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Mass Spectrometric Investigation of Hydrocarbon Ions Produced Via Catalytic Oxidation

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The mass spectrometric identification of the charged and neutral species produced during the catalytic oxidation of 2,2-dimethylbutane is reported. The chemical composition of the ions produced is temperature and pressure dependent. At temperatures below 750°C polymeric or clustered ions are observed at *m/e* ratios up to 298. Ions which are typically found in flames are detected above 900°C. The data suggest that at lower temperatures the oxidation process takes place on the surface. At high temperatures ($>900°C$) the ion producing mechanism extends into the vapor phase.

INTRODUCTION

For many years charged particles have been known to form in high temperature hydrocarbon–oxygen flames (*1*). It is now well established that the primary ions are produced within flames by radical–radical reactions. At our Laboratory measurable quantities of ions have been observed during the low temperature oxidation occurring when a hydrocarbon–air mixture is passed over a heated platinum filament (*2*). This earlier investigation was performed by monitoring the electrical current in a combustion cell. The experimental evidence presented here supports the proposal (*2*) that, at least at low temperatures ($<750°C$), these ions are produced by catalytic oxidation on the heated platinum surface and shows that the chemical composition of the ions is temperature and pressure dependent.

To facilitate a better understanding of the catalytic processes generating the above ions, an ion source for a time-of-flight mass spectrometer was constructed which permits the sampling and mass identification of ions and neutrals produced by catalytic methods.

APPARATUS AND PROCEDURES

In a conventional electron-impact ion source, ions are produced by bombarding neutral molecules with energetic electrons. The ion source built for this study, in addition to the conventional electron impact arrangement, incorporates a heatable catalytic surface in the ionization chamber. This ion source configuration permits the independent or simultaneous generation of ions within the conventional ion source or within the catalytic oxidation region. Thus, we have the capability to identify both the ions and neutral species generated by catalytic oxidation reactions. Hereafter, the ions produced in the catalytic oxidation region will be referred to as "catalytic ions."

Figure 1 depicts a "closed" high pressure ion source (*3*) for a Bendix time-of-flight mass spectrometer modified to include a heatable platinum wire as a catalytic surface. The temperature of the platinum was calibrated with an optical pyrometer. This ion source is differentially pumped with a high capacity diffusion pump (1400 liters/sec), which allows its operation to pressures of 150 Torr. A conventional electron gun, operated in a pulsed

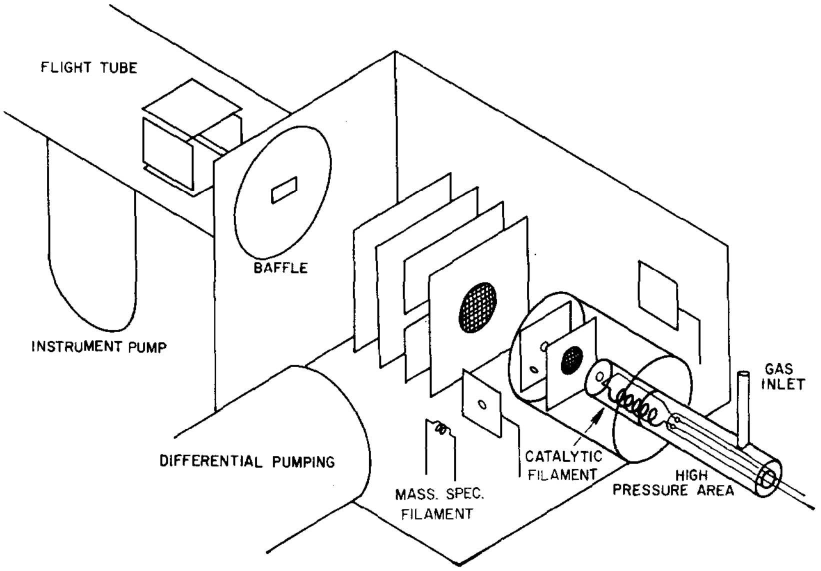

FIG. 1. Schematic diagram of the modified ion source for a time-of-flight mass spectrometer.

mode, is used for electron-impact ionization. A positive blocking pulse applied to the second grid of the ion source in synchronization with the focusing pulses prevents spurious ions from entering the focusing region. The focused ions are accelerated down the flight tube and separated according to their mass-to-charge (*m/e*) ratio. The instrument has a mass range of 1 to 500 *m/e*.

All mixtures were oxygen rich and prepared by injecting 0.5 to 2.0 mmoles of the hydrocarbon liquids or gases into an evacuated 13-liter reservoir and then pressurizing to 1 atm with the appropriate mixture of nitrogen and oxygen. The prepared gas mixtures were introduced into the ion source from the reservoir through a variable leak; the ion source pressure was monitored with a MKS Baratron pressure gauge, Model No. 100A, and was held constant.

Ions generated exclusively from the catalytic surface could be observed by shutting off the electron-impact gun. Activating the electron gun while the catalytic process was occurring produced additional ionic species. These new ions were formed by the ionization of neutral molecules and radicals during the catalytic reactions, and from unreacted hydrocarbon. Subtraction of the normal electron-impact spectrum of the hydrocarbon–nitrogen–oxygen mixture and of the ions produced by the catalytic oxidation permitted the identification of the neutrals generated by the catalytic process.

To insure that the mechanism producing the ions was indeed a catalytic process, the platinum filament was replaced with a gold wire; under these conditions, no ions were detected. In addition, no ions were observed using a platinum catalyst when O_2 was replaced by N_2.

RESULTS AND DISCUSSION

Umstead, Woods and Johnson (*2*) noted that the total ion current produced by catalytic oxidation varied as a function of Pt catalyst temperature, and that the greater the branching of a hydrocarbon the greater its ion yield. The temperature dependence of the production of catalytic ions was verified by summing the ion currents detected by the mass spectrometer at all *m/e* values and plotting these sums as a function of catalyst temperature (Fig. 2). The agreement between these data and the data reported by Umstead, Woods and Johnson (*2*) shows that, although the experimental

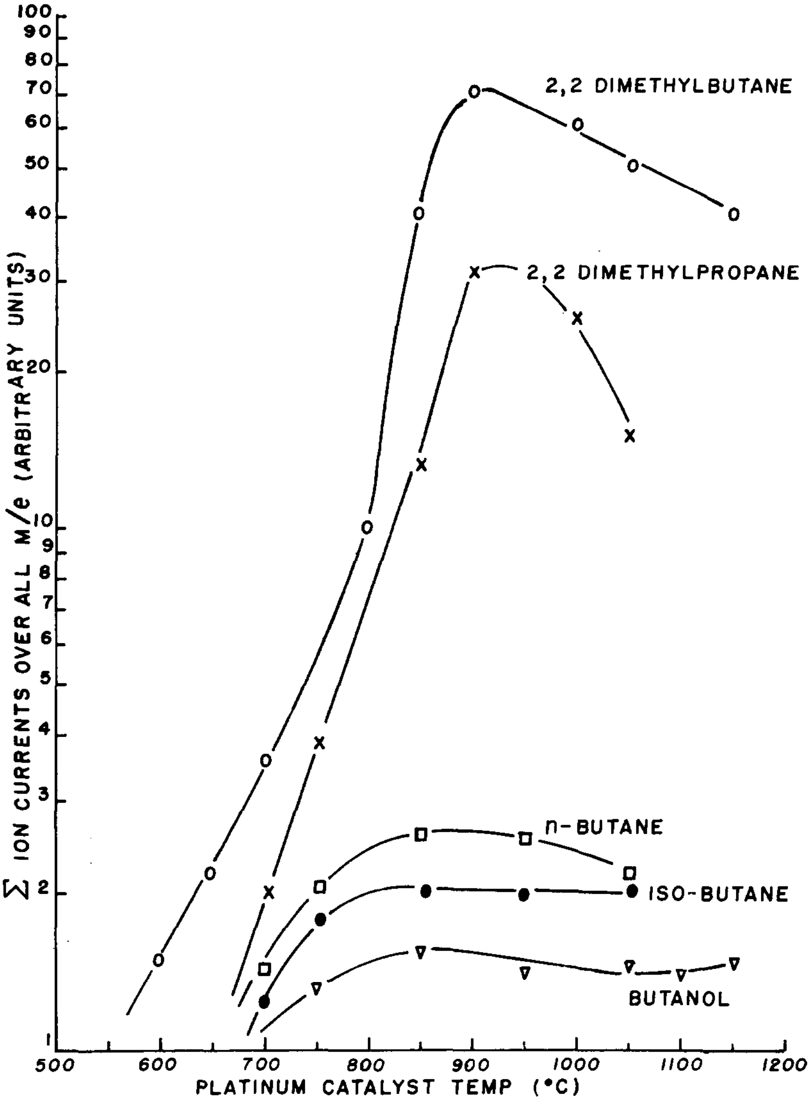

FIG. 2. Total ion current as a function of platinum filament temperature.

procedures used are different, the ion-producing mechanism is the same in both studies. Of the hydrocarbons tested, 2,2-dimethylbutane (DMB) yielded the greatest number of ions and was used in the remainder of this preliminary study.

A significant question to be answered is whether the ionizing reactions are occurring on the surface of the catalyst, in the gas phase, or at the catalyst–gas interface. Further, if the reactions directly involve the catalytic surface, do they proceed via the interaction of two species adsorbed on adjacent sites, or via the direct impact of a molecule from the gas phase with an adsorbed radical or atom? Insight into these questions may be gained by comparing the amount of hydrocarbon oxidized as a function of the catalyst temperature (Fig. 3) with the total catalytic ion intensity variation as a function of the catalyst temperature (Fig. 4). The quantity of hydrocarbon oxidized was estimated by conventional electron-impact analysis of the

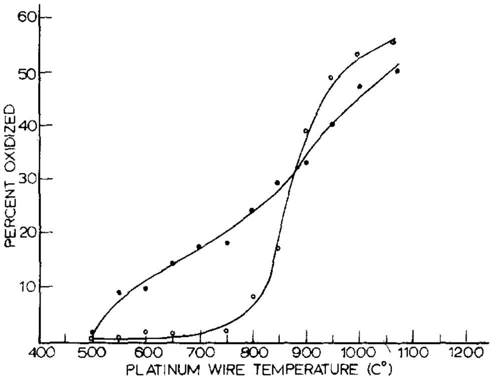

FIG. 3. Percentage of DMB oxidized as a function of the catalyst temperature. (○) 60% O_2, 40% N_2; (●) 21% O_2, 79% N_2.

decrease in DMB. The observed increase in CO and CO_2 also corresponded to the DMB consumed.

More DMB is oxidized at lower temperatures (<750°C) in the 21% O_2 mixture than in the 60% mixture. At higher temperatures (>900°C), however, more DMB is oxidized in the 60% O_2 mixture. Within the margin of experimental error, the total catalytic ion intensity is the same at lower catalyst temperatures for both oxygen concentrations. However, at higher temperatures (>900°C), the total ion current observed is significantly greater in the 60% O_2 mixture. From this examination, we can divide the data presented in Figs. 3 and 4 into three parts: a low temperature region (<750°C), a high temperature region (>900°C) and a transition region (750–900°C).

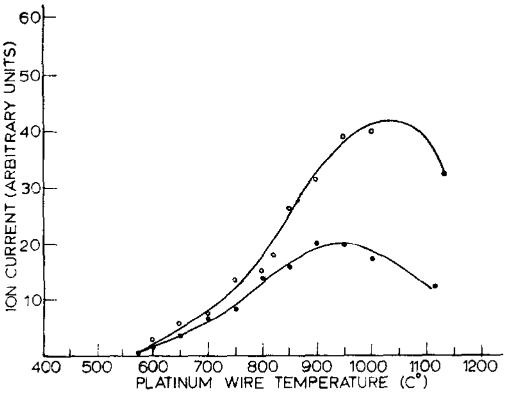

FIG. 4. Total catalytic ion current as a function of the catalyst temperature. (○) 60% O_2, 40% N_2; (●) 21% O_2, 79% N_2.

These observations can be interpreted to support the suggestion (*2*) that in the low temperature region oxidation occurs on the surface of the platinum catalyst. At the higher O_2 concentration, the preferential adsorption of oxygen over hydrocarbon (*4*) and its subsequent surface dissociation interferes with the adsorption of DMB; thus, fewer sites are available for DMB adsorption and less DMB is oxidized, as shown in Fig. 3. This indicates that both oxygen and DMB must be adsorbed on the catalyst surface for the oxidation reaction to take place, in accord with the Langmuir–Hinshelwood (*5*) mechanism.

The shapes of the total catalytic ion current curves in the low temperature region, (Fig. 4) are qualitatively different from those of their respective oxidation curves (Fig. 3), suggesting that, in this region, the surface mechanism producing ionization must be more complex than a Langmuir-Hinshelwood process. The difference between the oxidation and ionization processes is further pointed out by the estimate (*2*) that approximately 10^6 DMB molecules are oxidized for each catalytic ion formed.

In the lower temperature range, $C_3H_3^+$ was the abundant ion and was the only low molecular weight ion observed (Table 1). The formation of polymeric or clustered ions was observed to *m/e* 298; a chemical composition for each of these ions is suggested in Table 1. It is noteworthy that the proposed compositions of the high mass ions all have some multiple of the $C_3H_3^+$ unit in their structures. Miller (*6*) has recently reported ion clustering in the low temperature catalytic oxidation of hydrocarbons but gives no information on the ion composition or mass.

No catalytic ions, except $C_3H_3^+$, were detected when the ion source pressure was reduced to 20 Torr or less. Since the catalytic surface is sparsely covered at these pressures (*7*), with very few adjacent sites occupied, we believe $C_3H_3^+$ to be a primary ion and to serve as the "building block"

TABLE 1

Catalytic Ions Produced from a 2,2-Dimethylbutane–Air Mixture

Platinum surface <750°C			Platinum surface >900°C		
Ratio mass/charge	Proposed chemical composition	Relative intensity	Ratio mass/charge	Proposed chemical composition	Relative intensity
39	$C_3H_3^+$	100	19	H_3O^+	100
94	$(C_3H_3)_2O^+$	50	29	CHO^+	25
117	$(C_3H_3)_3^+$	10	39	$C_3H_3^+$	50
156	$(C_3H_3)_4^+$	10	43	$C_2H_3O^+$	25
255	$(C_3H_3)_5O_2CO^+$	40			
298	$(C_3H_3)_6O_4^+$	5			

of all higher molecular weight ions observed during low temperature catalytic oxidation. The higher mass (m/e) ions appear only when the catalyst surface approaches saturation (ions source pressure $\geq$ 100 Torr) and the $C_3H_3^+$ ions can initiate polymerization by reacting with other adsorbed species.

$C_3H_3^+$ can be produced in the gas phase by thermal ionization of C_3H_3 radicals or by chemi-ionization reactions, and by reactions on the catalyst surface. The first involves the catalytic cracking of DMB to produce C_3H_3 radicals which then become thermally ionized. Electron impact analysis of the hydrocarbon–oxygen mixture, after passage over the catalyst, does indicate the presence of small amounts of C_3H_3 radicals. From the Saha-Langmuir relationship (*8*), however, the ratio of ions to their respective neutral species is very small and, even though the ion source used in this study is not an efficient detector of neutral species, a larger concentration of C_3H_3 should have been observed. Since only a low concentration of C_3H_3 was detected, either thermal ionization is unimportant in our system, or the C_3H_3 remains adsorbed on the catalytic surface.

A second mechanism, chemi-ionization, that may lead to $C_3H_3^+$ formation is (*9*):

$$CH^* + C_2H_2 \rightarrow C_3H_3^+ + e, \qquad (1)$$

where CH^* (electronically excited CH) can be produced by catalytic cracking of DMB. An examination of the electron-impact spectra of the DMB mixture after exposure to the catalytic surface shows evidence for the presence of a small amount of acetylene. The low concentration of C_2H_2 observed, however, compared to the intensity of the $C_3H_3^+$, suggests that the gas-phase reaction (1) is not the primary source of $C_3H_3^+$. Thus, the only alternative left is that the $C_3H_3^+$ is formed on the catalyst surface.

In the high temperature region more DMB is oxidized and more catalytic ions are formed in the 60% O_2 mixture than in the 21% O_2 mixture. However, the difference between the amount of DMB oxidized in the 60 and 21% mixtures is much smaller than the difference between the total catalytic ion intensities. We believe that in the high temperature region (>900°C) both surface processes and gas phase reactions contribute to the overall production of catalytic ions, since considerable amounts of atomic oxygen are driven off the catalyst and this desorbed atomic oxygen is available to participate in gas phase reactions. It is well established (*10*) that molecular oxygen is dissociated on a heated Pt catalyst beginning at 400°C and that the dissociation increases with increasing temperature. The data presented in Fig. 5 shows that in our hydrocarbon–air system the concentration of gas-phase atomic oxygen also increases with catalyst temperature and the desorption rate is large throughout the high temperature range.

Above 900°C substantial amounts of atomic oxygen are being desorbed from the catalyst surface. Consequently, the contribution from the surface mechanism, where adsorbed atomic oxygen is involved

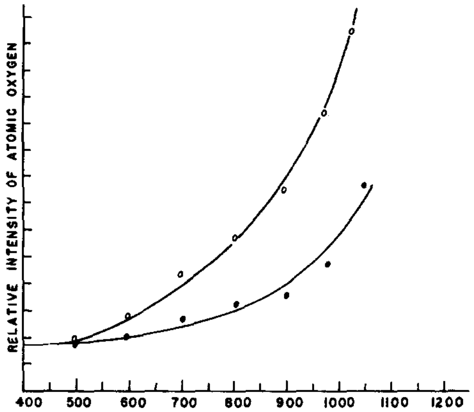

FIG. 5. The relative intensity of ion current from gas-phase atomic oxygen (m/e 16) as a function of catalyst temperature. (○) 60% O_2, 40% N_2; (●) 21% O_2, 79% N_2.

in the ionization process, diminishes and the overall catalytic ion intensity decreases (Fig. 4). The additional gas-phase atomic oxygen resulting from the desorption appparently does not increase any gas-phase ionization process sufficiently to compensate for the decrease in the surface reaction.

The rapid increase observed in the amount of DMB oxidized within the transition temperature range (750–900°C) indicates that the mechanism producing the catalytic ions is not the same throughout the temperature range (400–1100°C) investigated. The data in Table 1 support this interpretation since the catalytic ions produced in the low and high temperature ranges (400–750°C and 900–1100°C) differ significantly in composition. In the higher temperature region a completely different group of catalytic ions was detected which are characteristic of these observed in hydrogen flames (*11*). In this region it is possible that atomic oxygen reacts with hydrocarbon species both at the surface and in the gas phase to produce the ions observed.

In the combustion of hydrocarbons, atomic oxygen (O) is considered to be the major initiator of chemical reactions producing ions (*11*). Reactions leading to the observed ions are:

$$CH + O \rightarrow CHO^+ + e, \qquad (2)$$

$$C_3H_3^+ + O \rightarrow CHO^+ + C_2H_2, \qquad (3)$$

$$CHO^+ + C_2H_2O \rightarrow C_2H_3O^+ + CO, \qquad (4)$$

$$C_2H_2 + C_2H_3O^+ \rightarrow C_3H_3^+CH_2O, \qquad (5)$$

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO. \qquad (6)$$

The neutral hydrocarbon species identified in the high temperature catalytic oxidation of DMB are listed in Table 2. While only trace amounts of these species were observed, we cannot rule out their participation in gas-phase reactions leading to ionization. Their apparent low concentration, compared to that of the catalytic ions, may be due to the inefficient detection of neutral species in our ion source.

The transition region (750–900°C) appears to be a complex combination of the low and high temperature ranges. Future work is being planned to characterize this transition temperature zone.

CONCLUSION

This work has provided the first identification of some of the charged particles produced during the catalytic oxidation of hydrocarbons. Analysis of the data obtained on the formation of catalytic ions produced by passing a hydrocarbon–oxygen mixture over a heated platinum wire leads to the conclusions that below 750°C the oxidation process takes place on the surface via a Langmuir-Hinshelwood mechanism (*5*), and that the ionization process, while occurring on the surface, is more complex than the oxidation mechanism. We believe that the mechanism leading to catalytic ion production consists of the following steps: first, the adsorption of the hydrocarbon and oxygen on the catalytic surface; second, the dissociation of oxygen on the catalyst surface; and third, reaction of atomic oxygen with the hydrocarbon.

TABLE 2

NEUTRAL HYDROCARBONS OBSERVED DURING CATALYTIC OXIDATION OF DMB IN THE RANGE 700–1100°C

C_3H_3
C_2H_2
CH_2O

Polymerization or clustering is initiated by $C_3H_3^+$ resulting in ions of mass-to-charge ratios up to 298.

At catalyst temperatures above 900°C the data lead to the conclusion that the ions are produced in the gas phase as well as on the catalyst surface. The observation of typical flame ions in this region suggests that reactions similar to the ones occurring in flames are taking place on and in the vicinity of the surface.

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