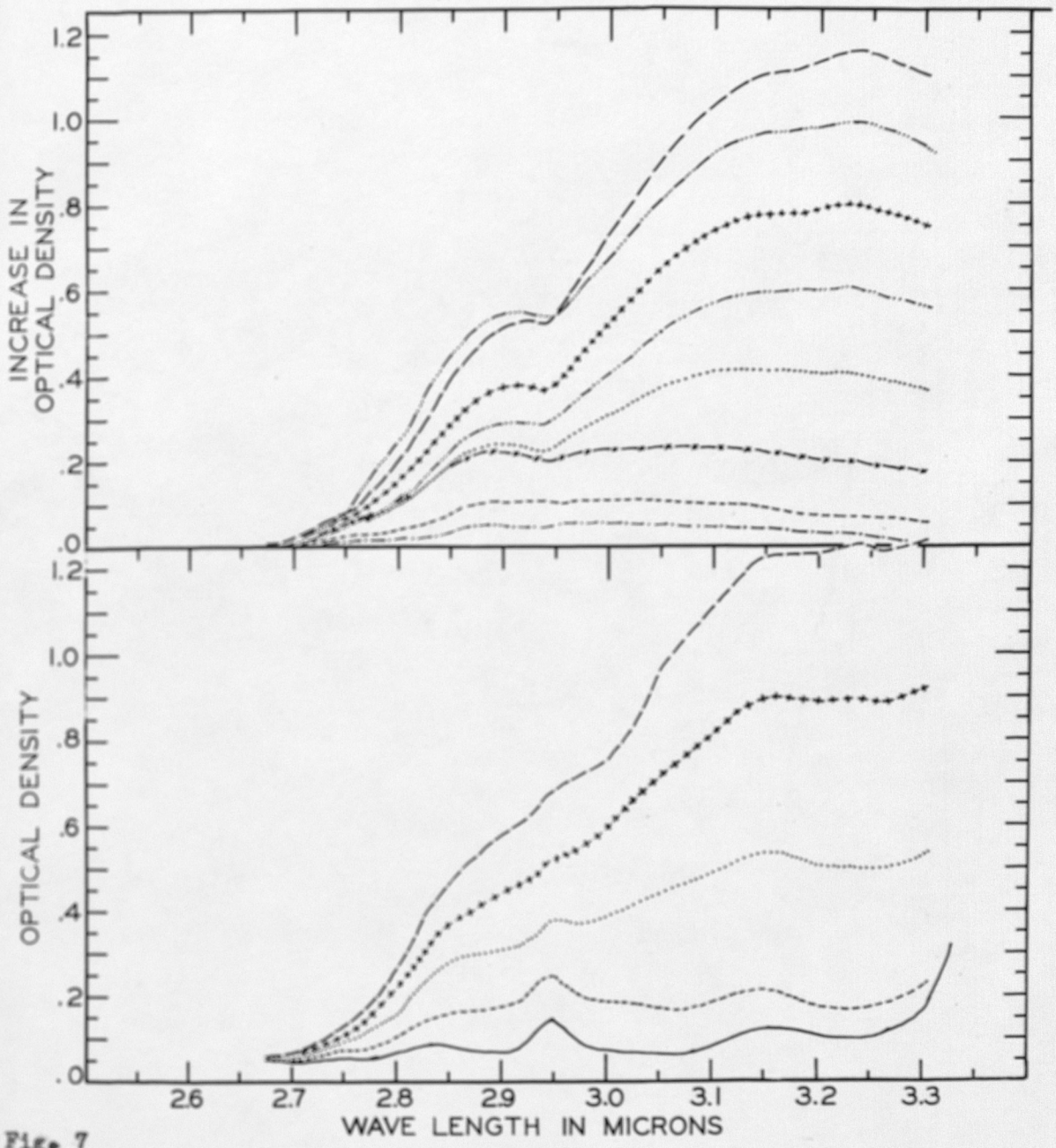


Fig. 7

SPECTRUM OF DI-ISO-BUTYL KETONE OXIDIZED AT 130° C
2.5 TO 3.4 MICRON REGION LI F PRISM 0.05 MM. CELL

KEY

—— PURE DI-ISO-BUTYL KETONE
—·—·— OXIDIZED 1.0 HOURS
- - - - OXIDIZED 18.0 HOURS
····· OXIDIZED 2.0 HOURS
·····+ OXIDIZED 23.0 HOURS
-·-·-·- OXIDIZED 5.0 HOURS
—··—·— OXIDIZED 31.0 HOURS
····· OXIDIZED 13.0 HOURS
— — — OXIDIZED 35.0 HOURS

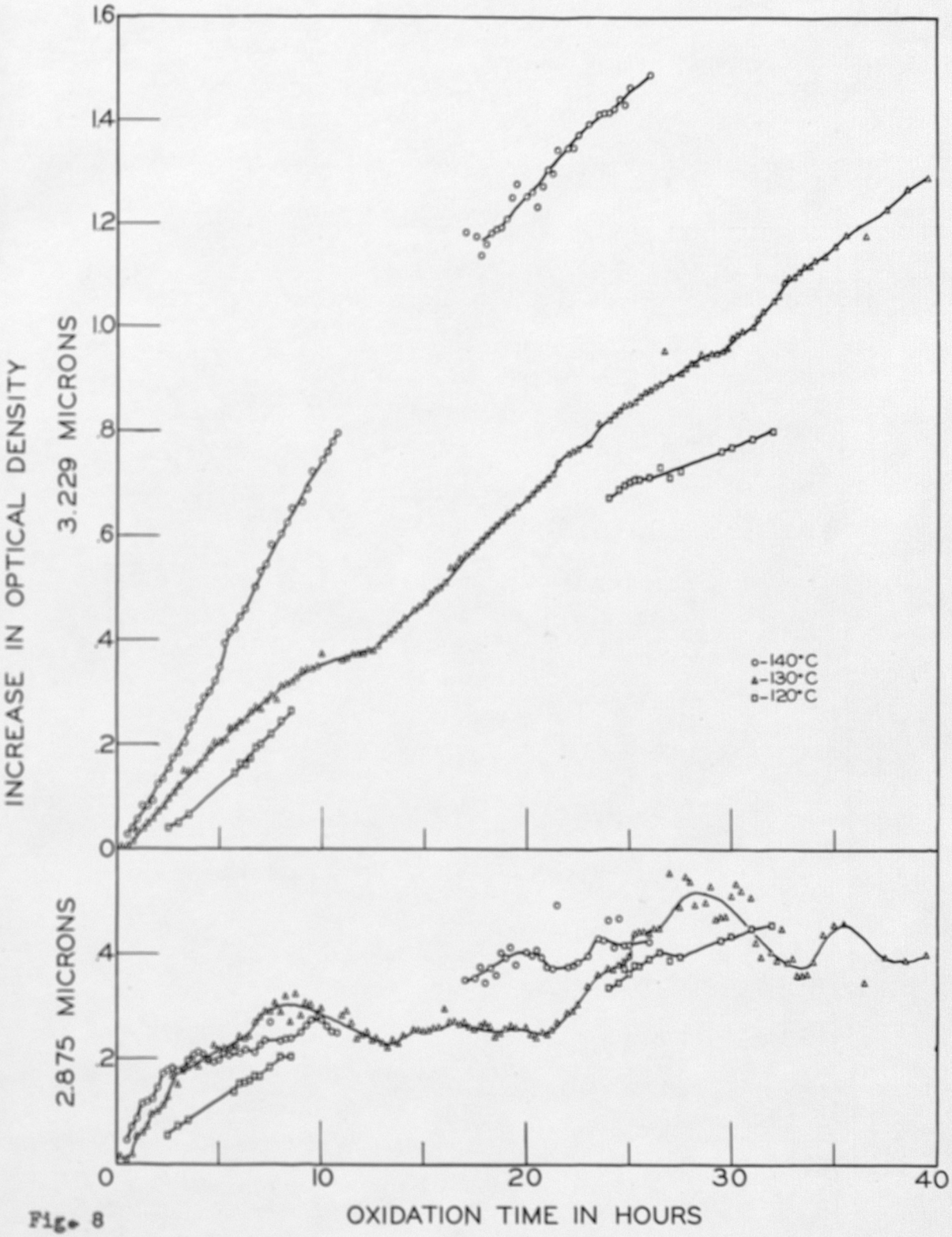


Fig. 8

CHANGE IN OPTICAL DENSITY VERSUS OXIDATION TIME OF DI-ISO-BUTYL KETONE

and three, in the 2.8 to 2.9 micron region were due primarily to the hydroperoxide. In order to calculate the concentrations of the products throughout the period of oxidation it was necessary to run the spectra of several mixtures of the two acids in di-iso-butyl ketone and to determine their extinction coefficients. It was found that these coefficients were not constant as predicted by Beers Law. A plot of concentration versus Optical Density for the two acids are shown in Fig. 9. Since the chemical results indicate the two acids to be in equal concentration at all times, these curves were added together to produce those shown in Fig. 9.

By taking the observed optical densities at these wave lengths during the oxidation runs, it was possible to determine the total concentration of the two acids throughout the run. This was done for all five wave lengths then the average concentrations were computed. A comparison curve between chemical and infrared acid concentration data is shown in Fig. 10. It can be seen from this figure that the data from the two different sources are in close agreement indicating that at these wave lengths the hydroperoxide produces very little absorption.

At the other three wave lengths chosen, it is found that the absorption is due to both the acids and the hydroperoxide. Therefore it was necessary to subtract the optical density due to the acids at these wave lengths from the observed optical densities in order to calculate the concentration of the hydroperoxide. The procedure for this is simply an inverse of the above operation; i. e., by using the computed concentration of acids to calculate the optical density due to acid at these wave lengths for each sample

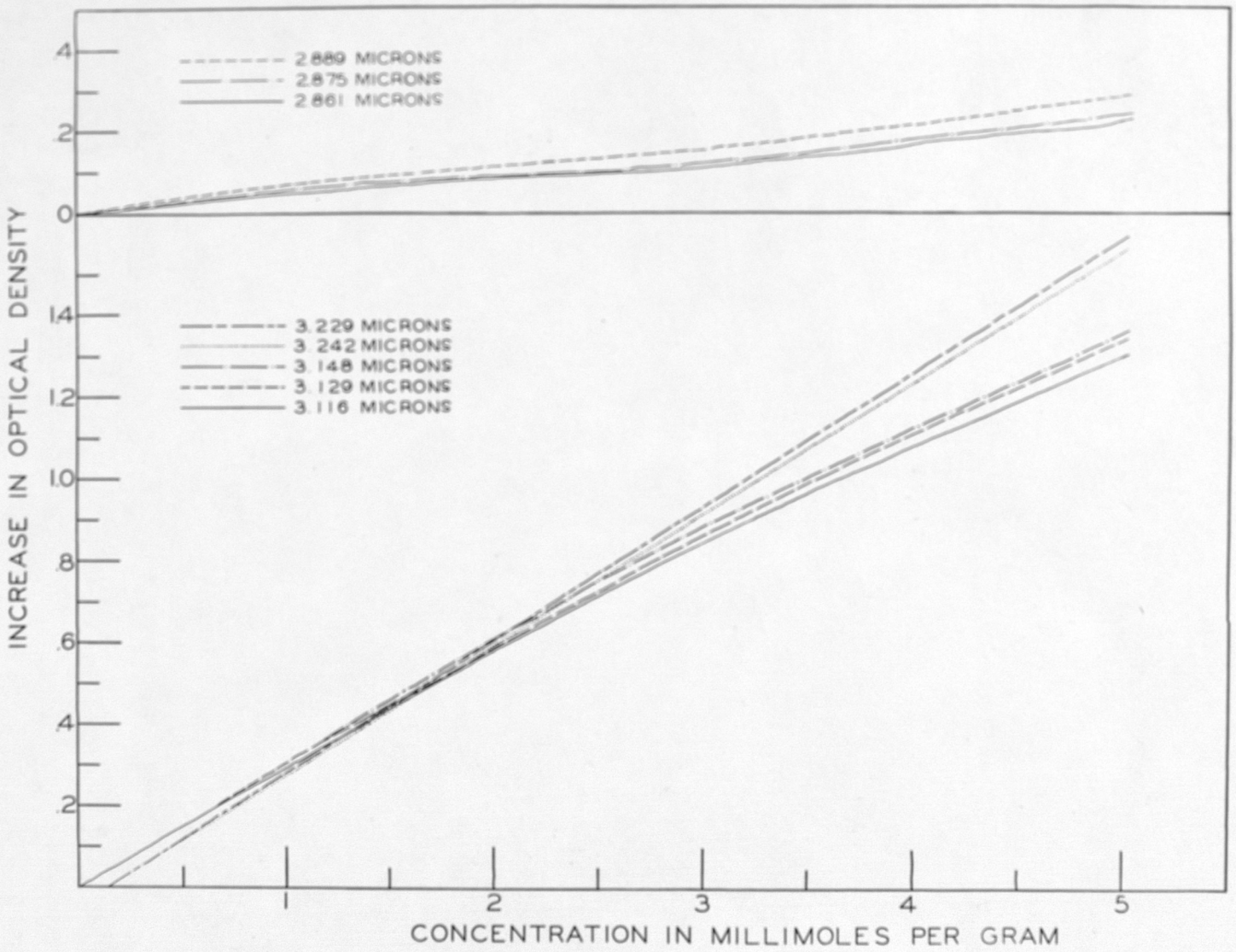


Fig. 9 INCREASE IN OPTICAL DENSITY DUE TO INCREASE IN ACID CONCENTRATION

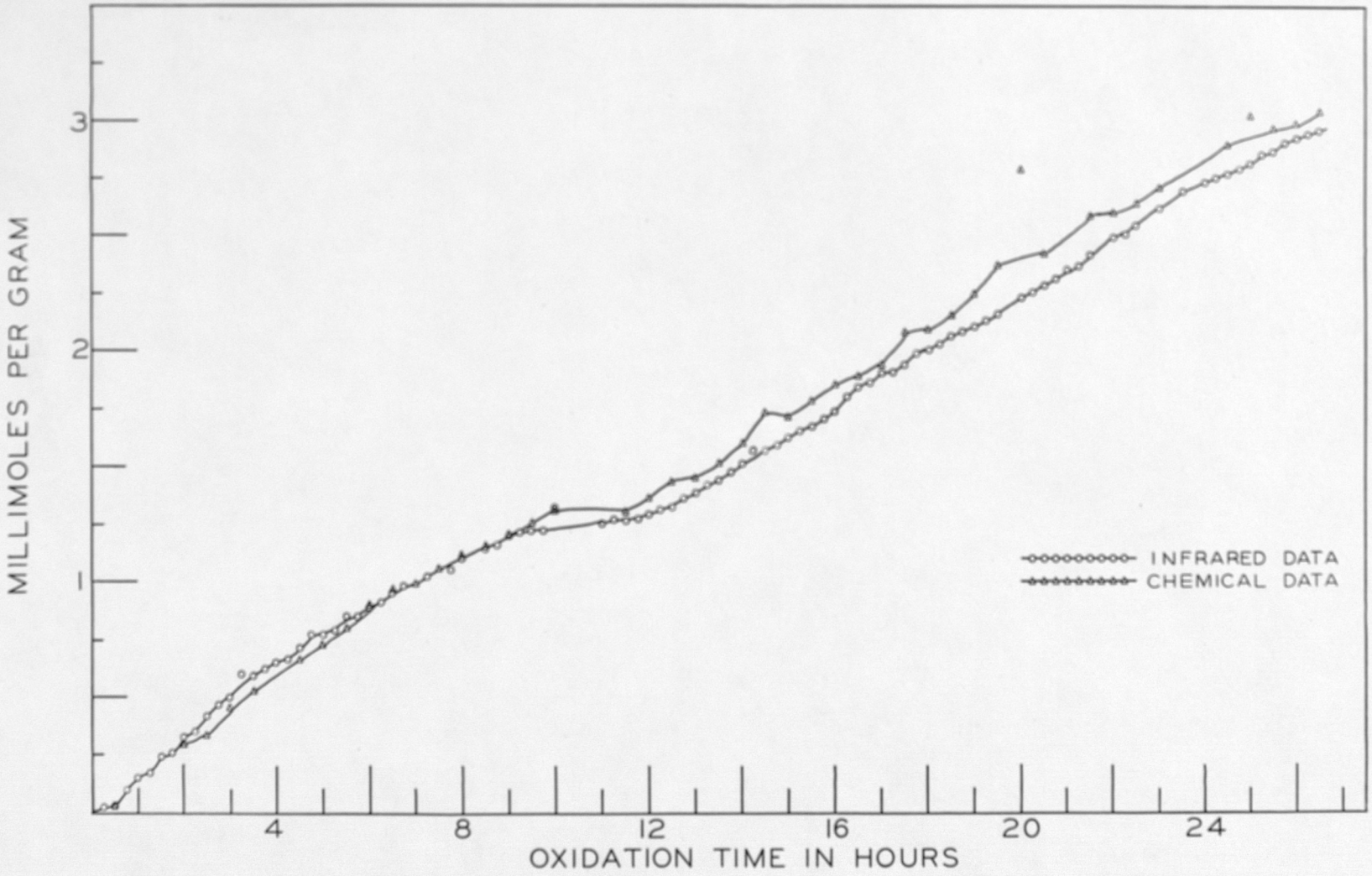


Fig. 10 INCREASE IN ACID CONCENTRATION DURING OXIDATION RUN

then subtracting them from the observed optical densities to obtain the optical density due to hydroperoxide.

In order to compute the concentrations of the hydroperoxide it was necessary to know the extinction coefficients due to the hydroperoxide for the three wave lengths. At the beginning of an oxidation run it was assumed that nothing but the hydroperoxide and the two acids were present in any great amount. Therefore for early oxidation times, these optical densities were plotted against chemically observed concentrations of the hydroperoxide and the curves were extended according to Beers Law for oxidation time later than five hours. These curves are shown in Fig. 11. The concentrations of the hydroperoxide was then computed at each of the three wave lengths for the entire run from these curves. The concentrations given by each wave length were then averaged and were compared on a plot of concentrations versus time with the chemical data (Fig. 12).

The concentration of the main constituents are now known for the complete run and are shown in Fig. 13. This completes all of the data that are obtainable from infrared analysis in the 2.4 micron region.

ASSUMPTIONS

The following arguments are presented in order to try to justify assumptions made during this analysis.

One assumption that was made was that isobutyric acid and isovaleric acid were in equal molar concentrations at all times during a run. The justification of this is that at the end of

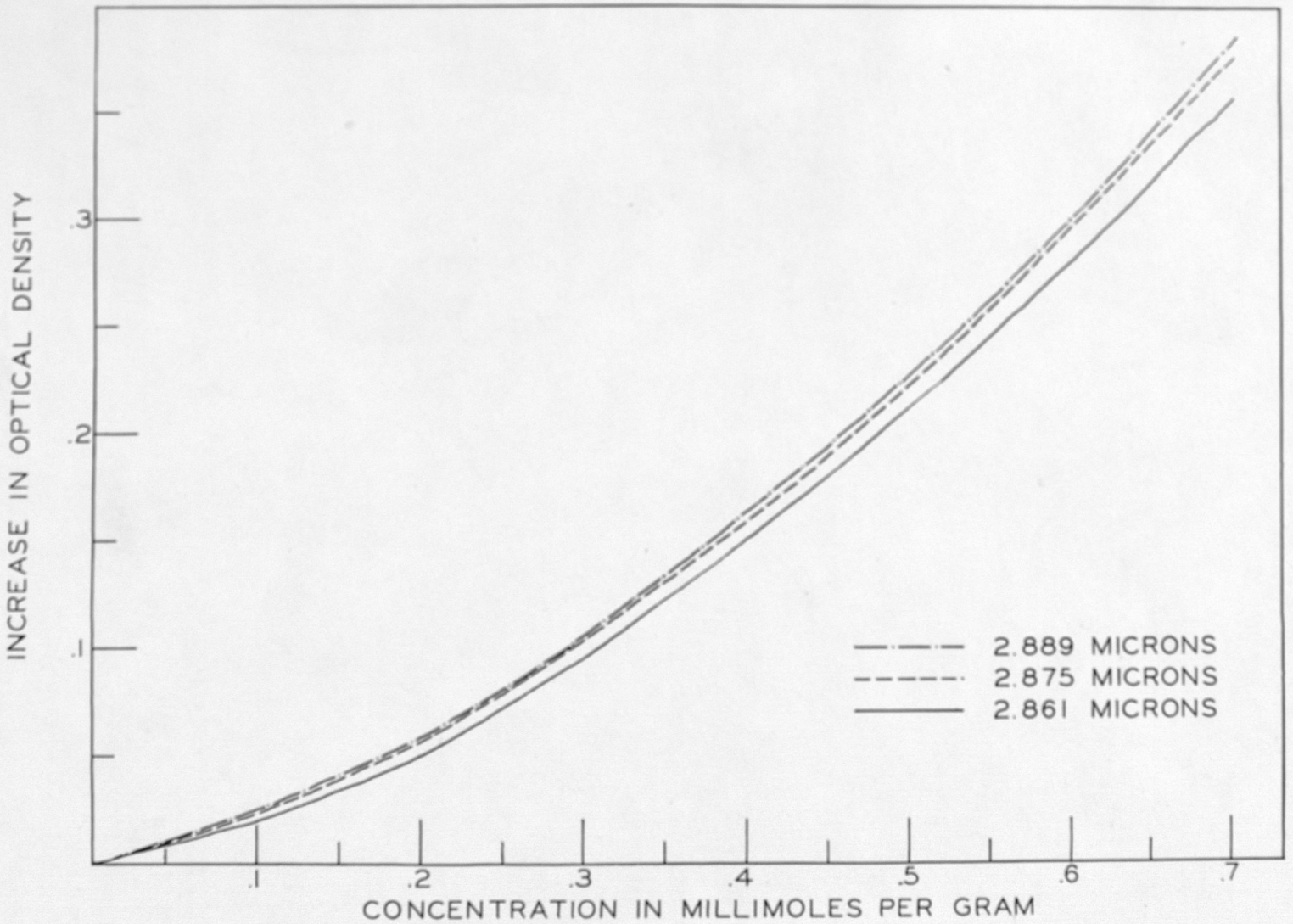


Fig. 11 INCREASE IN OPTICAL DENSITY DUE TO INCREASE IN HYDROPEROXIDE CONCENTRATION

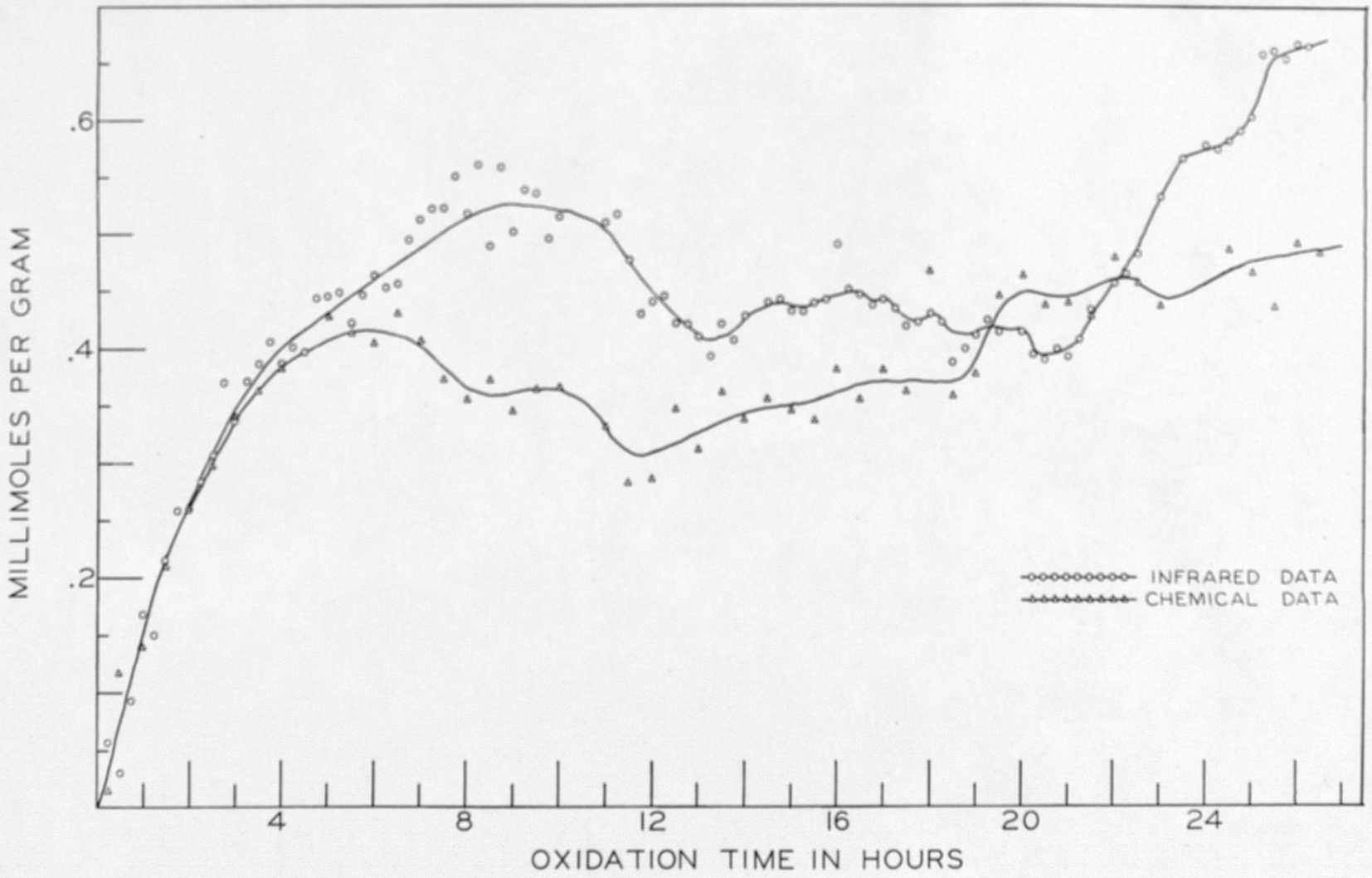


Fig. 12 INCREASE IN HYDROPEROXIDE CONCENTRATION DURING OXIDATION RUN

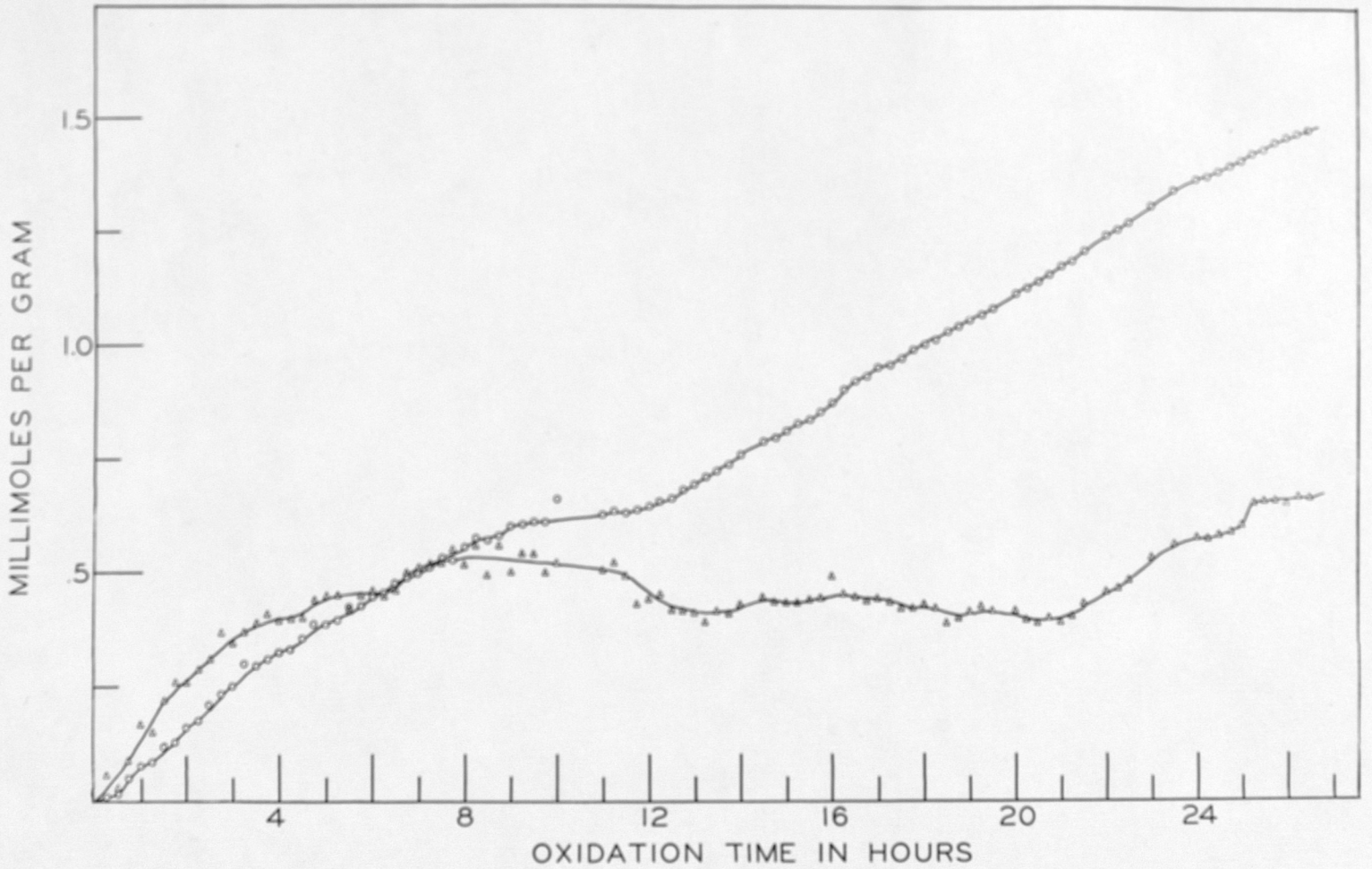


Fig. 13 INCREASE IN CONCENTRATION OF:

ooooooooooo ISO-BUTYRIC ACID

ooooooooooo ISO-VALERIC ACID

▵▵▵▵▵▵▵▵▵▵▵ HYDROPEROXIDE

the run when the end products were separated their proportions were found to be equal. Therefore it appears to be a reasonable assumption that the two acids were formed in the same reaction from the same parent molecule in equal proportions.

Another assumption which was made was that for early oxidation times the only products in any great proportions in the solution were isobutyric acid, isovaleric acid, di-iso-butyl ketone and hydroperoxide. Since hydroperoxide is the parent compound of the other products formed during the reaction this is a safe assumption and is justified by an investigation of Fig. 12 which shows the chemical curve of concentration versus time for hydroperoxide for the run and shows the rapid rise in concentration of hydroperoxide. Therefore it is doubtful whether, for the first six hours, other secondary products such as peroxides, aldehydes, acetone, etc. were present in any measurable concentration.

Some discrepency occured at oxidation time twenty-six and one-half hours when there was a jump in the optical density which more than doubled that of the previous sample at twenty-six hours and fifteen minutes. After this time for two or three hours the data was considered unreliable. This discrepency occurred in only this one run and it was over looked as an experimental failure either in the spectrometer or operation technique.

At approximately ten and one half hours the oxygen was obstructed by the diffusion plate and it was off for about two hours before it was noticed. Results from this can be noted in the Fig. 8 from the ten to fourteen hour region where the slope

is decreased for the 120° run. It may appear that the author is at fault for choosing a run in which such faults appear but only three runs were made in this region and only one was continuous, the latter being the run analyzed. The other two runs were made primarily to determine a temperature at which the best analytical run could be made.

The last assumption that is necessary to justify is that no peroxide is formed during the run. At the end of the run when the end products were separated by Mr. Yao Hsiung, who handled the chemistry phase of this work, a product was crystallized out which was believed to be the hydroperoxide and an infrared spectra of it was run, the results of which are shown in Fig. 14. As can be seen from this figure there is no absorption due to the compound in the O-H region proving without question that it was not a hydroperoxide. Further examination of the spectrum shows absorptions in the seven to nine micron region which is indicative of an ether linkage. The general absorption in the ten to fourteen micron region is most probably caused by a cyclic compound and also indicates the possibility of a C-O-C-C linkage. This information was given to the chemists and they made all possible tests to try and determine its structure. The following properties of the compound have been determined by chemical (13) and infrared analysis; 1) A compound of molecular weight 189.5, 2) Nine carbon atoms, 3) Four oxygen atoms, 4) From sixteen to eighteen hydrogen atoms, 5) An ether linkage, 6) A peroxide linkage, 7) A carbonyl group, 8) An active hydrogen and 9) it very probably contains a cyclic structure.

The assumption was made that the above peroxide does not

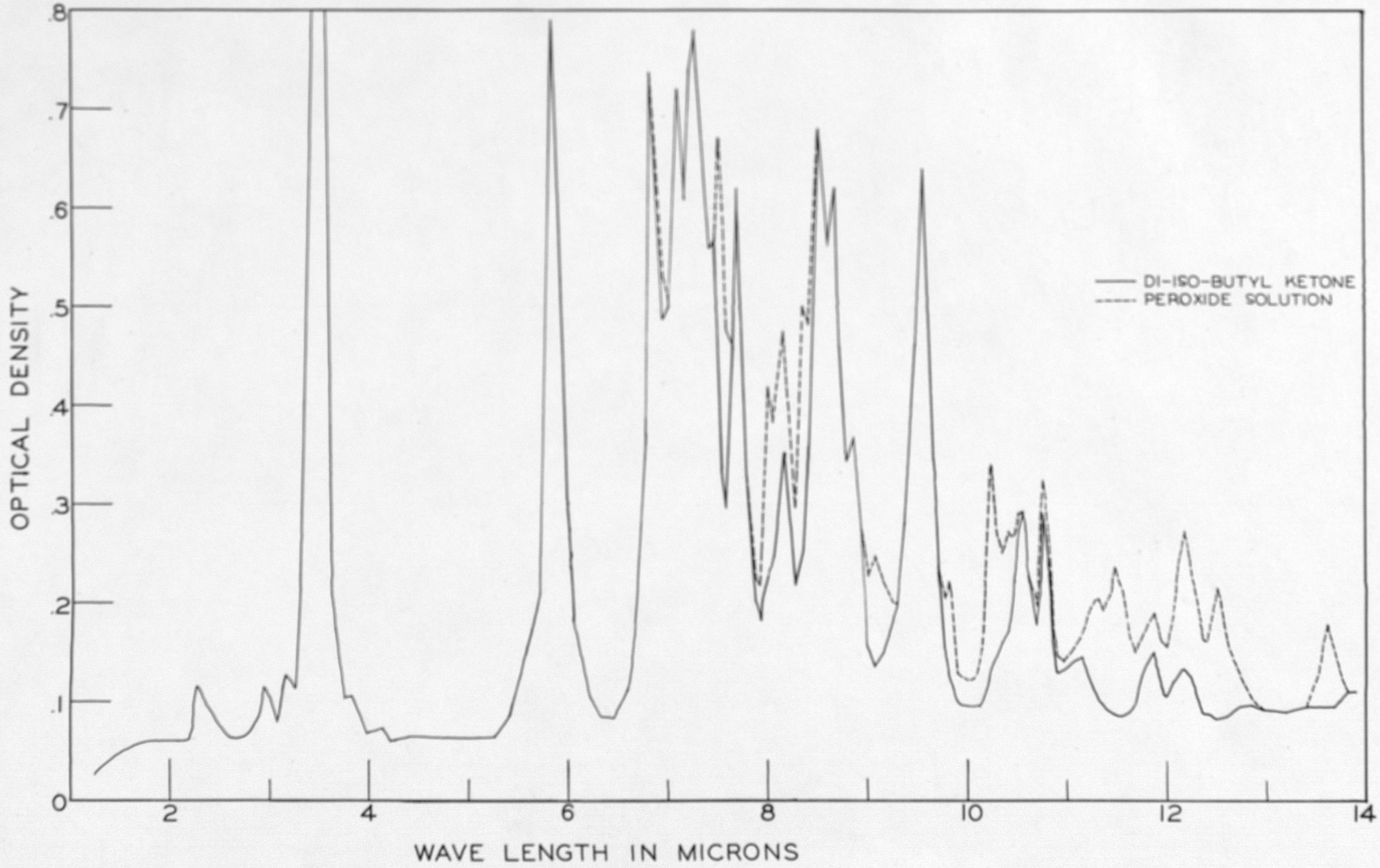


Fig. 14 INFRARED SPECTRA OF DI-ISO-BUTYL KETONE AND SOLUTION OF PEROXIDE IN DI-ISO-BUTYL KETONE

enter into the reaction and is not formed during the oxidation period covered by this study. Two justifications of this assumption can be advanced: 1) Figure 12 shows that the infrared hydroperoxide concentration follows the chemical curve and in the chemical titration for oxides the hydroperoxide could not be distinguished from the peroxide but the infrared curve is of hydroperoxide alone thus the chemical data must be of hydroperoxide alone. 2) On another oxidation run, in which the sodium choloride prism was used, the absorption band at 13.6 microns observed in the spectrum of the peroxide would be expected to increase with time if the peroxide were present.. No appreciable increase is observed at this wave length.

SUMMARY

By infrared and chemical analysis it is fairly well ascertained that the autoxidation of di-iso-butyl ketone reacts to yield an unstable hydroperoxide which in turn decomposes to give isobutyric acid, isovaleric acid, water and possibly very small quantities of other compounds such as acetone, aldehydes, etc..

Further it is seen that infrared spectroscopy can be very useful both quantitatively and qualitatively in the determination of the mechanisms of organic reactions..

ACKNOWLEDGMENT

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APPENDIX

Table 1. Tentative assignment of absorption bands.

Wave-length	Isobutyric acid	Isovaleric acid	Hydroperoxide	Peroxide	Di-iso-butyl Ketone
2.88			X		X
3.23	X	X			X
3.57					X
5.70	X	X	X		
5.95	X	X	X		X
6.75			X		
6.80					X
6.95	X	X			
7.25					X
7.35					X
7.57				X	X
7.75					X
8.00	X			X	
8.20					X
8.30	X	X	X		
8.65	X		X		X
8.80			X		X
8.90					X
9.00	X	X		X	
9.60					X
9.80	X		X	X	
10.25				X	
10.45	X	X	X		
10.60					X
10.70	X	X			X
10.90	X				X
11.50	X	X		X	
11.90					X
12.10			X		
12.25					X
12.50	X	X		X	
13.60				X	

Note: X indicates known products of the autoxidation which have relative strong absorption bands at the position of the band found in the spectrum of the oxidized ketone.

Table 2. Increase in optical density as a function of oxidation time at seven wave lengths.

Oxidation Time:	Wave lengths in microns 3.166:	3.129:	3.148:	3.227:	2.861:	2.875:	2.889:
0:15	.006	.005	.005	.006	.016	.015	.013
0:30	.008	.007	.007	.007	.008	.009	.012
0:45	.035	.028	.012	.015	.018	.017	.052
1:00	.047	.041	.044	.034	.048	.052	.055
1:15	.052	.050	.049	.040	.031	.059	.063
1:30	.073	.067	.068	.052	.067	.071	.079
1:45	.080	.076	.074	.110	.091	.095	.101
2:00	.100	.103	.090	.074	.096	.100	.108
2:15	.107	.100	.099	.083	.107	.113	.119
2:30	.121	.116	.114	.099	.119	.129	.139
2:45	.139	.131	.138	.109	.163	.167	.173
3:00	.147	.142	.139	.122	.143	.150	.159
3:15	.176	.171	.172	.151	.170	.176	.186
3:30	.175	.172	.169	.150	.180	.184	.191
3:45	.187	.183	.179	.157	.195	.199	.208
4:00	.197	.191	.188	.619	.181	.186	.194
4:15	.197	.192	.190	.175	.193	.201	.207
4:30	.213	.207	.206	.190	.192	.200	.207
4:45	.232	.222	.222	.208	.220	.226	.234
5:00	.231	.227	.224	.207	.209	.217	.225
5:15	.236	.232	.232	.210	.211	.221	.232
5:30	.255	.249	.248	.233	.205	.215	.222
5:45	.269	.252	.252	.232	.213	.221	.232
6:00	.271	.265	.265	.244	.235	.243	.253
6:15	.273	.267	.267	.249	.230	.238	.249
6:30	.284	.282	.279	.264	.233	.243	.253
6:45	.293	.289	.293	.272	.266	.270	.272
7:00	.305	.301	.301	.265	.273	.280	.287
7:15	.306	.304	.303	.286	.282	.290	.296
7:30	.320	.313	.314	.312	.284	.290	.300
7:45	.322	.313	.308	.319	.300	.307	.317
8:00	.335	.330	.329	.321	.284	.288	.295
8:15	.346	.342	.344	.332	.313	.319	.329
8:30	.343	.338	.338	.340	.262	.270	.277
8:45	.351	.348	.349	.344	.318	.325	.331
9:00	.357	.353	.353	.345	.275	.282	.292
9:15	.359	.358	.357	.350	.301	.307	.312
9:30	.361	.358	.358	.375	.300	.304	.310
9:45	.359	.360	.362	.362	.273	.281	.287
10:00	.393	.392	.390	.367	.287	.296	.302

Table 2 (cont.)

Oxidation Time:	Wave lengths in microns 3.116:	3.129:	3.148:	3.227:	2.861:	2.875:	2.889
11:00	.367	.369	.367	.362	.277	.281	.286
11:15	.374	.374	.376	.367	.290	.293	.298
11:30	.371	.372	.374	.369	.262	.268	.274
11:45	.375	.375	.378	.371	.231	.238	.245
12:00	.379	.382	.384	.374	.240	.245	.250
12:15	.386	.387	.388	.384	.242	.251	.258
12:30	.391	.390	.391	.385	.227	.235	.242
12:45	.400	.399	.404	.390	.232	.241	.252
13:00	.409	.409	.411	.405	.220	.230	.240
13:15	.420	.423	.419	.413	.210	.220	.234
13:30	.425	.425	.427	.422	.226	.236	.255
13:45	.434	.434	.439	.431	.219	.229	.246
14:00	.446	.447	.449	.443	.233	.243	.256
14:30	.469	.462	.465	.459	.243	.254	.267
14:45	.470	.472	.474	.468	.246	.257	.271
15:00	.477	.480	.482	.476	.240	.253	.268
15:15	.488	.490	.490	.491	.241	.254	.269
15:30	.491	.490	.495	.498	.245	.259	.274
15:45	.504	.505	.506	.507	.250	.261	.278
16:00	.515	.516	.520	.516	.284	.295	.308
16:15	.523	.526	.535	.541	.257	.270	.287
16:30	.534	.538	.543	.547	.256	.270	.287
16:45	.539	.546	.551	.560	.251	.266	.286
17:00	.550	.555	.559	.566	.256	.271	.289
17:15	.552	.557	.564	.575	.246	.262	.282
17:30	.562	.566	.575	.587	.241	.257	.279
17:45	.574	.581	.586	.596	.245	.263	.280
18:00	.583	.587	.593	.604	.252	.267	.284
18:15	.587	.594	.600	.615	.243	.262	.280
18:30	.594	.601	.607	.626	.225	.241	.259
18:45	.602	.608	.616	.632	.231	.249	.286
19:00	.614	.619	.624	.643	.238	.256	.277
19:15	.620	.624	.631	.649	.246	.263	.285
19:30	.626	.629	.638	.660	.241	.259	.281
20:00	.642	.652	.660	.677	.242	.260	.284
20:15	.651	.656	.663	.686	.228	.246	.270
20:30	.656	.663	.673	.695	.225	.240	.268
20:45	.664	.669	.682	.704	.231	.250	.278
21:00	.677	.684	.692	.717	.226	.246	.273
21:15	.681	.690	.702	.725	.235	.254	.282

Table 2 (concl.).

Oxidation Time:	Wave lengths in microns 3.116:	3.129:	3.148:	3.227:	2.861:	2.875:	2.889:
21:30	.702	.709	.715	.745	.251	.270	.297
22:00	.718	.723	.730	.761	.266	.278	.314
22:15	.721	.726	.736	.769	.271	.291	.320
22:30	.730	.737	.745	.770	.284	.303	.332
23:00	.750	.763	.770	.799	.316	.338	.364
23:30	.769	.779	.790	.821	.344	.361	.391
24:00	.780	.790	.798	.828	.351	.374	.401
24:15	.787	.796	.806	.838	.352	.370	.397
24:30	.790	.798	.811	.845	.354	.379	.402
24:45	.798	.809	.815	.851	.365	.385	.414
25:00	.802	.810	.821	.855	.376	.397	.422
25:15	.815	.826	.833	.861	.419	.439	.461
25:30	.819	.826	.839	.873	.422	.443	.464
25:45	.828	.838	.850	.878	.424	.444	.471
26:00	.834	.841	.854	.887	.419	.440	.464
26:15	.844	.845	.853	.891	.429	.449	.472
26:30	.838	.850	.862	.892	.425	.449	.475

Table 3. Concentration of hydroperoxide and acids during oxidation period both chemical and infrared data.

Oxidation Time	Total Acid		Hydroperoxide	
	Infrared	Chemical	Infrared	Chemical
0:15	.02		.057	.015
0:30	.03	.03	.030	.118
0:45	.10		.093	
1:00	.15		.166	.140
1:15	.17		.150	
1:30	.24		.215	.211
1:45	.26		.258	
2:00	.33	.299	.260	.262
2:15	.35		.283	
2:30	.42	.342	.305	.298
2:45	.47		.370	
3:00	.50	.455	.336	.339
3:15	.60		.371	
3:30	.59	.529	.386	.363
3:45	.62		.405	
4:00	.65		.386	.381
4:15	.66		.400	
4:30	.71	.665	.395	.395
4:45	.77		.443	
5:00	.77	.738	.445	.428
5:15	.79		.448	
5:30	.85	.807	.422	.411
5:45	.85		.445	
6:00	.89	.890	.463	.405
6:15	.91		.453	
6:30	.95	.973	.465	.405
6:45	.98		.495	
7:00	.99	.991	.512	.407
7:15	1.02		.522	
7:30	1.06	1.070	.523	.398
7:45	1.05		.550	
8:00	1.11	1.121	.519	.356
8:15	1.15		.560	
8:30	1.14	1.160	.488	.375
8:45	1.16		.558	
9:00	1.20	1.200	.501	.348
9:15	1.21		.538	
9:30	1.22	1.260	.535	.365
9:45	1.22		.495	
10:00	1.32	1.310	.515	.367

Table 3 (cont.).

Oxidation Time	Total Acid		Hydroperoxide	
	Infrared	Chemical	Infrared	Chemical
11:00	1.25		.510	.333
11:15	1.27		.516	
11:30	1.26	1.300	.477	.295
11:45	1.27		.430	
12:00	1.29	1.365	.440	.318
12:15	1.31		.445	
12:30	1.32	1.430	.422	.346
12:45	1.36		.420	
13:00	1.38	1.451	.410	.330
13:15	1.38		.392	
13:30	1.44	1.520	.421	.362
13:45	1.47		.407	
14:00	1.51	1.600	.426	.339
14:30	1.57	1.240	.440	.356
14:45	1.59		.443	
15:00	1.62	1.724	.432	.354
15:15	1.65		.432	
15:30	1.67	1.785	.440	.338
15:45	1.70		.443	
16:00	1.74	1.850	.491	.382
16:15	1.80		.452	
16:30	1.84	1.890	.447	.375
16:45	1.86		.438	
17:00	1.90	1.940	.443	.282
17:15	1.91		.435	
17:30	1.94	2.080	.420	.363
17:45	1.98		.423	
18:00	2.00	2.090	.430	.468
18:15	2.03		.423	
18:30	2.06	2.160	.388	.390
18:45	2.08		.400	
19:00	2.11	2.520	.412	.378
19:15	2.13		.425	
19:30	2.16	2.370	.417	.472
20:00	2.23	2.790	.417	.465
20:15	2.25		.395	
20:30	2.28	2.430	.390	.424
20:45	2.31		.400	
21:00	2.35		.393	.341
21:15	2.37		.408	

Table 3 (concl.).

Oxidation Time	Total Acid		Hydroperoxide	
	Infrared	Chemical	Infrared	Chemical
21:30	2.42	2.595	.433	.446
22:00	2.49	2.605	.458	.480
22:15	2.51		.467	
22:30	2.54	2.645	.483	.458
23:00	2.62	2.710	.532	.438
23:30	2.69		.567	
24:00	2.73		.578	
24:15	2.75		.575	
24:30	2.77	2.895	.582	.486
24:45	2.79		.590	
25:00	2.81	3.020	.603	.466
25:15	2.85		.655	
25:30	2.87	2.960	.659	.438
25:45	2.90		.661	
26:00	2.92	2.980	.655	.492
26:15	2.94		.667	
26:30	2.95	3.040	.666	.486

INFRARED SPECTROSCOPY APPLIED TO THE STUDY OF THE AUTOXIDATION OF DI-ISO-BUTYL KETONE

by

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The infrared spectra of di-iso-butyl ketone which had been subjected to the action of molecular oxygen for periods up to forty-eight hours were observed from two to fifteen microns using a sodium chloride prism. The changes in these spectra were observed as a function of oxidation time. Frequencies characteristic of the chemically observed products of the oxidation of the ketone (di-iso-butyl ketone, hydroperoxide, isobutyric acid, and isovaleric acid) were chosen by consideration of the spectra of the prepared solutions of these products in the ketone. From these spectra a tentative assignment of the characteristic absorption bands were made for each of the products. It was determined that a quantitative analysis could be made in the two to four micron region using the highly dispersive lithium fluoride prism. In this region there were two main absorption bands. One was due to the acids formed during the reaction and the other was due to the hydroperoxide and the acids formed during the reaction. By computing the extinction coefficients for the acids at the former band from known solution spectra, the concentration of the acids could be computed during the oxidation period. By substracting the optical density due to the acids from the observed optical density during the oxidation time at the band which was due to both the acids and the hydroperoxide the concentration of hydroperoxide could be determined with the use of its extinction coefficients at this band. Since the hydroperoxide could not be separated it was necessary to assume that for early oxidation time the absorption at this band was due to hydroperoxide and acid so that the extinction coefficients could be determined. The concentrations

which can be shown as a function of oxidation time are in good agreement with the chemical data. Other products were formed during the oxidation (acetone, water and other undetermined compounds) but their concentrations were so small that they were neglected. It was necessary to make several assumptions during this study and they are discussed.