BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (7), 2007—2008 (1976)

A Shock-tube Investigation of Ethylene-Oxygen-Argon Mixtures. Chemi-ionization and Apparent Activation Energy

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(Received December 25, 1975)

Synopsis. The reaction of ethylene–oxygen mixtures highly diluted with argon was studied over the temperature range of 1400—1800 K behind reflected shock waves by monitoring the total ionization. A kinetic study of the chemi-ionization in the ethylene oxidation was undertaken. It was inferred that the mechanism of CHO^+ formation was dependent on the composition and the temperature, and that the rate-determining step for the chemi-ionization was $C_2H_3+O_2 \rightarrow C_2H_3O+O$.

The oxidation of ethylene has been previously studied by shock-tube techniques.[1–4)] Kinetic studies have been mainly done by various optical methods[2–4)] and mass spectrometric methods;[1)] also, we ourselves have reported our results monitoring the emission from CH*, C_2*, and OH*.[5)] The oxidation of ethylene and other hydrocarbons in the shock tube is accompanied by an intense chemi-ionization. In the present paper, we wish to report the results of our simultaneous measurements of CH* emission and chemi-ionization and to discuss the formation mechanism of ions. Another purpose of this paper is to determine the apparent activation energy of the total ionization in the ethylene oxidation.

Experimental

The shock tube and the techniques for measuring the chemiluminescence have already been described.[5)] In the present experiment, the time intervals for the shock-speed measurements were determined by the use of a universal counter (Iwatsu US-6141) with a precision of ±0.1 μs. For the measurement of the ion current, the Langmuir probe was located at the same distance as the quartz window, 1 cm from the reflected plate of the shock tube.

The compositions of the reaction mixtures used were:

(A) 0.5% C_2H_4, 1.0% O_2, 98.5% Ar
(B) 0.5% C_2H_4, 1.5% O_2, 98.0% Ar
(C) 0.5% C_2H_4, 2.0% O_2, 97.5% Ar

The ethylene, oxygen, and argon were commercial gases; then purities were 99.99%, 99.9%, and 99.99% respectively. The initial pressures of the reaction mixtures were about 100 Torr. The ion current (+6.5 V bias on the Langmuir probe) and CH* emission (4315 Å, with a half-width of 25 Å) were simultaneously measured behind reflected shock waves.

Results and Discussion

Some typical oscillograms on the oscilloscope are shown in Fig. 1 (a) and (b). The following characteristics were seen from the profiles of each run:

(1) The onset of the ion signal was earlier than that of the CH* emission signal in the (A) and (B) mixtures below 1700 K. However, in the (A) and (B) mixtures above 1700 K and the (C) mixture over the temperature range of 1400—1800 K, the reverse tendency was true.

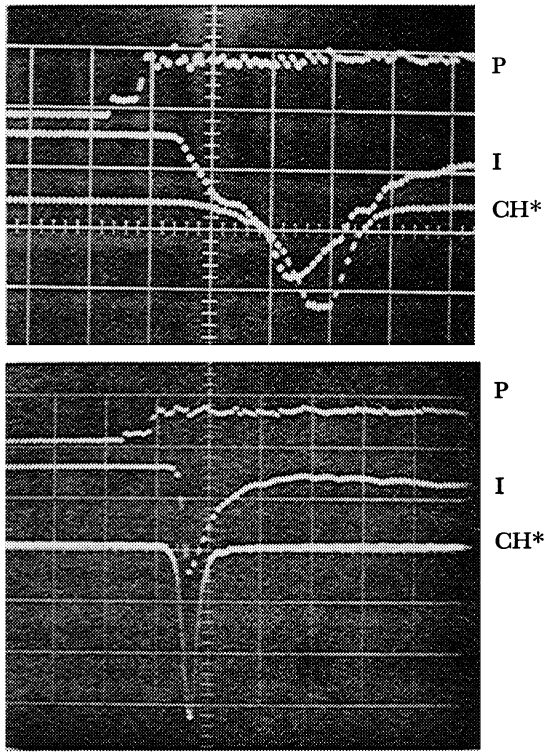

Fig. 1. Time histroy of CH* emission and ion currents.
Upper trace: Pressure signal.
Middle trace: Ion current signal.
Lower trace: CH* emission signal.
(a) T_5=1593 K, P_5=4.04 atm, Sweep=50 μs/div., 1.0% O_2+0.5% C_2H_4.
(b) T_5=1610 K, P_5=4.48 atm, Sweep=50 μs/div., 2.0% O_2+0.5% C_2H_4.

(2) In most profiles of the (A) mixture over the temperature range of 1400—1800 K, the arrival time to the peak of the ion signal was earlier than that of the CH* emission signal. In the lower-temperature regions of the (B) mixture (below 1700 K) and the (C) mixture (below 1500 K), the arrival time to the peak of the ion signal was later than that of the CH* emission. In the higher-temperature regions of the (B) and (C) mixture, they were almost identical.

The maximum intensities of the ion signals are plotted against the temperature at the C_2H_4/O_2 ratios of 1/2 (A mixture), 1/3 (B mixture), and 1/4 (C mixture) respectively in Fig. 2. These results indicate that the maximum intensity, I_{max}, increased with the increase in the temperature and the O_2 concentration over the temperature range of 1400—1800 K.

Mass-spectral analysis has shown that, in the oxidation of ethylene in a shock tube, the $C_3H_3^+$ ion is dominant

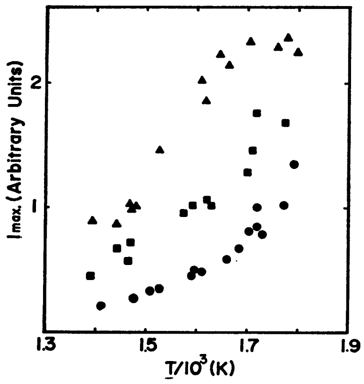

Fig. 2. Comparison of maximum intensity of total ionization at various temperatures.
●: 1.0% O_2+0.5% C_2H_4, ■: 1.5% O_2+0.5% C_2H_4, ▲: 2.0% O_2+0.5% C_2H_4.

and the H_3O^+ ion is not observed in the O_2-lean mixture; on the other hand, in the O_2-rich mixture, the $C_3H_3^+$ ion is rapidly succeeded by the H_3O^+ ion, which becomes the most abundant species.[1]

From has been mentioned above, it may be considered that the increase in the total ions with the increase in the O_2 concentration is based on the increase in the number of H_3O^+ ions and that the most abundant ion is the H_3O^+ ion. The generally accepted steps for the $C_3H_3^+$ formation are:

$$\mathrm{CH} + \mathrm{O} \longrightarrow \mathrm{CHO}^+ + \mathrm{e}^- \qquad \Delta H = +20\ \mathrm{kcal/mol} \qquad (1\mathrm{a})$$

or

$$\mathrm{CH}^* + \mathrm{O} \longrightarrow \mathrm{CHO}^+ + \mathrm{e}^- \qquad \Delta H = -46\ \mathrm{kcal/mol} \qquad (1\mathrm{b})$$

$$\mathrm{CHO}^+ + \mathrm{H_2O} \longrightarrow \mathrm{H_3O}^+ + \mathrm{CO} \qquad \Delta H = -34\ \mathrm{kcal/mol} \qquad (2)$$

However, there is controversy concerning the electronic state of CH in (1) reactions.[6–10] Considering that the onset of the ion signal occurs earlier than that of CH* emission, and that the arrival time to the peak of the ion signal was earlier than that of the CH* emission, as has been mentioned above, it may be difficult for the (1b) reaction to be the main route of the CHO^+ formation in a lower-temperature region at comparatively O_2-lean mixtures. The CH* concentration increased with increases in the temperature and the O_2 concentration;[5] the O concentration may also increase with increases in the temperature and the O_2 concentration. In a higher-temperature region and an O_2-rich mixture, it was found that the onset of the ion signal occurred later than that of the CH*emission, as has been mentioned above. Hence, in a higher-temperature region and an O_2-rich mixture, the (1b) reaction may occur.

The lag time in the total chemi-ionization was defined as the time elapsing between the reflected shock arrival and the time at which the probe current reached a constant value, 2.5×10^{-6} A. The lag time, τ_I increased with decreases in the temperature and O_2/C_2H_4 ratios. The plot of log τ_I *vs.* 1/T of each composition fit a single line, and the log τ_I increased with the decrease in the O_2 concentration. A plot of log $\tau_I[O_2]$ *vs.* 1/T for three compositions fits a single line, as is shown in Fig. 3. The temperature coefficient of the lag time can be obtained from the slope of the line; the value is 26.4 kcal/mol. Over the experimental temperature and concentration ranges we covered, the lag time can be represented as:

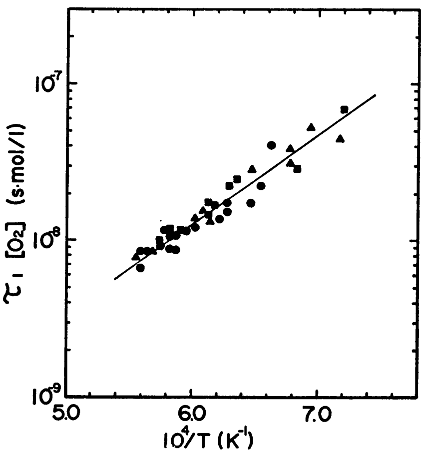

Fig. 3. A plot of log $\tau_I[O_2]$ *vs.* $1/T$ for reaction mixtures.
●: 1.0% O_2+0.5% C_2H_4, ■: 1.5% O_2+0.5% C_2H_4, ▲: 2.0% O_2+0.5% C_2H_4.

$$\log \tau_I[\mathrm{O_2}] = -11.35 + 26.4 \times 10^3/4.58T$$

in units of s mol l^{-1}. This equation agrees with the following equation, which was determined from the measurements of the CH* emission in our previous work:[5]

$$\log \tau_{\mathrm{CH}^*}[\mathrm{O_2}] = -11.45 + 27.5 \times 10^3/4.58T$$

Thus, we estimate that the following reaction is the rate-determining step for the ethylene oxidation in a shock tube:

$$\mathrm{C_2H_3} + \mathrm{O_2} \longrightarrow \mathrm{C_2H_3O} + \mathrm{O} \qquad (3)$$

also, the apparent activation energy obtained from our measurements in the total ionization is 26.4 kcal/mol, and the values, ΔH, of individual ionization reactions would be less than 20 kcal/mol.[6] Hence, it may be concluded that Reaction 3 is the rate-determining step for chemi-ionization in the ethylene oxidation under the present experimental conditions.

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