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A Study of the Ionization Produced by the Catalytic Combustion of Hydrocarbons

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Studies have been made of the ionization produced during the catalytic combustion of hydrocarbons on a platinum catalyst. The ion yield varies widely depending upon the molecular structure of the hydrocarbon and the catalyst temperature. Highly branched alkanes have produced the greatest ionization among the hydrocarbons studied. The ions produced per mole of hydrocarbon burned are of the same order of magnitude as those produced from a hydrocarbon burning in a hydrogen flame.

INTRODUCTION

Several years ago a study was conducted in this Laboratory concerning the catalytic oxidation in air of low concentrations of hydrocarbons and other organic compounds (*1*, *2*). The striking fact which emerged from this study was that under these conditions, very small amounts of organic compounds were oxidized with no evidence of intermediate oxidation products. Only unburned hydrocarbon, carbon dioxide, and water were found in the effluent. About this same time a considerable interest had developed concerning the nature of the ionization which occurred in hydrocarbon flames (*3*). Of particular note was the development of the hydrogen flame-ionization detector for use in gas chromatography (*4*). To further the understanding of the catalytic combustion process, it was of interest to compare it with noncatalytic vapor-phase oxidation, and with flame combustion. As a consequence, work was begun to explore the possibility of ion formation during catalytic combustion at temperatures much lower than in flames. The possibility was enhanced by the theory that ions in hydrocarbon flames are the result of chemi-ionization (*3*). It was soon demonstrated that the catalytic combustion process did in fact yield collectible ions.

Since the initiation of the current work, several papers by Perkins and co-workers (*5*, *6*, *7*) have been published which showed that ions are produced during catalytic combustion. The work of Perkins *et al.* had a strong emphasis on the possible application of this catalytic ionization phenomenon as a detector for gas chromatography. In this respect, it appeared that this process would be unsuitable as a chromatographic detector except for special situations.

Nevertheless, it was deemed desirable to study the phenomenon of ionization during catalytic oxidation further to gain more insight into the general catalytic oxidation process. Of particular interest was the exploration of the effect of molecular structure, with emphasis on hydrocarbons in the studies presented here. In addition, attention was given to establishing that the ionization observed was indeed a function of the catalytic oxidation process itself, and not due simply to thermal emission of ions from the catalyst.

METHODS

The experimental apparatus for studying ionization due to catalytic combustion consisted of a brass cell block containing a platinum combustion filament and an ion collector, together with a shielded battery, electrometer, and recorder. This arrangement is shown in the schematic diagram in Fig. 1. Figure 2 is a detailed drawing of the combustion cell and Teflon plug insert. As may be seen from Fig. 2, the gas enters the cell through a suitable hole in the Teflon plug in which is mounted the cylindrical platinum ion collector, and flows up around the spirally wound platinum catalytic filament, and out near the top of the cell.

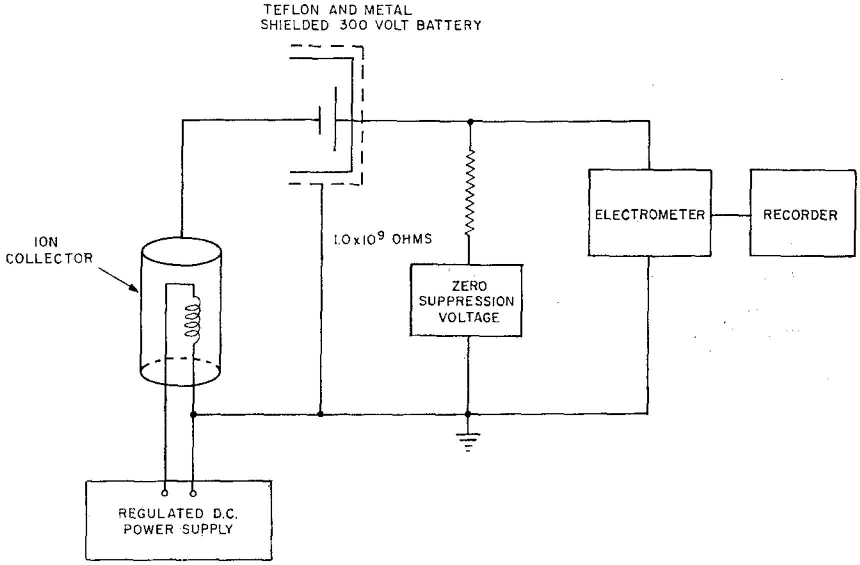

FIG. 1. Schematic diagram of circuit used with catalytic combustion cell.

The platinum combustion filaments were obtained from the Precision Scientific Co. They were spirally wound and mounted as shown in Fig. 2. The filament was powered by a transistorized DC variable voltage power supply. A 300-V battery provided the collector potential, usually 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. Each new filament was noisy after installation until exposed to several temperature cycles with air or nitrogen flowing through the cell. After filaments were so conditioned, the background current was no higher than 0.015×10^{-9} amp, even at the highest filament current used, 1.2 amp.

The temperature of the filament was measured at the three highest current settings, 1.0, 1.1, and 1.2 amp, by means of an optical pyrometer. From the resistance of the filament at room temperature, the optical pyrometer values and literature data on the change of resistance of platinum with temperature, along with the applied currents and voltages, filament temperatures at intermediate currents were calculated.

In order to measure the temperature rise of the filament due to the combustion of the sample on its surface, the filament was made one leg of a Wheatstone bridge circuit. The bridge was balanced with air flowing through the cell, and the subsequent unbalance caused by the combustion of the sample was measured. This data enabled the heating effect of the various samples on the filament to be compared.

The mixtures of liquids and gases used were prepared in 1.7-liter stainless steel bottles by injecting the liquid or gas into

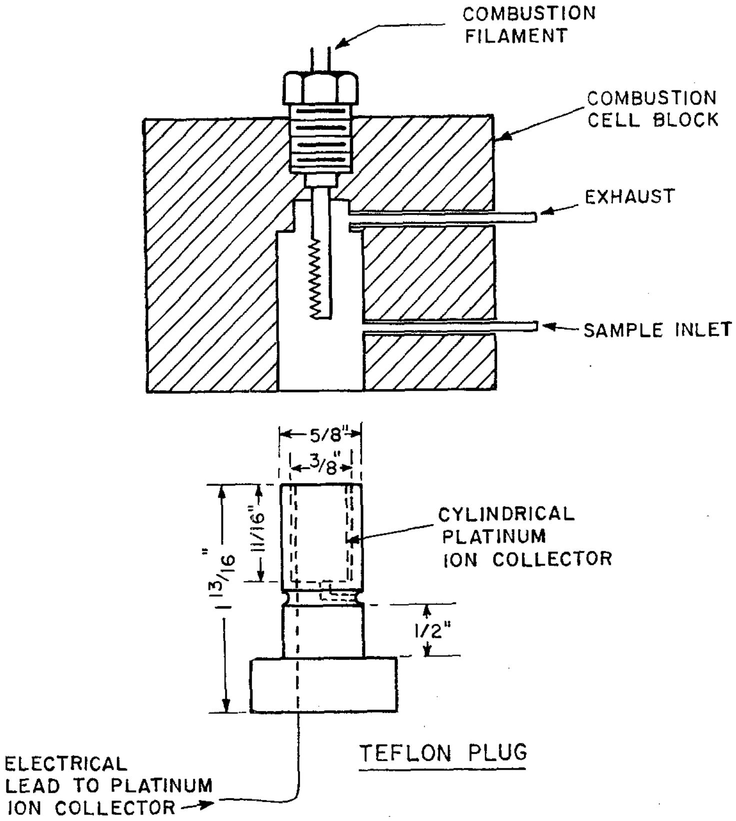

FIG. 2. Catalytic combustion cell.

the evacuated bottle and then pressurizing to 10 atm with breathing quality compressed air. A four-way valve was used to introduce the sample into the combustion cell. The two-position valve was operated as follows: In position one, air alone flowed through the combustion cell at a metered rate. At the same time the sample mixture was flowing through the other loop of the valve through a flow meter so that the flow rate could be matched to the air flow rate. In position two, the two streams were reversed so that the sample mixture flowed through the combustion cell. The flow rates used were either 50 or 100 cc/min. The exhaust gases were passed through appropriate analytical instruments to determine the extent of oxidation. Carbon dioxide (CO_2) and carbon monoxide (CO) were analyzed with Model 15A Liston-Becker nondispersive infrared gas analyzers. Hydrocarbons and hydrogen were determined by gas chromatography. For hydrocarbons, a DC-550 silicone oil column was used in either a Laboratory-built chromatograph or a Beckman GC-2A. Both instruments were equipped with Beckman hydrogen-flame detectors. Hydrogen was measured with a Fisher Gas Partitioner, Model 25M, containing a 5A Molecular Sieve column.

The hydrogen and carbon monoxide used were obtained from the Matheson Co. The hydrocarbons were Phillips Chemical Co. pure grade (99 plus mole %), used as received.

RESULTS AND DISCUSSION

Some effort was expended in establishing the effect of certain operating parameters on the extent of ionization. However, details of these studies will not be presented except in a few instances, because the primary emphasis is put on the chemical aspects of the ionization which occurs. Analytical instrumentation was provided to determine the disappearance of fuel molecules and the appearance of oxidation products. The stability of the combustion system was excellent, no baseline noise being observed at relatively high filament temperatures. A small background current occurred at 1.2-amp filament current (about 1190°C) which was the highest used. Reproducibility of ionization current at a level of about 5×10^{-10} amp and higher was about $\pm 2\%$.

A potential of 300 V was maintained between the collector and the heated filament. When the collector (cylindrical outer electrode) was operated at a potential negative with respect to the heated filament, the ionization currents obtained were as given in the data in this paper. When the collector was positive, no measurable ion current was observed under the conditions of these experiments. This observation agrees with that published by Perkins and Folmer (*6*).

Although hydrocarbon mixtures have been found to give an ionization signal at concentrations as low as 0.004 mg/liter, higher concentrations were usually used to allow better analyses for CO_2, CO, and the temperature rise of the filament. A detailed study of concentration effect has not been made. However, in the range of approximately 0.1 to 1.0 mg/liter the ion current is roughly proportional to concentration.

Relationship of the Ionization Phenomenon to Catalytic Oxidation

All of the results presented in this paper were obtained using platinum as the catalyst as described under "Methods." However, some experiments were made using gold-plated platinum filaments. For example, with platinum the maximum ionization of 2,2-dimethylbutane was found in the temperature range of 800–900°C, as shown in Fig. 3. In addition, considerable oxidation of the hydrocarbon occurred, as is shown by the CO_2 production. In this same temperature range, no CO_2 or ionization were detectable when gold-plated filaments were used. This fact clearly establishes the intimate relationship between the ionization phenomenon and the catalytic properties of platinum. The close relation of ionization with catalytic oxidation is shown by the fact that no ionization occurred with platinum catalyst when nitrogen was substituted for air.

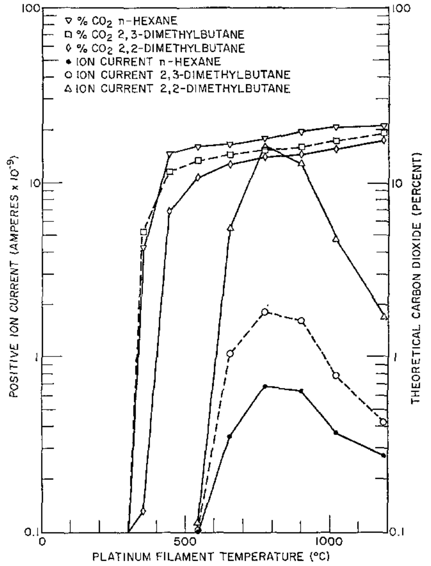

FIG. 3. Effect of filament current on ion current and carbon dioxide yield.

Catalytic Combustion of Hydrocarbons

To illustrate the general results obtained with hydrocarbon/air mixtures, representative data for the catalytic oxidation of the three isomeric hexanes, *n*-hexane, 2,2-dimethylbutane, and 2,3-dimethylbutane are presented in Fig. 3. In addition to the ionization current and CO_2 yield given in this figure, simultaneous measurements were made of CO production, disappearance of hydrocarbon, and temperature rise of the filament.

CO_2 is the dominant carbon-containing oxidation product. Curves of hydrocarbon loss roughly parallel the CO_2 yield. Only a trace of CO is found at lower filament temperatures, building up to $<5\%$ of theory at the highest temperatures used.

From Fig. 3, it is immediately apparent that there is no direct relationship between extent of oxidation for a given hydrocarbon and the ion current produced. For example, although significant

CO_2 production (4.3%) is measured for *n*-hexane at a filament temperature of 350°C, no measurable ion current is recorded until a filament temperature of 650°C is reached (CO_2 production is 16.7%). A sharp increase in ion population occurs as the filament temperature is increased, with maximum ionization at 770° to 900°C, followed by a rather sharp decrease. All of these characteristics are typical of the results obtained for all the aliphatic hydrocarbons studied. In all cases substantial oxidation occurs at filament temperatures considerably below those at which ionization begins.

It is observed in Fig. 3 that the highly branched hexanes were less easily oxidized than was *n*-hexane, based on conversion to CO_2 and temperatures for onset of oxidation. This is corroborated by data for the disappearance of hydrocarbon. This is similar to the case of uncatalyzed vapor-phase oxidation in air, where branched-chain paraffinic hydrocarbons are more difficultly oxidized than straight-chain paraffins (*8*, *9*).

The most intriguing fact observed in Fig. 3, however, is that *n*-hexane, although more easily oxidized, shows considerably less ionization than the branched-chain hexanes at a given filament temperature. This large difference in ionization has been corroborated for these three hydrocarbons several times under these and other conditions.

The ionization currents measured during the catalytic oxidation of several additional hydrocarbons are given in Table 1 for comparison with these three hexanes. Benzene produces almost no ions under these conditions. It appears evident that the effect of chain branching for the alkanes is a general phenomenon, and is not a random effect. The order of magnitude increase in ionization for the highly branched 2,2-dimethylbutane and 2,2,4-trimethylpentane over the *n*-alkanes, hexane and octane, is well demonstrated, and has been substantiated by experimentation using several different platinum coil catalysts, hydrocarbon concentrations, and flow rates.

TABLE 1
IONIZATION PRODUCED BY CATALYTIC COMBUSTION OF HYDROCARBONS

Hydrocarbon[a]	Ionization current (amperes × 10^9)
n-Hexane	0.67
2-Methylpentane	1.11
3-Methylpentane	1.45
2,3-Dimethylbutane	1.81
2,2-Dimethylbutane	15.8
n-Octane	0.87
2,2,4-Trimethylpentane	9.9
Benzene	0.02
tert-Butylbenzene	1.65

[a] Hydrocarbon concentration in air was 3.8 mg/liter. Flow rate of mixture through combustion cell was 50 cc/min.

Ion Yield

The ion yields from the catalytic combustion of hydrocarbons were calculated from the number of gram atoms of carbon passing through the cell per unit time, the extent of burning, and the ion currents produced. Table 2 lists the yields for the three isomeric hexanes. By way of comparison, combustion of hydrocarbons in a hydrogen flame produces about 0.25 coulomb/g atom carbon (*10*). The efficiency of ionization of hydrocarbon is extremely low in both the hydrogen flame and in the catalytic combustion cell. In the catalytic combustion of 2,2-dimethylbutane, one ion is formed for each 300 000 carbon atoms burned; of *n*-hexane, one for each 15 000 000.

TABLE 2
ION YIELD FROM THE CATALYTIC COMBUSTION OF HYDROCARBONS

Hydrocarbon	Hydrocarbon concentration, (mg/liter)	Coulomb/g atom C burned
n-Hexane	3.8	0.0067
n-Hexane	0.42	0.0066
2,3-Dimethylbutane	3.8	0.021
2,2-Dimethylbutane	3.7	0.28
2,2-Dimethylbutane	0.41	0.26

For *n*-hexane and 2,2-dimethylbutane, samples of each differing in concentration by a factor of almost 10 were compared. Although the data in Table 2 are limited, a degree of linearity of ion current with hydrocarbon concentration is indicated by the close agreement of the ion yields. The values are probably within experimental error.

Catalytic Combustion of Carbon Monoxide and Hydrogen

Since it has been well established (*10*) that no significant ionization occurs in flame combustion of hydrogen (H_2) and carbon monoxide (*CO*), it was of interest to determine the extent of ionization during catalytic combustion of these two gases. A mixture of 1% of H_2 in air was passed through the catalytic combustion cell under experimental conditions which have yielded substantial ionization currents with hydrocarbons. Although oxidation of the H_2 was considerable when compared to hydrocarbons at the same filament temperatures (see Fig. 4 and Table 3), there was no evidence of ionization even at filament temperatures as high as 1020°C, where H_2 oxidation was complete. The extent of H_2 oxidation was followed by gas chromatography of the H_2 and the temperature rise of the filament. Oxidation of H_2 began at a lower filament temperature and was more complete than for hydrocarbons or CO, as shown in Fig. 4.

A similar mixture of CO in air also showed no ionization over the same wide range of filament temperatures, even though considerable oxidation occurred as shown by the disappearance of CO (see Fig. 4) and production of CO_2.

It was not unexpected that catalytic oxidation of H_2 and CO did not generate ions. In this respect the catalytic process is the same as flame combustion. However, this finding appears to be at variance with Perkins and Folmer (*6*), who state that they observed ionization for these two compounds which was about as great as for other compounds.

The absence of an ion current during the combustion of H_2 and CO demonstrated that the current produced during the burning of a hydrocarbon was indeed due to ions formed in the combustion process and was not caused by thermal emission from the platinum catalyst. In all cases, the temperature rise of the filament due to the burning of the H_2 was greater than, and for the CO equivalent to, that produced by the hydrocarbon at a given applied filament temperature. If the ion current was due to thermal emission, the H_2 and CO should have produced equal or higher currents.

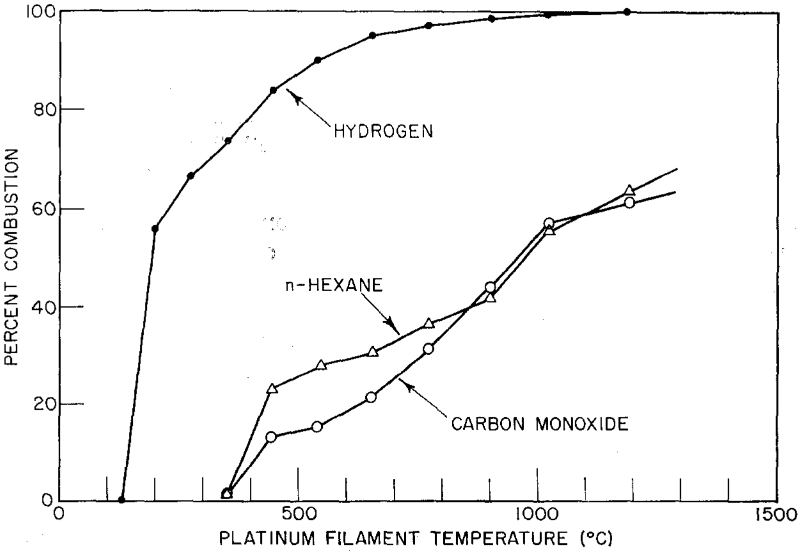

FIG. 4. Effect of filament current on combustion of hydrogen, carbon monoxide, and *n*-hexane.

TABLE 3

COMBUSTION AND IONIZATION OF *n*-HEXANE AND HYDROGEN

Filament temperature, (°C)	Percent combustion				Ion current (amperes × 10^9)		
			H_2-*n*-Hexane mixture[c]				
	H_2[a]	*n*-Hexane[b]	H_2	Hexane	H_2	*n*-Hexane	H_2-*n*-Hexane mixture
130	0.0	0.0	0.0	0.0	0.0	0.0	0.0
200	61.5	0.0	0.0	0.0	0.0	0.0	0.0
270	77.8	0.0	21.9	0.0	0.0	0.0	0.0
350	80.6	0.0	67.5	0.0	0.0	0.0	0.0
440	82.6	0.0	81.8	18.8	0.0	0.0	0.0
540	91.3	13.3	88.5	25.4	0.0	0.0	0.0
650	92.3	15.1	89.5	27.5	0.0	0.009	0.003
770	93.2	33.5	91.5	29.3	0.0	0.051	0.051
900	95.0	39.3	92.2	33.7	0.0	0.078	0.061
1020	97.0	43.8	98.0	44.6	0.0	0.096	0.060

[a] 1% H_2 in air.

[b] 0.42 mg/liter *n*-hexane in air.

[c] 1% H_2 plus 0.42 mg/liter *n*-hexane in air.

Catalytic Combustion of n-Hexane in the Presence of H_2

Recent theories on the mechanism of flame ionization of hydrocarbons (*3*) are based primarily on mass spectrometric data which show that the predominant positive ion is H_3O^+. One theory suggests that the ultimate reaction is

$$CHO^+ + H_2O \rightarrow CO + H_3O^+$$

Consequently, it seemed possible that the oxidation of large amounts of hydrogen at the surface of the catalyst simultaneously with the catalytic oxidation of the hydrocarbon might enhance the production of ions.

As stated earlier, the catalytic oxidation of H_2 was not accompanied by a measurable ion current. A relatively low concentration of *n*-hexane (0.42 mg/liter) in air containing 1% H_2 was passed through the combustion cell. The combustion of this amount of *n*-hexane does not cause a significant increase in filament temperature compared to that produced by the hydrogen. The data are tabulated in Table 3, in comparison with H_2 alone and *n*-hexane alone.

It was found that this mixture yielded somewhat more oxidation of *n*-hexane and less ionization than the *n*-hexane alone in air. The combustion of the H_2 was decreased by the presence of hydrocarbon.

SUMMARY AND CONCLUSIONS

Not enough information is available at present to suggest a mechanism for the ionization associated with the catalytic oxidation of hydrocarbons. However, a number of facts have been established which will be helpful in any explanation by limiting some of the possibilities.

(a) No ions are collected during the catalytic combustion of CO or H_2.

(b) Substantial ion currents are produced during the catalytic oxidation of hydrocarbons at 550°C or greater.

(c) At low filament temperatures, 300° to 400°C, no ions are produced even when substantial oxidation of the hydrocarbon occurs.

(d) There appears to be an optimum catalyst temperature for the production of ions. The fact that this temperature is nearly the same for all hydrocarbons studied suggests that a similar mechanism is involved in all cases.

(e) The production of ions is as much as an order of magnitude greater for highly branched hydrocarbons than for straight chain hydrocarbons. In contrast to flame ionization, the hydrocarbon structure has a profound effect on ionization induced by catalytic combustion.

(f) Extent of ionization is not related to ease of oxidation of a particular hydrocarbon. For example, 2,2-dimethylbutane yielded many times more ions than *n*-hexane, although the latter was oxidized more readily.

(g) As with flame ionization, the number of ions produced is an exceedingly small fraction of the number of carbon atoms oxidized.

It seems premature to postulate a mechanism to account for the ions produced during oxidation of hydrocarbons over a platinum catalyst. However, it seems likely that this phenomenon is another instance of chemi-ionization, that is, ionization resulting from the reaction of two or more atoms or molecules. This is in contrast to thermal ionization. Chemi-ionization is suggested by several observations: (a) the absence of ions when nitrogen is substituted for air; (b) the absence of ions when gold is substituted for platinum; (c) the absence of ions when hydrogen and carbon monoxide are oxidized in this system; and (d) the tremendous influence of molecular structure of the hydrocarbon on the extent of ionization realized.

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