

Vapor-Phase Oxidation of Hydrocarbons

Part 2 - Effect of Oxygen Concentration on Platinum-Catalyzed Combustion and Ionization

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February 7, 1969



NAVAL RESEARCH LABORATORY
Washington, D.C.

PREVIOUS REPORT IN THIS SERIES

"Part 1 — A Study of the Ionization Produced by the Catalytic Combustion of Hydrocarbons," F. J. Woods, M. E. Umstead, and J. E. Johnson, NRL Report 6316, Oct. 1, 1965

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ABSTRACT

The catalytic combustion of hydrocarbons has been studied further, with particular attention given to the ionization phenomena associated therewith. The greater ion yield of highly branched alkanes relative to straight-chain alkanes was confirmed.

The effect of the concentration of O_2 in the gas mixture on the extent of oxidation and ionization varied with the hydrocarbon used. In general, increase in O_2 content caused considerable enhancement of the ion yield. However, with some hydrocarbons the fraction oxidized decreased markedly with increased O_2 concentration. The data seem consistent with an explanation based on lower temperature oxidation occurring only on the Pt surface, whereas at higher temperatures the catalytic process extends itself to some degree into the vapor phase. It is also suggested that dissociative adsorption of O_2 at higher temperatures is involved in the ion-producing process.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C01-03
Project RR 001-06-41-5850

Manuscript submitted October 9, 1968.

VAPOR-PHASE OXIDATION OF HYDROCARBONS

PART 2 - EFFECT OF OXYGEN CONCENTRATION ON PLATINUM-CATALYZED COMBUSTION AND IONIZATION

INTRODUCTION

During the past several years, it has been observed that measurable quantities of ions are formed when hydrocarbons in an air stream are oxidized in the presence of a heated Pt filament (1-3). The experimental evidence suggests that these ions are produced by the chemical oxidation reactions catalyzed by the Pt surface (1,2). That this process is one of chemi-ionization is supported by the following experimental observations (1,2): (a) although ions have been collected when hydrocarbons were oxidized in this manner, no ions were obtained when H_2 or CO was oxidized, (b) no ions or oxidation products were obtained when Au was substituted for the Pt surface, (c) no ions were obtained when N_2 was substituted for air, and (d) the extent of ionization depended highly on the molecular structure of the particular hydrocarbon being oxidized. For example, the maximum ion yield from 2,2-dimethylbutane (2,2-DMB) under the conditions used was 20 times as much as from n-hexane.

These catalytic ionization results present the intriguing prospect of a new approach to the study of the important, but complex, subject of surface catalysis. For example, heterogeneous catalytic combustion is now linked to flame combustion by the additional fact that ions are produced in both oxidation processes. However, one large difference which already has been observed is that, in contrast to flame ionization, the hydrocarbon structure profoundly affects the amount of ionization produced by catalytic oxidation. The great similarity in hydrocarbon flames, e.g., in regard to reaction products and flame speeds, suggests a great deal of similarity in the chemical reactions involved. This is particularly true of the ionization measured in flames, since the rate of ionization (ionization current) for saturated hydrocarbons, for example, does not appear to depend in any way on the molecular structure but only on the number of carbon atoms available per unit time (4).

The marked influence of hydrocarbon structure on the ionization from catalytic oxidation prompted extension of this study to other selected hydrocarbons. In addition, the effect of the O_2 content of the gas mixture has been explored. The results have led to certain suggestions in regard to the processes involved in these examples of catalytic oxidation.

APPARATUS AND PROCEDURES

The experimental apparatus and procedure for studying the ionization related to catalytic combustion are similar to those which have been described previously (1,2). The schematic diagrams given in Figs. 1 and 2 show the salient features of the apparatus. The Teflon-insulated Pt ion collector was mounted in the brass insert as shown in Fig. 2. Figure 2 shows further that the gas sample enters the cell through a tube in the brass insert, flows up around the spirally wound catalytic Pt filament and out near the top of the cell.

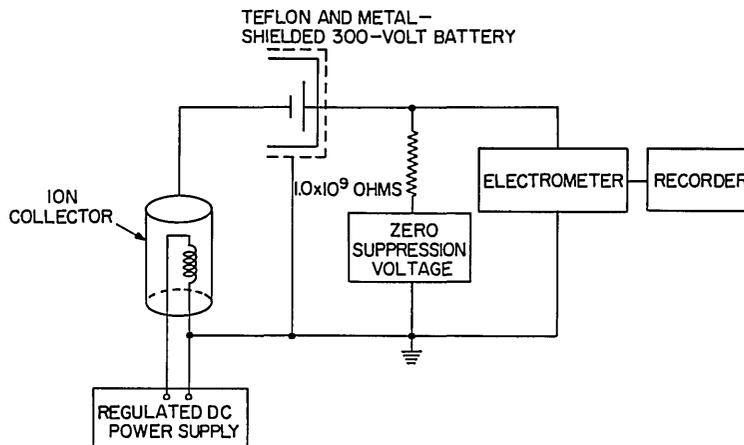


Fig. 1 - Circuit used for measuring ion current

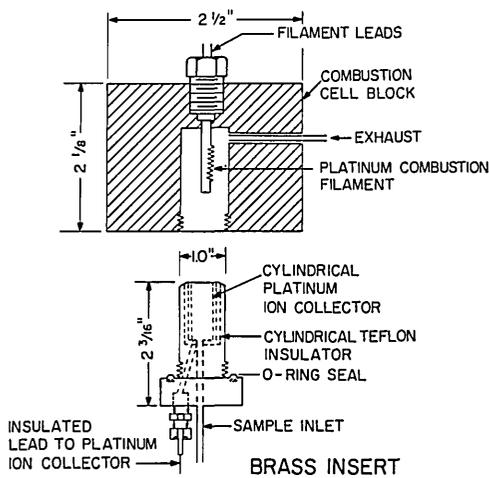


Fig. 2 - Catalytic combustion cell

The Pt combustion filaments were obtained from the Precision Scientific Company. New filaments were "noisy" when first installed; i.e., they emitted positive ions when heated, starting at about 700°C . This noisy condition occurred with used filaments after a period of idleness or a series of tests. This positive-ion emission subsided after the filaments were heat-cycled several times to 900°C with air or N_2 flowing through the cell. After the filament was conditioned, the background current dropped to less than 0.01×10^{-9} Amp, even at the highest filament temperature used (900°C).

The filament was powered by a Sorensen model QR36-15A dc voltage power supply. A 300-V battery provided the negative collector potential. The ion collector was operated at 300 V negative with respect to the filament. The output signal was developed across a 1.0×10^{-9} ohm resistor and a zero suppression network and amplified by a Keithley Model 220 electrometer which fed into a recorder. The filament temperatures used in this report were determined by a method described previously (1,2).

The mixtures of gases and liquids were prepared by injecting a measured amount of the selected liquid or gaseous hydrocarbon into an evacuated stainless-steel bottle, 1.7-l capacity, and then pressurizing with a gas mixture containing the desired concentration

of O₂ to higher pressure, usually 10 atm. The hydrocarbon concentrations were usually about 4.0 mg/l.

The prepared gas mixtures were passed through the combustion cell at a metered rate, usually 50 cc/min. Appropriate analytical measurements were made of the influent and effluent gases as needed. CO₂ and CO were analyzed using Beckman L/B Model 15A nondispersive infrared analyzers. Hydrocarbons were determined by gas chromatography using a DC-550 silicone column and a Beckman GC-2A hydrogen flame detector.

The H₂, CO, and CH₄ were obtained from the Matheson Co. The other hydrocarbons used were Phillips Petroleum Co. pure grade (99+ mole-%). The liquid hydrocarbons were percolated through silica gel before using.

EXPERIMENTAL RESULTS

All of the data presented in this report were obtained using a Pt filament as the catalyst. Under the experimental conditions used, a maximum of about 35 to 60% of the hydrocarbon in each case was oxidized. That portion of the hydrocarbon which was oxidized was converted almost entirely to CO₂, especially at temperatures below about 750°C. It has been shown in earlier experiments also that during the oxidation of hydrocarbons a small yield of CO occurs which increases to several percent at higher temperatures. Although the ion yields can be expressed in several ways, for the most part they are presented as "coulombs per mole of hydrocarbon oxidized."

Effect of Hydrocarbon Molecular Structure on Ionization from Catalytic Oxidation in Air

Figure 3 contains the data for the ion yields obtained for several hydrocarbons during the oxidation in air over a Pt filament in the approximate temperature range of 400 to 900°C. The hydrocarbons fall into two broad categories; those which produced about 0.04 coulomb per mole of hydrocarbon oxidized and those which produced about 1.0 coulomb or more per mole. The latter yield is similar to that obtained during combustion of hydrocarbons in a H₂ flame (4).

Table 1 contains a summary of the data shown in Figs. 3 and 4 in terms of maximum ion yields plus a few other hydrocarbons taken from previous data (1). These data show the strong influence of the t-butyl group in producing a relatively high ion yield. This is in spite of the fact that these compounds generally were more difficult to oxidize than the normal paraffins.

It is interesting that in the series of compounds containing the t-butyl group, when oxidized in air, the tendency was to produce a higher ion yield as the molecular weight decreased, with 2,2-dimethylpropane having the highest ion yield per mole of hydrocarbon oxidized. However, when the series was extended all the way to isobutane, this progression no longer held. Although isobutane is the smallest hydrocarbon containing the t-butyl group, it yielded relatively few ions. These results suggest that perhaps the scission of a C-C bond may be an important contributor to ion formation. The facility with which the compounds such as 2,2-dimethylpropane produced ions compared with the other hydrocarbons investigated suggests that the t-butyl group somehow plays an important role in the ion-producing process. The relative stability of the trimethylcarbonium ion may be an important factor in this regard. It appears that the ease of removal of an H atom from the hydrocarbon molecule is not a requirement for ionization because of the preeminence toward ionization of 2,2-dimethylpropane, which has a relatively high energy requirement for hydrogen abstraction compared to isobutane, for example (5).

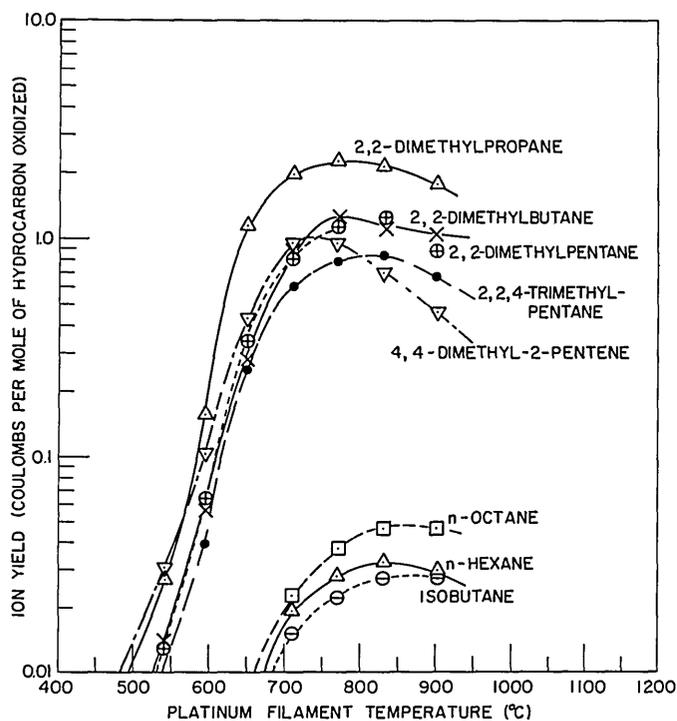


Fig. 3 - Effect of filament temperature on ion yield in air

Table 1
Maximum Ion Yield

Hydrocarbon	Ion Yield (coulombs/mole hydrocarbon burned)	
	In Air	In 60% O ₂ /40% N ₂
2,2-Dimethylpropane	2.28	2.47
2,2-Dimethylbutane	1.26	3.43
2,2-Dimethylpentane	1.21	2.21
4,4-Dimethyl-pentene-2	0.93	2.22
2,2,4-Trimethylpentane	0.83	1.77
2,3-Dimethylbutane*	0.14	-
t-Butylbenzene*	0.13	-
3-Methylpentane*	0.12	-
2-Methylpentane*	0.09	-
n-Octane	0.05	0.10
n-Hexane	0.03	0.09
Isobutane	0.03	0.05
Benzene*	0.002	-
Methane	<0.002	-

*Taken from Ref. 1.

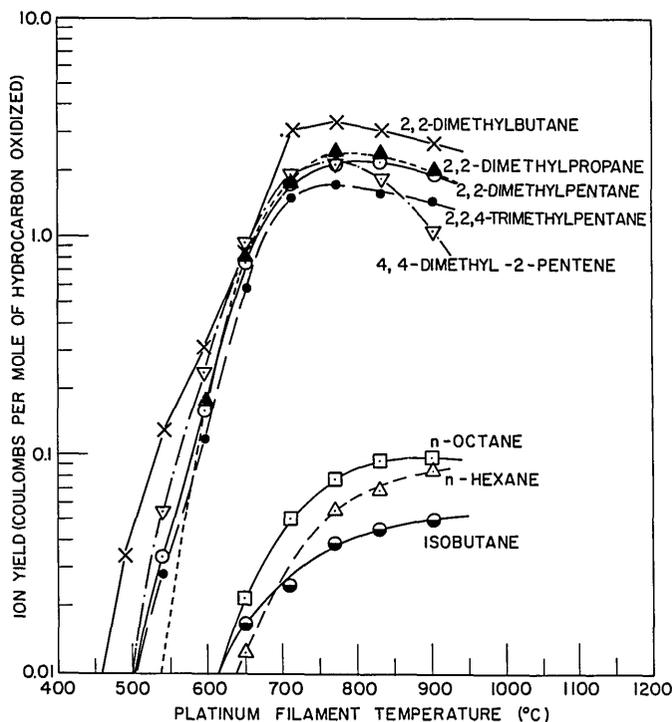


Fig. 4 - Effect of filament temperature on ion yield in 60% O₂ and 40% N₂

It was observed that 4,4-dimethylpentene-2 was much more readily oxidized than the saturated hydrocarbon, 2,2-dimethylpentane, although the latter gave a significantly larger ion yield. It was noted also that in the case of this olefin, which was used as the stereoisomeric mixture, the cis and trans isomers were equally attacked in terms of hydrocarbon oxidized.

Effect of Oxygen Concentration on Catalytic Oxidation and Ionization

A number of the hydrocarbons studied were oxidized over Pt using a mixture of 60% O₂ and 40% N₂ instead of air. The results are plotted in Fig. 4. In all cases the increased O₂ content resulted in increased ion yields. In many instances, the maximum ion yield was about twice that in air, as is shown also in Table 1. The relative position of each hydrocarbon in terms of ion yield remains about the same as in air, with the principal exception that 2,2-DMB had the highest ion yield at 60% O₂. The temperature at which maximum ion yield was obtained was about the same for air and 60% O₂ except for the groups which had the low yields. In these cases, it appeared that the peak ionization had not yet been reached at 900°C.

During these experiments, it was observed that at temperatures below 600° to 700°C, the percentage of hydrocarbon oxidized was less at 60% O₂ than at 21% O₂. In some cases this difference was substantial. Reyerson and Swearingen (6) showed earlier that platinized gel catalyst was much less efficient for the oxidation of CH₄ when the O₂ content of the gas was increased from 28% to 73% in the temperature range of 250° to 400°C. In the present work several additional experiments were performed to study the effect of O₂ concentration on both the ionization and oxidation of hydrocarbons.

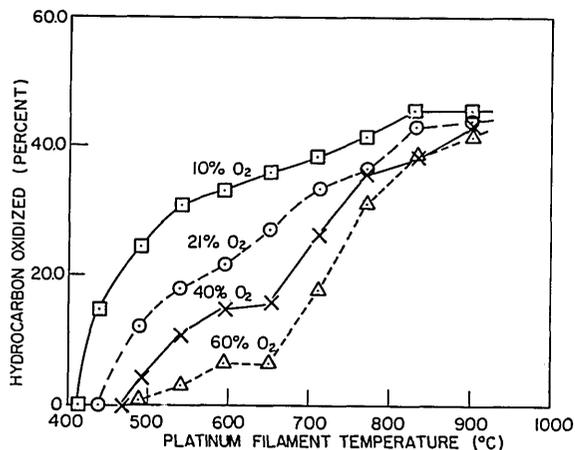
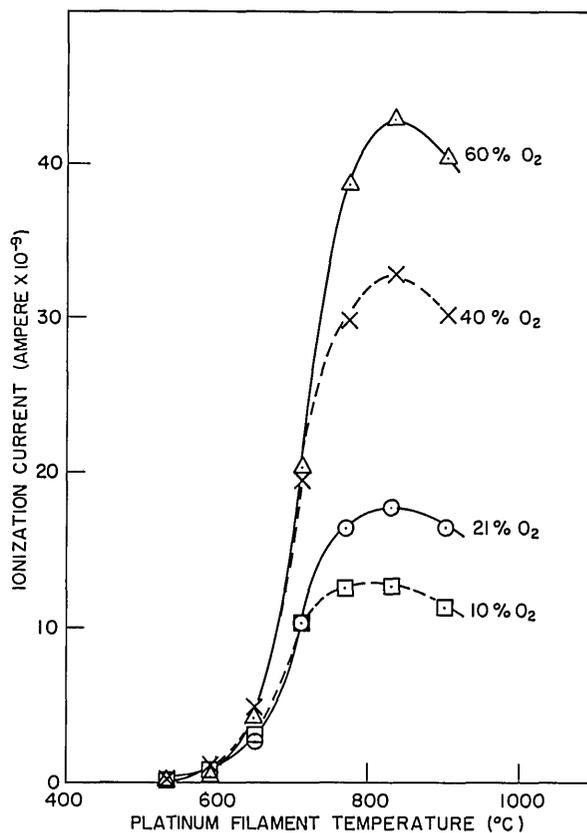


Fig. 5 - Effect of O₂ concentration on the catalytic oxidation of 2,2-DMB

Fig. 6 - Effect of O₂ concentration on ionization during the catalytic oxidation of 2,2-DMB



For example, gas mixtures were prepared containing 3.8 mg/l of 2,2-DMB in O₂-N₂ mixtures ranging from 10% O₂ to 60% O₂. The percent of the hydrocarbon which was oxidized was determined over a catalyst surface temperature range of 400° to 900°C. These data are given in Fig. 5. At the lower temperatures, it is evident that increased O₂ content results in a markedly lesser attack on the hydrocarbon.

The ionization current measured during the oxidation of 2,2-DMB as a function of O₂ concentration is plotted in Fig. 6. The ion current increases significantly as the O₂ content is increased, in spite of the fact that at lower temperatures the hydrocarbon oxidation yield is less with increased O₂. It is noted also in Fig. 6 that the temperature

Fig. 7 - Effect of O₂ concentration on the catalytic oxidation of n-hexane

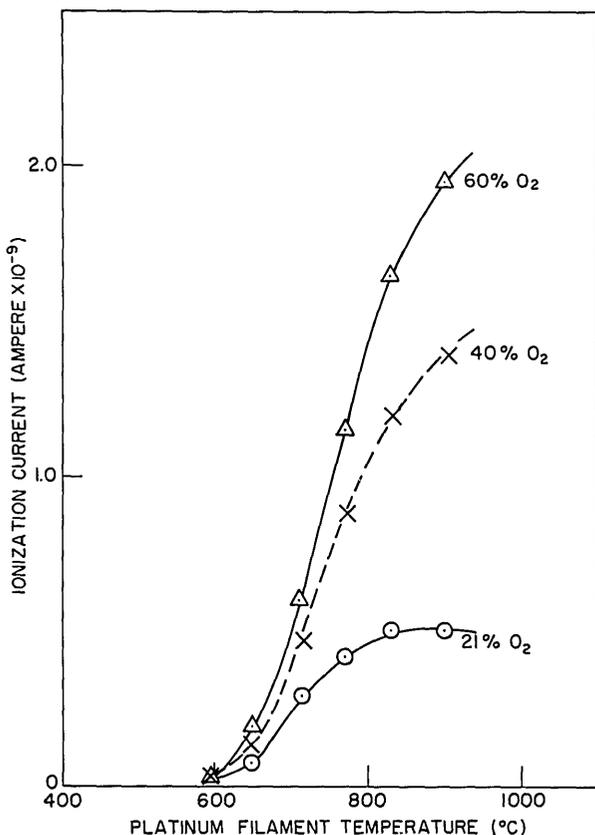
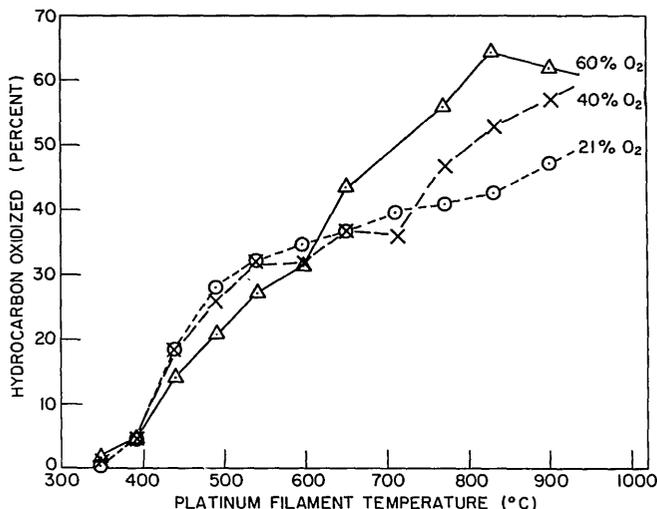


Fig. 8 - Effect of O₂ concentration on ionization during the catalytic oxidation of n-hexane

at which significant quantities of ions are collected is nearly the same regardless of O₂ concentration. In Fig. 5, it is seen that a knee in the hydrocarbon oxidation curve appears, and it becomes more pronounced as O₂ concentration is increased. The temperature range at which this knee occurs is about the same as the temperatures where the ion current increases markedly.

Additional data relative to these oxidation phenomena were obtained for n-hexane. In similar experiments, n-hexane was oxidized in 21%, 40%, and 60% O₂ in N₂ mixtures. The percent hydrocarbon oxidized over the temperature range of 300° to 900°C is shown in Fig. 7. Only a slight decrease in n-hexane conversion with increased O₂ content at lower temperatures was observed, and at temperatures above about 600° to 700°C, higher O₂ concentration resulted in more oxidation of n-hexane. The ionization current, Fig. 8, increases markedly in the temperature range where the oxidation curves exhibit an apparent change in reaction mode. Data for the oxidation of n-octane at 21% and 60% O₂ result in curves similar to n-hexane.

For comparison with n-hexane and 2,2-DMB, data obtained for 2,2-dimethylpropane are plotted in Fig. 9, because it gave among the highest ion yields of the hydrocarbons studied. Very little oxidation of 2,2-dimethylpropane in 60% O₂ occurred until the Pt surface temperature exceeded 600°C. The oxidation curve showed a strong increase in conversion of hydrocarbon at about the same temperatures at which the ion yield increased markedly. At 21% O₂, the ion-yield curve showed a break at approximately 600°C

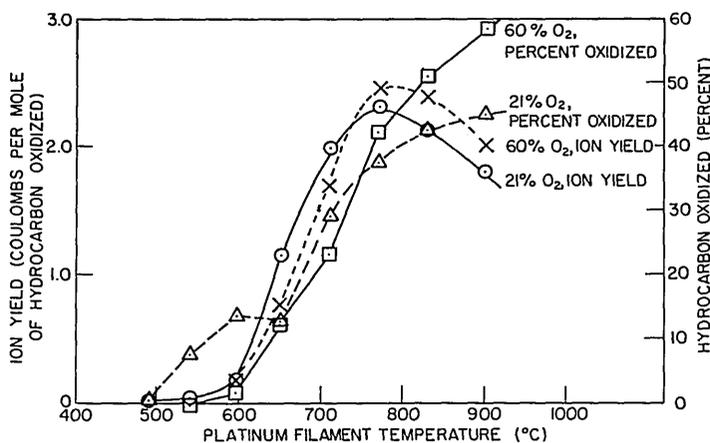


Fig. 9 - Effect of O₂ concentration on the catalytic oxidation and ionization of 2,2-dimethylpropane

also. However, the hydrocarbon oxidation curve was quite different from that at 60% O₂, in that substantial oxidation occurred below 600°C, with a pronounced knee in the curve at about 650°C.

Effect of Substitution of Helium for Nitrogen as Diluent

It was of interest to observe the effect on the oxidation and ionization processes of changing the diluent gas from N₂ to He. Making this change has the physical effect of substantially increasing the thermal conductivity of the gas mixture flowing past the Pt wire surface. Mixtures of 15% and 20% O₂ in He were used for the oxidation of 2,2-DMB, the latter at a concentration of 3.8 mg/l. The ionization yields are plotted in Figs. 10 and 11 in comparison with similar mixtures containing N₂. It is concluded from these data that no profound difference occurs when He is substituted for N₂. The maximum ionization measured is somewhat less in He, and there appears to be a slight shift in temperature dependence. Further experimentation would be needed to establish these changes as real.

The extent of hydrocarbon oxidation is shown in Fig. 12. Two confirmatory facts are noted. First, significantly less hydrocarbon is oxidized as we increase from 15% O₂ to 20% O₂. Second, a pronounced knee effect occurs with a plateau extending from 500° to 600°C and breaking upward between 600° to 700°C as with N₂.

Catalytic Oxidation of Mixtures Containing Carbon Monoxide

It has been shown that neither H₂ (7) nor CO (4) contributes to the ionization in flames. Nor does a mixture of H₂ and CO in flames produce ionization (8). Analogously, it was shown previously (1,2) that neither H₂ nor CO produced ions when oxidized catalytically under conditions such as those prevailing in the present work. In further experiments with mixtures in air containing both 0.5% CO and 0.5% H₂, it was found that although as much as 75% of the CO and 90% of the H₂ in the mixture were catalytically oxidized to CO₂ and H₂O, there was no measurable ion current ($< 0.01 \times 10^{-9}$ Amp). The absence of positive ion formation in this instance is an additional item of similarity between the ionization phenomena in catalytic oxidation and in flames. This information is a further indication that we are dealing with a chemi-ionization process when ions are produced during hydrocarbon combustion, that the mere presence of both carbon and hydrogen atoms in some form to be oxidized is not sufficient.

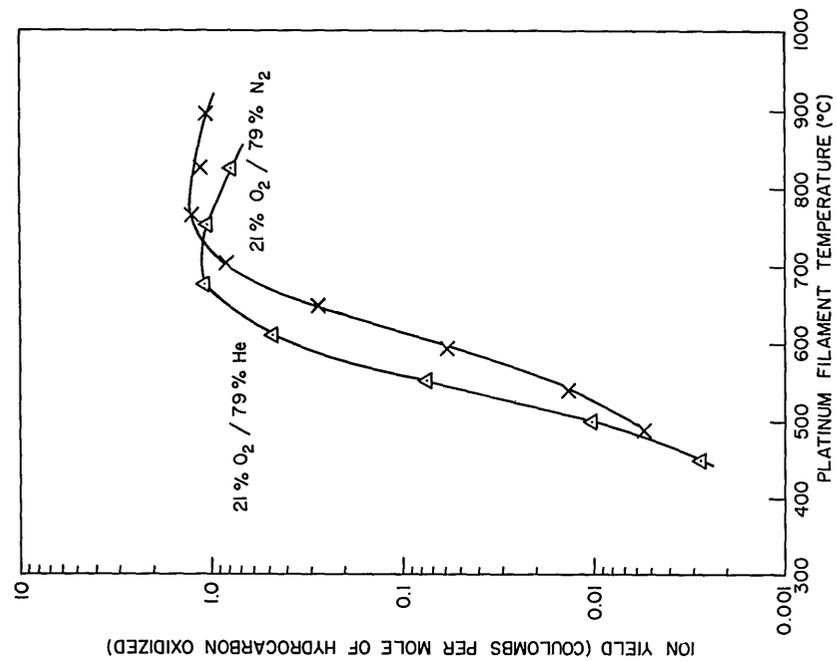


Fig. 11 - Effect of N₂ and He as diluents on the ion yield during the oxidation of 2,2-DMB with 21% O₂

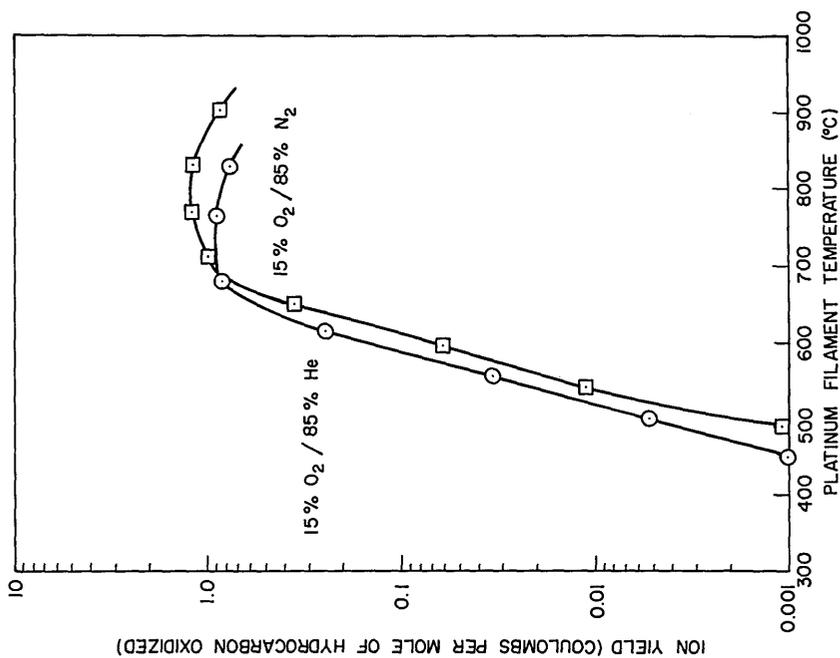


Fig. 10 - Effect of N₂ and He as diluents on the ion yield during the oxidation of 2,2-DMB with 15% O₂

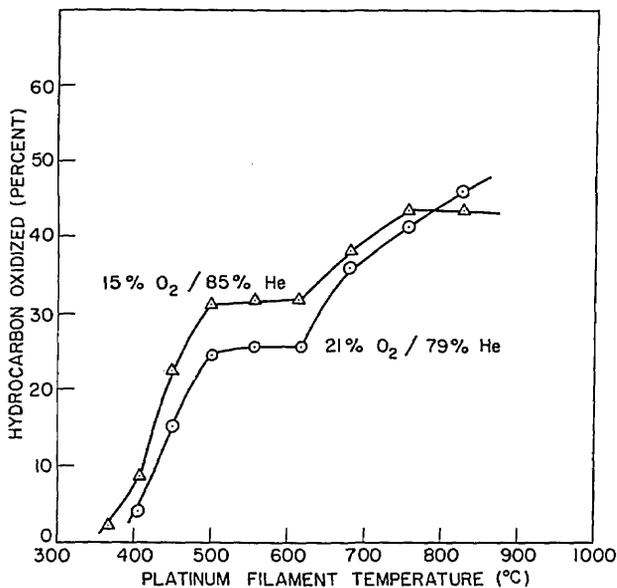


Fig. 12 - Catalytic oxidation of 2,2-DMB in He-O₂ mixtures

Because CO is strongly adsorbed on Pt, a mixture containing 3.8 mg/l of 2,2-DMB and 0.5% CO in air was passed over the Pt filament at temperatures ranging from 400° to 900°C. The CO did not appear to interfere significantly with the oxidation of 2,2-DMB. For example, at 830°C, 35.4% of the 2,2-DMB was oxidized in the presence of CO and 34.1% without CO added. At the same time the ion current was 6.5×10^{-9} Amp with CO and 11.7×10^{-9} Amp without CO, indicating a possible inhibiting effect of CO on the ion yield.

Halogenated Hydrocarbons

A few halogenated hydrocarbons were studied by the usual procedure using mixtures in air over the Pt filament. Neither dichlorodifluoromethane nor 1,1-dichloroethene yielded a measurable ion current at temperatures up to 900°C. 1,1,1-Trichloroethane, however, did yield a modest ion current, but the results were erratic and not reproducible. There was some indication that the halogen compounds changed the behavior of the filament. Consequently, no further experiments with halogenated compounds were conducted. This erratic behavior was in contrast with the results with hydrocarbons, which were very reproducible.

DISCUSSION

The data collected in these experiments suggest the following explanation: As the concentration of O₂ in the gas stream increases, the strong adsorption of O₂ molecules on the catalyst surface (9) interferes with adsorption of the hydrocarbon molecules. The result is that at lower temperatures fewer hydrocarbon molecules are oxidized as the O₂ concentration increases. This explanation implies that both types of molecules, O₂ and hydrocarbon, must be adsorbed for reaction to occur, in accord with the Langmuir-Hinshelwood mechanism (10). It may be that the lesser effect of increased O₂ content on the oxidation at lower temperatures for n-hexane is due to a stronger adsorption of n-hexane compared to the branched hydrocarbons, particularly neopentane. No confirmatory data in this regard has been found, however.

It appears from Fig. 5 that at about 600°-700°C a change occurs in the oxidation process. For example, at 60% O₂, further temperature increase results in a pronounced increase in oxidation yield, until at 850° to 900°C, the conversion of hydrocarbon is nearly the same at 10% O₂ and 60% O₂. Several different explanations can be offered to account for this effect. First, it may be suggested that the adsorption of O₂ relative to hydrocarbon may change to permit a higher percentage of hydrocarbon to be adsorbed and oxidized, with no real change in mechanism. Second, it may be that an increase in the rate of oxidation at higher temperatures decreases the residence time of adsorbed molecules on a given site. This permits more hydrocarbon molecules to be adsorbed and oxidized. Third, it may be that the mode of reaction has changed to permit more and more oxidation of the hydrocarbon to occur by the Rideal mechanism, i.e., reaction between O₂ on the surface with hydrocarbon molecules in the gas phase (10). The latter explanation seems favored by the abrupt change in the hydrocarbon oxidation curves in Fig. 5, rather than a more gradual change which might be expected for either of the first two explanations. However, the absence of products other than CO₂ and CO seems to speak against the Rideal mechanism. It would be expected that partially oxidized products should become significant, if the process tended to occur to a larger extent in the vapor phase. Vapor-phase oxidation of hydrocarbons usually produces a number of oxygenated products (11).

It is further apparent that the onset of ionization is closely related to the break in the oxidation curve at 600° to 700°C. These combined observations may be explained by suggesting a relationship to the dissociation of O₂ on the Pt surface, yielding adsorbed O atoms. Margolis (12) gives evidence for the dissociative adsorption of O₂ on Pt beginning at temperatures above 400°C and becoming significant at higher temperatures. Such atoms may be very reactive and may attack hydrocarbon molecules or radicals readily. It has been postulated in flame chemistry (7), for example, that ions are produced primarily from the reaction of two free radicals, CH and O, because such a system has the very high energies required to produce ionization. Also chemi-ions have been produced at room temperature by the vapor-phase reaction of O atoms and hydrocarbon molecules (13). Here again the CH radical is proposed as the most likely reactant with the O atom. It is suggested, therefore, that in the present situation an adsorbed O atom may react with a free radical from the hydrocarbon source to yield an ion. Whether this hydrocarbon-derived radical reacts in the adsorbed or vapor state is an open question.

The suggestion that the dissociative adsorption of O₂ on the Pt surface is a controlling factor would also explain the similarities in temperature dependence of the oxidation and ionization phenomena from one hydrocarbon to another. The similarities in the curves in Figs. 3 and 4, for example, certainly indicate that a common feature of the oxidation reaction is occurring, which is easiest explained at this point of our knowledge as being due to the one common reactant, O₂.

SUMMARY AND CONCLUSIONS

Additional information has been gained concerning the catalytic oxidation of hydrocarbons which may be summarized as follows:

1. The ion yield for the oxidation of hydrocarbons containing the t-butyl group tends to increase with decreasing molecular weight. However, isobutane gives a much smaller ion yield than does 2,2-dimethylpropane.

2. As O₂ concentration of the gas mixture is increased up to 60%, a substantial increase in ion yield occurs.

3. As O₂ concentration of the gas mixture increases, the oxidation of the hydrocarbon decreases in the lower temperature range, 400° to 700° C. This effect is particularly pronounced for branched hydrocarbons such as 2,2-dimethylpropane and 2,2-dimethylbutane.

The information obtained in this study gives additional insight into the process of heterogeneous catalysis involved in the oxidation of hydrocarbons in the presence of a Pt surface. Observation of the chemi-ionization process in this manner adds another tool which will be useful in gaining better understanding of the complexities of heterogeneous catalysis. Consequently, studies of these phenomena are continuing.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE VAPOR-PHASE OXIDATION OF HYDROCARBONS, PART 2 - EFFECT OF OXYGEN CONCENTRATION ON PLATINUM-CATALYZED COMBUSTION AND IONIZATION		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim report; work is continuing		
5. AUTHOR(S) (First name, middle initial, last name) F.J. Woods, M.E. Umstead, and J.E. Johnson		
6. REPORT DATE February 7, 1969	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. NRL Problem C01-03	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6816	
b. PROJECT NO. RR 001-06-41-5850	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360	
13. ABSTRACT <p>The catalytic combustion of hydrocarbons has been studied further, with particular attention given to the ionization phenomena associated therewith. The greater ion yield of highly branched alkanes relative to straight-chain alkanes was confirmed.</p> <p>The effect of the concentration of O₂ in the gas mixture on the extent of oxidation and ionization varied with the hydrocarbon used. In general, increase in O₂ content caused considerable enhancement of the ion yield. However, with some hydrocarbons the fraction oxidized decreased markedly with increased O₂ concentration. The data seem consistent with an explanation based on lower temperature oxidation occurring only on the Pt surface, whereas at higher temperatures the catalytic process extends itself to some degree into the vapor phase. It is also suggested that dissociative adsorption of O₂ at higher temperatures is involved in the ion-producing process.</p>		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Surface catalysis Hydrocarbon oxidation Platinum-catalyzed combustion Platinum-catalyzed ionization Chemi-ionization						