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The products of the gas phase ozonolysis of tetramethylethylene

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THE PRODUCTS OF THE GAS PHASE OZONOLYSIS OF TETRAMETHYLETHLENE

by

Anthony R. DeAngelo
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Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

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ABSTRACT

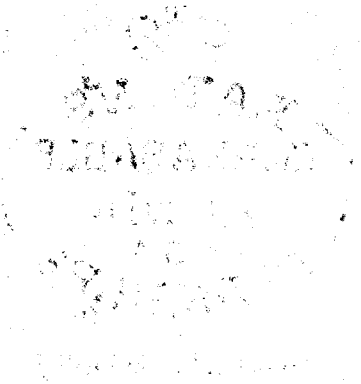
The products of the ozonolysis of tetramethylethylene (TME) in the gas phase was studied. Reactions were run at concentrations between 10 and 400ppm TME and lower concentrations of ozone. The reactions were run at room temperature and atmospheric pressure.

Gaseous products were studied by gas chromatography, mass spectrometry and HPLC analyses, the latter using 2,4-dinitrophenylhydrazine derivatives of carbonyl products. Ozone concentrations and the determination of possible peroxidic products was accomplished by measuring the absorbance of a buffered KI solution (352 nm) after reaction with a known volume of gas. The possibility of acetone/ozone and TME/peroxides reactions were experimentally determined.

Significant amounts of acetone and formaldehyde were detected. Traces of methylglyoxal were also found. Methyl acetate, ethyl acetate, acetyldehyde, glyoxal, and dimethyl glyoxal were not detected in any significant amounts. Carbon dioxide, carbon monoxide, methanol, acetic acid, and formic acid were all determined to be undetectable with the methods used.

At initial TME concentrations of 100ppm, acetone appeared with nearly a 1:1 ratio with TME consumed. At TME concentrations of 400ppm a 50% increase in the yield of acetone was detected. The yield of formaldehyde to TME consumed

was approximately 1:5 with a slight decrease in the yield of formaldehyde with increasing concentrations. A variation of the Criegee mechanism of ozonolysis was a better explanation for the results observed than the O'Neal-Blumstein mechanism.



ACKNOWLEDGEMENTS

Many individuals have helped or hindered me in the completion of this project, I wish to thank the former. At the top of the list is Professor Leslie Hull whose advice, support, and penetrating questions about when I was going to do my lab work made him instrumental in my finishing. Next I'd like to thank Professor Robert Schaefer and the rest of the Chemistry Department Faculty because their advice, support, and understanding were instrumental in my staying at Union. Special thanks go to my girlfriend Karen McHugh, my roommate Richard Dubs, and my family and friends who had the good sense to stay out of my way when I finally sat down to write all this up.

It is not the critic who counts; not the man who points out how the strong man stumbles, or where the doer of deeds could have done better. The credit belongs to the man who is actually in the arena, whose face is marred by dust and sweat and blood; who strives valiantly; who errs, and comes short again and again, because there is no effort without error and shortcoming; but who does actually strive to do the deeds; who knows the great enthusiasms, the great devotions; who spends himself in a worthy cause; who at best knows in the end the triumph of high achievement, and who at worst, if he fails, at least fails while daring greatly, so that his place shall never be with those cold and timid souls who know neither victory nor defeat.

Theodore Roosevelt

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INTRODUCTION

An important atmospheric reaction of pollutants is the ozonolysis of alkenes.[1] Certain alkenes discharged into atmosphere may be oxidized by ozone to products which will have different properties from the original reactants. In regulating such discharges a knowledge of possible reaction pathways is essential. Regulations of discharges should be created with intermediate and final products taken into account. An effective way of predicting possible products is by studying the reaction mechanism(s).

At the present time there is a controversy about the mechanism of ozonolysis of alkenes in the gas phase. In liquid phase ozonolysis the accepted mechanism is the Criegee mechanism.[2] The Criegee mechanism is shown in Fig. 1.

Recent studies in the gas phase have identified products which are not easily explained by the Criegee mechanism.[3,4] A possible mechanism to explain such products is the O'Neal-Blumstein mechanism.[3] This mechanism departs from the Criegee mechanism by suggesting a biradical intermediate after the primary ozonide (see Fig. 2). The biradical mechanism suggests radical abstraction pathways which can account for ketones, aldehydes, carboxylic acids, alkanes, esters, alcohols, ketenes, peroxides, dicarbonyls, and dioxetanes.

In this thesis the mechanism of ozonolysis of tetramethyl-

Figure 1: The Criegee Mechanism and Products

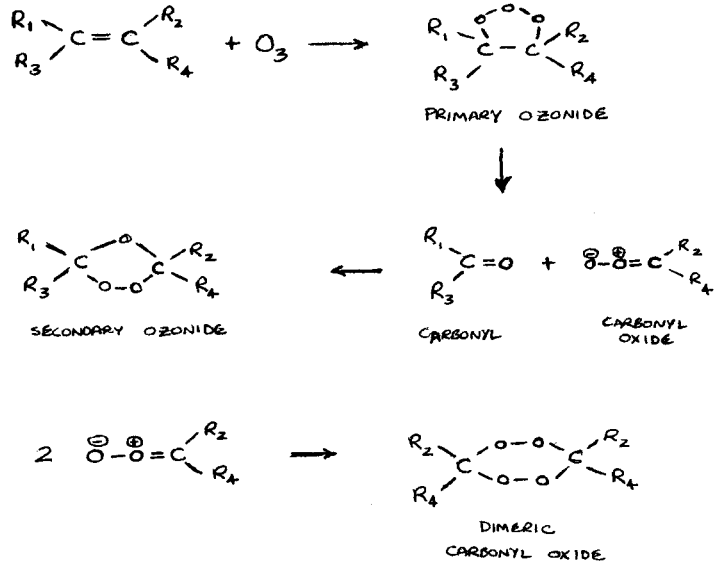
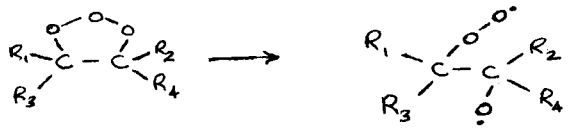


Figure 2: O'Neal-Blumstein Biradical Intermediate



ethylene (TME) was examined by product analysis. All reactions were carried out at concentrations much lower than past research and at room temperature. Several techniques were employed in this study. Concentrations of products were reported whenever possible.

EXPERIMENTAL

Reproducible results in this project were dependent on a wide variety of techniques, reagents, and instrumentation. In order to judge the results presented a thorough knowledge of the above is required. Therefore a comprehensive description of all major stages of the project follows.

Flow Gauge Calibration:

Any work depending on the accurate measure of concentrations of compounds in a gas media requires a dependable technique of measuring reproducible volumes of gas. The tool used for this work was a floating ball gauge. The glass tubing containing a steel ball is marked off in units of centimeters. The gauge operates by the height of the ball in the tube being nearly a direct relation to the flow rate in the line to which it is attached. In actual operation this relationship isn't exactly linear. The exact mathematical relation was not, and is still not, known. Calibration was by experimentation.

This problem was overcome by comparing ball height to a known (or measureable) flow rate. For flow rates less than 0.5 liter/minute the optimal set-up was the one depicted in Fig. 3.

The gas flow was set at a constant rate, the height of the ball was noted, then soap bubbles were produced. Using a stopwatch the time was measured for a bubble to pass through a

Figure 3: Set-up for Measuring Flow Rates (< 0.7 l/min.)

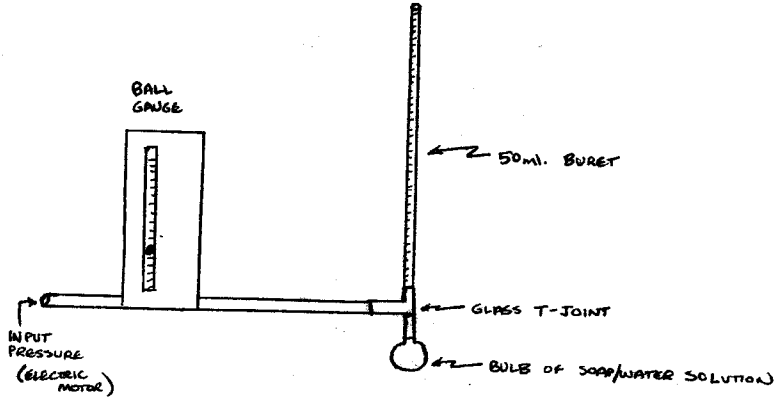
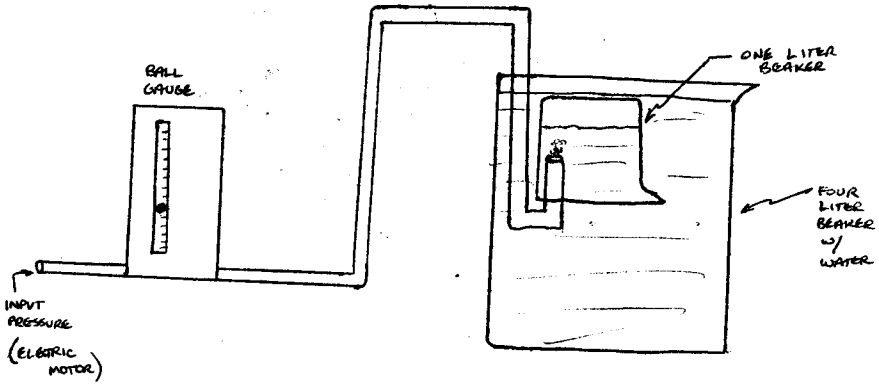


Figure 4: Set-up for Measuring Flow Rates (> 0.7 l/min.)



volume of 50.0 milliliters (see Table 1 for results).

At a flow of 0.7 liters/minute it was decided that the soap bubble was moving too fast to be accurately timed with a stopwatch. For this reason a new set-up was made for the higher flow rates (see Fig. 4). The one liter beaker was submerged upside down in the water filled four liter beaker. Any air bubbles in the smaller beaker were aspirated out. A plastic tube was connected to the ball gauge then fed into the upended beaker. A stopwatch was then used to time the time it took to fill a one liter volume (see Table 2 for results). This technique was not acceptable for lower flow rates because it allowed too much error in judgement for choosing exactly when a liter was filled.

The following standard settings were chosen for delivering uniform flows:

Gauge Reading	Flow Rate	Estimated Error
8.0	1.00	± 3%
1.5	0.10	± 2%

The standard settings are used and the time controlled in order to deliver reproducible volumes of gas. The graph in Fig. 5 shows the overall characteristics of the ball flow gauge.

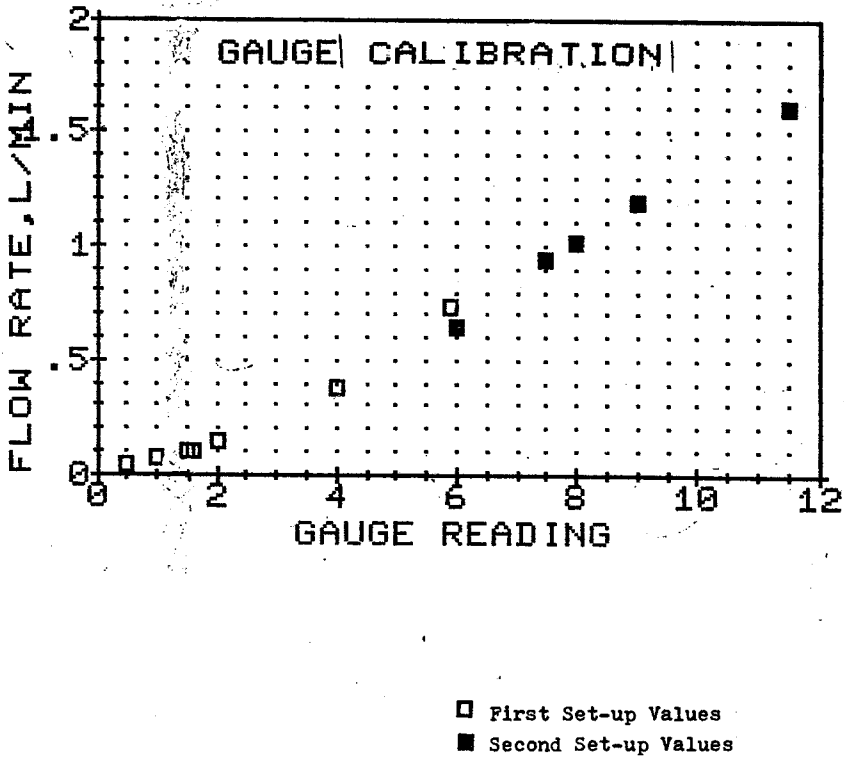
Table 1: Flow Rates Using First Set-up

Gauge Reading	Time (min.)	Flow Rate (l/min.)	Average Flow Rate (l/min.)
0.5	1.236	0.040	0.040 ± 2.5%
	1.210	0.041	
1.0	0.744	0.067	0.067 ± 0%
	0.745	0.067	
1.5	0.512	0.098	0.098 ± 0%
	0.510	0.098	
	0.512	0.098	
	0.510	0.098	
1.6	0.492	0.102	0.103 ± 1%
	0.482	0.104	
	0.482	0.104	
2.0	0.355	0.141	0.140 ± 1%
	0.358	0.140	
	0.358	0.140	
4.0	0.130	0.385	0.381 ± 1%
	0.132	0.379	
	0.132	0.379	
5.9	0.068	0.740	0.740 ± 3%
	0.072	0.700	
	0.070	0.710	

Table 2: Flow Rates Using Second Set-up

Gauge Reading	Time (min.)	Flow Rate (l/min.)	Average Flow Rate (l/min.)
11.5	0.624 0.620 0.615	1.60 1.61 1.63	1.61 ± 1%
9.0	0.840 0.834	1.19 1.20	1.20 ± 1%
8.0	0.972 0.982	1.03 1.02	1.02 ± 1%
7.5	1.070 1.060	0.934 0.943	0.938 ± 4%
6.0	1.584 1.500	0.631 0.667	0.649 ± 3%

Figure 5: Flow Gauge Calibration Graph



Reaction Bag Construction:

Since all reactions studied would be in the gas phase an air tight vessel was needed for five to ten liter volumes. The vessel used was a heat sealed Tedlar® bag with a Swagelok® Quick-Connect™ fitting for introducing and removing the gases.

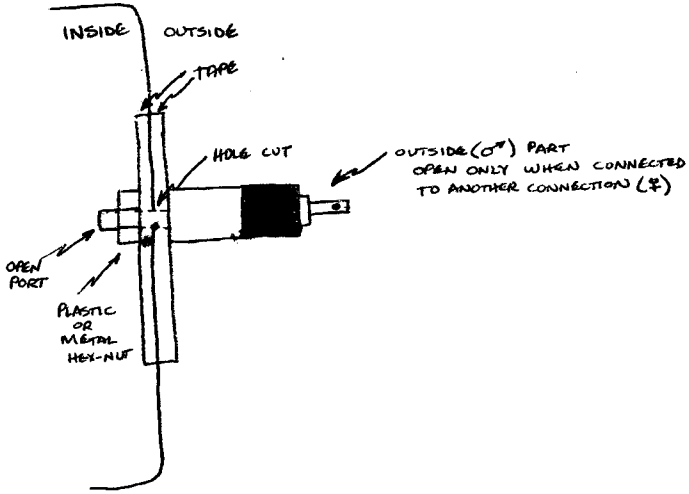
The bags were constructed as follows. First a large sheet (approx. 1 m^2) of Tedlar® was cut from a roll. At this point which side would be the outside of the bag was decided on and that will be the only side which can be touched by hands, counters, etc. where organic contaminants may be present. A small section (approx. 2 in. x 4 in.) is then covered on both sides with pieces of Polyrex™ all purpose tape. A piece of thick cardboard is placed under the covered section. Then a cork hole borer is used to cut a small hole (approx. 0.25 in.) which is centered on the taped section. A male Swagelok® fitting is then attached (see Fig. 6).

The sheet is then folded so that the sheet is halved with inside touching inside. The sheet is then sealed on the remaining three edges with a Vertrod Thermal Impulse Heat Sealing Machine (model 30A/CAB). It was found that a better seal is made (no folds in seal) if the sides adjacent to the halved fold are evened up simultaneously, then sealed one at a time before sealing the end opposite the initial fold. It was found that sticking was held to a minimum if the jaws are held together for ten seconds after the heat is off, then allowed to cool for ten seconds with the jaws open, then the bag may

be peeled off. Occassionally spraying of the jaws with a silicone lubricant also prevents sticking.

The process is finished with two more steps. First the bag is assigned a number for reference, which is written on the tape with a grease pencil. Second, if injections are made into a bag with a microsyringe the hole may be covered with a piece of tape. It is easier to remove and replace the tape if a corner is covered with a "chip" of paper so that a "lip" is presented to ease in grasping with fingers.

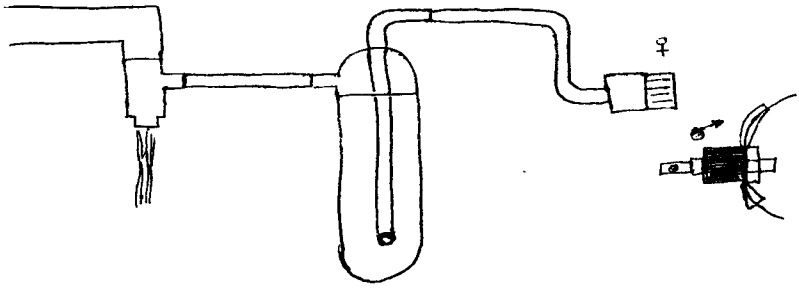
Figure 6: Fitting Attached to Reaction Bag



Filling a Reaction Bag:

Before a reaction bag can be filled it should be emptied of all past contents. This is accomplished with a running water aspirator. Because no water should enter the bag a trap is attached to the suction hose. The inlet of the trap has a female Swagelok fitting to attach to the bag (see Fig. 7). A second protection against water entering the bag is to release the bag from the trap, attach a "false" male fitting to the trap, then turn off the water.

Figure 7: Emptying a Reaction Bag



It may be noted here that leaks may be avoided in the bags by using the tape around the fitting on the bag as a surface to exert force with. The "false" male part is easily attached by pressing it against a hard flat surface.

After being emptied completely the bag may be checked for leaks by allowing it to sit for a while. If crackling is heard, or the bag begins to fill with air, then the bag is leaking. Leaking should be at an absolute minimum for any quantitative

run. Once the bag is found to be sufficiently leakproof it is ready to be filled with the reaction medium.

In this case the reaction medium is dry, hydrocarbon free air (Linde®). The inlet of the ball gauge is attached to the outlet on the reducing valve of the air tank. A "false" (unattached) male fitting is attached to the outlet (female fitting) of the flow gauge. This allows the outlet of the flow gauge. This allows the outlet of the flow gauge to be open. The knob on the reducing valve is then used to set the flow at a constant one liter/minute rate. Once this is set, the "false" male fitting is popped off, then the outlet (female) of the flow gauge is attached to the male part of the bag. The instant the bag is attached a stopwatch is started. When the appropriate time is reached the bag is popped off.

Producing Ozone:

Ozone is generated with a Welsbach Ozonator (Model T-408). The turn on procedure for the ozonator is as follows[5]

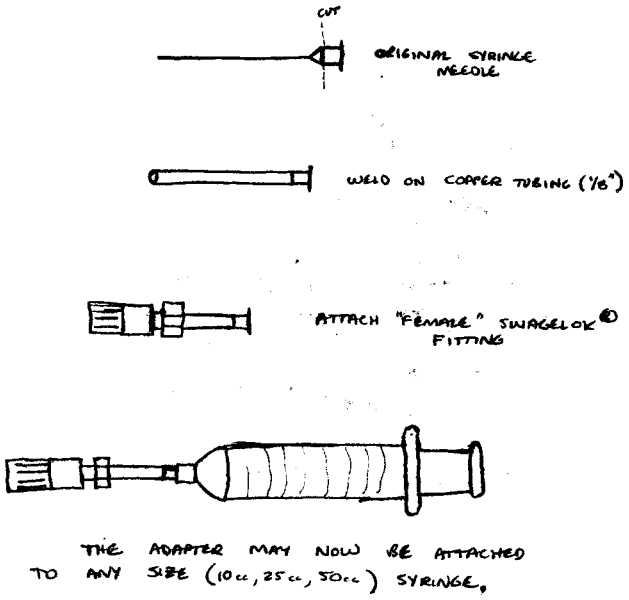
1) turn on oxygen flow
2) turn on water coolant
3) set air pressure at 8 psi
4) set flow at ozone port to zero
5) set flow at sample port at 0.6 (This is because the ozone is collected out of the sample port.)
6) turn on power
7) set at 90 volts

The ozonator is allowed to run like this for several minutes, then it can be assumed that the ozonator is delivering a constant flow (and concentration) of ozone.

A bag is then connected to the sample port to collect the product. The ozone/air mixture in this bag is then extracted with a 50 cc syringe (with a special adapter, see Figure 8), then injected into the reactant ozone bag. It was found that this process is simpler if the syringe is allowed to rest on the counter, as opposed to holding in the hand. This allows the user to be more precise because nothing is lost in the transfer due to the inevitiable effect of gravity on the plunger of the syringe.

It has been found by trial and error that a 20 milliliter injection of ozone /air mixture will produce approximately a 100 ppm concentration (a little on the high side) in a ozone reaction bag with a six liter volume.

Figure 8: Syringe Adapter for Bag Injections



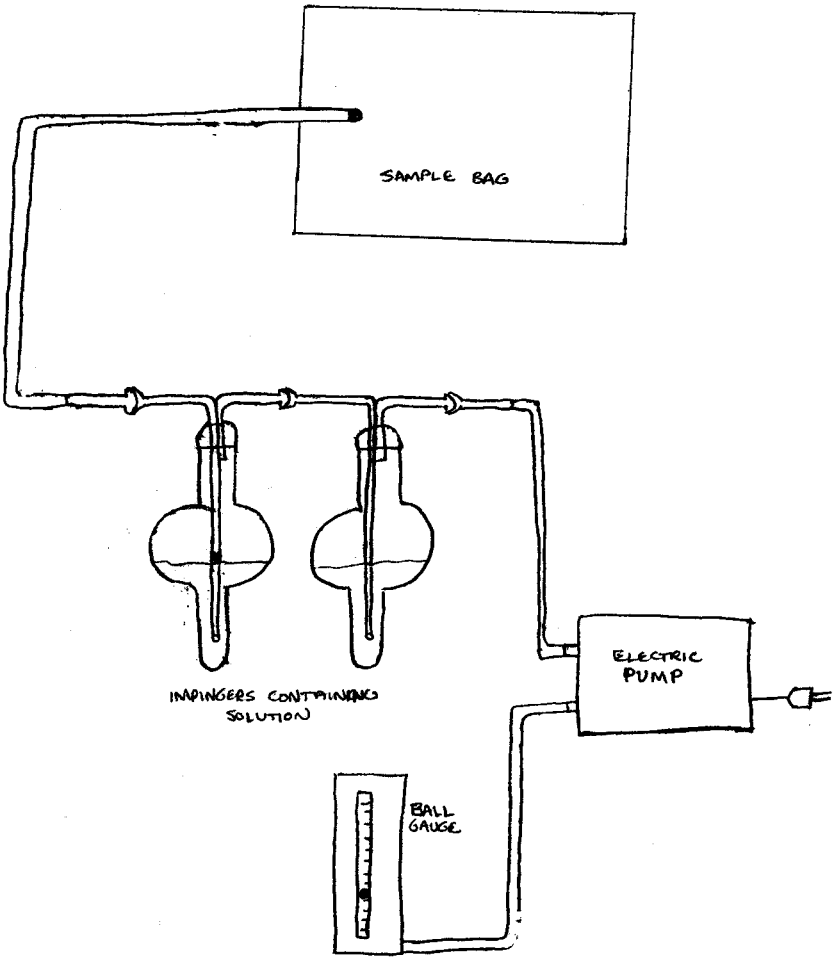
Determining Accurate Ozone Concentrations:

Ozone concentrations were determined by spectrophotometry.[5] The technique consists of drawing of a known quantity of gas from a bag, bubbling the sample through a solution of acid buffered KI solution. Ozone converts I^- to I_2, then by measuring the absorbance of the I_2 produced the concentration of ozone present may be accurately known.

The solution used for detection is a buffered potassium iodide (0.1M H_3BO_3, 1% KI). All solutions were prepared in the following manner; 20.00g of KI and 12.37g of H_3BO_3 into a two liter volumetric flask, then diluted to the mark. Since it is somewhat difficult to dissolve all H_3BO_3 it is usually a good idea to allow the solution to sit a day or two to equilibriate. The solution is both light sensitive and susceptible to air oxidation. Therefore when not in use it should be kept in a dark colored container, with the cap wrapped with tape, and stored in a closed cabinet.

For analysis the above solution was placed in two impingers set up in series (see Fig. 9). The impinger flasks are wrapped in aluminum foil to shut out any light. A known volume (usually one or one-half liter) of sample is bubbled through the gas impinger flasks which contain a known amount (25, 50, 75, or 100 milliliters) of solution in each. The second impinger is used to detect any ozone that the first impinger missed. It has been tentatively found that if the first impinging flask is totally filled (150 milliliters) there seems to be no ozone

Figure 9: Ozone Measuring Set-up



left to be caught by the second impinger. After the desired amount has been bubbled through the KI solution the pump is stopped, the bag is disconnected, and the solutions stored in the dark to be transported for analysis.

The solution's absorbance is measured with a Cary 118 UV/Vis Spectrophotometer. Any solution not being used is kept in darkness. When measurements were not being taken a piece of cardboard was used to block the light beam to preserve the standard, but even with this precaution the Cary was rezeroed frequently with fresh standards. The reaction being used for detection is:

$$O_3 + 2I^- + 2H^+ \rightleftharpoons I_2 + H_2O + O_2 \qquad (1)$$

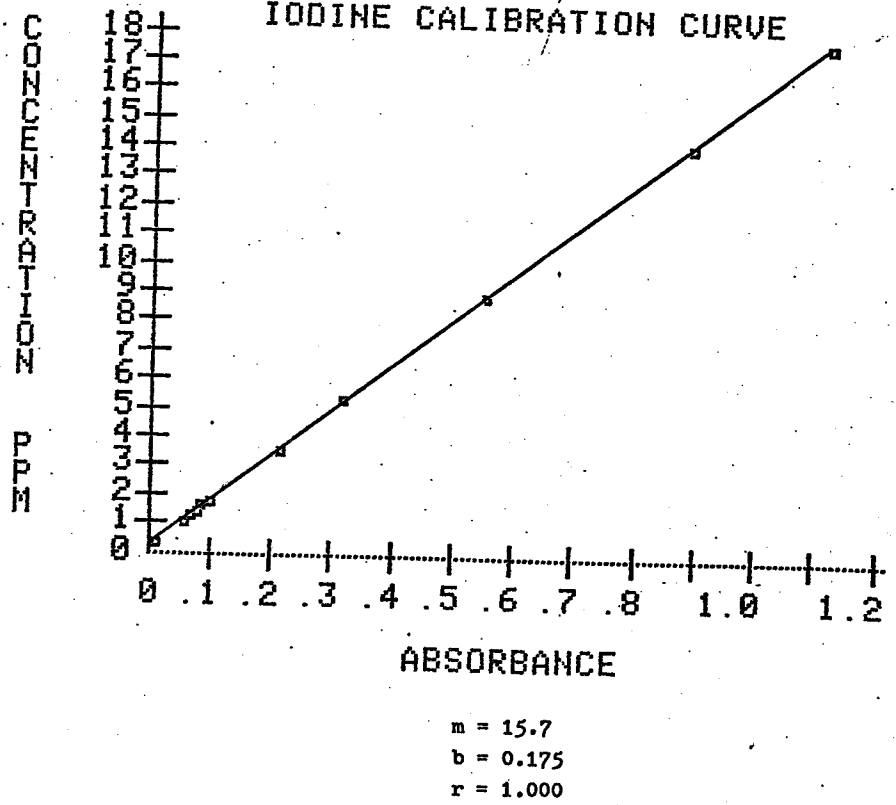
The absorbance being measured is that of I_2 (or more specifically I_3^-). Figure 10 shows the correlation between absorbtion and concentration. The following formula may be used in determing ozone concentrations from absorbance measurements:

$$\left(\begin{matrix}\text{ppm.}\\ O_3\end{matrix}\right) = \frac{\left(15.7[\text{ABSORBANCE}] + 0.175\right)\left(\begin{matrix}\text{MILLILITERS OF}\\ \text{SOLUTION IN}\\ \text{IMPINGERS}\end{matrix}\right)/10\text{ml.}}{\left(\begin{matrix}\text{NUMBER OF LITERS}\\ \text{SAMPLED}\end{matrix}\right)} \qquad (2)$$

The following settings were used on the Cary 118:

wavelength:	352 nm.	source:	vis, normal
mode:	autoslit	gain:	0.30
period:	5 seconds		

Figure 10:
Calibration Curve--Iodine in Buffered KI Solution[6]



Work was started on finding out if this method could be used as a detection method for peroxides. It was calculated that air sampling of one liter of a 100ppm H_2O_2/air mixture through 100ml of buffered KI solution would give the same result as injecting 0.322 microliters of 30% H_2O_2/water solution directly into 100ml of buffered KI. Since this amount was too small for precise injections, 3.2 microliters were injected into 100ml buffered KI, then diluted ten-fold.

The first time this was performed one sample was exposed to intermittent light for three hours while the other sample was exposed to the same type of lighting only a half hour. The results were appreciably different (see Table 4). It was concluded that exposure to light had an appreciable effect on the results. Another run was performed but with the following precautions taken:

1) volumetrics wrapped in paper towel
2) pipetting second dilution was performed in dim lighting
3) final sample was stored a half hour in dark to equilibriate.

The sample was then measured for absorption several times because of unstable output on the Cary 118 (see Table 5 for results). It should be noted that it is believed that the unstable output of the Cary 118 was due to the gain being adjusted too high.

A vapor phase sample was then prepared by injecting 3.2 microliters of 30% H_2O_2/water solution into ten liters of air. Absorbances were measured at different times after injection, and at different flow rates (see Table 6 for results)

The results of the gas phase sample were poor because enough

Table 4: Results of Initial Liquid Injection

Sample	Time in Light	Absorbance	Equivalent ppm H_2O_2
1	3 hr.	0.914 0.914	145 ± 15%
2	0.5 hr.	0.597 0.599	95.6 ± 15%

Table 5: Results of Second Liquid Injection

Sample	Absorbance	Equivalent ppm H_2O_2	Average ppm H_2O_2
1	0.5290	84.8	
2	0.5550	88.9	87.0 ± 2.2
3	0.5450	87.3	

Table 6: Results of Gas Phase Sample

Elapsed Time (min)	Flow Rate (l/min)	Impinger Absorbances 1st	2nd	Combined Equivalent ppm H_2O_2
60	1.0	0.0164	0.0088	5.7
65	0.10	0.0128	0.0112	5.5
120	1.0	0.0170	0.0152	6.8
125	0.10	0.0189	0.0168	7.4
300	1.0	0.0140	0.0080	5.2
305	0.10	0.0360	0.0340	12.7

Note: Equivalent ppm of H_2O_2 was derived from Fig. 10.

time was not allowed for all the H_2O_2 to react with the I^-. The need for this extra time is due to the fact that H_2O_2 is much less reactive than O_3. It was later determined that if the samples were allowed to sit in the dark for 2-3 hours results were obtained which were the same as the direct injection sample.

Producing Known Vapor Concentrations

From gas phase calculations it was determined that 4.0×10^{-6} moles of any volatile compound will produce a 100 ppm (volume/volume) concentration in one liter of air. With this number it was straight forward to calculate required injection amounts from molecular weights and liquid densities.

$$\left(\begin{matrix}\text{REQUIRED}\\ \text{INJECTION}\\ \text{AMOUNT}\end{matrix}\right) = \left\{\frac{(4.09 \times 10^{-6}\ \text{moles})\left(\begin{matrix}\text{MOLECULAR}\\ \text{WEIGHT}\end{matrix}\right)}{(\text{LIQUID DENSITY})}\right\}\left(\begin{matrix}\text{NUMBER OF}\\ \text{LITERS}\\ \text{TOTAL VOLUME}\end{matrix}\right)\left(\frac{\text{DESIRED PPM. CONC.}}{100}\right) \quad (3)$$

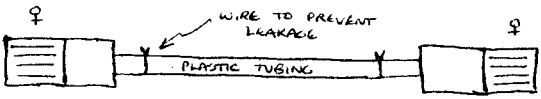
Injections are made with a 10 microliter syringe through a puncture hole in the reaction bag. When no injections are being made the hole is covered with plastic tape. Sufficient time should always be left for the compound to vaporize before further work is done.

It should be noted here that the total volume should be the final reaction volume after mixing, and not the initial reactant bag volume.

Bag to Bag Injections[5]

In a regular ozonolysis run ozone and TME (or other reactants) are prepared in seperate reaction bags. When it is desired to initiate the reaction the contents of each bag must be somehow combined. This combination is accomplished by the device shown in Fig. 11. It consists of two female Swagelok® fittings connected together with a piece of plastic tubing. The device is attached to the male outlets of each bag. Then hand pressure is exerted on one bag (usually the ozone bag) in order to transfer all its contents into the other bag.

Figure 11: Bag to Bag Injection Device



Gas Chromatography

Unless otherwise noted, all GC work was done at 40°C, with a six foot, one eighth inch diameter, 10% Carbowax 20M column and a 35 cc/min flow rate. All GC data was produced by a Perkin-Elmer 900 Gas Chromatograph with a FID detector. All samples were injected in the gas phase (see Fig. 12).

Peak areas were found by measuring height and width at half height with a ruler. Variations in peak areas for consecutive runs was occassionally a problem. Whenever detected the problem could be traced to leakage in the gas injection apparatus attached to the GC.

Mass Spectrometry at Below Room Temperature

Several runs of varying success were made on a Hewlett-Packard 5992 GC/MS System at temperatures below room temperature. The device depicted in Fig. 13 to attain temperatures as low as -38°C. This apparatus produced cooling by blowing compressed air through a aluminum coil submerged in liquid N_2, then into the GC oven. A shield was placed in front of the dewar containing the coil as a precaution in case any liquid O_2 might condense out of the air and detonated from the air pressure in the line. Luckily no such explosion occurred.

Figure 12: Gas Injection Port on GC

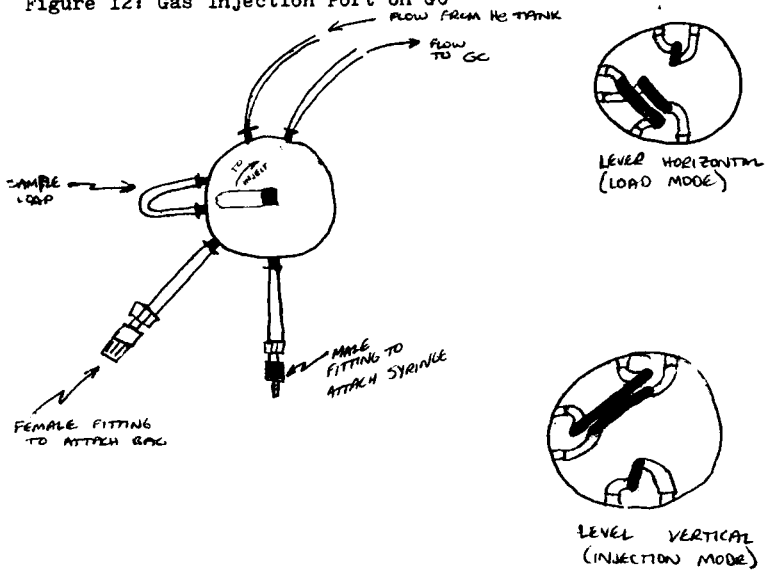
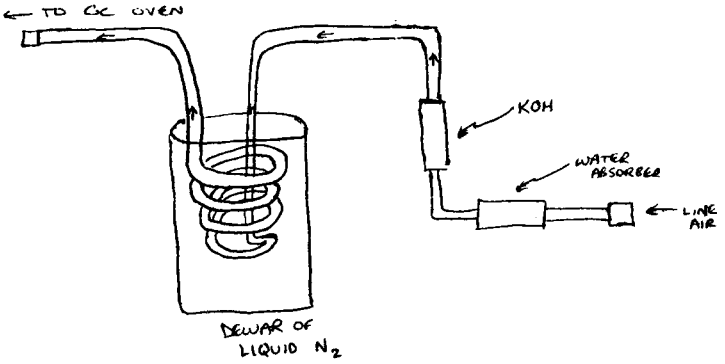
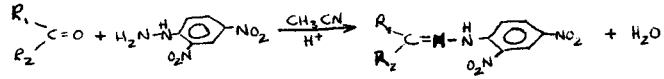


Figure 13: GC/MS Cooling System



Carbonyl Determination

Determination of identity and concentration of carbonyl compounds was accomplished by reacting carbonyls with 2,4 dinitrophenylhydrazine (DNPH) in an acidic (0.002% H_2SO_4) acetonitrile solution? DNPH reacts with carbonyls by the following reaction:



(4)

HPLC analysis was used to identify various derivatives by retention time and absorbance (254 and 360 nm). The carrier was a 65% acetonitrile with water solution, with a flow of 1.5 ml/min. The HPLC used for analysis was a Varian 502 with a Altech reverse phase C18 (4cm x 4mm) column.

The solution was made in the following manner. Approximately 0.25 g of once recrystallized DNPH was dissolved in one liter acetonitrile. In this form the indicator could be stored. Prior to use 0.2 ml H_2SO_4 was added to each liter of solution.

The sample was taken from the reaction bag in the same manner as the ozone measurement (see Fig. 9). A known volume of gas (0.5 or 1.0 liters) was bubbled through two impingers in series, each impinger containing a known concentration of acidic DNPH solution (10 or 25 ml). The samples were then ready to run on the HPLC.

Concentrations were calculated from peak areas. Values used for identification and concentration calculations may be seen in Table 7.

Table 7: Carbonyl Detection Characteristics

Compound	Retention Time (min)	Wavelength (nm)	Response Factor (10^{-7})
Formaldehyde[8]	3.8	254	3.39
		360	1.62
Acetone[8]	6.2	254	3.30
		360	1.57
Methylglyoxal[9]	14.2	254	2.78
		360	2.75

Note: The responce factor is in units of molarity/mm^2 for an absorbance factor of 0.08 and a chart speed of 10mm/min. The response factor was derived from the slope of a concentration-response plot. The following equation was used to convert a peak area in millimeters to a bag concentration of parts per million (volume/volume):

$$\text{ppm of carbonyl} = \text{peak area } (mm^2) \times \text{response factor} \times \text{absorbance setting} \times \left[\frac{(4.70 \times 10^7)\, V_D \left(\frac{\text{chart speed in cm/min}}{\text{cm/min}}\right)^{-1}}{(1000) V_s (8)}\right] \quad (5)$$

where V_D = volume DNPH solution in impinger

V_s = volume of gas sampled

RESULTS

The results presented here consist both of product analyses by various techniques of the ozonolysis of TME, and several stability tests to demonstrate the likelihood of certain possible secondary reactions, specifically acetone/ozone and TME/peroxides.

Product Analysis by Gas Chromatography

The method of identification of products was by retention times (see Table 8). Several possible products were not able to form identifiable peaks under the conditions of analysis; they were acetic acid, formic acid, and formaldehyde. All three compounds are small and highly polar. The high polarity probably caused the above compounds to be too spread out by the column used. When this possibility is coupled with their low FID response, it becomes very plausible that they are unidentifiable with this technique.

The reaction product identified and most easily studied under various initial reactant concentrations was acetone. An increase in baseline height in the region of methanol's retention time does not allow it to be ruled out as aproduct. Very low concentrations of methanol is still a possibility. At this stage ethyl acetate may be safely ruled out as a significan reaction product.

Table 9 shows acetone concentrations produced from various initial reactant concetrations. Concentrations were calculated from the FID response of known concentrations.

Table 8: GC Retention Times

Compound	Retention Time (min)
Tetramethylethylene	0.72 ± 0.01
Acetone	1.31 ± 0.06
Ethyl Acetate	1.87 ± 0.05
Methanol	2.2 ± 0.1
Formaldehyde	no peak
Acetic Acid	no peak
Formic Acid	no peak
Methyl Acetate	1.31 ± 0.06

Note: Injections were made to produce a calculated concentration of 600ppm in the gas phase.

Formaldehyde was attempted by the injection of 30% solution of formaldehyde in a water/methanol mixture as a liquid directly into the bag.

Table 9: GC Analysis Results

Run	Initial TME conc. (ppm)	Initial O_3 conc. (ppm)	TME Reacted conc. (ppm)	Acetone conc. (ppm)	$\frac{T}{O_3}$ @	$\frac{A}{T}$ @	$\frac{A}{O_3}$ @
1	100	47	34	41	0.72	1.2	0.87
2	100	49	56	50	1.1	0.89	1.0
3	100	50	47	47	0.94	1.0	0.94
4	100	24	26	25	1.1	0.96	1.0
5	100	69	76	67	1.1	0.88	0.97
6	100	14	24	18	1.7	0.75	1.3
7	100	14	14	16	1.0	1.1	1.1
8*	100	75	68	46	0.91	0.68	0.61
9*	100	64	51	37	0.89	0.72	0.58
10	50	20	22	20	1.1	0.91	1.0
11	50	34	18	32	0.53	1.8	0.94
12	50	28	20	28	0.71	1.4	1.0
13	50	25	31	30	1.2	0.97	1.2
14	200	96	31	78	0.32	2.5	0.81
15	200	74	66	100	0.89	1.5	1.4
16	220	172	162	150	0.94	0.92	0.87
Error	±15%	±10%	±25%	±25%	±50%	±50%	±25%

Table 9: GC Analysis Results (con't.)

Run	Initial TME conc. (ppm)	Initial O_3 conc. (ppm)	TME Reacted conc. (ppm)	Acetone conc. (ppm)	$\frac{T^@}{O_3}$	$\frac{A^@}{T}$	$\frac{A^@}{O_3}$
17	390	283	98	220	0.35	2.2	0.78
18	390	264	154	240	0.58	1.6	0.91
19	400	264	150	240	0.58	1.6	0.91
20	400	283	98	220	0.35	2.2	0.78
21	400	---	150	170	---	1.1	---
22	400	300	270	440	0.90	1.6	1.5
23	400	350	300	540	0.86	1.8	1.5
24*	400	281	270	270	0.96	1.0	0.96
25*	400	300	240	200	0.80	0.83	0.67
26*	400	324	270	300	0.83	1.1	0.92
27*	400	---	150	210	---	1.4	---
28*	400	266	390	360	1.5	0.92	1.4
29	490	170	120	120	0.70	1.0	0.70
30	10	7	10	12	1.4	1.2	1.7
31	25	19	11	18	0.58	1.6	0.95
Error	±15%	±10%	±25%	±25%	±50%	±50%	±25%

* Means that carbonyl analysis was done on same samples.

@ T: tetramethylethylene A: acetone

In determining retention times it was noticed that the peaks for acetone and methyl acetate were unresolvable on the 10% carbowax 20M column used. The compound peaks were resolvable on a 25 foot, 1/8 inch diameter, 25% TCEP on chromosorp P column. On this column methyl acetate and acetone had retention times of 12.0 and 14.0 minutes, respectively, when injected in gas phase.

A run was made of the products of a 600ppm TME/240ppm O_3 reaction. Three peaks were discernable at retention times of 7.0, 14.2, and 17.8 minutes. The first peak was found to be TME and the third peak was a contaminant in the stock bottle of TME. The middle peak was assumed to be acetone. From this analysis it was concluded that methyl acetate is not a product of the reaction (≤6%).

Acetone/Ozone Stability Test

Since acetone accounts for approximately half of the carbon of the TME consumed, and there is the possibilty of more moles of ozone consumed than TME, the question arose whether ozone reacted with acetone. To answer this question four sets of various concentrations were followed with time to look for any disappearance of acetone. Acetone and ozone concentrations were generated in separate bags, then mixed as described previously. The concentration of acetone was followed with time, and the initial and final (when run was terminated) concentrations of ozone were determined. Table 10 gives initial concentrations after mixing and Table 11 shows the results (Fig. 14 is a plot of the values from Table 11).

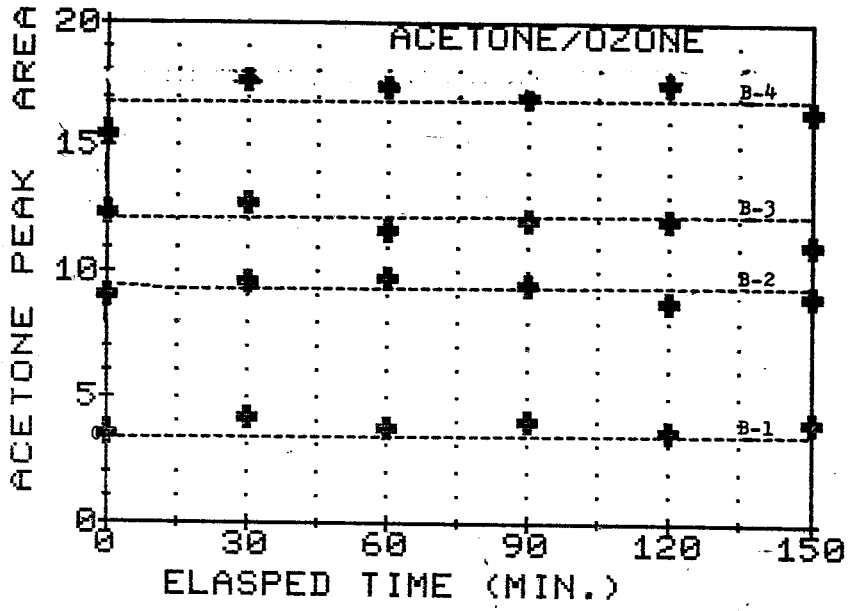
Table 10: Concentrations in Acetone/Ozone Stability Test

Bag	Acetone Conc. (ppm)	Initial O_3 Conc. (ppm)	Final O_3 Conc. (ppm)
B-1	100	144	96
B-2	200	262	204
B-3	300	410	320
B-4	400	450	337

Table 11: GC Peak Area of Acetone With Time

Time (min)	B-1	B-2	B-3	B-4
0	3.4 ± 0.4%	9.1 ± 0.1%	12.8 ± 11.1%	15.4 ± 0.7%
30	4.2 ± 10.5%	9.6 ± 0.8%	12.7 ± 4.3%	17.6 ± 0.6%
60	3.7 ± 1.7%	9.7 ± 1.5%	11.6 ± 0%	17.4 ± 1.2%
90	4.0 ± 6.2%	9.4 ± 0.6%	12.2 ± 3.3%	17.0 ± 3.0%
120	3.6 ± 1.8%	8.8 ± 0.6%	12.0 ± 2.9%	17.4 ± 2.9%
150	4.1 ± 6.9%	9.1 ± 3.1%	11.1 ± 1.8%	16.3 ± 0.2%

Figure 14: Plot of Acetone/Ozone Stability Results



It was assummed that any reaction of acetone would result in a noticeable decrease in the acetone peak area. The concentration of acetone was followed for 150 minutes and there was no deperciable loss of acetone. From these results it was assumed that acetone and ozone do not react to an extent that the reaction need be taken into account.

Carbonyl Analysis by HPLC

Carbonyl analysis was accomplished by the method described previously. Significant quantities of formaldehyde and acetone were found. Reproducibility of data for acetone concentrations between GC and HPLC methods was getting better with practise (runs 8 and 9 were the last runs attempted). Table 12 is a compilation of carbonyl concentrations.

The results also gave an indication of the presence of methylglyoxal. The positive identification of methylglyoxal was difficult because it has a tendency to remain adhered to the Tedlar bags, even after being emptied by a vacuum. Methylglyoxal also remains on glassware if they are given only a single rinse of solvent. When new bags were used 5 and 4ppm of methylglyoxal were found in runs 8 and 9, respectively. This area still needs clarification.

There were no indications of any significant amounts of acetaldehyde, glyoxal, or dimethylglyoxal. No significant peaks were unidentified.

Table 12: Carbonyl Analysis Results

Run	Formaldehyde* Conc. (ppm)	Acetone* Conc. (ppm)	TME Consumed (ppm)	Initial O_3 Conc. (ppm)	$\frac{F}{A}$@	$\frac{F}{T}$@	$\frac{F}{O_3}$@
Error	±10%	±10%	±25%	±10%	±20%	±35%	±20%
8	12	64	68	75	0.19	0.18	0.16
9	10	46	51	64	0.22	0.20	0.16
24	58	250	270	281	0.23	0.21	0.21
25	48	330	240	300	0.14	0.20	0.16
26	30	200	270	324	0.15	0.11	0.09
27	56	450	150	---	0.12	0.37	----
28	25	150	390	266	0.16	0.06	0.09

* Concentrations are the mean average of the areas derived from responses at 254 and 360 nm.

@ T: tetramethylethylene A: acetone F: formaldehyde

Peroxidic Products

The spectrophotometric technique used to determine ozone concentrations was also used with some success to determine if peroxidic products were present. This method of determining peroxide concentrations was only used briefly in the project. More work must be done in this area before any positive conclusions may be reached.

A single run was performed to check for peroxidic products. The results are in Table 13.

Table 13: Detection of Peroxidic Products

Run	TME Conc. (ppm)	O_3 Conc. (ppm)	Absorbance Impinger 1	Absorbance Impinger 2	Peroxide Conc. (ppm)
1	54 ± 5%	53 ± 10%	0.6520	0.0150	12 ± 15%
2	224 ± 5%	225 ± 10%	2.820	0.0340	40 ± 20%

A GC analysis was not performed on the above samples. The results show the possiblity of peroxidic products.

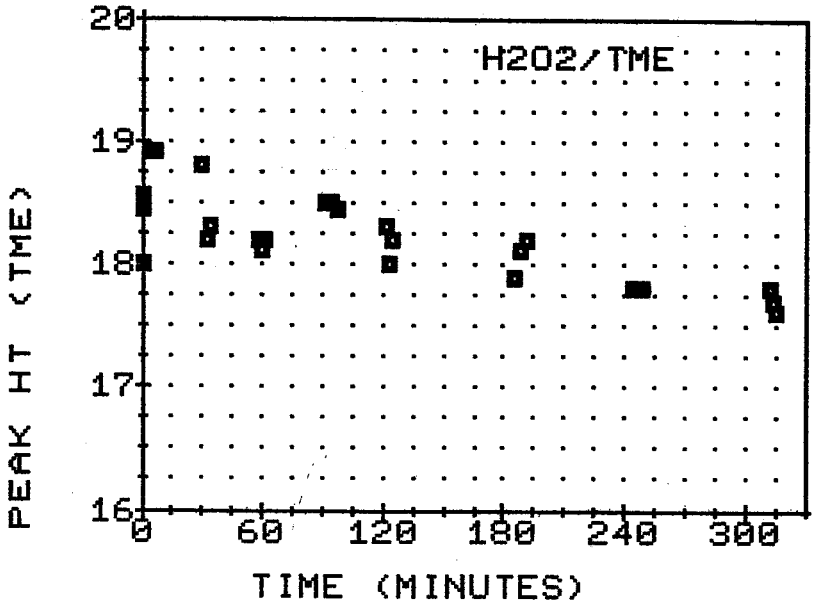
Peroxide/TME Stability Test

Since the possibility of peroxidic products had been demonstrated to a limited degree, the question arose if peroxidic products could consume excess TME. A bag initially containing 200ppm TME in ten liters of air was injected with 6.80 microliters of 30% H_2O_2/water solution (enough to produce 200ppm H_2O_2 when fully vaporized). The TME concentration was followed by GC as a function of time. The results are listed in Table 14 and plotted in Fig. 15.

Table 14: Results of H_2O_2/TME Stability Test

Time(min)	TME Peak Height (cm)
0	18.0
4	18.9
7	18.9
30	18.8
32	18.2
34	18.3
58	18.2
60	18.1
62	18.2
92	18.5
94	18.5
97	18.4
122	18.3
123	18.0
125	18.2
186	17.9
189	18.1
191	18.2
245	17.8
247	17.8
249	17.8
312	17.8
314	17.7
316	17.6

Figure 15: Plot of H_2O_2/TME Stability Test



From the results of the H_2O_2/TME stability test it was concluded that peroxides would not react with TME to any appreciale degree in one to two hours (6% over five hours, $k = 1.7 \times 10^{-8} ppm^{-1} sec.^{-1}$). Time between TME/ozone reaction and analysis was never more than two hours. Therefore they will not be considered as an interference of the product analysis.

Mass Spectrometry Analysis

Work in this area was initiated to detect the possibility of the TME peak masking the peak of a product. The spectrum produced for pure TME and reacted TME were similar enough to conclude that TME was not masking another peak. For this analysis the column used was a 10% carbowax 20M column.

The possibility of products with a mass higher than TME was then examined. It was assumed that such compounds, if present, would probably be a carbonyl compound, a hydroxy compound, an acid compound, or any combination of such. Such compuonds would likely have long retention times and, since they may be in low concentrations, would probably produce broad peaks which would be indistinguishable from the background response. In an attempt to remedy this problem the column was changed to a 2% OV 101 ultrabond 20M (100/120 mesh) column. The reason was to promote shorter retention times, and sharper peaks.

The new column worked too well. With the column TME, acetone, and any other potential products appeared in a single peak with no other peaks at longer retention times. To re-

solve the peak into its components the temperature was lowered. The cooling apparatus described previously was used here.

At temperatures of about -10 to -13°C a potential unknown peak was detected at 4.8 minutes (on this run TME was 2.0 minutes) but it was barely distinguishable with a total abundance of 131, with the background about 70. Several times the temperature was slowly raised, but what might have been a peak would merge with the TME peak without ever being distinguishable enough from the background to reach any conclusions.

This phase of the project was temporarily abandoned to pursue the carbonyl analysis.

DISCUSSION

This project presents a wide variety of data. Enough results were not produced to make any positive statements about the reaction mechanism, but enough results were produced to supply insights into the various possibilities.

Error Estimates

The nature of this work produced many possibilities for error. For example, volumes were not measured with factory calibrated glassware, but by a flow gauge calibrated by the experimenter. Gas phase work has the constant possibility of leaks, relatively rough measurements of volume, and leakage of improvised equipment attached to factory made instruments. With careful work reproducible results are still possible.

Volume measurements of gases were performed with the flow gauge mentioned previously. The flow gauge had several inherent difficulties. First an error of 3% was calculated as the best possible accuracy for flow rates due to the scale on the gauge. Second, a 1% error was allotted for the fact that when the line was attached to fill a bag, and there was always pressure in the line since the flow had to be set with the bag unattached, there was an initial surge of gas that would make the ball hit the top of the gauge. The 1% accounts for this error. Finally a 5% was allotted for errors in injected liquid samples.

An error of 10% was allotted to ozone concentrations for the following reasons; 5% was allotted for measuring the flow for the analysis (this is higher than previously because a smaller volume is measure and timing must be taken into account). 2% was allotted for filling the impingers with a graduated cylinder, and 3% was allotted for error in the standardization plot.

A 25% error was assigned to consumed TME amounts because it is the result of mixing two bags (5% and 4% error), then subtracting two peak areas at 8% each, this includes calculation of the FID response.

An error of 25% was assigned to GC acetone concentrations because the FID response for acetone was calculated from a single bag (described previously as 5% TME bag and 4% ozone bag), and 8% variation each is allotted for measuring two peaks (one for calculating the FID response, the other for the product peak).

An error of 10% is allotted to each carbonyl analysis concentration due to flow error, error in filling impingers, and error in measuring peaks (HPLC peaks had sharper lines and wider peaks than GC peaks).

The above errors are assumptions. They do not take into account bag leakage, leakage in the impinger fittings, and leakage in the gas injection port of the GC. On some runs the leakage in the gas injection port resulted in unusual values (see runs 14 and 17).

One last error which wasn't taken into account, but critical, was the half life of ozone (465 minutes).[5] Frequently much time was lost between measuring ozone concentration and final injection (especially when repairs had to be made on the gas injection port), sometimes as much as three or four hours. No attempted was made to correct for this error since it was variable between each run. All ozone values should be taken as upper limits.

Any other errors assigned in this paper were statistical variations due to reproducibility of runs.

Classification of Possible Products

Many possible products were found or ruled out, but many were undetectable by means used in this project. Table 15 shows the classification of each compound.

Table 15: Classification of Possible Products

Found	Ruled Out	Undetectable
acetone	methyl acetate	carbon dioxide
formaldehyde	ethyl acetate	carbon monoxide
methylglyoxal	acetaldehyde	methanol
	glyoxal	acetic acid
	dimethyl glyoxal	formic acid

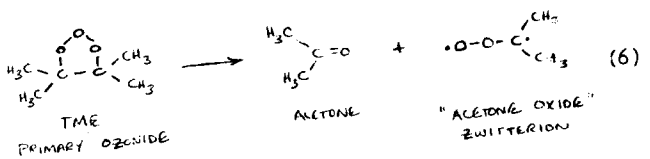
Analysis of Results

There appears to be a variation in results with a change in initial reactant concentrations.

Initial TME	Average T/O_3	Average A/T	Average A/O_3	Average F/T
100	1.0 ± 17%	0.91 ± 15%	0.93 ± 17%	0.19 ± 5%
400	0.88 ± 21%	1.4 ± 24%	1.1 ± 28%	0.14 ± 43%

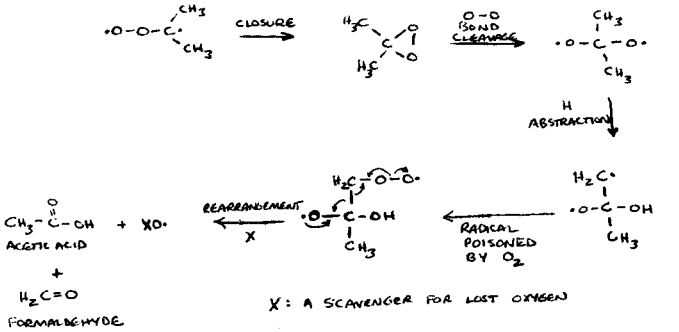
At higher reactant concentrations more ozone appears to be consumed than the 1:1 ratio of the lower concentration runs, though the values may be the same within experimental error. A higher percentage of acetone is produced at the higher reactant concentrations. The results for formaldehyde are sketchy due to the fact that insufficient runs were made to produce a reliable average, but from the data available there appears to be a decrease in formaldehyde produced with increasing reactant concentraions.

A possible explanation for these results is by the Criegee mechanism. As mentioned before, the primary ozonide, the mechanism suggests, splits into a carbonyl component and a carbonyl oxide. For TME the reaction would be:



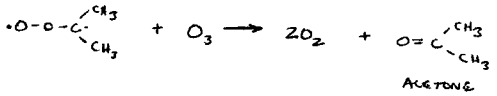
(6)

Two possible reactions of the zwitterion would be:



(7)

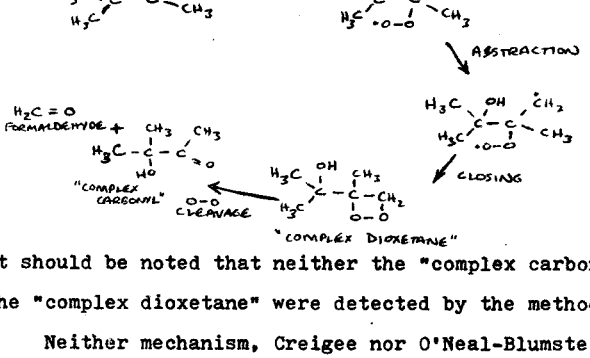
or



(8)

It may be assumed that the second pathway (8) will be more probable with increasing reactant concentrations. With the above pathways the conversion of approximately 50% of the TME to acetone may be rationalized. After the initial breakdown of the primary ozonide to acetone and the "acetone oxide" zwitterion, the two suggested pathways of zwitterion will be in competition. At relatively low initial reactant concentrations the first possible reaction (7) will be more prevalent and formaldehyde and acetic acid would be formed. At higher concentrations the possible reaction between the zwitterion and ozone (8) will be more prevalent and this would account for the increase in yield of acetone and decrease in formaldehyde yield at higher concentrations.

One type of pathway suggested by the O'Neal-Blumstein mechanism is an abstraction of a hydrogen from a β-carbon. The reaction would be:



(9)

It should be noted that neither the "complex carbonyl", nor the "complex dioxetane" were detected by the methods used.

Neither mechanism, Creigee nor O'Neal-Blumstein, offers a possible pathway to produce methylglyoxal.

There is still the possibility for other mechanisms since all the products of the ozonolysis are not accounted for. In the lower concentration runs only 48% ± 15% of the carbon mass of TME is accounted for. In the higher concentration runs 72% ± 25% of the carbon mass is accounted for. If you assume that there is the same amount of acetic acid as formaldehyde (assuming formaldehyde is formed by decomposition of the carbonyl oxide) then the percentages of carbon mass accounted for would be 55% ± 16% and 77% ± 27%, respectively. Even with this assumption all the TME carbons are not yet accounted for. Anymore mechanisms suggested before the rest of the carbons are accounted for would be premature.

Future Work

The most promising area for future work should be in the carbonyl analysis by DNPH. This should give an accurate value of formaldehyde present. It will also further prove or disprove the actual presence and amount of methylglyoxal.

New methods should be developed to detect acetic acid, formic acid and methanol. This may be possible with different GC columns, or more likely, a reagent which will react stoichiometrically with the above compounds. No work has been done in this area to date.

More work needs to be done to draw more supportable conclusions.

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