ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

Final Report

EFFECT OF OZONE UPON FLAME SPEEDS OF SOME COMBUSTIBLE MIXTURES

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Project 2279

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March 1957

FOREWORD

This report describes the continuation of a study of the effects upon combustion resulting from the addition of small amounts of ozone to gaseous mixtures. It covers the work done between January 1, 1956, and January 31, 1957. The previous work had been conducted from May 5, 1954, to July 14, 1955, and has been discussed in ARDC Technical Report No. OSR-TN-55-227, by Martin E. Gluckstein, Richard B. Morrison, and Tariq B. Khammash. That work, as well as its presently reported extension, had been engaged under the terms of Contract No. AF 18(600)-1186, Air Research and Development Command, U. S. Air Force. Dr. Richard B. Morrison has continued as local supervisor of the project, known to the Engineering Research Institute as No. 2279. Mr. Gluckstein, who was project leader in the previous work, continued as such on the present extension, but found it necessary to limit his activities because of other commitments. In the month of December, 1956, Mr. Gluckstein resigned his appointment with the Engineering Research Institute to accept a position with the Ethyl Corporation, 1600 West Eight Mile Road, Ferndale 20, Michigan, where he may now be reached.

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SUMMARY

A study was made of the effect of ozone addition in amounts up to three percent of total mass flow upon the flame speeds of propane, hexane, and carbon monoxide burned with air. It was found that in the combustion of all three fuels the effect of ozone was to increase flame speed. Some specification is made as to the possible mechanism of the observed effects. A qualitative examination was also made of the pre-flame reaction product of ethylene and an air-ozone mixture. Resulting from this, an additional discussion is presented of the possible mechanism that causes decrease in the flame speed of ethylene-air mixtures when ozone is added. The latter phenomenon had been observed in a previously reported phase of the present project.

OBJECTIVE

The objective of the project was to determine the effect of addition of ozone in small amounts on the flame speeds of combustible gas mixtures. It was also desired to attempt an explanation of the observed results.

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12. Abstract: A study was made of the effect of ozone addition in amounts up to three percent of total mass flow upon the flame speeds of propane, hexane, and carbon monoxide burned with air. It was found that in the combustion of all three fuels the effect of ozone was to increase flame speed. Some specification is made as to the possible mechanism of the observed effects. A qualitative examination was also made of the pre-flame reaction product of ethylene and an air-ozone mixture. Resulting from this, an additional discussion is presented of the possible mechanism that causes decrease in the flame speed of ethylene-air mixtures when ozone is added. The latter phenomenon had been observed in a previously reported phase of the present project.

INTRODUCTION

This study of the effect of ozone addition upon the combustion of gaseous mixtures was originally inspired by the desire to define some characteristics of power plant operation in the ozone layer of the atmosphere at high altitude. It was thought that ozone, being at a comparatively high energy level, would give rise to an improvement in flame characteristics through its inclusion in a combustible mixture. During the period of the original contract, studies were made of flame speeds in the combustion of acetylene, ethylene, and ethane.[1] Superimposed photographic comparisons were made with both (1) no conversion of the air to ozone and (2) conversion of air to ozone in the amount of about one percent by weight. In general it was found, at least qualitatively, that the flame speed was increased in the combustion of ethane and that it was decreased in the combustion of acetylene and ethylene. A tentative explanation of the results obtained was that two different types of mechanism were involved in the opposing results. In the first case—increase of the ethane-air flame speed—it was concluded that the ozone effectively assumed the role of an atomic oxygen "donor," thus enhancing the reaction in those steps of the normal reaction scheme where atomic oxygen is of significance. The second case—decrease in flame speed of acetylene or ethylene with air—was accounted for by the possibility of ozonide formation and subsequent decomposition in the mixing section of the burner assembly.

As a result of the observed effects it was decided to extend the time and funds for the project in an attempt to determine more conclusively the type of phenomena that take place. These determinations were to take the form of possbily more accurate flame speed measurements, and also of measurements of changes in stability limits and pressure drop across the flame front under the influence of ozone. In addition, attempts were to be made to verify the supposition that ozone reacts with ethylene prior to passage through the flame front.

It was decided during the dourse of the project to dispense with the studies of stability limits and pressure drop across the flame front. The reason for this is given in the text of the report.

The report, then, is concerned (1) with the results of studies of the reaction of ethylene with ozone prior to the flame front, (2) with the study of the effect of ozone addition upon the flame speeds of propane, hexane, and carbon monoxide, all burned with air, and (3) with conjectures which may be made concerning the observed results.

APPARATUS AND METHOD

OBSERVATION OF ETHYLENE-OZONE REACTION

The reaction between ethylene (C.P.) and ozone was qualitatively observed by bringing the ethylene and ozonized air streams together in a glass reaction chamber. This chamber, a drawing of which is shown in Fig. 1, was equipped with a series of sampling ports equally spaced along its length. Exhaust products from the reaction were removed at the top of the chamber and carried through about 20 ft of Tygon plastic tubing to an exhaust blower, where they were discharged into the atmosphere. The length of tubing was necessitated simply because the exhaust blower could not be properly placed with the test equipment.

In conjunction with visual observation of the reaction, samples were drawn off at the various ports and subjected to the Fehling test for aldehydes. A positive test could provide only an inference of the presence of ozonide, since it is known that ethylene ozonide decomposes to formaldehyde as one of its products in the presence of water. Continuous operation of the apparatus resulted in enough accumulation of a liquid reaction product, thought to be ethylene ozonide, so that this material could be collected for further qualitative examination. A period of operation of two or three hours enabled the collection of several ml of the liquid. Further details of this experiment are covered in the discussion section of the report.

FLAME SPEED DETERMINATIONS

The reader is referred to Figs. 2 and 3 which are drawings of the burner assembly and of the overall system, respectively. The fuels selected for study were propane, hexane, and carbon monoxide. It is pointed out that propane is gaseous under normal atmospheric conditions, while hexane is normally liquid. The fuel under consideration and the air, or air-ozone mixture, were brought together at the base of the mixing chamber, and the total mixture was ignited at the burner nozzle by means of an electric arc. After stabilization of the flame, a photograph was taken and readings were made of the metering pressures and temperatures of the two streams, and of the burner-head temperature. This was done for a sequence of pictures first, when no ozone was present in the mixture, and then in the presence of increasing amounts of ozone.

In the combustion of propane, air was taken from 2000-psi steel cylinders through a reducing valve and, after being passed through a chemical drier, was fed to a Welsbach Model T-23 laboratory ozone generator. In this experiment it may or may not have been partially converted to ozone accordingly as desired.

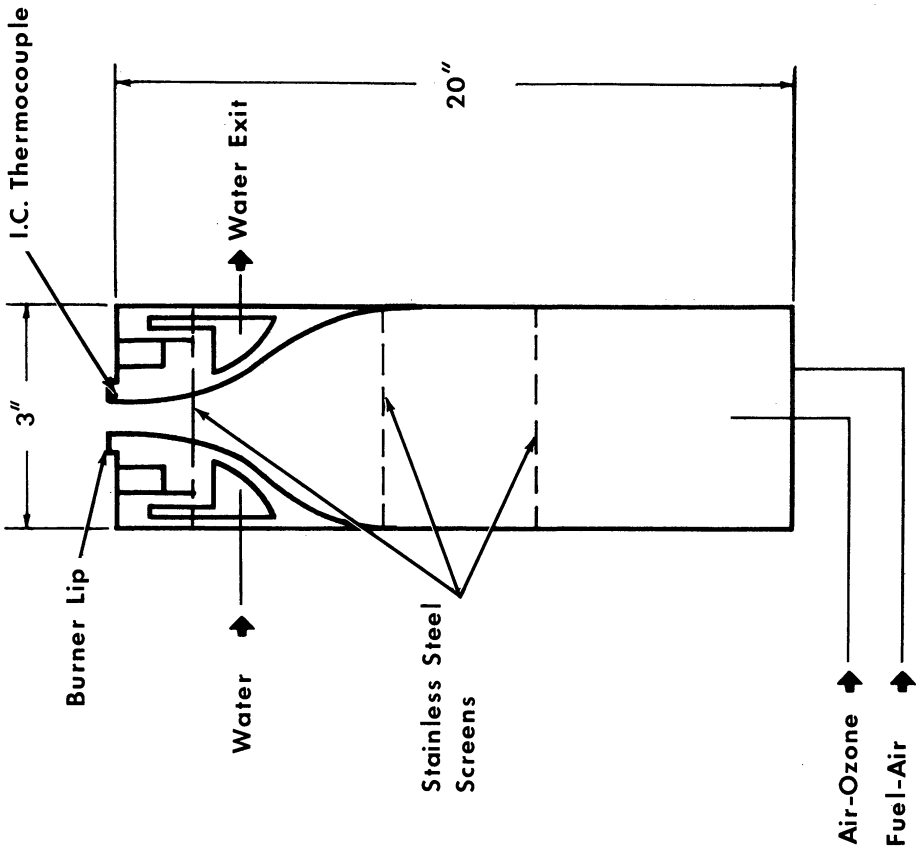

Fig. 2. Cross-sectional view of burner.

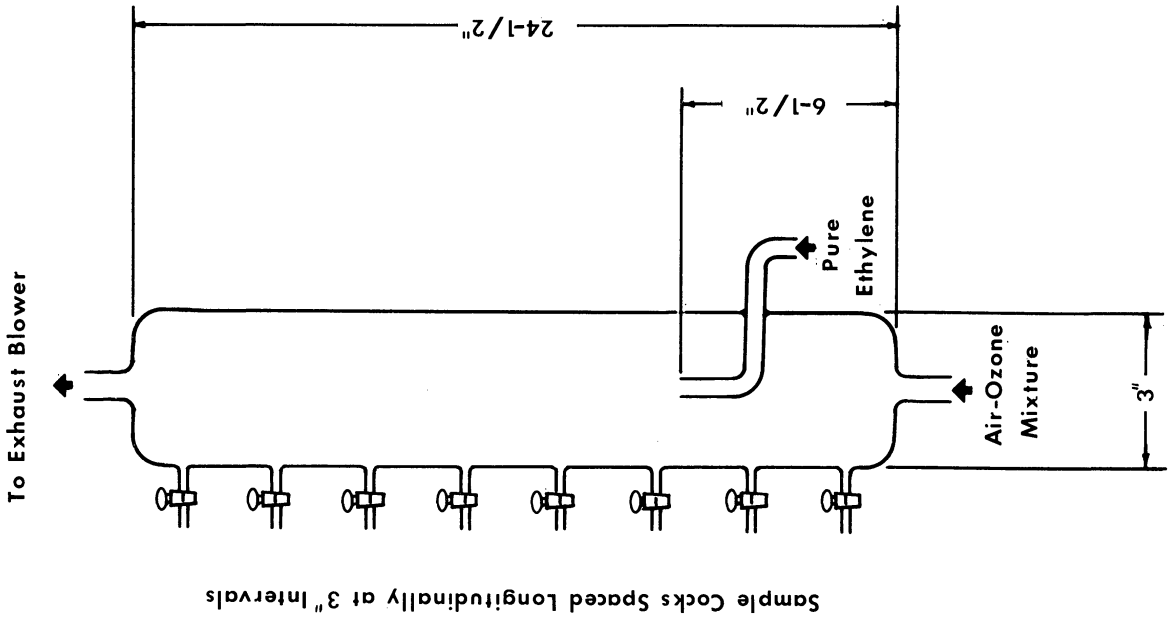

Fig. 1. Glass reaction chamber used for observation of reaction between ethylene and an air-ozone mixture.

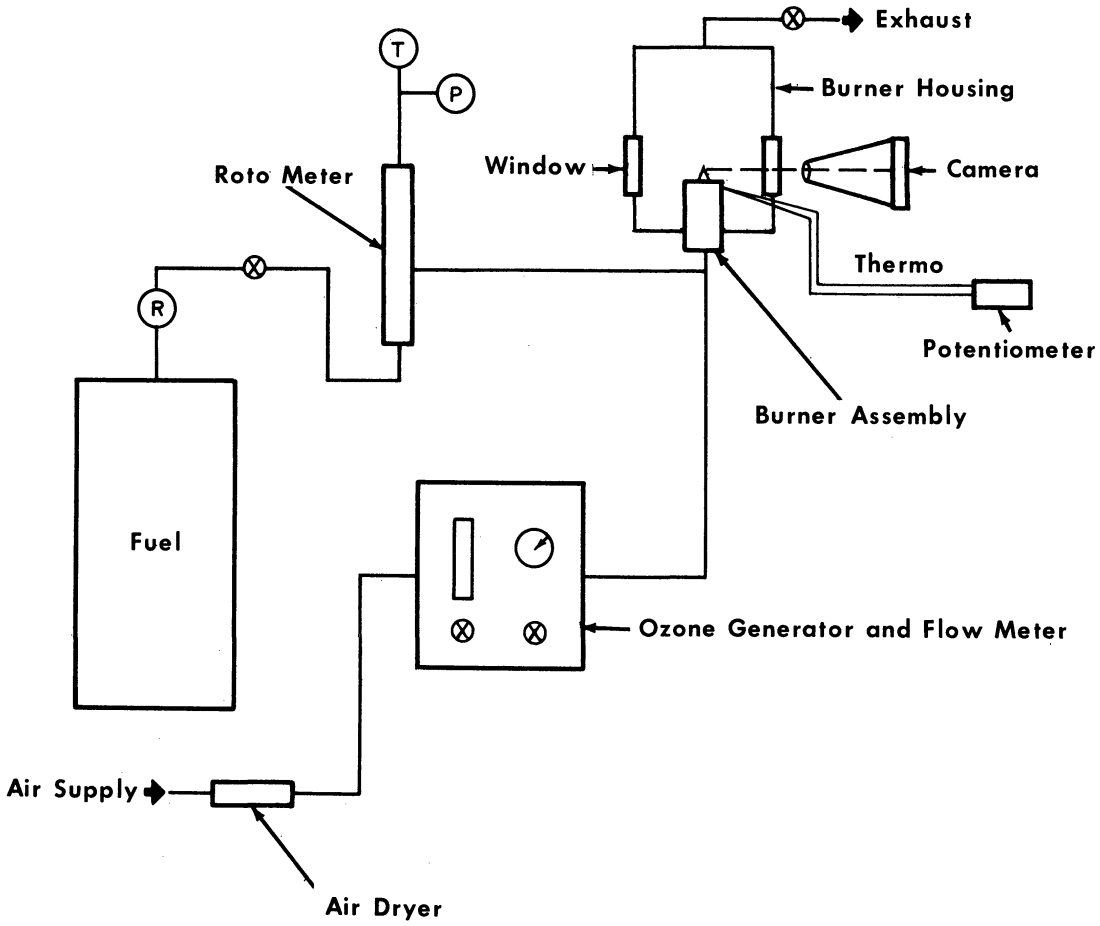

Fig. 3. Schematic diagram of equipment for propane runs.

Upon leaving the ozonator, the air stream was then passed on to the mixing chamber as stated above. Metering of the air stream was done with a rotameter which was integral with the ozonator itself. Ozone concentration in the air stream was governed by regulation of applied voltage drawn off the building's 120-volt supply line. Maximum concentration of ozone by weight resulting from conversion of oxygen was from 1.5 to about 3.0 percent in the air stream, depending upon the flow rate of the air stream. Tubing for the air stream was of copper between the supply source and the ozonator, while ozone-resistant Tygon plastic tubing was used between the ozonator and the burner itself. Chemically pure propane was taken from a steel storage cylinder through a reducing valve, passed through a rotameter for flow rate measurement, and then brought to the mixing chamber of the burner.

For the combustion of hexane, which is a liquid fuel under normal atmospheric conditions, the system was altered in the following manner. About 400 cc of 95% hexane liquid was placed in a glass absorption tower, and part of the air stream was diverted to pass through the tower and liquid, thus becoming saturated with hexane vapors. The absorption tower was operated at controlled temperature and pressure so that the saturated humidity ratio of the exit stream

could be calculated at any time. This hexane-air stream was then brought to the mixing chamber of the burner where it was combined with the main air stream which had been brought through the ozonator. Knowing the saturated humidity ratio, the total mass and volume flow through the absorber, and the total mass and volume flow through the ozonator, the fuel-air ratio and total volumetric flow rate could be readily calculated and controlled.

The combustion of carbon monoxide involved one change from the propane system. This consisted of the insertion of a quartz tube filled with alumina chips in the fuel line immediately after the point of withdrawal of the fuel from the steel cylinder. The tube and cylinder were heated, and were very effective in removing iron carbonyl particles from the fuel stream, which had been present as a result of solvent action of carbon monoxide on the walls of the storage cylinder. This step was necessary to eliminate a strong luminosity from the flame front which existed under ozonized conditions as a result of the presence of the particles. After removal of the carbonyl particles from the fuel stream, the latter was passed through the flow meter apparatus and then to the burner's mixing chamber, where it was combined with the air stream.

If pressures and temperatures were closely regulated, and if bone-dry air was fed into the ozonator, it was found that ozone concentrations were readily reproducible as functions of applied voltage and volumetric flow rate. Therefore these concentrations were determined, and charts were made wherein the percent concentration by weight was plotted against volumetric flow rate in a series of curves representing various constant applied voltages. Once having been made, the charts were used to read directly the ozone concentration in a given run. In constructing the charts, ozone concentration was determined by absorbing the ozone in a two-percent potassium iodide solution and titrating with 1/10 normal sodium thiosulphate, using starch as an indicator.

The stainless-steel burner and mixing chamber are shown in longitudinal section in Fig. 2. The converging-nozzle type of burner head is threaded so that it may be removed from the mixing chamber, thus permitting the use of a series of nozzles interchangeably on the same burner. These nozzles range in cross-sectional lip diameter from 3/16 in. up to 1-1/8 in. In all propane and hexane runs a 3/8-in. nozzle was used, and in the carbon monoxide runs a 1/4-in. nozzle was used.

The gaseous mixture was ignited with the use of a continuous spark which was generated with the aid of a spark coil. The electrodes consisted of a movable heavy iron wire and of the burner head itself. While combustion was taking place, the burner head was cooled by means of water circulation through the annular section at the top of the burner assembly.

The burner assembly was enclosed by a cylindrical chamber having two removable heavy glass windows through which the flame could be observed and photographed and a valved exhaust port at the top. The latter could be left

open or closed, as desired. The window through which the photographs were taken was equipped with an electric heating element which was effective in keeping the interior surface clear of moisture of combustion. Pictures were taken of each run on Eastman Kodak Tri-X Safety film, for which an exposure time of 1/25 sec and a stop setting of f16 were found to be satisfactory. Only one run was included on each picture, thus eliminating possible confusion in flame surface area measurement.

After a picture had been taken and developed, it was placed in a slide projector and the enlarged image was traced upon a sheet of vellum drawing paper. Since the lip of the burner head showed up readily in the photographs, its outside diameter was measured with a micrometer and this was used as a gauge for converting the areas measured on the enlarged drawings down to the normal scale. Having obtained the flame surface areas in this manner, using the method of conical sections, and having determined the volumetric flow rate from the data which were recorded, it was now possible to calculate the average flame speed by the relationship $v = Q/A$. Here, v is the average flame speed, Q is the volumetric flow rate of the gases at the burner exit, and A is the area of the conical surface of the flame.

Finally, the percent increase in flame speed over the no-ozone condition was calculated for the various runs, and these were plotted against the percent by weight of ozone present in the air stream. The curves that are shown were simply estimated visually as best-fit, since it is desired only to infer a trend of the data rather than to establish any mathematical relationship.

Originally it had been planned to take measurements concerning the effect of ozone addition upon pressure drop across the flame front and upon the blow-off limits of the mixture. It became apparent, however, that any data of this type taken from the system as it existed would be quite without meaning. Fluctuations in the system together with the time periods involved in measuring the extremely small differences at the various points would preclude obtaining the precision that was required. It is pointed out that the pressure drop across the flame front is related to the flame speed^2 and, therefore, predictions can be made about the effect of ozone on the pressure drop. It was decided to omit these observations until such a time as the system could be better stabilized, taking the obtaining of more precise flame speed data as the criterion of stability. The stability that was thought to be desirable was not attained and so the observations were not made.

NOTES ON THE EXPERIMENTAL PROCEDURE

Although the considerations upon which the design of the experiment was based are simple, it was found that construction of the experimental equipment was faulty in several respects.

Since the experiments were to be carried out in a rather large room which also houses several other projects, it was decided to enclose the burner in a chamber that would protect the flame from stray air currents. It was felt that this same chamber could then be used in regulating the external pressure around the flame by operation of a connected vacuum pump. Unfortunately, the relative geometry of the burner assembly and the enclosing chamber turned out to be such that resonance effects were induced under certain conditions. This resulted in oscillation of the flame front, and in extreme cases "singing flames" were produced. In addition the flame was very sensitive to external noises emanating from various parts of the laboratory. These phenomena made it impossible, of course, to obtain proper photographic data. Insertion of fine-mesh metal screens at various levels in the burner's mixing section resulted in substantial elimination of resonance effects for most operating conditions. But this contributed nothing toward the elimination of sensitivity to externally produced sound waves. It was decided to take some of the data at night when almost all other operations in the building were shut down. This did not, however, completely resolve the difficulties. For example, the flame was sensitive enough to go into violent oscillation whenever an airplane flew directly over the laboratory buildings. These airplanes came from Willow Run Airport about 15 miles eastward, and were probably at an altitude of about 2000 ft upon passing overhead. Since all windows and doors of the building were closed, the noise of the engines was not unduly loud. Until this time it had been customary to operate with the exhaust valve at the top of the outer chamber in an open position. It was now discovered that if the valve was tightly closed, sensitivity to external noise no longer existed. It should be added that, at any time during the operations described, one could rap the side of the outer chamber with a hammer and produce no apparent effect on the flame. At any rate, operations went back to a daytime basis, and the exhaust port was closed about one min prior to the taking of each photograph. This time was long enough to ensure insensitivity to external noises, but yet short enough so that there was no appreciable build-up of pressure within the chamber due to accumulation of exhaust gases.

In spite of the above precautions which resulted in elimination of vibrational effects, the values obtained for flame speed were still found to vary more than desirable. After ascertaining that all valves, metering devices, and components of the tubing in the system were in proper working condition, the source of the trouble was sought in the ozonator, the burner assembly itself, and in the methods of measurement of the flame areas. The flame areas had previously been measured by several different persons on different runs. Since various persons may see such measurements differently, the same person repeated all these measurements and some further uniformity of trend in the values was obtained. This was especially so in the case of the carbon monoxide runs. As stated previously, the ozone concentrations generated by the ozonator were found to be quite reproducible, signifying that the variations were not due to variable ozone production. Finally it was decided that the trouble came from incomplete mixing of the feed streams in the burner's mixing chamber. The first hint of this possibility was provided by the behavior, mentioned previously, of

iron carbonyl particles as they entered the flame front in the presence of ozone. When the air-feed line was adjusted in the burner so that mixing of air and fuel took place near the top of the mixing chamber, the combustible mixture going into the flame front was incompletely blended. Under this circumstance, the poor mixing became evident because the luminous particles of iron carbonyl imparted a marble-like appearance to the flame surface. The marble-like streaks moved about the surface so that the whole effect was one of undulation. By moving the air-feed line to lower positions in the mixing chamber, the effective mixing length was made greater and the undulating wave-like motion became less sharp. After the feed line was moved to its limit and the aforementioned fine-mesh screens were inserted, the luminosity at the surface had reached the most nearly uniform appearance that could be obtained, but the effects just described were still discernible. Along with the progressive changes in the appearance of the flame surface, there seemed to be proportionate changes in the extent to which the conical area of the flame was altered over a given time period. This was taken as evidence that proper mixing of the two streams could not be attained in the burner assembly as designed, simply because the mixing length was not great enough. Another point worthy of note is that one of the feed streams was axially centered in the mixing section while the other was somewhat off-center. In spite of the rather bad scatter of points, especially in the propane and hexane runs, it has still been possible to infer a trend for the effects of ozone on combustion. Because of this and the expense and time involved, it was decided not to construct a new burner assembly.

DISCUSSION OF RESULTS

MIXTURE OF ETHYLENE WITH OZONIZED AIR

Upon combination of air containing about one percent by weight of ozone with pure ethylene gas, visual evidence was obtained of immediate reaction between the two streams. Extremely fine droplets of liquid were seen to form and swirl through the glass reaction chamber as a fog. This was accompanied by a slight, but noticeable, warming of the chamber walls opposite the point of injection of the air stream. The droplets seemed quite stable and it seemed possible that reaction was substantially complete by the time the mixture had reached the exit point of the chamber. It could be seen further that the droplets remained stable and were readily carried along through the approximately 20 ft of Tygon exhaust tube. As the flow continued at a steady rate a portion of the drops collected upon the chamber and tubing walls, conglomerating into larger drops which flowed to low points as they became larger and heavier. The degree of denseness in which the cloud of drops formed depended on how dry the reaction chamber had been when the flow of gases was started. Unless the chamber was bone-dry, the visible reaction was not evident to its maximum extent. If the substance formed is ethylene ozonide, as is believed, then the

phenomenon would seem to be in keeping with the tendency of the ozonide to decompose by hydrolysis.

A search of the literature showed that while much work is reported relative to ozonides in general, little of it is concerned with ethylene ozonide in particular.[3,4] Some indication of the characteristics of the substance, including the probability that it exists in polymeric, as well as monomeric, form, was found. Existence of the monomer as an extremely unstable compound is an established fact. The possibility of a relatively stable polymeric form is definite, but some discussion arises whether this is a dimer, or is of some greater chain length. The point of interest to us, however, is that the two forms have properties at great variance with each other, and that the properties that are attributed to the polymer are similar to those observed in the substance under consideration here.

To determine some of the qualitative properties of the liquid substance, some of it was collected by baffling the fluid flow and accumulating the liquid at a low point in the system. In this manner it was possible to collect several ml over a period of time, and this liquid was subjected to various expedient examinations which are now described. The liquid was colorless and clear, and viscous or oily in nature, having a consistency similar to that of glycerine when rubbed between the fingers. Upon being permitted to stand in a test tube, small bubbles were seen to appear slowly in the liquid. The test tube was immersed in a bath of dry ice and acetone, and the liquid became more viscous and then solid with no fairly sharp freezing point. As it became more viscous it also assumed a grayish opacity and any gas bubbles that were present became entrapped throughout the body of the substance. It was not determined whether the "bubbles" had now changed phase. This is mentioned because of the possibility that the bubbles were formaldehyde, having a boiling point of -21°C, which is higher than the temperature of the bath.

A small quantity of the substance was placed in a test tube in a water bath, which was then heated. At a temperature somewhat below that of boiling water, fairly vigorous action was started in the liquid. This seemed to be a decomposition rather than boiling, that is, the liquid was still quite viscous while the bubbles were forming in its mass.

A few drops of the liquid were placed on the surface of a piece of tool steel. Reaction started immediately and the metal was stained almost immediately. After standing a few sec, the liquid was ignited with a direct application of a bunsen-burner flame and fairly vigorous burning resulted. The same experiment was repeated, using a wood surface rather than steel. In this case there was no apparent effect on the wood and no apparent reaction in the liquid. Application of the direct bunsen-burner flame resulted in much more vigorous burning than was the case with a steel surface. It is additionally noted that there was a very short, yet distinctly noticeable, period between the application of the burner flame and the onset of burning.

The blade of a spatula was heated to a rather high temperature over a bunsen burner after which a drop of the liquid was applied to the blade surface with a glass stirring rod. An abrupt flare-up and vigorous burning resulted. As the blade cooled, successive drops of the liquid were brought into contact in the same manner. Down to a certain point in blade temperature, the burning seemed to become more vigorous, finally seeming to have a detonative quality and giving off a sharp cracking sound. Below that certain point burning did not take place; rather, a vigorous decomposition reaction seemed to occur. Reaction in this latter manner became successively less vigorous as the blade cooled.

A small amount was subjected to the impact of an 8-oz brass weight dropped from various heights up to about one ft. There seemed to be no effect, but attempts were not made to determine whether any decomposition had taken place.

These experiments, which had been conducted prior to a study of the references cited above, agreed quite well with the findings discussed in those references. These results, then, were taken as sufficient qualitative evidence that the substance found in the glass reaction chamber, and also in the mixing section of the burner assembly itself, was ethylene ozonide in some form, presumably dimeric.

In an attempt to associate the reduced flame speeds of the ethylene-air-ozone flame with the formation of ethylene ozonide in the mixing chamber, two sequences seem possible, the difference in them being a matter of reactivity and time. One could be that the two streams, upon combining in the mixing section, form ethylene ozonide which then substantially decomposes before entry into the flame front. The resulting products would have a lower energy release upon combustion. Heat generated in the two exothermic steps involved would be said to be lost to the walls of the mixing section. Or it could be assumed that the ethylene ozonide does not decompose before entry into the flame front, but rather enters, as such, in liquid droplet form. Assuming initiation of the decomposition reaction to have a time lag, a large part of the substance would be pictured as coming through the flame front in the form of its incomplete decomposition products without actually burning. Indeed, perhaps some of the drops could actually pass intact through the flame front. Besides the loss of energy involved, the comparatively large droplets may hinder the normal reaction schemes by altering the collision probabilities of active species. Essentially, what is visualized is the possibility that we are now dealing with heterogeneous reactions and that the liquid droplets may act as chain-breaking catalysts. Of the two possibilities discussed, it seems that the second is the more likely. The bases for such a conclusion lie in the properties of comparative stability described in the experiments and in the references, and also in the belief that energy lost as heat through the burner assembly walls is not as great as was previously supposed.

COMBUSTION OF PROPANE OR HEXANE WITH OZONIZED AIR

It had been suggested in the previous report[1] concerned with this project that in the combustion of ethane the role of ozone in general would be that of an atomic oxygen "donor" by the reaction

$$O_3 = O_2 + O \quad .$$

The resulting atomic oxygen would then react directly with oxidizable material or with another molecule of ozone to give two activated oxygen molecules:

$$O + O_3 = 2O_2^* \quad ,$$

which would then further react with O_3 to generate atomic oxygen again:

$$O_2^* + O_3 = 2O_2 + O \quad ,$$

or be deactivated by collision with nitrogen molecules. The latter was held to be most likely because of the relatively large proportion of nitrogen in the air mixture. Figures 4, 5, and 6 show the results obtained in the determination of percent change in propane flame speed as a function of ozone concentration in the air stream. Figures 7 and 8 are exhibits of the same data for hexane-air-ozone flames. In these figures the abscissa has been placed on an exaggerated scale so that the trend of the curves can be more readily visualized. In all cases it is seen that the most reasonable curves, estimated by eye, would seem to be approximately straight lines of quite large slope. It is also seen that if the curves are given straight-line extrapolation to the zero ordinate they will not intercept at the origin, or alternatively an extrapolation to the origin will require relatively abrupt changes in slope. Furthermore, comparison of the various figures shows that the curves may all be of approximately the same slope, regardless of the fuel-air ratio or even of the hydrocarbon that is being considered. Allowing for different curve placement by different interpreters, any reasonably interpreted curves would almost certainly give rise to the same observations as those listed above. One inference that can be drawn is that, whatever the phenomenon taking place, a certain minimum concentration of ozone is required before appreciable action takes place. Otherwise the slopes would tend toward the origin in a more uniform manner. Another reasonable inference is that the phenomenon is not dependently related to the two fuels involved, since the curves themselves do not seem dependent upon the fuel.

These observations now place in question the original supposition that ozone may be effectively an atomic oxygen donor to the reactions that follow. If this were the predominant role, then it would seem reasonable to suppose that the curves would show a more nearly uniform correlation from the range shown down to the origin. At least the adjustment to the ultimately steep slope

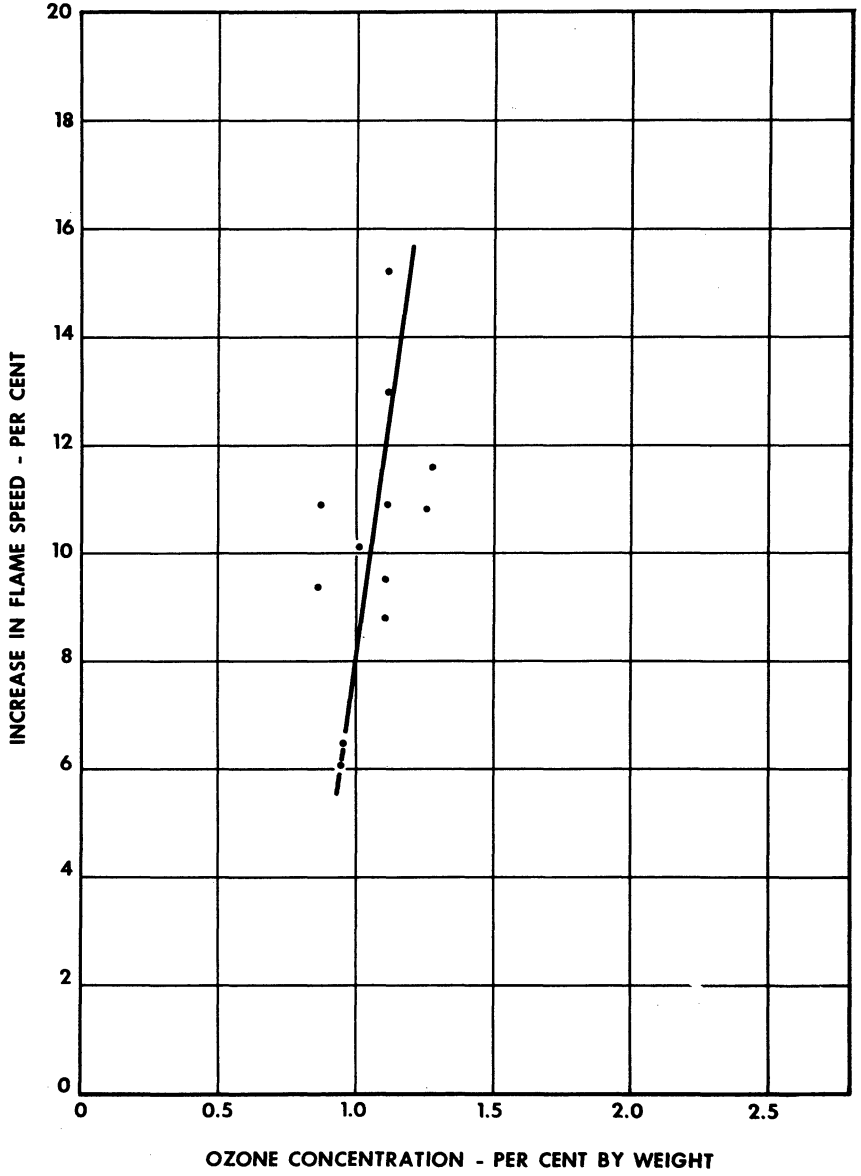

Fig. 4. Effect of ozone concentration on flame speed of hexane-air-ozone mixtures. Fuel-air ratio 0.057 to 0.060. Run series 19, 20, and 21.

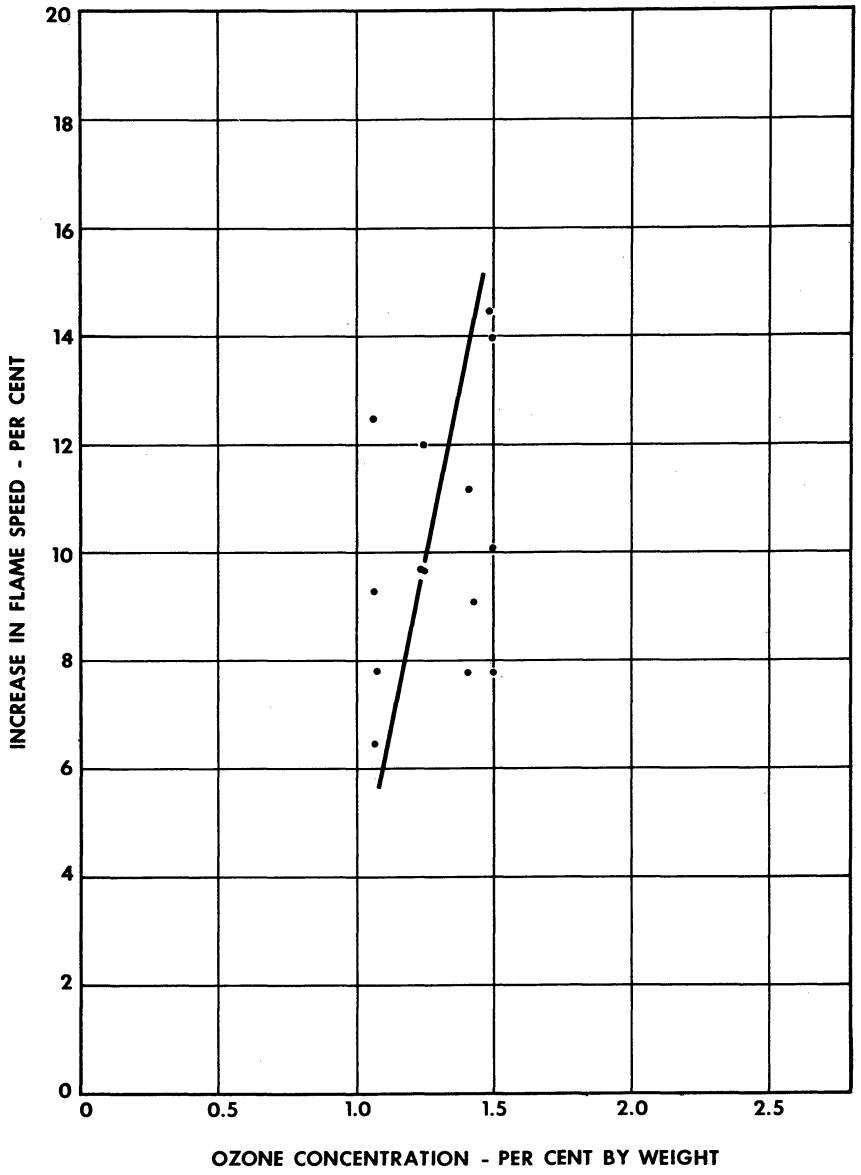

Fig. 5. Effect of ozone concentration on flame speed of propane-air-ozone mixtures. Fuel-air ratio 0.059 to 0.061. Run series 11 and 16.

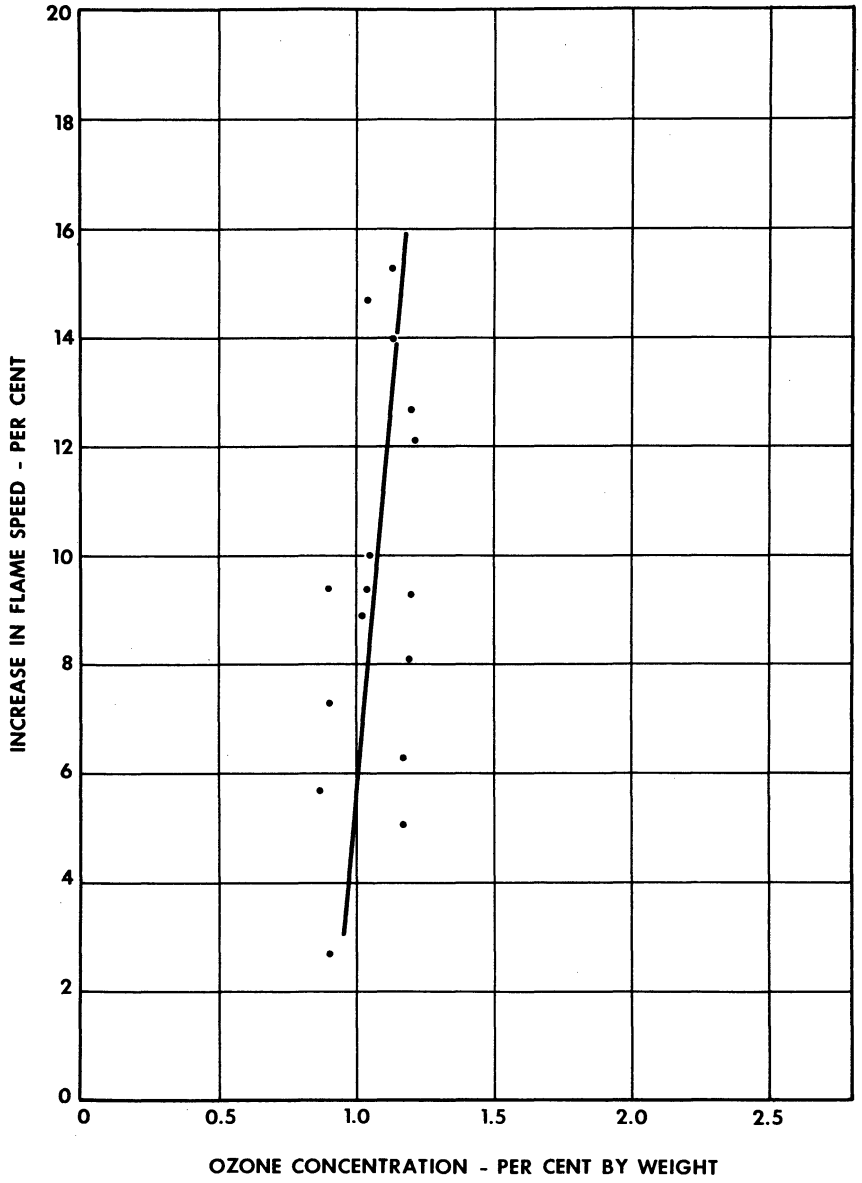

Fig. 6. Effect of ozone concentration on flame speed of hexane-air-ozone mixtures. Fuel-air ratio 0.065 to 0.068. Run series 20, 21, and 22.

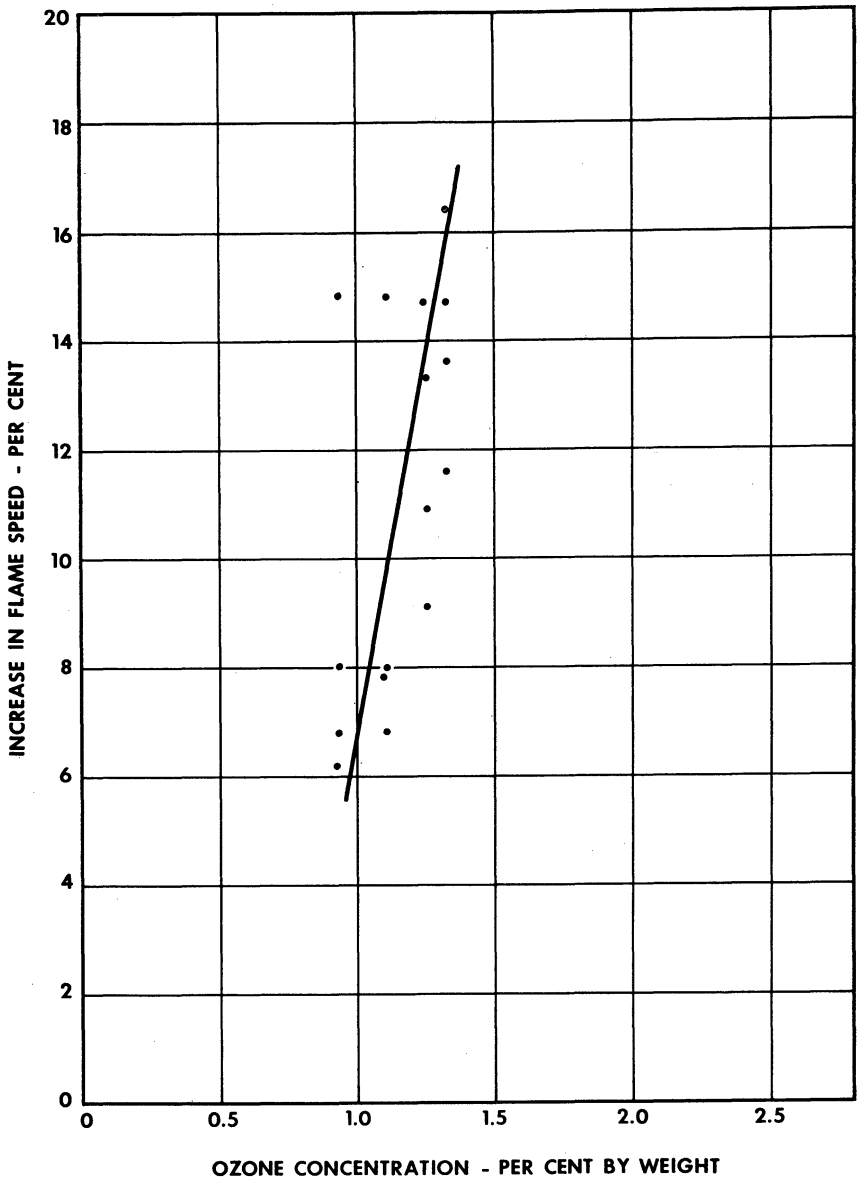

Fig. 7. Effect of ozone concentration on flame speed of propane-air-ozone mixtures. Fuel-air ratio 0.047 to 0.049. Run series 12 and 17.

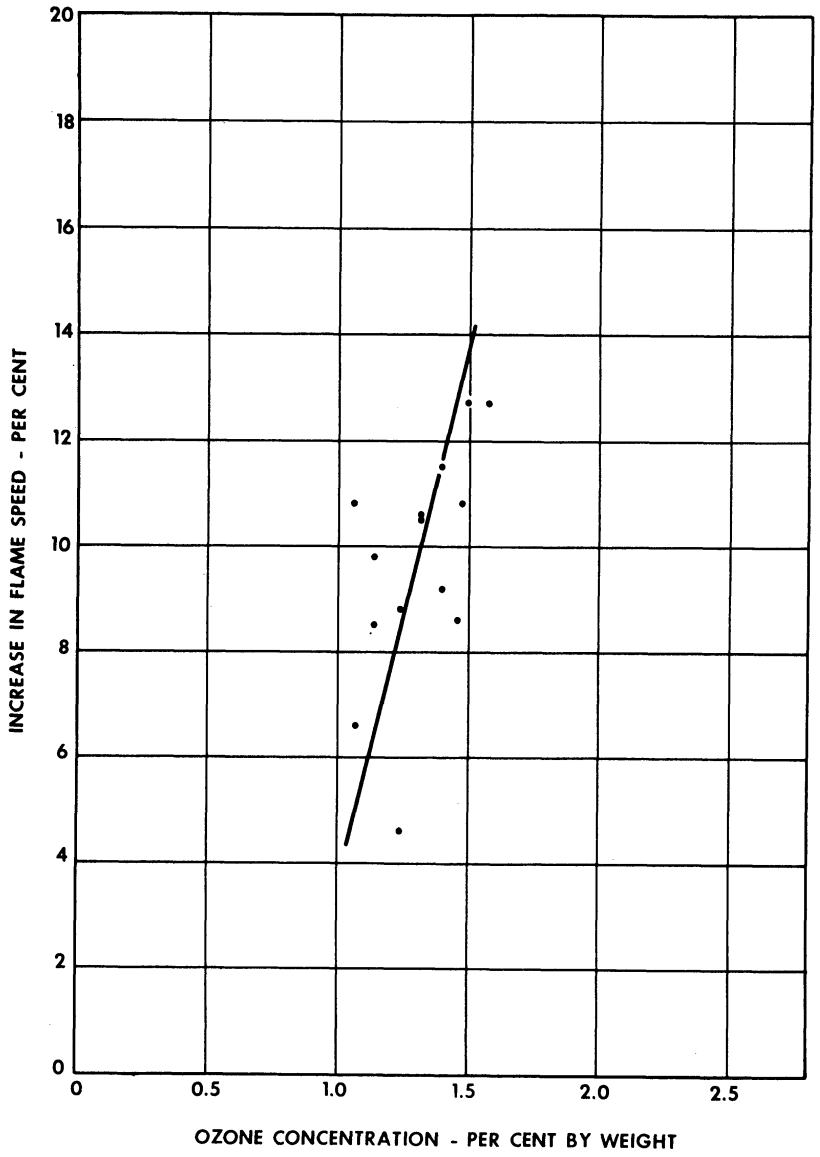

Fig. 8. Effect of ozone concentration on flame speed of propane-air-ozone mixtures. Fuel-air ratios 0.064. Run series 13 and 15.

should not be as abrupt as the trend of the curves would imply. On the other hand, a reasonable argument can be presented for assuming energy release as the basis of the phenomenon. It is possible that the energy released in decomposition of the ozone would increase the rate of those reactions in the overall scheme that produce active radicals. If the production of such radicals is the rate-controlling step, then the overall reaction would experience a rate increase and the flame speed would be increased. The requirement of a threshold energy for such a situation could then explain the fairly abrupt onset of the steep slope shown in the curves. For example, it might be speculated that after a certain level of energy production is reached, breaking of carbon-to-carbon or carbon-to-hydrogen bond in the hydrocarbon is facilitated. The combustive decomposition of ozone in ozone-oxygen mixtures has been suggested to occur as follows:[5]

$$M + O_3 + 24.1 \text{ kcal} = O_2 + O + M \quad (1)$$

$$O + O_3 = 2O_2 + 93.2 \text{ kcal} . \quad (2)$$

In the reactions under consideration here, it is possible that the endothermic first step is at least partially eliminated due to the existence of atomic oxygen from sources other than ozone in the flame. Thus the exothermic second step in the above reaction might to a large extent be directly effected by atomic oxygen that normally is produced in a hydrocarbon-air flame, resulting in a greater net energy release at the flame front. Effectively, the M of the first step is an atomic oxygen and the reaction becomes identical with that of step two. Ultimately, of course, what this amounts to is an addition of energy to the flame front from an external source, that is, part of the energy that went into generating the ozone in the first place.

In the discussion of the decomposition of ozone in ozone-oxygen mixtures it is suggested that much of the excess energy released in reaction (2) above is used up in the dissociation of oxygen by the reaction

$$M + O_2 + 117.4 \text{ kcal} = 2\,O + M .$$

Perhaps, however, when the hydrocarbon fuel is made part of the system a large part of the excess energy is used up in producing hydrocarbon radicals and atomic hydrogen. Energies for dissociation of carbon-to-carbon and hydrogen-to-carbon bonds in the fuels being considered are believed to be at about the same values.[6] Either of these energies is somewhat lower than that required for the dissociation of oxygen, above. Consequently, it seems probable that dissociation of the hydrocarbon is favored.

COMBUSTION OF CARBON MONOXIDE WITH OZONIZED AIR

Figure 9 shows results obtained in percent increase in flame speed for the combustion of carbon monoxide with ozonized air. Data obtained for the three ranges of fuel-air ratio that were used are all shown in the same figure, for ready comparison. It is unfortunate that more data were not taken so that the trend of the curves could be drawn with a greater degree of confidence.

Lewis and von Elbe have proposed that ozone is required as an intermediate in the carbon monoxide-oxygen reaction scheme to reconcile the phenomenon of the second explosion limit.[2] The reactions they propose are as follows:

$$O + O_2 + M = O_3 + M \quad (3)$$

$$O_3 + CO = CO_2 + 2\,O \quad (4)$$

$$O_3 + CO + M = CO_2 + O_2 + M \quad (5)$$

$$O + CO + M = CO_2^* + M \quad (6)$$

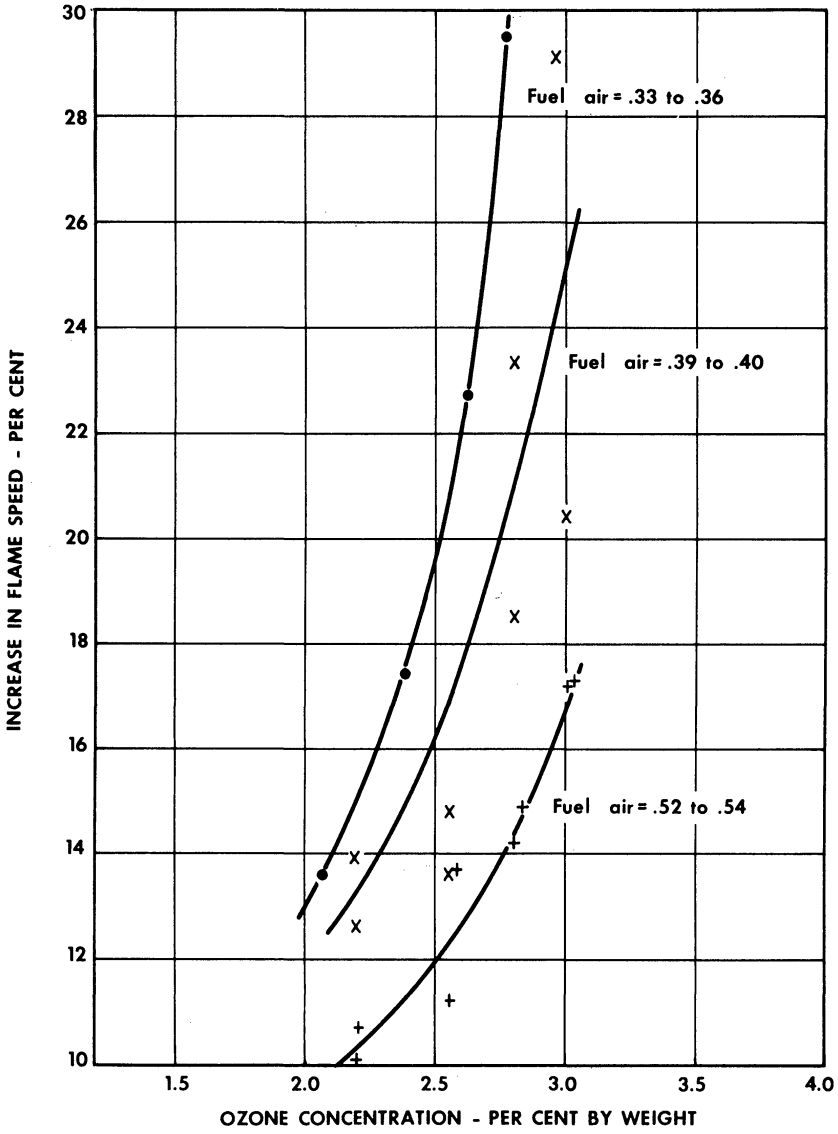

Fig. 9. Effect of ozone concentration on flame speed of carbon monoxide-air-ozone mixtures. Fuel-air ratios 0.33 to 0.36, 0.39 to 0.40, and 0.52 to 0.54.

Later steps for the deactivation of the excited carbon dioxide molecule in reaction (6) have been omitted from the present discussion. Of the competing reactions shown, (3) occurs more readily than (6), and reaction (5) occurs more readily than (4). But reaction (6) is the only possible reaction in collisions of O + CO + CO [where one CO is now the M of reaction (6)]; therefore the relative reaction rates of (3) and (6) are dependent upon the fuel-air ratio, with (6) increasing relative to (3) as the fuel-air ratio increases.

With these points in mind we may now discuss the curves of Fig. 9. Within the limits of the small number of data that was obtained, it seems that the curves would not be straight lines over the range shown. This is perhaps in contrast to the hydrocarbon-air-ozone curves. Another manner in which they seem to differ from the hydrocarbon curves is that they are parametric with

fuel-air ratio. The smaller the fuel-air ratio, the higher is the percent increase in flame speed. A third manner in which they differ is that all three curves tend to converge toward the origin without an abrupt change of slope. In examining the reactions above, it is seen that the addition of ozone to the combustion mixture constitutes a source that is auxiliary to ozone supplied by reaction (3). The added ozone goes directly into reactions (4) and (5). In three-body collisions (5) would be a normally favored reaction, but the addition of ozone would increase the chances for reaction (4) because of the greater possibility of the occurrence of sufficiently energetic two-body collisions of CO_3 and CO. The presence of ozone as an intermediate in the scheme proposed by Lewis and von Elbe seems to be in agreement with the curves as the effect of externally added ozone is greater at lower fuel-air ratios. With more carbon monoxide in the mixture there is greater probability that the M molecule of reaction (6) is carbon monoxide, and the reaction competes to a greater extent with reaction (3). The result is that ozone production by reaction (3) is relatively lower, and externally added ozone increases the flame speed to a lesser extent. Thus the primary role of added ozone in a carbon monoxide-air flame would seem to result simply from an increase in its concentration available for direct reaction with carbon monoxide.

REFERENCES

1. Gluckstein, M. E., Morrison, R. B., and Khammash, T. B., "Combustion with Ozone-Modification of Flame Speeds C_2 Hydrocarbon-Air Mixtures," Univ. of Mich., Eng. Res. Inst. Report 2279-1-T, Aug., 1955 (ARDC Report No. OSR-TN-55-227).

2. Lewis, B., and von Elbe, G., Combustion, Flames, and Explosions of Gases, Academic Press, Inc., New York, 1951.

3. Reiche, A., Alkylperoxyde und Ozonide, Theodor Steinkopff, Dresden und Leipzig, 1931.

4. Briner, E., and Schnorf, P., Helv. Chim. Acta, 12, 154 (1929).

5. Cook, G. A., Spadinger, E., Kiffer, A. D., and Klumpp, C. V., Ind. Eng. Chem., 48, 736-41 (1956).

6. Steacie, E. W. R., Atomic and Free Radical Reactions, Vol. I, Reinhold Publishing Corp., New York, 1954.