

CONVERSION OF OLEFINS
TO UNSATURATED CARBONYL COMPOUNDS
BY MERCURIC SULFATE

By

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1940

Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College
In partial fulfillment of the requirements
For the Degree of
MASTER OF SCIENCE

1949

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ACKNOWLEDGMENT

The author wishes to express his gratitude for the inspiration and helpful suggestions from Dr. Otis C. Dermer.

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INTRODUCTION

Acrolein has classically been prepared by the dehydration of glycerol. Owing to the relatively high cost of glycerol and low yields this process has not been used commercially.

There is now a semi-commercial plant in operation for producing acrolein from diallyl ether, a by-product of another chemical process.

Recent U. S. patents describe a process for converting propylene to acrolein by oxidation with mercuric sulfate. Since propylene is available at low cost, the present work was undertaken to evaluate these patents by systematic study of the variables.

HISTORICAL DISCUSSION

Acrolein was first prepared in the pure state by von Redtenbacher (29) in 1843 after earlier scientists had obtained an impure grade in a volatile liquid from distillation of fats.

The distillation of glycerol in presence of a dehydrating agent to produce acrolein has long been known and studied. Acid catalysts, especially sodium or potassium hydrogen sulfate, have always been preferred. Besides the literature reviewed by Beilstein (3), Hanyu and Yanagibashi (14) heated both pumice impregnated with ferric phosphate and Japanese acid clay and dropped glycerol upon them. With pumice 50-51% and with acid clay 37% yields of acrolein were obtained. A patent to Schering-Kahlbaum A. G. (33,35) described the use of ferric phosphate and lithium phosphate as dehydrating agents. Another to N. V. de Bataafsche Petroleum (28) claimed the action of acid catalysts upon polyhydric alcohols such as glycerol and methylglycerol to produce acrolein and methacrolein. Trimethylene glycol (27) can be dehydrated instead of glycerol to produce acrolein.

Another method of preparing acrolein which has been extensively studied is the union of acetaldehyde and formaldehyde in the presence of silica gel or alumina (23) gel catalyst at a temperature sufficiently high (200°-260°C) to dehydrate the primary aldol condensation product to form acrolein. A patent issued to I. G. Farbenindustrie (20) prescribed heating to 800°C for the preparation of the alumina gel catalyst. With this catalyst acrolein is formed from acetaldehyde and formaldehyde at 180°-200°C. Wagner (40) reacted acetaldehyde and formaldehyde at

temperature between 200°-400°C over a catalyst which contained calcium phosphate as active ingredient and which may contain 1% lithium phosphate or 5% aluminum phosphate. This method was adapted to preparation of methacrolein by substituting acetone for acetaldehyde. Schulz and Wagner (34) described a similar process for producing acrolein with unspecified catalyst at 200°-400°C but with exclusion of all iron and aluminum from the catalyst and material of construction. Gallagher and Masche (13) also described a vapor phase, catalytic process at temperature of 250°-350°C for producing acrolein from acetaldehyde and formaldehyde. Brant (4) found that a lead acetate catalyst at temperature 200°-400°C was effective to produce acrolein from acetaldehyde and formaldehyde. Smart (39) controlled the temperature of the exothermic reaction (10-12 kcal/mole) of acetaldehyde and formaldehyde by replacing acetaldehyde with paraldehyde which by endothermic depolymerization (24 kcal/mole) furnishes acetaldehyde. Distillers Co. (9) used a vapor phase process with a fluidized catalyst to convert formaldehyde and acetaldehyde to acrolein. Walter and Schulz (41) obtained acrolein by reacting acetylene and formaldehyde in presence of sodium silicate or zinc phosphate catalyst at temperature above 150°C.

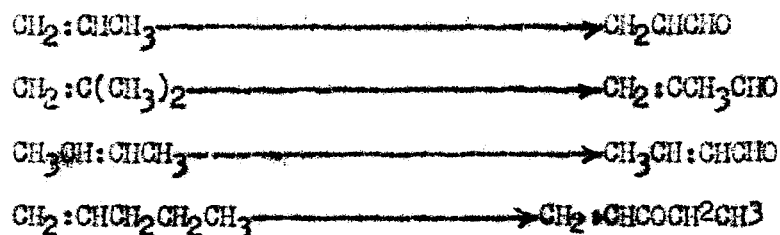
Fitzky (12) described a process for preparing the intermediate aldol by reaction of formaldehyde and acetaldehyde in slightly alkaline solution. A patent (10) issued to du Pont described the preparation of aldols in presence of condensation reagents when one of the aldehydes was present as a bisulfite addition product.

Allyl alcohol can be converted to acrolein by reaction with oxygen in standard vapor-phase methods (36). It is of interest to note that the oxidation of propylene with selenium dioxide (37) in acetic acid-

acetic anhydride solvent yields not acrolein, but allyl alcohol.

Tetrahydrofurfuryl alcohol (30) yields acrolein when heated above 400° C. in vapor-phase with an aluminum silicate or titanium dioxide catalyst. Acrolein can also be formed by the little-studied reaction of ethylene and carbon monoxide (26).

Clark and Shutt (5) investigated the catalytic oxidation of unsaturated hydrocarbons to unsaturated carbonyl compounds. They used a mixture of air and hydrocarbon in volume ratio 9:1 and passed it over a silver selenite catalyst promoted with cupric oxide at 175°-450° C. The catalyst was regenerated with air alone or air containing ozone or oxides of nitrogen. The hydrocarbons investigated and products obtained were:



There was claimed 20% per pass conversion of propylene to acrolein with 0.6% of propylene destructively oxidized; with isobutylene 30% per pass conversion to methacrolein was achieved and only 1% isobutylene was destructively oxidized.

Rust and Vaughn (31) found the vapor-phase oxidation of propylene in presence of hydrogen bromide to yield acrylic acid, bromoacetone, and allyl bromide, but no acrolein. Tests with cyclohexene gave cyclohexenone in low yield (6.3%). Acrolein is produced along with formaldehyde, acetaldehyde, etc., in partial oxidation of petroleum oils (11), either liquid-phase or vapor-phase, but not in important quantity.

Converse (6) described a method for pyrolyzing diallyl ether at 500°-600° C. to obtain acrolein and propylene. This process can be applied to methallyl ether to obtain methacrolein and isobutylene. Shell Chemical Corporation (12) has recently placed in operation at Houston, Texas a semicommercial plant for producing acrolein from diallyl ether obtained as by-product from the hydrolysis of allyl chloride.

Mercuric sulfate has long been known to oxidize unsaturated hydrocarbons to form unsaturated aldehydes or ketones. Deniges (8) observed the formation of acrolein when the complex formed by propylene and a mercury salt was decomposed by heating; however, the object of his research was the isolation and characterization of the complex. The formula he proposed was: $(SO_4 \cdot Hg \cdot HgO)_3 R^n$, in which R^n represents an olefin. Deniges (7) studied the reaction of tertiary butyl alcohol with mercuric nitrate and, finding the complex to contain only the isobutylene radical, proposed the formula: $NO_3 \cdot HC_2 \cdot C_4 Hg \cdot HgNO_3$. Sand and Hofman (32) isolated propanol-mercury complex and both butanol and isobutylene-mercury salts from isobutylene-mercury complex, all made in slightly basic solutions. With ethylene (19) there are two series of complexes obtainable depending upon the experimental conditions, a substituted alcohol series, $HOCH_2CH_2HgX$, and a substituted ether series, $O(CH_2CH_2HgX)_2$.

Keller (21) concludes a review of olefin-inorganic salt complexes as follows: "Perhaps no theory has been advanced which satisfactorily explains all of the questions relating to the various inorganic salt-olefin compounds. It is entirely possible that the metal-olefin bonds in these complexes are not all of the same type: in that case any one theory concerning the mechanism of their formation would obviously be

inadequate."

Yale and Hearne (43) investigated the reaction of mercuric salts of oxygen-containing acids with non-tertiary, acyclic olefins having more than three carbon atoms. The mercuric reagent was predominantly a suspension of mercuric oxide in a dilute aqueous acid (1-2%). Under these conditions it was found that a CH_3 group adjacent to a double linkage was unaffected but that the reaction occurred at a CH_2 group adjacent to the double linkage or at the double-bonded carbon atoms. That is, an olefin $\text{RCH}_2\text{CH}=\text{CH}_2$ gave $\text{RCOCH}=\text{CH}_2$ and the olefin $\text{RCH}=\text{CHCH}_3$ gave the isomers $\text{RCOCH}_2\text{CH}_3$ and $\text{RCH}_2\text{COCH}_3$.

Macallum (25) claimed good yields of acrolein from propylene by employing a reagent which contained 3-24% mercuric sulfate and even as high as 50% but the exceedingly high concentrations of slurried mercuric sulfate were difficult to pump. The maximum acidity recommended is 15% and 2-5% is preferred, for low acidity favored production of acrolein, although none was formed in neutral suspensions. The yields were increased by control of acidity from 4% to as high as 75% based on mercuric sulfate used. The yield based on olefin consumed was not given.

Herstein (16) recommended the use of a reagent composed of 16.7% mercuric sulfate, 22% sulfuric acid and 61.3% water. The reagent and propylene were mixed concurrently in a spray tower at temperature below 70°C . preferably 20°C . The reagent saturated with propylene was then heated to $85^\circ\text{-}105^\circ\text{C}$ and sprayed into a second tower wherein the physically absorbed propylene was released, carrying with it some acrolein. From the second spray tower the reagent passed to a digestion tank where the temperature was maintained at $85^\circ\text{-}105^\circ\text{C}$ for one-half hour to convert

propylene to acrolein. The acrolein was separated from the reagent by steam distillation.

In the second process Herstein described (1,18), the propylene was concurrently absorbed in a spray tower at a temperature of 85°-105°C. The reagent next entered a second spray tower at the top while propylene was introduced at the bottom to strip out the acrolein, which was recovered from propylene by absorption in water. Other gases which may be used for the stripping operation are carbon dioxide, nitrogen, suitable hydrocarbons, or water vapor.

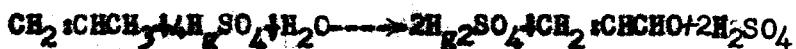
EXPERIMENTAL

Consideration of the work of Harstein, Yale and Hearn, and Macallum suggests two questions which would have considerable influence upon the commercial adaptation of the process: (a) will other cheaper oxidants produce the aldehyde and (b) what is the yield of acrolein, based upon propylene reacted, in various concentration of acid.

A qualitative test to verify the patent claims was made with propylene and mercuric sulfate reagent (10% H_2SO_4 , 15% H_2SO_4 , and 75% H_2O). The hydrocarbon was slowly introduced below the surface of the reagent. The reagent was then heated to $85^{\circ}-90^{\circ}C$, when a yellow precipitate formed. Steam was directly introduced to distill the acrolein. The characteristic odor of acrolein was very evident and a yellow precipitate formed upon the addition of 2,4-dinitrophenylhydrazine to a portion of the distillate.

The method was next tested to determine if methacrolein could be obtained from isobutylene, this not having been claimed by the patents under test. The isobutylene was prepared by passing tertiary butyl alcohol vapor over alumina heated to $400^{\circ}-500^{\circ}C$. A procedure was followed similar to that used with propylene. The steam distillate smelled like acrolein and yielded an orange-yellow precipitate with 2,4-dinitrophenylhydrazine. After one recrystallization from alcohol the precipitate had a melting point of $200^{\circ}C$. This compares so favorably with the literature value (38) of $206^{\circ}C$ that it was concluded the product was methacrolein.

To produce one mole of acrolein from one mole of propylene with mercuric sulfate reagent according to the equation



requires 4 moles of mercuric sulfate. The mercurous sulfate formed must be regenerated electrolytically (15), by fuming with sulfuric acid (17), or by oxidizing with chlorine or nitric acid (25). These operations would be difficult and expensive on a commercial basis. With the purpose of finding a reagent which could be regenerated more easily the following salts and acids in various concentrations were tested with propylene:

Cupric chloride in hydrochloric acid.

Cupric chloride plus potassium chloride in hydrochloric acid.

Cupric sulfate in sulfuric acid.

Cupric sulfate plus potassium sulfate in sulfuric acid.

Cupric sulfate plus silver sulfate in sulfuric acid.

Ferric chloride in hydrochloric acid.

Ferric sulfate in sulfuric acid.

Silver nitrate in very dilute nitric acid.

Cupric salts were tested since cupric chloride oxidizes mercaptans to disulfides and is easily regenerated by oxygen of the air. Ferric chloride is known to oxidize certain compounds such as hydrazobenzene. Nevertheless, none of the salts yielded any acrolein: apparently the effect of mercury is specific.

Stronger oxidizing agents such as potassium dichromate, potassium permanganate, ceric sulfate, and hydrogen peroxide were not tested since they attack the double bond of the olefin and the yield of acrolein would be very low or zero.

A qualitative test made with propylene and mercuric nitrate dissolved in nitric acid just strong enough to prevent hydrolysis yielded acrolein. No acrolein was produced by mercuric chloride, phosphate, or

acetate in the corresponding dilute acid nor by mercuric acetate in the glacial acid. Thus it appears that only mercuric sulfate and mercuric nitrate can be made to produce unsaturated aldehydes from olefin.

The second phase of the experimental work was devoted to determination of yield of carbonyl compounds based upon the mercuric sulfate used and hydrocarbon consumed. These data were determined for isobutylene, propylene, and cyclohexene.

The method used for isobutylene and propylene was as follows: From a calibrated bottle of $2\frac{1}{2}$ liters capacity the hydrocarbon gas was caused to flow by displacement with water. The inlet gas volume was recorded as difference in the reading of initial and final water levels. The gas then passed through a gas-washing bottle of 200 ml. capacity which contained 170 ml. of mercuric sulfate reagent. The unreacted gas then passed to a second gas-washing bottle which contained water to dissolve any acrolein that might have been carried out with the unreacted gas. However, no acrolein was ever detected in the second gas-washing bottle. From this second bottle the gas flowed to an aspirator bottle in which it was collected by displacement of water. The volume of water displaced was recorded as volume of unreacted gas. The difference in inlet gas volume and unreacted gas volume gave the quantity of hydrocarbon gas which reacted with the mercuric sulfate reagent.

The mercuric sulfate reagent was prepared by diluting concentrated sulfuric acid to 1*M* normal. The required volume of 1*M* acid was then measured to give 170 ml. of acid of the desired concentration, and mercuric sulfate (C.P. Reagent) was added to give a predetermined concentration. For solutions containing 10% acid and less, the mercuric sulfate dissolved faster when the 1*M* acid was added directly to mercuric sulfate, and then the water slowly added. If 5% acid were added to the mercuric sulfate, for example, hydrolysis resulted and the yellow

mercuric oxide would not dissolve even on heating the acid. It was determined that the minimum concentration of acid required to prevent hydrolysis of mercuric sulfate in concentration of 5 g. per 100 ml. is between 2 and 5%.

After 900 ml. to 1200 ml. of hydrocarbon gas had been passed through the mercuric sulfate reagent, the flow was stopped and the gas-washing bottle containing the reagent placed into a beaker of water at 90°C and maintained at that temperature for an hour. A current of steam was passed through for a few minutes to sweep out desorbed propylene. The reagent was next transferred to a two-liter, long-neck Flask (at this point the reagent had no odor of acrolein) and subjected to steam distillation. The first 10 to 25 ml. of distillate collected still had no odor of acrolein; then suddenly the acrolein began to come over and continued to be present in the distillate until 1000 to 1500 ml. of distillate were collected. The distillation was discontinued when only a very slight turbidity was noticeable upon adding 2,4-dinitrophenylhydrazine solution to a portion of the distillate. These observations indicate that the formation of acrolein is a slow reaction, probably resulting from the hydrolysis of the mercury-olefin complex in the presence of steam.

The quantity of aldehyde produced was determined by the hydroxylamine hydrochloride method. Hydroxylamine hydrochloride solution (5%) was prepared and bromophenol blue indicator added. To a 50 ml. aliquot of distillate was added the same indicator to make equal intensities of color. With sodium hydroxide solution both the sample and hydroxylamine hydrochloride were adjusted to the same intermediate greenish color between yellow and blue. A portion of the hydroxylamine hydrochloride

solution was then added to the 50 ml. aliquot and the required volume of standard sodium hydroxide determined to again match the color of the sample with the original hydroxylamine hydrochloride solution. This procedure eliminated errors due to extraneous acidity the sample may have contained and the effect of dilution upon the shade and intensity of the color of the indicator. From these data was calculated the total quantity of aldehyde that was produced since one mole of aldehyde releases 1 mole of hydrochloric acid from hydroxylamine hydrochloride.

Tables 1, 2, and 3 show the per cent yield of aldehyde calculated on basis of both mercuric sulfate and the hydrocarbon which reacted. The variables were the concentrations of mercuric sulfate and acid.

Graph 1 also shows the per cent yield of methacrolein based upon isobutylene consumed. It can be seen that optimum acid concentration is approximately 10% and that higher per cent yields were obtained with mercuric sulfate concentration of 5 g. per 100 ml. (Curve 1) than with 10 g. per 100 ml. acid (Curve 2). There are probably two reasons for this. With more concentrated mercuric sulfate solution considerably more precipitate was formed during the introduction of isobutylene; this probably absorbed mercuric sulfate and prevented it from contacting the hydrocarbon gas. Again, when the methacrolein was steam-distilled from the reagent, more of the product would be consumed by successive reactions if the mercuric sulfate were more concentrated.

Graph 2 shows the per cent yield of methacrolein from isobutylene based upon the mercuric sulfate used. This method of expressing the data is not very accurate since the calculations were based upon the change of mercury only from mercuric to mercurous sulfate, whereas actually, part of the mercury is completely reduced. This was evident

TABLE I

Yield of Methacrolein from Isobutylene at Various Acidities

Reagent Concentration 5 g. H_2SO_4 /100 ml. Acid

Run No.	Concentration of H_2SO_4 -- Wt. %	Aldehyde Produced		Per Cent Yield	
		g.	moles	Based on Isobutylene	Based on H_2SO_4
1	1	.0074	.00011	.17	1.5
2	5	.11	.0016	13.	22.
3	10	.08	.0012	16.	16.
4	15	.065	.0009	12.	13.
5	20	.054	.0008	9.	11.

Graph 1
Yield of methacrolein
based upon isobutyrene.
Absorption temperature 24.00

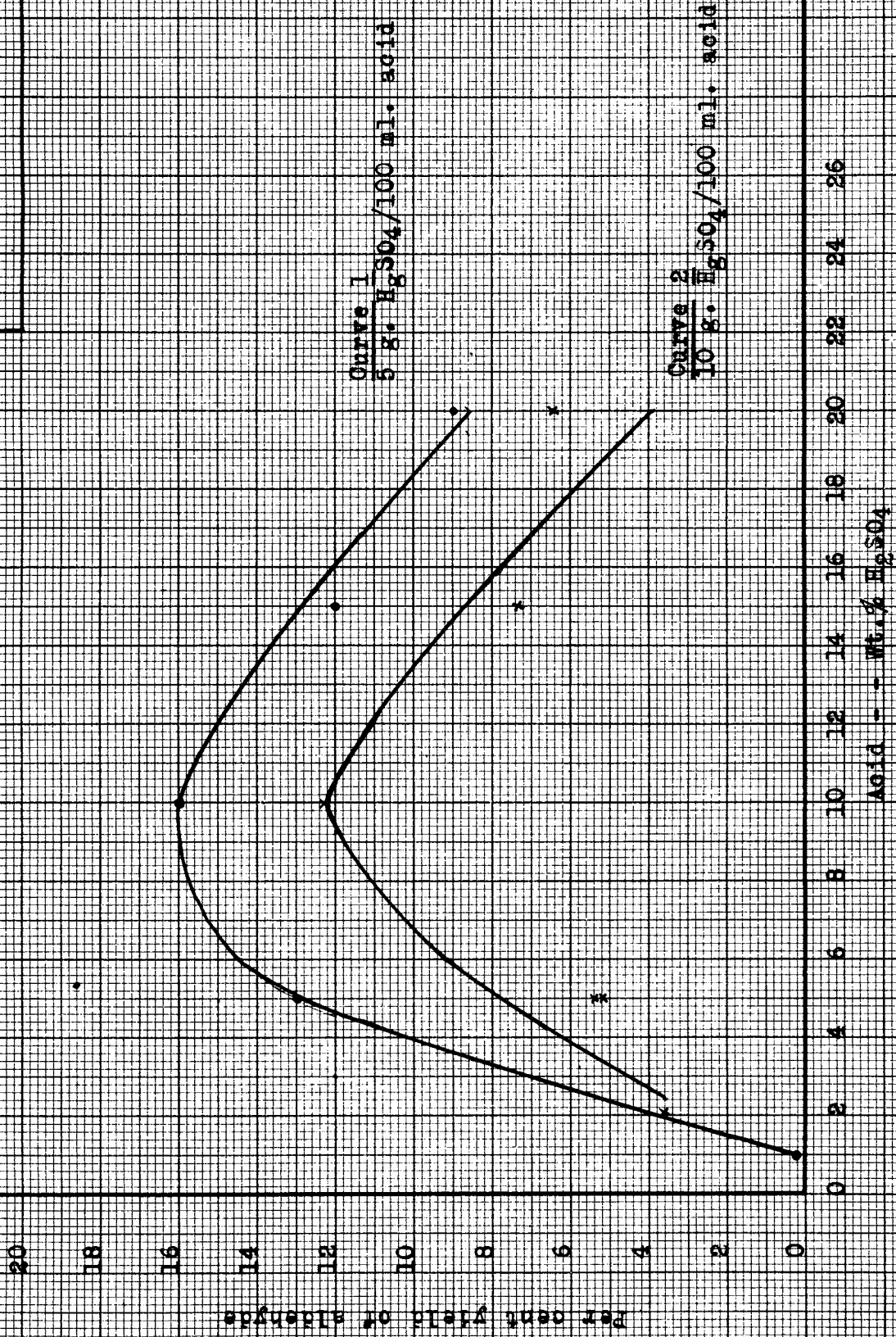


TABLE II

Yield of Mithersolein from Isobutylene at Various AciditiesReagent Concentration 10 g. H_2SO_4 /100 ml. Acid

Run No.	Concentration of H_2SO_4 -- Wt.%	Aldehyde Produced		Per Cent Yield	
		g.	moles	Based on Isobutylene	Based on H_2SO_4
6	2	.041	.00058	3.7	3.0
7	5	.094	.0014	5.4	7.0
8	5	.10	.0014	5.2	7.4
9	10	.117	.0017	12.3	8.7
10	15	.082	.0012	7.3	5.6
11	20	.061	.00088	6.5	4.6

Graph 2

Yield of methacrolein
based upon H_2SO_4
Absorption temperature $24^{\circ}C$

Curve 1 $H_2SO_4/100$ ml. acid

Curve 2 $H_2SO_4/100$ ml. acid

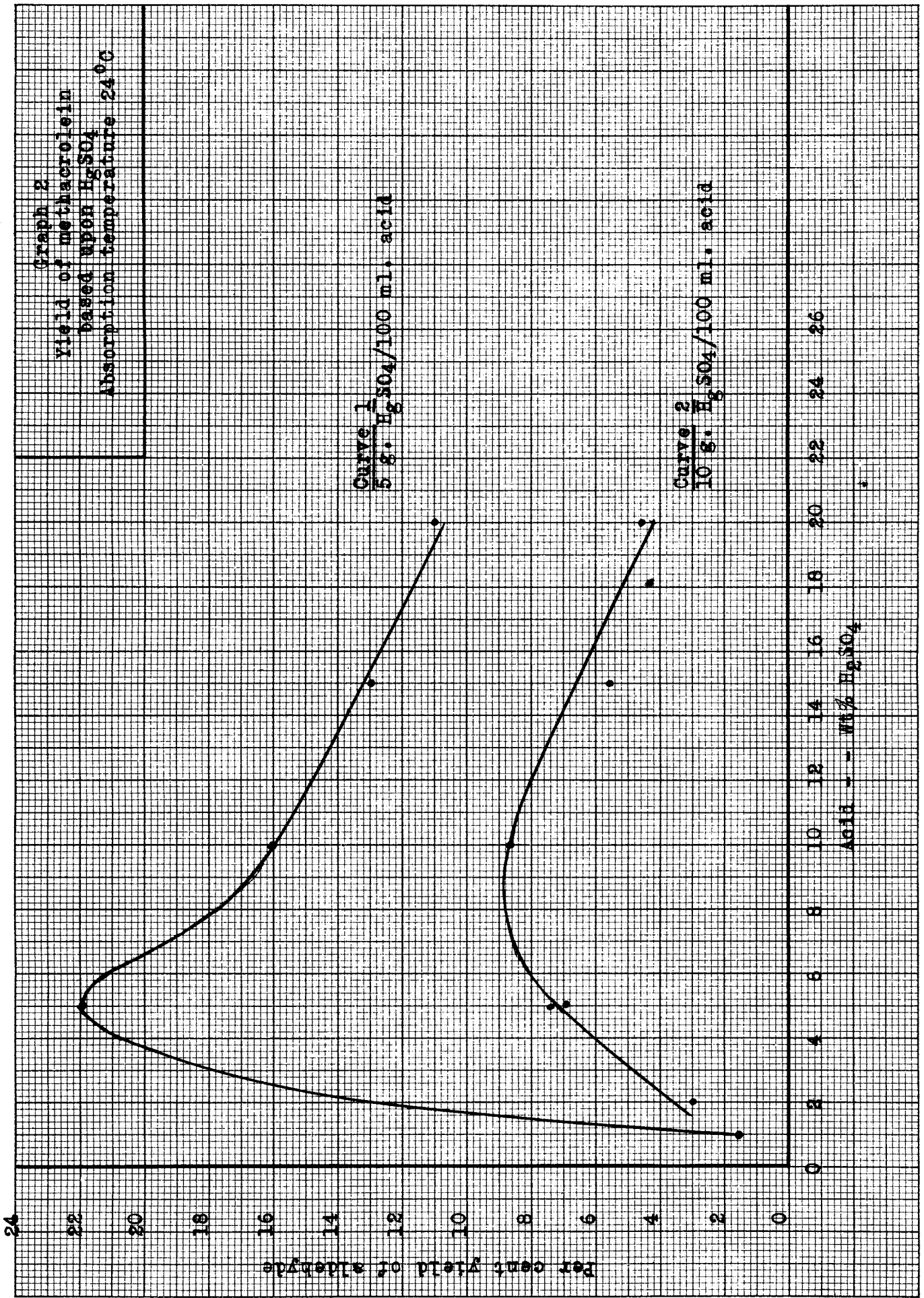


TABLE III

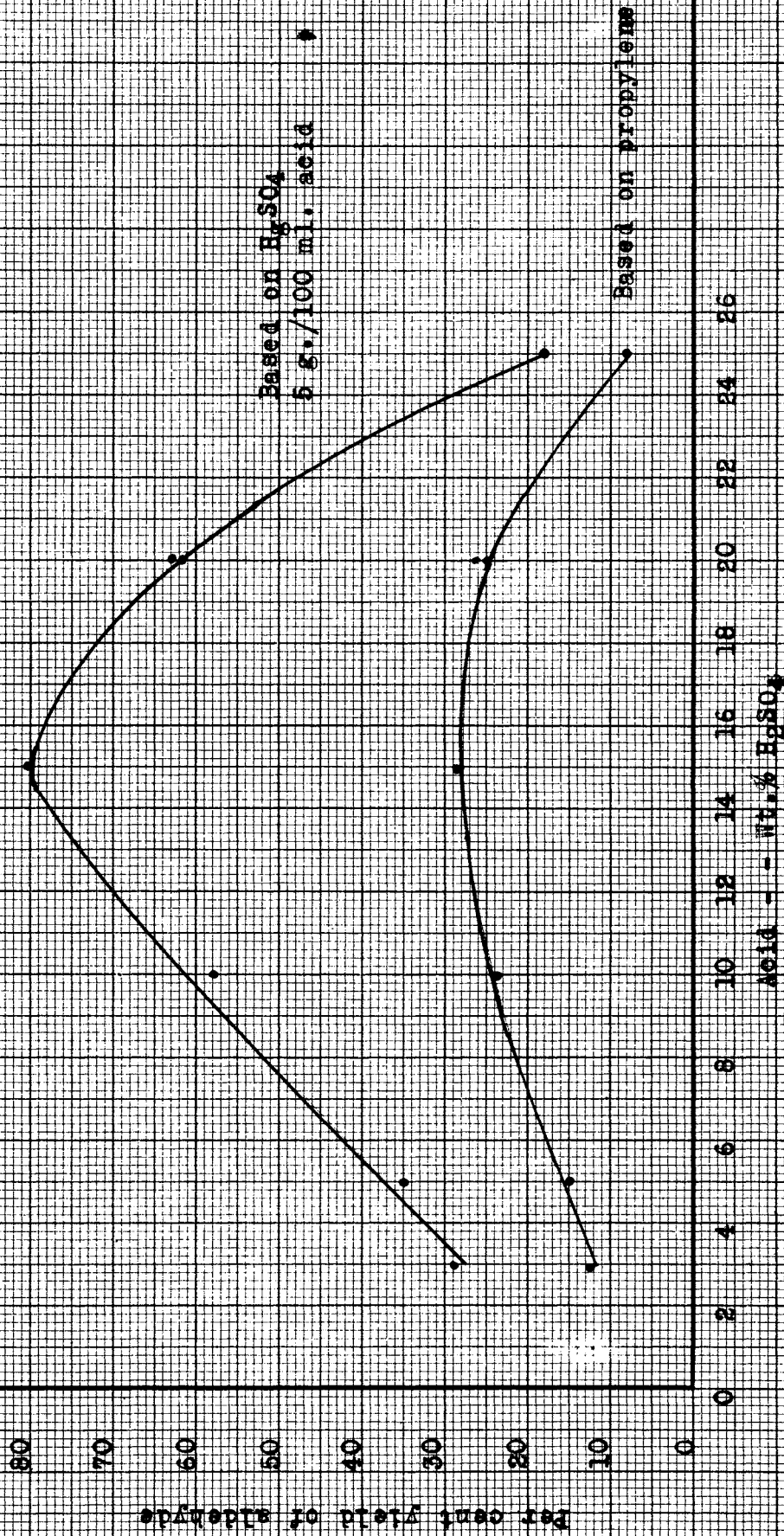
Yield of Acrolein from Propylene at Various Acidities

Reagent Concentration 5 g. H_2SO_4 /100 ml. Acid

Run No.	Concentration of H_2SO_4 — Wt. %	Aldehyde Produced		Per Cent Yield	
		g.	moles	Based on Propylene	Based on H_2SO_4
12	3	.12	.0021	12	29
13	5	.14	.0025	15	35
14	10	.23	.0041	24	58
15	15	.32	.0057	28	80
16	20	.25	.0044	25	62
17	20	.25	.0045	26	63
18	25	.07	.0013	7	18

Graph 3

Yield of acrolein
Absorption temperature 24.00



by observing free mercury in the reagent during steam-distillation and also appreciable quantities in the distillate. The tendency toward complete reduction of mercury seemed to be greater with more dilute mercuric sulfate and acid solutions.

Table 3 and Graph 3 present the per cent yield of acrolein from propylene produced by 5 g. mercuric sulfate per 100 ml. acid. The comments on the method of expressing the per cent yield apply to propylene as well as isobutylene. The mercuric sulfate shows the greatest activity with propylene in 15% sulfuric acid. The yield of acrolein is not so sensitive to changes in acid concentration as the yield of methacrolein. This is to be expected since branched-chained higher members of the series are more reactive.

To test the effect of the temperature at which the absorption of hydrocarbon in the reagent was performed, runs were made at 0° C. and at 60° C. to compare with the runs made at 24° C. The reagent contained 5 g. of mercuric sulfate per 100 ml. of 10% sulfuric acid. The results are given in Table 4 and Graph 4. As was expected the temperature did not change the results appreciably since the acrolein is formed during the steam-distillation process (see page 11). The yield based on mercuric sulfate increased slightly with increasing temperature, which indicates a greater activity of the mercury. The yield based on propylene decreased only slightly.

Since 28% yield of acrolein, based on propylene consumed, was the highest obtained, the question arose what products were formed from the remaining 72% of the hydrocarbon. Two possibilities were immediately suggested: hydration of the olefin to form the alcohol and polymerization to form higher-boiling polymers. To determine isopropyl alcohol

TABLE IV

Yield of Acrolein from Propylene at Various Absorption Temperatures

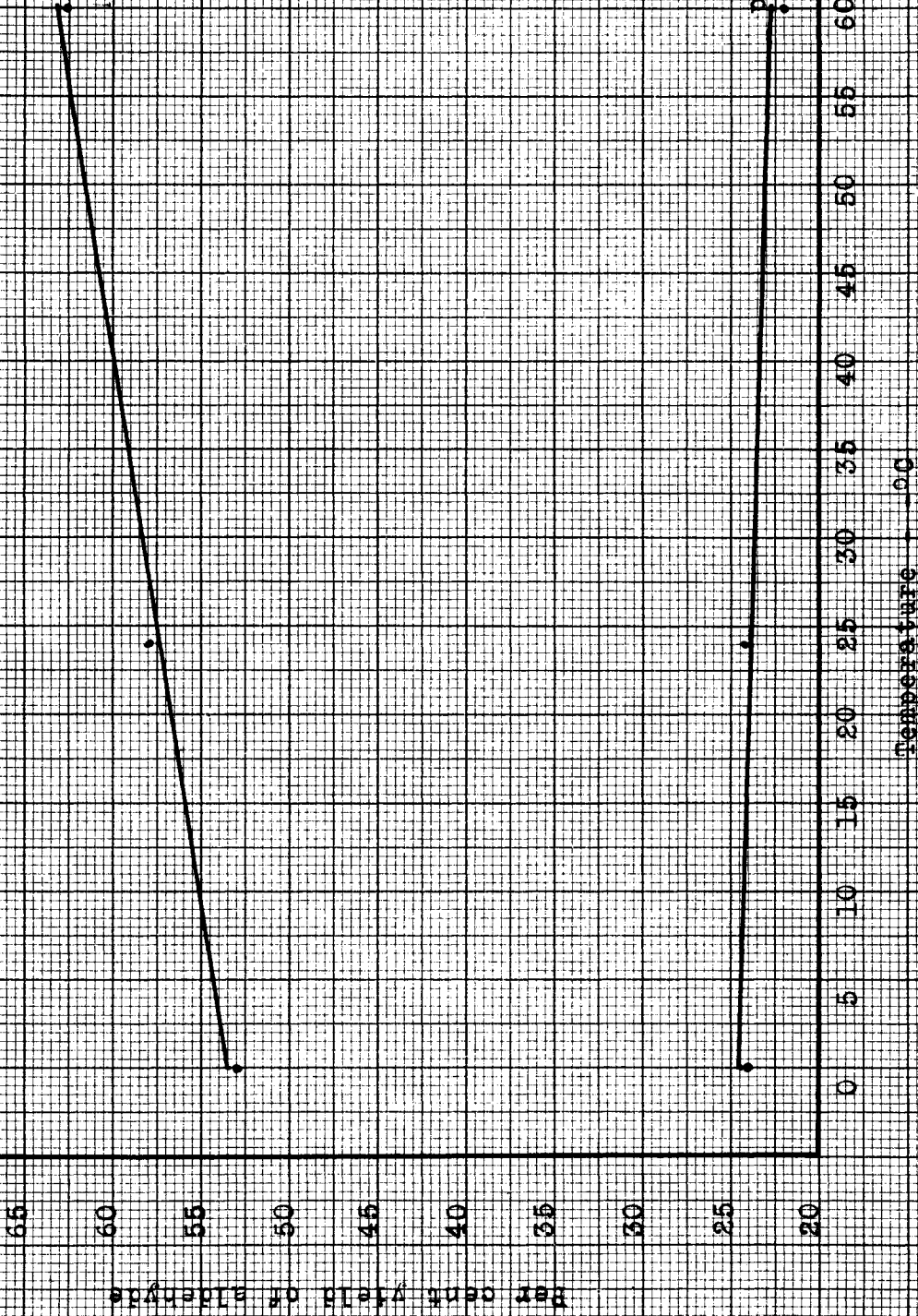
Reagent Concentration 5 g. H_2SO_4 /100 ml. 10% Sulfuric Acid

<u>Run No.</u>	<u>Temperature of Reagent</u>	<u>Aldehyde Produced</u>		<u>Per Cent Yield</u>	
		<u>g.</u>	<u>moles</u>	<u>Based on Propylene</u>	<u>Based on H_2SO_4 g</u>
18	0°C	.21	.0038	24	53
14	24°C	.23	.0041	24	58
19	60°C	.26	.0045	22	63

Graph 4

yield of acrolein
from propylene at varying
absorption temperatures

Based on H₂SO₄
5 g./100ml. 10% acid



Based on
propylene reacted

an aliquot of the distillate from the run with propylene using 5 g. mercuric sulfate per 100 ml. of 10% acid was analyzed according to the following method (22). For each 15 ml. of the aliquot were added 0.4 g. of powdered potassium dichromate and 3 ml. of 4% sulfuric acid. The solution was shaken until the potassium dichromate dissolved and allowed to stand for 24 hours. This oxidized the isopropyl alcohol to acetone. The solution was made slightly basic with 1 N sodium hydroxide and diluted with water to 5 times its original volume. The acetone was stripped out by transferring the entire solution to a 2-liter distilling flask and distilled until 250 ml. of distillate were collected. The cited literature described an iodoform method for the determination of the acetone content of the distillate, but the hydroxylamine hydrochloride method previously described in the present work was used. The quantity of alcohol so determined in two trials accounted for only an additional 1.7% of the propylene consumed.

The residue and distillate from steam-distillation of acrolein from the mercuric sulfate reagent were next analyzed for oils by ether extraction. An aliquot of each was shaken with ether in a separatory funnel and the ether layers evaporated at low temperature with a carrier gas. Only a slight indication of oil was present. It was therefore concluded that a negligible quantity of propylene had polymerized.

Since negligible hydration and polymerization indicated that the propylene was not converted directly to by-products, a test was made to determine if successive reactions between acrolein and mercuric sulfate were occurring. Pure acrolein obtained from the storeroom was distilled to remove the hydroquinone stabilizer. A quantity was dissolved in water and the concentration determined by the hydroxylamine hydrochloride

method. A known volume of this standard acrolein solution was added to the reagent which contained 5 g. mercuric sulfate in 100 ml. of 10% acid. The usual procedure of steam-distilling the acrolein from the mercuric sulfate solution was followed. The distillate was tested for acrolein with 2,4-dinitrophenylhydrazine and none was found present. This result shows that acrolein is so reactive that it cannot be removed from acid mercuric solution before much of it is destroyed by oxidation.

A quantitative run was made with a reagent composed of 5.1 g. of mercuric nitrate in 100 ml. of 10% nitric acid. The propylene was brought in contact with the reagent in the usual manner and then the reagent subjected to steam-distillation. The distillate gave no test for acrolein with 2,4-dinitrophenylhydrazine. Evidently acrolein cannot exist long in such a high concentration of nitric acid.

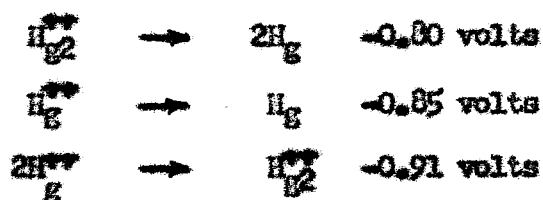
A quantitative run also was made using cyclohexane and 5 g. of mercuric sulfate in 100 ml. of 10% sulfuric acid. Exactly two ml. of cyclohexene were added to 170 ml. of the reagent, which was maintained at 90°C for an hour. The mixture was steam-distilled and the quantity of ketone produced determined by the hydroxylamine hydrochloride method. Since there are two possible ketones that can be produced by oxidizing cyclohexene, 2-cyclohexen-1, 4-dione and 2-cyclohexen-1-one, the 2,4-dinitrophenylhydrazine derivative of the product was prepared and recrystallized once from alcohol to determine which was the main product. The observed melting point was 155°C which compares to 163°C as reported in the literature (2) for the melting point of the 2-cyclohexen-1-one derivative. It was necessary to alter the procedure for determination of unreacted hydrocarbon since cyclohexane is a liquid. The method of Lewis and Bradstreet (24) was used for determination of total unsaturated compounds. To an aliquot of the steam distillate (taken after vigorous

shaking) were added 10 ml. of 10% sulfuric acid saturated with potassium bromide. Standard potassium bromate was added until a faint color of bromine persisted and an additional 1 ml. added in excess. Saturated potassium iodide was added and the liberated iodine titrated with standard sodium thiosulfate using starch indicator. From these data the moles of cyclohexene and 2-cyclohexen-1-one, present were calculated and the moles of 2-cyclohexen-1-one, as determined by the hydroxylamine method, subtracted to obtain moles of cyclohexene. The yield of ketone was 19% based on hydrocarbon consumed and 51% based on mercuric sulfate. This yield of ketone based on mercuric sulfate is fair but not as high as expected considering that the ketone, unlike acrolein, cannot be oxidized further at the carbonyl group; presumably the double bond of the hydrocarbon or the ketone is attacked by even mercurous sulfate; at least the residue from the steam-distillation had a very gray appearance due to the presence of an unusually large amount of free mercury.

DISCUSSION

Mercury salts are the only inorganic salts which will oxidize olefins to unsaturated carbonyl compounds. This property is unquestionably related to the tendency to form complexes with olefins. The carbonyl compounds probably result from decomposition of the complex in the presence of steam. In the case of cupric and ferric salts, both of which have oxidizing properties, there is no evidence of metal-olefin complexes in aqueous solution and neither will oxidize propylene.

The failure of ferric iron to oxidize propylene is probably not due to low oxidation-reduction potential. For the reaction $Fe^{+++} \rightarrow Fe^{++}$ the potential is -0.77 volts, which compares favorably to potentials of the following reactions:



Mercuric sulfate is superior to the nitrate in producing acrolein but none was produced with the chloride. Sand and Hofmann (32) prepared in alkaline solution mercury-olefin complexes of the composition $(CH_2)_2C:CH_2HgI$ and HOC_3H_5HgI and it was observed that when these complexes were acidified with 20% hydrochloric acid the olefin was regenerated. Deniges (6) isolated the complex $(3O_{1/2}H_gH_2O)_3R^u$, in which R^u represents the olefin; this complex also dissolved readily in hydrochloric acid. This indicates there is no tendency for complex formation with mercuric chloride in hydrochloric acid and consequently no carbonyl formation.

The stoichiometric equation for oxidizing propylene is based upon mercuric sulfate changing to mercurous sulfate. The mercurous sulfate which is formed possesses oxidizing properties and may

still react with propylene, acrolein, or carbon-carbon double bonds. That it does so is evident by observing free mercury in the residue and distillate of the steam-distillation step.

Macallum (25) claimed best yields of acrolein with acid concentrations ranging from 2 to 5% when mercuric sulfate concentration was about 25%. In the present work it was experimentally determined that highest yield was obtained in acid concentrations of 15% when mercuric sulfate was present in 5% concentration.

Herstein recommended sweeping the acrolein out of the reaction mixture with excess propylene at a temperature of 85°-105° C. This does not seem reasonable, since acrolein is not formed in any appreciable quantities during the heating of the reagent at 90° C. for an hour but only after the reagent is subjected to steam distillation and 10 to 25 ml. of distillate are collected. There appears to be no special advantage to absorbing the hydrocarbon in the reagent at any particular temperature below 90°, but it might be possible that effecting the absorption and reaction simultaneously at about 105° C. would decrease consecutive oxidation of the aldehyde and thus increase yields based on hydrocarbon.

Owing to the low yield of acrolein (28% maximum based on propylene consumed), the mercuric sulfate process does not seem economically feasible for commercial installation. The competitive process involving vapor-phase oxidation of olefins with air over silver selenite promoted with cupric oxide (5) appears much more attractive and is recommended for further study.

SUMMARY

The ability of various inorganic salts to oxidize unsaturated hydrocarbons to unsaturated aldehydes or ketones has been tested. Only mercury salts have this property, mercuric sulfate being most effective.

Quantitative yield data are presented for the conversion of propylene to acrolein, isobutylene to methacrolein, and cyclohexene to 2-cyclohexene-1-one. The variables investigated were concentration of mercury salt, concentration of acid, and the temperature of the absorbing reagent. Determination of some by-products is also reported. It was shown that the low yields based on hydrocarbon are due, not to hydration nor polymerization of the olefin, but to over-oxidation at either the carbonyl group or the double bond.

The low conversions of hydrocarbon to carbonyl compounds, the high cost of mercuric salts as oxidants, and the difficulty of regenerating mercuric sulfate combine to render the process of little commercial promise.

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AUTOBIOGRAPHICAL SKETCH

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