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Hydrogen Peroxide Laboratory
Massachusetts Institute of Technology
ONR Contract No. N5ori-07819

August 10, 1953

Figures 2,3, and 4 of report No. 38 entitled
"Separation of Hydrogen Peroxide from the Products of
the Partial Oxidation of Propane", may be missing in
the copy to you. This oversight is regreted and copies
of these figures are enclosed for attachment to the report.

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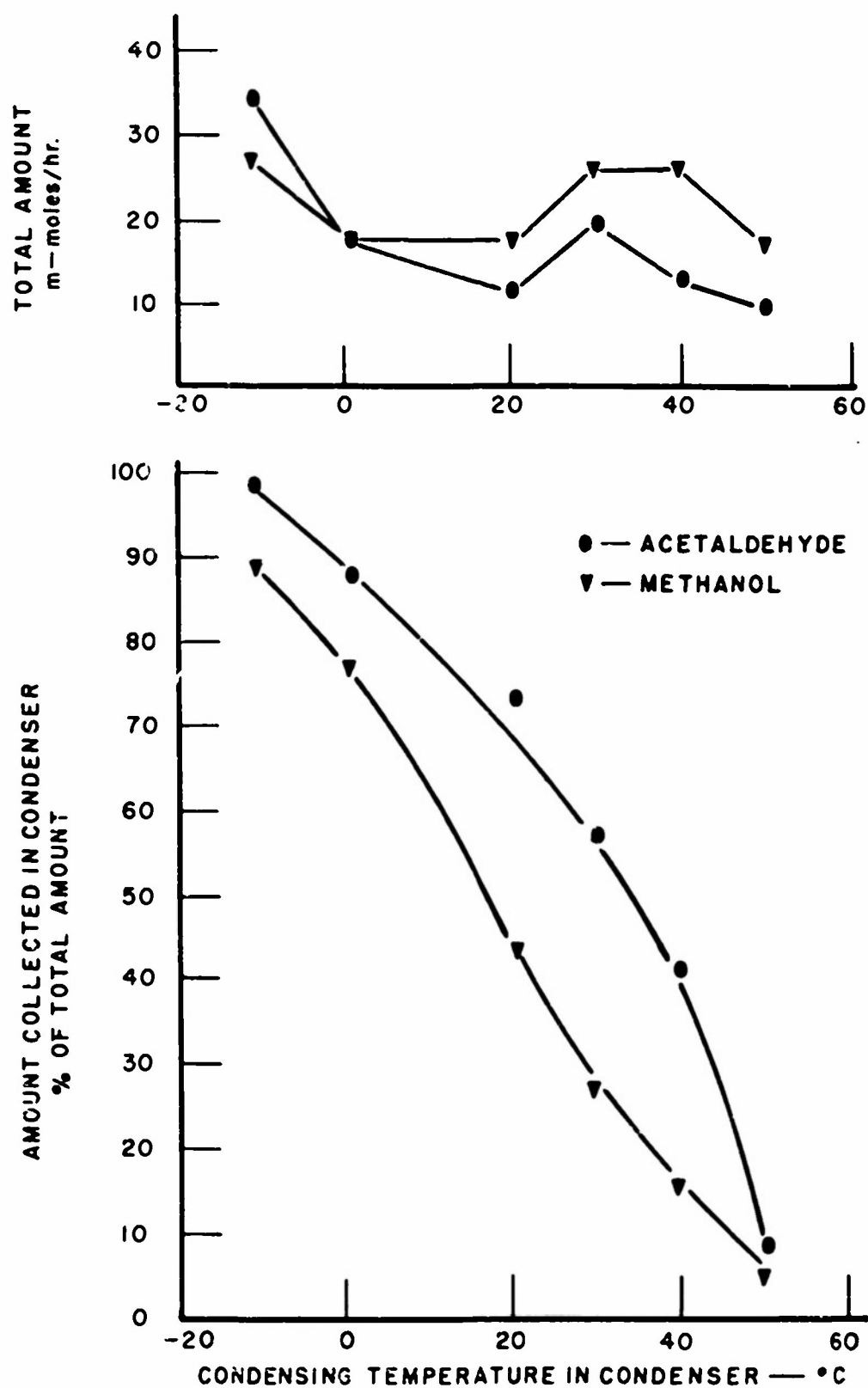


FIGURE 2
EFFECT OF TEMPERATURE ON AMOUNT OF
ACETALDEHYDE AND METHANOL COLLECTED

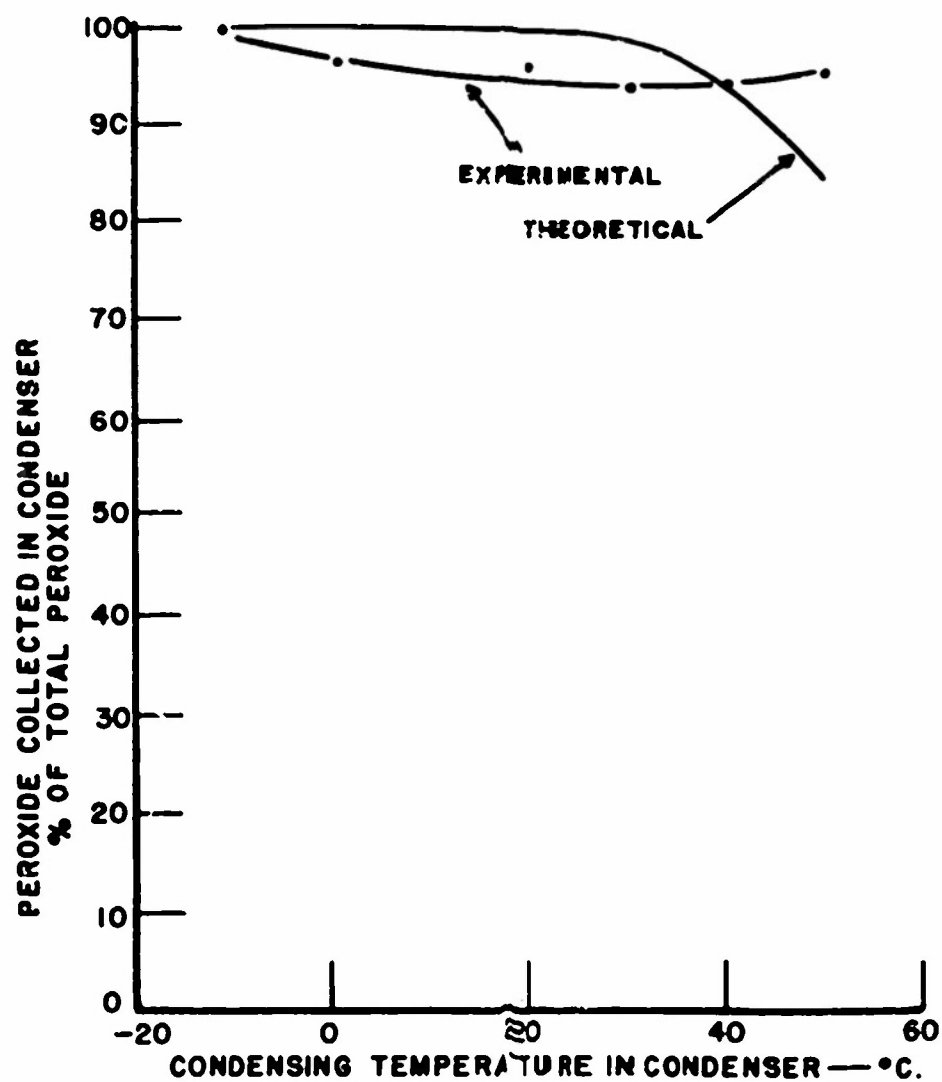
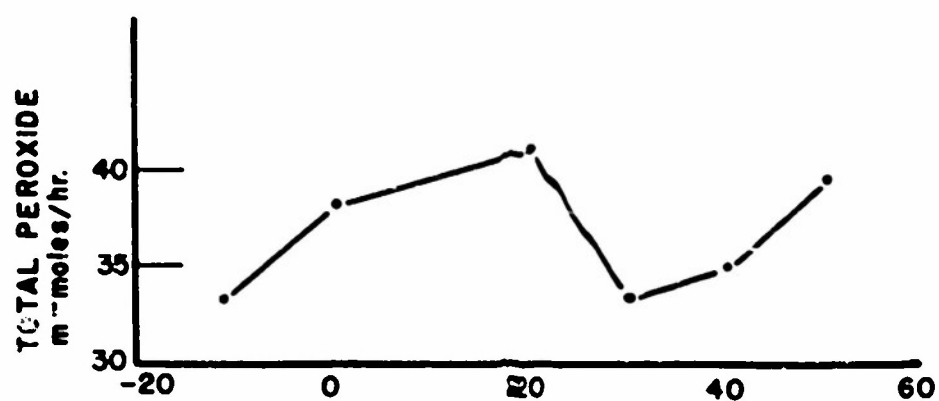


FIGURE 3
EFFECT OF TEMPERATURE ON AMOUNT OF
PEROXIDE COLLECTED

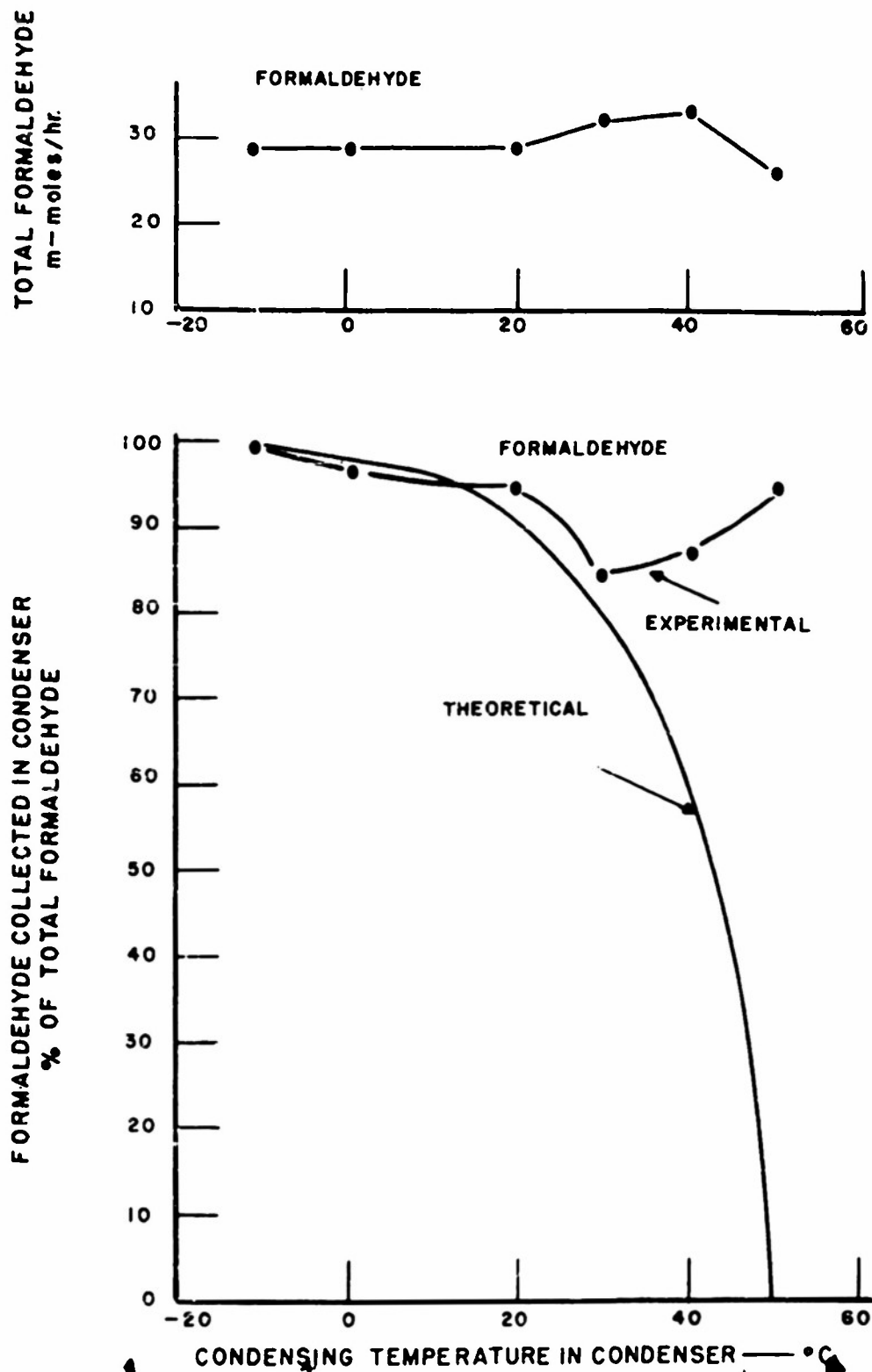


FIGURE 4
EFFECT OF TEMPERATURE ON AMOUNT
OF FORMALDEHYDE COLLECTED

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REPORT NO. 38

SEPARATION OF HYDROGEN
PEROXIDE FROM THE PRODUCTS
OF THE PARTIAL OXIDATION
OF PROPANE

Prepared for the
Office of Naval Research
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BY

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April 10, 1953

Separation of Hydrogen Peroxide from the
Products of the Partial Oxidation of Propane

by

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Abstract

Three methods were studied for separating hydrogen peroxide from the condensable product of the partial oxidation of propane, which forms an aqueous solution of hydrogen peroxide, formaldehyde, acetaldehyde, and methyl alcohol. The problem of separation is crucial in evaluating the possible industrial potentialities of the production of hydrogen peroxide by partial oxidation of hydrocarbons. One method, fractional condensation of the product gas mixture, gave partial separation, yielding a condensate composed chiefly of hydrogen peroxide, formaldehyde, and water. A second method, removal of formaldehyde from hydrogen peroxide-formaldehyde solutions by distillation, was hindered greatly by decomposition reactions. The addition of excess methyl alcohol

aided the removal, but not by the formation of methylal as had been previously reported. A third method, removal of hydrogen peroxide from the condensate by the addition of calcium hydroxide to form insoluble calcium peroxide, was satisfactory at low mole ratios of aldehyde to peroxide or in the absence of formaldehyde.

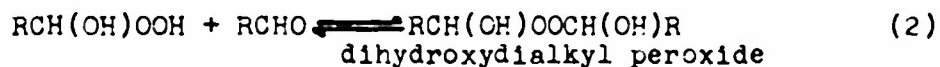
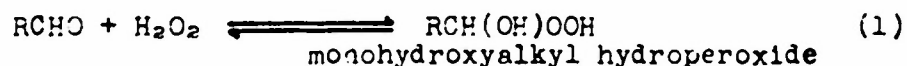
The results presented here have clarified the essential problems which exist in proposed separation procedures and suggest the directions in which future work should be concentrated.

Moderate amounts of hydrogen peroxide can be formed by the partial oxidation of a considerable number of hydrocarbons. At the same time various oxygenated hydrocarbons may also be formed, in addition to olefins and hydrocarbons of lower molecular weight than the starting material. For example, if propane is allowed to react with oxygen in a continuous-flow reactor, using propane : oxygen mole ratios greater than 4:1 at temperatures exceeding 450°C, rapid cooling of the product gas mixture to ambient temperatures after a few seconds reaction time yields a gas phase mixture plus a condensate consisting of an aqueous solution of hydrogen peroxide, formaldehyde, acetaldehyde, and methyl alcohol. A study of the formation of hydrogen peroxide by propane oxidation is reported elsewhere by the two senior authors of this paper (9). If the hydrogen peroxide thus formed could be easily separated from the organic components present, it is possible that partial oxidation of propane or other hydrocarbons might become of industrial interest as a manufacturing process for hydrogen peroxide. Therefore three different methods of separation have been investigated and are reported in this paper.

The separation of hydrogen peroxide from the condensed mixture is complicated by the fact that hydrogen peroxide reacts with the aldehydes present to form organic peroxides. Although the ratio of aldehyde to peroxide in the product gas can be varied somewhat by varying the reaction conditions, substantial

amounts of aldehydes are always formed under conditions yielding hydrogen peroxide. One method of separation studied was that of fractional condensation of the gaseous products from the reactor. A second method was the removal of the organic components from the condensate by distillation. A third method was the removal of hydrogen peroxide from the condensate by the addition of calcium hydroxide, forming calcium peroxide which is insoluble and therefore can be filtered out and then readily converted to hydrogen peroxide in a subsequent reaction. Each of these methods will be described in more detail below.

The reaction between hydrogen peroxide and an aldehyde proceeds in two consecutive, reversible steps:



The equilibrium constants for reactions (1) and (2) have been determined by Dunicz, Perrin, and Style (2) at 25°C for mixtures of formaldehyde and hydrogen peroxide and by Kooijman and Ghijsen (7) at 0°C for mixtures of formaldehyde and hydrogen peroxide, and acetaldehyde and hydrogen peroxide. The equilibrium constants reported by Kooijman and Ghijsen indicate that, if the mole ratio of initial aldehyde to peroxide in a 15 wt. % aqueous hydrogen peroxide solution exceeds 1.5:1, nearly all of the peroxide will be present as organic peroxide.

Thus, to attain high percentage recovery of hydrogen peroxide, it is necessary either to remove it before it can react with the aldehydes, or else to use techniques causing substantially complete reversal of reactions (1) and (2).

The reaction rate constants for reactions (1) and (2) were evaluated by Dunioz, Perrin, and Style (2) for formaldehyde - hydrogen peroxide mixtures. Calculations from their results show that formaldehyde and hydrogen peroxide react rapidly when present in a solution having the typical concentrations obtained from partial oxidation of propane. For example, in a 15 wt. % hydrogen peroxide solution containing initially a formaldehyde : hydrogen peroxide mole ratio of one, the uncombined formaldehyde is calculated to decrease to approximately one-half its initial value at the end of two minutes reaction at room temperature. The dihydroxydimethyl peroxide formed by the reaction of formaldehyde and hydrogen peroxide decomposes readily, especially in basic solution.



The reaction is unimolecular with a rate constant of $1.86 \times 10^{-4} \text{ min}^{-1}$ at 25°C in neutral solution. The activation energy is 24.9 kcal/gm. mole (2). At 25°C the half-life is therefore approximately 5400 minutes, while at 100°C the half-life is only 1 or 2 minutes. Results of the present investigation indicate that dihydroxydiethyl peroxide, formed from acetaldehyde-hydrogen peroxide reaction, is very stable to decomposition in neutral solution.

Fractional Condensation of the Products

The necessity of separating hydrogen peroxide from the condensate itself would be eliminated if the separation could be accomplished by a partial condensation process. The difficulties caused by reactions (1), (2), and (3) might thereby be alleviated. Harris (5) suggested that if the gaseous products of propane oxidation were passed through a condenser maintained at 40°C, an aqueous solution containing primarily hydrogen peroxide is obtained. Under these conditions the more volatile organic components would be expected to pass through uncondensed. The feasibility of this method was studied by making six runs in which the hot product gases from a reactor were passed through two surface condensers in series, the first being held at some fixed temperature in the range of -10° to + 50°C for each run, and the second being held at a constant temperature of -35°C for all runs. From the quantity and composition of the condensate collected in each condenser, the percent of each component formed which condensed in the first condenser could be calculated.

Experimental procedure: The equipment which was used has been described in an article on the partial oxidation process itself (9). The following reactor conditions were maintained for each run: inlet gas temperature, 472°C; propane: oxygen mole ratio, 8:1; residence time, 5 seconds. The condensate was analyzed for total peroxide, total aldehyde, formaldehyde,

and methyl alcohol by procedures developed for this system (10). A test of the condenser efficiencies using product gas containing only water vapor besides non-condensables, showed that for each condenser the partial pressure of the water vapor in the exhaust gas was reduced essentially to the equilibrium vapor pressure of water at the condenser-coolant temperature.

The results of the study are presented in Figures 1,2,3, and 4. The lower curves of the figures show the fraction of each condensable component which was recovered in the first condenser. The slight irregularity in the total amounts of the products recovered in the different runs, which is shown in the upper curves, was caused by slight variations from run to run in the inlet temperature and inlet flow rates in the propane - oxidation reactor, which affected the degree of reaction. The experimental data for water, hydrogen peroxide, and formaldehyde are each compared with a theoretical curve which was calculated from vapor-liquid equilibrium data. That for hydrogen peroxide is based on vapor - liquid equilibrium data for a hydrogen peroxide-water system (11), and that for formaldehyde is based on a formaldehyde - water system (12). The theoretical curve for water is based on vapor pressure data for water over condensate assumed to obey Raoult's Law for vapor pressure lowering.

It is seen that the percent of the total condensate which condensed in the first condenser decreased regularly from -10° to +50°C and at 60°C no condensate was obtained.

The amount of water condensed, shown in Figure 1, followed the trend calculated assuming establishment of vapor-liquid equilibrium at the exit of the condenser. The amounts of acetaldehyde and methyl alcohol condensed, shown in Figure 2, also followed a trend very similar to that of water, as would be expected. As can be seen from a comparison of the theoretical and the experimental curves in Figure 3, the hydrogen peroxide condensed in the first condenser, however, did not follow the theoretical curve. Above 30°C, the theoretical curve drops off rapidly whereas the experimental curve actually increases. The deviation of formaldehyde from its theoretical curve, shown in Figure 4, is even more marked, particularly above 30°C. The collection in the first condenser actually increased from 85% to 94% as the condensing temperature increased from 30° to 50°C. In summary these indicate that fractional condensation will separate acetaldehyde and methyl alcohol from the hydrogen peroxide, but will not produce a separation of formaldehyde, at least in the apparatus used here. As a specific example the condensate collected in the first condenser at 50°C coolant temperature had a composition of 23 wt. % hydrogen peroxide, 13 wt. % formaldehyde, 63 wt. % water, and less than one percent each of acetaldehyde and methyl alcohol. It is possible that the use of a condenser so as to cause a short residence time of the condensate may give better separation, as discussed

in more detail below.

Since hydrogen peroxide and formaldehyde show similar trends in Figures 2 and 3, one explanation of the experimental results is that these two compounds react, either in the gas phase or the liquid phase, to form hydroxyalkyl peroxides, as shown in reactions (1) and (2). These organic peroxides are presumably relatively non-volatile. If the hydroxyalkyl peroxides were formed in the gas phase, they would be expected to condense in the first condenser. If they were formed in the liquid phase, they would reduce the concentrations of uncombined hydrogen peroxide and formaldehyde and thereby reduce the vapor pressures of these two compounds over the condensate on the condenser surface, thereby leading to the same result.

The following investigation by Egerton, Harris, and Young (3) is of importance in considering the possibility of gas phase reaction of formaldehyde with hydrogen peroxide. Pure, crystalline dihydroxydimethyl peroxide was prepared, and the ultraviolet absorption spectra of its vapor was studied. Little or no dissociation of the vapor was detected at 105°C and a pressure of 15 mm. of mercury. The appearance of strong formaldehyde bands at 190°C indicated a large amount of dissociation at this temperature. Similar results were obtained with the acetaldehyde compound, dihydroxydiethyl peroxide. As

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reaction rate is faster under the present experimental conditions. This would be indicated by calculations from their data. Presumably acetaldehyde has a slower reaction rate with hydrogen peroxide than formaldehyde, and thus does not react with hydrogen peroxide while the condensate is on the condenser plate.

The possibility then arises that the separation of organic compounds by fractional condensation may be improved by removing the condensate from the condenser before the reactions of formaldehyde and hydrogen peroxide can occur. This could be effected by using a condenser of smaller diameter and shorter length and possibly adding water at a slow rate to help wash out the condensate rapidly. The minimum size of the condenser would be limited by the condensing efficiency desired. If these proposed techniques indeed gave better separation, it would strongly support the belief that the gas phase reactions of hydrogen peroxide with aldehydes do not occur during the partial oxidation of hydrocarbons, an important point in the theory of the mechanism of hydrocarbon oxidation.

The Distillation of Formaldehyde-Hydrogen

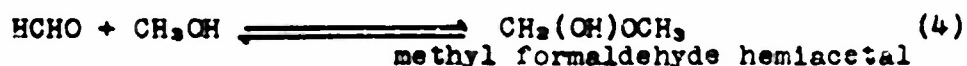
Peroxide Solutions

Upon first examination the process of distillation appears to offer some promise of separating the organic compounds from the condensate, for formaldehyde, acetaldehyde, and methanol

each have a lower boiling point than either water or hydrogen peroxide. However, the process would be greatly hindered by the fact that a considerable fraction of the aldehydes are present as hydroxyalkyl peroxides, which are presumably relatively non-volatile. Overhoff (8) reported that the addition of a large excess of methyl alcohol aided in the removal of formaldehyde from an aqueous solution initially containing formaldehyde and hydrogen peroxide. The methyl alcohol was presumed to have reacted with formaldehyde to form methylal, which being relatively volatile, distilled off. The present investigation was directed primarily at evaluating his proposal.

The investigation of fractional condensation methods discussed above revealed that condensates could be obtained containing primarily hydrogen peroxide, formaldehyde, and water. Thus the distillation studies were conducted on such an aqueous solution. Also, formaldehyde - hydrogen peroxide mixtures offered a more severe test of the practicability of a distillation process because of the instability of the hydroxyalkyl peroxides which are formed in this system. It was felt that if formaldehyde could be removed from hydrogen peroxide by a distillation process, it certainly would be feasible for solutions containing acetaldehyde and the other volatile organic compounds present.

The reaction between formaldehyde and methyl alcohol proceeds in two consecutive, reversible steps.



If the equilibria for these reactions lie very far to the right, the amount of formaldehyde combined with hydrogen peroxide would be reduced appreciably. Although reactions (4) and (5) have been investigated previously (1,4) no true equilibrium constants are known. The actual effects of adding methyl alcohol had to be determined experimentally.

Experimental procedure: Distillation was carried out in an apparatus consisting of a 1000-ml round-bottomed flask, topped with a distilling head containing a thermometer, but with no fractionation equipment. A tubular surface condenser was cooled with tap water during runs at atmospheric pressure, and with a methanol-water solution circulated through a bath containing solid carbon dioxide during runs at sub-atmospheric pressure. The initial and final bottoms were analyzed for total hydrogen peroxide (combined and uncombined), total formaldehyde, and acid. The distillate was analyzed for formaldehyde at the end of all runs and for acetal at the end of one run. The hydrogen peroxide was analyzed by a hydrogen iodide-glacial acetic acid method described elsewhere (10). The formaldehyde was determined using the alkali hydrogen peroxide method described

by Walker (12). Methylal was calculated as the difference between formaldehyde and the sum of methylal plus formaldehyde, the latter sum being determined by the alkali hydrogen peroxide method after first hydrolyzing any acetal present to formaldehyde and methanol. Acetals are stable in alkali hydrogen peroxide (1), but are rapidly hydrolyzed to equilibrium concentrations in acid solution. For each run the formaldehyde-hydrogen peroxide solution to be distilled was prepared by adding 37 ml. of 90% hydrogen peroxide to 112 ml. of water, followed by the addition of 68 ml. of 37% formaldehyde. This solution was allowed to stand at room temperature for several hours to permit reactions (1) and (2) to proceed to equilibrium. Prior to distillation, 18.5 ml. of concentrated sulfuric acid was added as a catalyst for acetal formation, and the solution was diluted to a total volume of 500 ml. with water or methyl alcohol. The solutions which were distilled all had the following initial compositions:

	<u>Dilution with Water</u>	<u>Dilution with Methyl Alcohol</u>
H ₂ O ₂	46.5 gms.	46.5 gms.
HCHO	26.0	26.0
CH ₃ OH	7	218
H ₂ SO ₄	32.5	32.5
H ₂ O	423	159
Total	<u>535 gms</u>	<u>482 gms</u>

The results of the distillation studies, which are presented in Table I, show the conditions existing after the collection of 250 ml. of distillate; at this point essentially one-half of the initial mixture had been distilled. For any one run, the difference between the sum of columns 6 plus 7 and 100 is the percent of formaldehyde disappeared, presumably by decomposition according to reaction (3).

To determine the effects of added methyl alcohol, distillations were performed at atmospheric pressure and the distillate was analyzed for methylal by the method described above. It is interesting to compare run 1, which had no added methyl alcohol, with run 2, which contained added methyl alcohol. The first observable effect was a reduction in the distillation temperature when added methyl alcohol was present. The analysis of the distillate revealed that the amount of formaldehyde volatilized doubled when methyl alcohol was present, but the bottoms also contained more formaldehyde. Evidently considerably less formaldehyde was decomposed by reaction (3), and as is shown in column 8, less hydrogen peroxide also decomposed. The analysis of the distillate from run 2 disclosed that, within an experimental error of 4% of the aldehyde present no methylal was found. Thus, contrary to the claim in the patent by Overnoff (8) it appears that methylal is not formed here and that the increased removal of formaldehyde in the presence

Table I

Distillation of Hydrogen Peroxide-Formaldehyde Solutions

Run	Pressure mmHg	Bottoms Temp. °C	Methyl Alcohol Initially Present gms.	Distillation Rate cc/min	% of initial HCHO found in distillate	% of initial HCHO found in residue	% of initial H ₂ O ₂ found in residue
1	760	100-101.5	7	4.2	25	1	35
2	"	68-83	218	5.0	53	32	66
3	"	62-80	218	1.9	49	20	58
4	190	40-51	218	2.5	19	62	84
5	15	19-25	218	1.8	1	7	84

of methyl alcohol is caused by other factors, as discussed below.

The increased quantity of formaldehyde found in the distillate of run 2 over that in run 1 is presumably due in part to a decreased rate of reaction (3) at the lower distillation temperature, and in part to an increase in the relative volatility of formaldehyde when methanol is present. This effect is illustrated by the following data on aqueous solutions at 20°C from Walker (12):

<u>Liquid-phase</u>		<u>Vapor-phase</u>
<u>Formaldehyde</u> <u>wt. %</u>	<u>Methanol</u> <u>wt. %</u>	<u>Formaldehyde</u> <u>Partial Pressure</u>
10.4	0	0.37 mm
10.4	61.5	1.16

It is interesting to compare run 3, which was conducted at a reduced distilling rate, with run 2. As would be expected, run 3 was accompanied by increased decomposition as a result of the increased time required for distillation.

The two runs, 4 and 5 were made at reduced pressure in order to lower the distillation temperatures. They resulted in an expected decrease in decomposition and also in a marked decrease in the amount of formaldehyde recovered in the distillate. Both these effects are presumably due to the lowered distillation temperature. Data presented by Walker

(12) show that the relative volatility of formaldehyde with respect to water decreases rapidly with decreasing temperature and therefore the removal of formaldehyde by distillation becomes more difficult at reduced distillation pressures. For example, a 6.82 wt. % aqueous formaldehyde solution at 20 mm Hg, approximately 20°C, is in equilibrium with a vapor containing 0.46 wt. % formaldehyde, while the same solution at 98°C forms a vapor containing 6.95 wt. % formaldehyde.

It is seen that the most important operational variable in the distillation of formaldehyde-hydrogen peroxide solutions is the temperature of distillation. A high temperature gives a high relative volatility of formaldehyde but also a high rate of decomposition. As the temperature decreases both the relative volatility and the decomposition decrease. It therefore appears that an optimum temperature exists, but it is doubtful that even the optimum temperature will produce an economical separation. These studies also suggest that the benefits gained by adding methanol result mainly from a reduced distillation temperature and partly from an increase in the formaldehyde relative volatility rather than from methyl formation. It is therefore likely that if this type of separation were to be considered most of these same benefits could be gained more economically by distilling the formaldehyde-hydrogen peroxide solution at subatmospheric pressures without

added methyl alcohol.

Precipitation of the Peroxide as Calcium Peroxide

Kooijman (6) has set forth a method for converting hydroxy-alkyl peroxides, such as are formed by reactions (1) and (2), to alkaline earth peroxides, which precipitate and can be filtered from the solution and then converted to hydrogen peroxide by treatment with acid. Both barium and calcium hydroxide form relatively insoluble peroxides.



Calcium hydroxide was used in the present study, however, because of the possibility of recycling the calcium compounds in an industrial process. For example, once the calcium peroxide has been filtered from the solution, it can be made into a slurry and the hydrogen peroxide regenerated by introducing carbon dioxide.



The calcium carbonate could be filtered from the slurry and then calcined to calcium oxide, which after slaking is ready for reuse in the precipitation step, reaction (6). Although barium hydroxide could be used in a similar manner, the calcination of barium carbonate is substantially more difficult than that of calcium carbonate. The process of calcium peroxide precipitation was studied using aqueous solutions containing hydrogen peroxide plus either formaldehyde alone, acetaldehyde alone, or else mixtures of the two aldehydes. The actual

product from the partial oxidation of propane was employed for two tests.

Experimental procedure: Fifty milliliters of aldehyde - peroxide solution, containing approximately 50 millimoles of total peroxide, was placed in a 300-ml round-bottomed flask immersed in ice water. Into this flask was introduced 100 ml. of calcium hydroxide slurry, containing 20% excess over the stoichiometric amount needed to react with the peroxide present. The slurry was added slowly, in 3 ml. increments, over a period of one and one-half hours, with constant agitation by a motor driven glass rod stirrer. The resulting slurry was maintained at about 0°C with slow stirring for an additional three hours. The contents of the flask were then filtered. The precipitate was dissolved in 2 N hydrochloric acid and analyzed for the hydrogen peroxide formed from the calcium peroxide. The filtrate was acidified and analyzed for the residual peroxide content. The difference between the sum of these two determinations and the initial hydrogen peroxide content is reported as the amount of peroxide destroyed. Two different methods were employed for peroxide analysis with equivalent results; in the first method, the hydrogen peroxide was titrated with standard potassium permanganate; in the second, excess potassium iodide was added and the iodine released was titrated with standard sodium thiosulfate. The procedures for the latter method are described in detail by Kooijman and Ghijsen (7)..

The results of the investigation are presented in Table II. The initial peroxide and aldehyde contents are given, and in addition the mole ratio of total aldehyde: total peroxide is listed. For solutions containing only hydrogen peroxide and acetaldehyde, approximately 90% of the initial peroxide content can be precipitated as calcium peroxide. It is important to note however, that for solutions containing only hydrogen peroxide and formaldehyde, the recovery was very low. Two additional observations should be noted in order to explain the difference between hydrogen peroxide-acetaldehyde solutions and hydrogen peroxide-formaldehyde solutions. First, Kooijman (6) reported that the precipitate corresponded to the formula of the octahydrate of calcium peroxide, which suggests that no organic peroxide is precipitated and that the calcium hydroxide reacts only with hydrogen peroxide. Second, it was noted here that essentially all of the peroxide not precipitated as calcium peroxide was destroyed by decomposition. The high recovery of calcium peroxide obtained from solutions of acetaldehyde and hydrogen peroxide indicates that the hydroxy-alkyl peroxides formed from acetaldehyde and hydrogen peroxide are relatively stable to decomposition under the experimental conditions. The rate of the reverse of reactions (1) and (2), at least for acetaldehyde, is evidently rapid relative to the time of contact of the calcium hydroxide with the slurry. However, the low yields of calcium peroxide obtained from solutions of

Table II

The Precipitation of Calcium Peroxide from Aldehyde-Peroxide Mixtures

Sample	Peroxide m.mole/gm	HCHO m.mole/gm	CH ₃ CHO m.mole/gm	Mole Ratio aldehyde/ peroxide	% of Initial Peroxide Recovered as CaO ₂	% of Initial Peroxide Destroyed
Synthetic	1.24	0	2.58	2.08	84.0	12.2
"	1.44	0	2.85	1.98	91.3	7.2
"	1.75	0	0.75	0.43	90.2	5.5
"	1.48	0	0.62	0.42	88.0	8.1
"	1.35	0	0.72	0.53	91.2	5.0
"	2.10	0	0.68	0.32	92.3	5.4
"	1.38	0	1.60	1.18	89.5	4.4
"	1.38	1.50	0	1.09	0	*
"	1.65	2.18	0	1.32	34.2	*
"	1.85	2.15	0	1.17	51.8	47.7
"	1.23	1.88	1.32	2.60	29.3	70.7
"	1.40	0.92	0.64	1.10	74.2	25.8
Propane Oxidation	3.18	5.18	3.32	2.67	0.2	99.7
"	2.03	1.16	1.61	1.36	56.5	43.5

* Not determined

formaldehyde and hydrogen peroxide indicates that the hydroxyl alkyl peroxides formed here are unstable and decompose before reactions (1) and (2) can shift to the left. Another indication of the relative stability of acetaldehyde-hydrogen peroxide solutions compared with formaldehyde - hydrogen peroxide solutions is given by the data presented in Table III which were obtained by allowing the two different solutions to stand at room temperature for a number of days. These data demonstrate not only the relative stability of acetaldehyde - hydrogen peroxide solutions, but also that both aldehyde - peroxide solutions are much more stable in neutral than in basic media.

From the above discussion it would be expected that solutions containing both aldehydes and hydrogen peroxide would give lower recoveries than solutions with only acetaldehyde and hydrogen peroxide, and higher recoveries than solutions with only formaldehyde and hydrogen peroxide. The data in Table II indicate that this is the case, if the data are compared at approximately the same mole ratio of total aldehyde : total peroxide. This ratio is an important factor in determining the fraction of the total peroxide which is combined with aldehydes. The higher the ratio of total aldehyde: total peroxide, the lower is the recovery of calcium peroxide. For example consider only the data obtained on the product of propane oxidation; for an aldehyde: peroxide ratio of 2.67:1 the recovery was 0.2%, for a

Table III

Relative Stability of Aldehyde-Hydrogen Peroxide Solutions

Formaldehyde
Hydrogen peroxide = 1.21

Acetaldehyde
Hydrogen Peroxide = 1.35

Initial H_2O_2 = 8.24 wt. %

Initial H_2O_2 = 5.57 wt. %

% of Initial H_2O_2	Time (days)	% of Initial H_2O_2
100.0	0	100.0 %
99.8	0.25	99.6
97.5	1	99.8
87.0	2	99.1
73.3	3.2	98.8
50.1	8.17	99.1
46.3	9.12	
22.1	16.17	99.8
12.5	23.0	99.3
5.8	32.0	99.4

ratio of 1.36:1 the recovery was 56.5%, for a ratio of one:one the recovery has been reported to be 75 to 80% (5), and for a ratio of approximately 0.75:1 the reported recovery was 96% (6). These results substantiate the suggestion made above, that the calcium hydroxide reacts primarily with the hydrogen peroxide present and only slightly, if at all, with the hydroxyalkyl peroxides.

Summary

It was found that the principal problem in the separation of hydrogen peroxide from the organic products formed in the partial oxidation of propane is caused by the presence of formaldehyde, which reacts rapidly with hydrogen peroxide to form unstable hydroxyalkyl peroxides. Although the ratio of hydrogen peroxide to formaldehyde in the product of a partial oxidation reaction is partly determined by the particular hydrocarbon specie oxidized, and also by the oxidation conditions, some quantity of formaldehyde will probably always be present under conditions yielding hydrogen peroxide.

The above work suggests that the most promising methods of separation would be ones in which the hydrogen peroxide and formaldehyde are removed from one another before they have sufficient time to react. This might well be accomplished by either fractional condensation of the product gases in a condenser with a short condensate residence time or total condensation at a low temperature. If the latter method were

used the condensate would have to be treated immediately to separate the hydrogen peroxide. It is seen that the peroxide could also be separated as an insoluble salt, calcium peroxide.

A solvent extraction process might be feasible to remove the organic compounds from solution before appreciable association of aldehydes with hydrogen peroxide had occurred. Alternately, it is possible that solvent extraction could be employed under conditions in which the hydroxyalkyl peroxides are stable, and which permit reactions (1) and (2) to reverse.

Acknowledgment

Some of the experimental data reported in Table II are taken from the M. S. thesis of Mr. R. M. LeClair, M.I.T., 1951.

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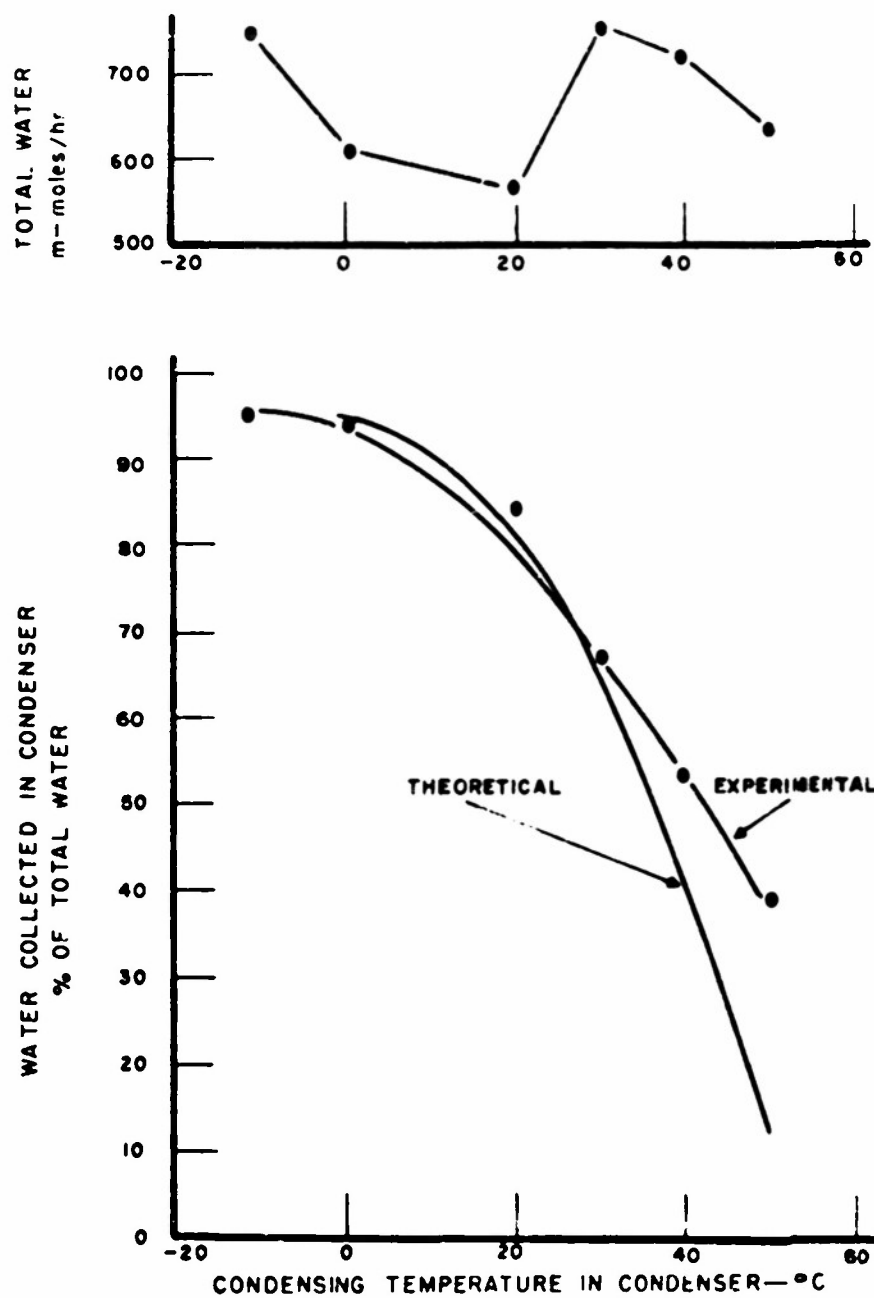


FIGURE 1
EFFECT OF TEMPERATURE ON AMOUNT
OF WATER COLLECTED