Chemi-ionization Reactions in High Temperature Hydrocarbon Oxidation

Joe V. Michael and Graham P. Glass

Chemistry Department, Harvard University, Cambridge, Mass.

Introduction

The mechanism of chemi-ionization in hydrocarbon oxidation reactions has attracted much interest in recent years. Ionization in hydrocarbon flames has been studied by means of Langmuir probes,[1,2] mass spectrometric sampling,[2,3] and microwave attenuation measurements.[4,5] By using these techniques the concentration of ions in the flames of lower hydrocarbons has been measured and has been shown to be too great to be accounted for by thermal excitation. Most investigators agree that the ions are formed by chemical reactions but the nature of these reactions as yet is not absolutely clear. The high heats of formation of most organic ions places severe energetic restrictions on the reaction which produces ions, and much effort has been spent considering reactions exothermic enough to do this. The reaction, $CH + O = CHO^+ + e^-$, has been suggested as a probable ion forming reaction, but no conclusive evidence for it has been found. To be sure CHO^+ (mass 29) has been observed by many investigators in flames, but it has always appeared in concentrations much below that of the more abundant ions (e. g. H_3O^+). Calcote[6] has pointed out that CHO^+ would be expected to undergo rapid proton transfer reactions with water, a product of these oxidations, thus explaining its presence in such low concentrations.

Calcote[2] has detected the $C_3H_3^+$ ion in a mass spectrometric investigation of low pressure acetylene-oxygen flames. This ion was observed in the flame profile ahead of H_3O^+ in quite large concentrations and its abundance was independent of the stoichiometry of the flame. It is diffucult to account for these observations on the basis of charge transfer reactions from CHO^+.

The work described in this paper was performed using shock tubes, and the reactions which occur during the oxidations of both methane and acetylene were studied by means of a Langmuir probe and also by means of a time-of-flight mass spectrometer which was adapted to detect the chemi-ions formed during the reactions.

Experimental

The apparatus in which the Langmuir probe measurements were made was substantially the same as that described by Hand and Kistiakowsky[5]. Shock waves were generated in a three inch I. D. steel tube and shock wave velocities were measured by gold film resistance gauges the outputs of which were displayed on a raster sweep oscilloscope. Radiation from the heated gas behind the shock wave passed through a lithium fluoride window and was detected by means of an RCA 1P28 photomultiplier. An interference filter was used to isolate the $A^2\Delta \rightarrow X^2\pi$ system of CH. The probe consisted of a 12 mil diameter tungsten wire placed in the shock tube in a plane defined by the optical slits. All but the last one-quarter inch of the wire was insulated with Armstrong A2 cement, the tip of the probe being near the shock tube axis. The major modification to the apparatus was the introduction of a removable piston which could be placed seven millimeters behind the cross sectional plane which contained the probe. This allowed the reactions in the stationary gas behind the reflected shock to be studied, thus removing the complicating effect of the aerodynamic interaction of the moving gas with the probe[7].

The second technique combines a shock tube and a Bendix time-of-flight mass spectometer in a redesigned apparatus which is a significant improvement over the one described by Bradley and Kistiakowsky[8]. Complete mass spectra of the reacting gases can be obtained every 20 or 50 μsec. Data is recorded by means of Polaroid 10000 ASA speed film. Normally a total of twenty-one spectra are displayed on three Tektronix 531-A oscilloscopes so that the amount of observable reaction time is a little over a millisecond with 20 KC operation. The mass range can be adjusted at will before the start of an experiment.

Sampling is through a small pinhole (.004 in. diameter) in the tip of a small conical nozzle (1 mm. by 1 mm. pointed away from the mass spectrometer) at the end of the shock tube. It is felt that this small nozzle reduces problems caused by boundary layer build up on the reflection plate onto which the nozzle is mounted.

The shock tube is one inch in diameter and 2.75 meters long. Shock velocities are measured with four thin film resistance gauges (either Pt or Au) spaced ten centimeters apart. The signals from these gauges are displayed on a raster oscilloscope. Shock temperatures are calculated using ideal shock relations in both incident and reflected shocks.

All experiments with the time-of-flight mass spectrometer reported here were carried out with five percent reactants in ninety-five percent krypton. The experiments with the Langmuir probe apparatus were carried out with one percent reactants in ninety-nine percent argon.

Results

Ions and stable products were observed using the time-of-flight mass spectrometer in the oxidations of both acetylene and methane. Both types of species arose concurrently after an induction period characteristic of a branching chain reaction. In both systems the total ionization was observed using the Langmuir probe technique. The ionization rises exponentially with time and the measured time constants provide a convenient method for determining the rates of the branching chain reactions. Ionization is not, however, a major part of the reaction since, for example, in the oxidation of acetylene, the maximum concentration which the ions achieved was about 10^8 ions/cc. This was 10^{-6} of the initial acetylene concentration.

The individual ions produced were indentified with the time-of-flight mass spectrometer. The largest mass peaks in the acetylene-oxygen system were 39 and 19. 39, 31, 19, and 37 were observed in the methane-oxygen system. By using deuterated acetylene and methane the following assignments were made for the different species:

$$39\text{-}C_3H_3^+ \; ; \; 31\text{-}CH_3O^+; \; 37\text{-}H_3O\cdot H_2O^+; \; 19\text{-}H_3O^+.$$

Figure 1 shows the time history of the ionization in two typical experiments with acetylene-oxygen. It is seen that $C_3H_3^+$ is the first ion observed followed later by H_3O^+. In these experiments the reactant mixtures were: (A) 3 O_2 + 2 C_2H_2 + 95 Kr, and (B) 3.75 O_2 + 1.25 C_2H_2 + 95 Kr. Ionization was not observed in mixtures where acetylene was in excess over oxygen.

$C_3H_3^+$ was also the first ion observed in the oxidation of methane. CH_3O^+ arose at nearly the same time as did $C_3H_3^+$ but its concentration was much lower. H_3O^+ and $H_3O\cdot H_2O^+$ arose concurrently at still later times.

In the acetylene-oxygen system the time constant measured for the growth of ionization, using the Langmuir probe technique, was found to be identical to that measured for the simultaneous growth of chemi-luminescent radiation from the CH ($A^2\Delta \longrightarrow X^2\pi$) system.

In earlier experiments with the time-of-flight mass spectrometer, the stable products observed in the oxidation of acetylene were CO, H_2O, CO_2, and C_4H_2.[8,9] These results were confirmed in the present study. CO, CO_2, H_2O, and C_2H_2 were observed as stable products in the methane-oxygen system. CO_2 was a major product in 3 O_2 + 2 CH_4 + 95 Kr, and it was absent in 1.4 O_2 + 3.6 CH_4 +95 Kr. C_2H_2 was found to be a major product in the latter mixture but was formed in quite small quantities in the former.

Discussion

$C_3H_3^+$ has been observed by several investigators in hydrocarbon

oxidation systems. As has been stated previously, Calcote[2] detected this ion ahead of H_3O^+ in a dilute low pressure flame of acetylene and oxygen. Green and Sugden[3] have also observed this ion in flames at somewhat higher pressures. The following reaction schemes have been suggested by these workers for the formation of $C_3H_3^+$.

Calcote:

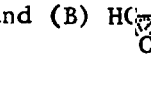
$$(1)\ CH + O = CHO^+ + e^-$$
$$(2)\ CHO^+ + H_2O = H_3O^+ + CO$$
$$(3)\ H_3O^+ + C_3H_2 = C_3H_3^+ + H_2O$$

Green and Sugden:

$$(1)\ CH + O = CHO^+ + e^-$$
$$(2)\ CHO^+ + H_2O = H_3O^+ + CO$$
$$(4)\ H_3O^+ + CH_2O = CH_3O^+ + H_2O$$
$$(5)\ CH_3O^+ + C_2H_2 = C_3H_3^+ + H_2O$$

In both of these mechanisms, $C_3H_3^+$ is formed by charge transfer reactions from CHO^+. However, the time history in the stationary gas behind a reflected shock wave is much better defined than in a flame where diffusion and cold boundary layer effects could invalidate measurements, and it is felt that $C_3H_3^+$, and not CHO^+, is the first ion formed since it is the first ion observed in these experiments.

Two structures appear to be feasible for the $C_3H_3^+$ ion:

(A) $HC{\equiv}C{-}CH_2^{\ +}$ and (B) 

The cyclopropenyl ion (B) is believed to be the more probable structure, since it has great stability due to delocalization of its π electron system. Tri-substituted aliphatic and aromatic analogs of the cyclopropenyl ion have been synthesized and halogen salts are completely dissociated in polar solvents.[10] Furthermore, a plausible mechanism for it can be suggested which is energetically possible, whereas such a mechanism for the formation of (A) is difficult to justify on an energetic basis.

If (B) is the correct species it should be extremely stable and should undergo little or no charge transfer. The ion probably is removed from the system by chemical reaction, perhaps with oxygen resulting in the production of other ions. Indeed in experiments where oxygen is in excess the rate of fall off for $C_3H_3^+$ is faster and the total yield of H_3O^+ is greater that in experiments where oxygen is present in stoichiometric quantities (see Figure 1).

The following mechanism is proposed for the formation of $C_3H_3^+$:

$$(6)\ CH + C_2H_2 = HC{\equiv}CH^+ + e^-$$

The heat of formation has been determined by Wiberg et al[11] for $C_3H_3^+$ to be 271 kcal/mole. This value is higher than that estimated by a simple molecular orbital calculation coupled with thermodynamic considerations, and the value measured by Wiberg et al may refer to structure (A). However if the Wiberg value does apply to (B) then reaction (6) is nearly thermoneutral if the CH radical is in its $A^2\Delta$ or $B^2\Sigma$ state. If the calculated value is correct then the CH radical could even be in its ground state and reaction (6) would be close to thermoneutrality. Both CH ($A^2\Delta$) and CH ground state are known to be present in the oxidation of acetylene.[12,13] Since there is some evidence for the existence of acetylene in the oxidation of methane, reaction (6) could also explain the observation of $C_3H_3^+$ in this system.

The above mechanism has recieved some support from the observation of chemi-ionization in the reaction of iodoform and acetylene. The chemi-ionization had an "activation energy of formation" much below that usually found (55 kcal/mole), and the ionization was believed to be produced from the reaction of acetylene with the breakdown products of iodoform (CH and CHI).

This mechanism is also consistent with the observation that the time constants for the rise of ion concentration and CH($A^2\Delta \rightarrow X^2\pi$) radiation were identical in the early stages of the acetylene-oxygen reaction. However the mechanism, CH ($A^2\Delta$) + O = CHO^+ + e^-, which has previously been proposed[7] for the formation of ions in these systems is not consistent with this observation. Both CH ($A^2\Delta$) and O would be expected to be intermediates in the branching chain reaction, and therefore the concentrations of both would be expected to rise exponentially in the early stages of reaction. Thus the inverse time constant for the growth of ionization would be equal to the sum of the inverse time constants for the rise of CH* and O concentrations.

The authors wish to thank Professor G. B. Kistiakowsky for his many helpful suggestions. We also wish to thank Dr. Hiromi Niki and Dr. J. L. Michael for help in the experiments with the time-of-flight mass spectrometer. The work with the Langmuir probe technique was supported by the Office of Naval Research and that with the time-of-flight mass spectrometer by the National Science Foundation.

Bibliography

1. Van Tiggelen, A.; Experimental Investigation of Ionization Processes in Flames, University of Louvain ARL Report 68, May, 1961.
2. Calcote, H. F.; Ninth Symposium (International) on Combustion, p. 622, Academic Press (1963).
3. Green, J. A. and Sugden, T. M.; Ninth Symposium (International) on Combustion, p. 602, Academic Press (1963).
4. Sugden, T. M.; Fifth Symposium (International) on Combustion, p. 406, Reinhold (1955).
5. Schneider, J. and Hoffman, F. W.; Phys. Rev. 116, 244 (1959).
6. Calcote, H. F.; Eighth Symposium (International) on Combustion, p. 184, Williams and Wilkins Co. (1962).
7. Hand, C. W. and Kistiakowsky, G. B.; J. Chem. Phys. 37, 1239 (1962).
8. Bradley, J. N. and Kistiakowsky, G. B.; J. Chem. Phys. 35, 256 (1961).
9. Dove, J. E. and Moulton, D. M.; To be published.
10. Breslow, R., Höver, H., and Hai Won Chang; J. Am. Chem. Soc. 84, 3168 (1962).
11. Wiberg, K. B., Bartley, W. J., and Lossing, F. P.; J. Am. Chem. Soc. 84, 3980 (1962).
12. Gaydon, A. G.; The Spectroscopy of Flames, p. 113, Chapman Hall, Ltd., (1957).
13. Gaydon, A. G., Spokes, G. N., and Van Suchtelen,J.; Proc. Roy. Soc. A256, 323 (1960).

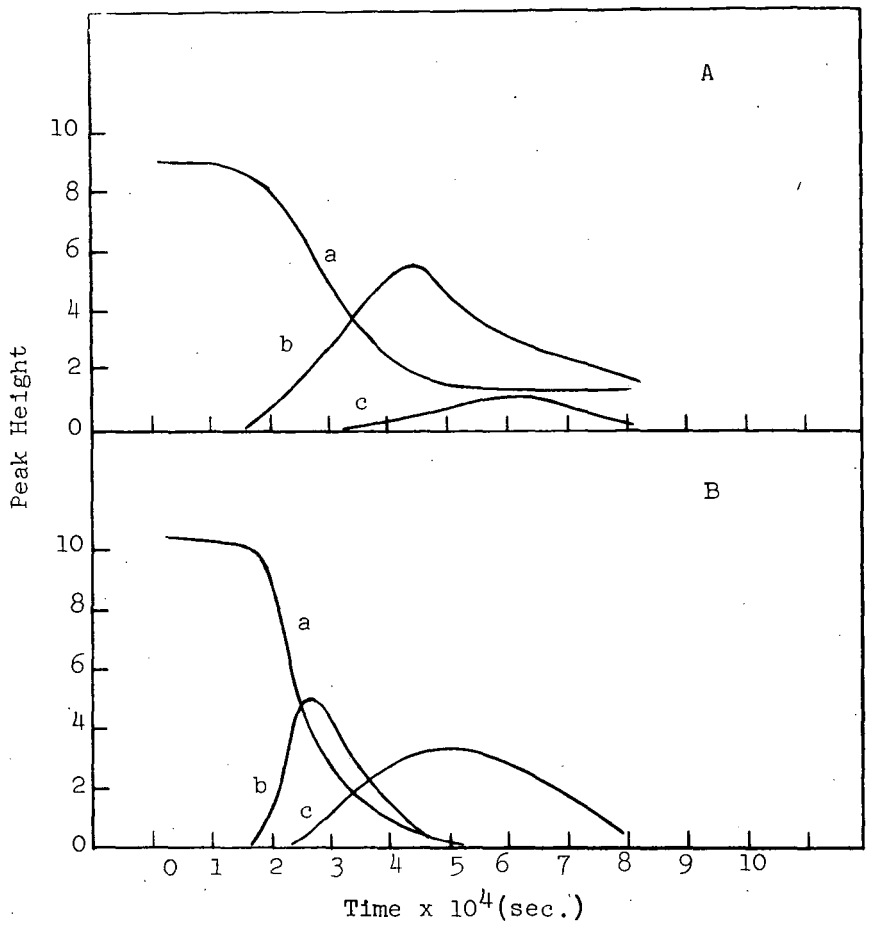


Figure 1. Height of ion peaks versus time in two experiments.

Experiment A:

$2\ C_2H_2 + 3O_2 + Kr$ at 1600°K;
curve a is acetylene, b is m = 39 ($C_3H_3^+$), c is m = 19 (H_3O^+).

Experiment B:

$1.25\ C_2H_2 + 3.75\ O_2 + 95\ Kr$ at 1700°K;
a, b, and c refer to the same species as in A.