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Mixture Dependences of OH($^2\Sigma$) Produced in the Oxidations of C_2H_2 and C_2H_6 in Shock Waves

Tohru Koike
Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239
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Synopsis. The OH($^2\Sigma$) emissions from shock-heated mixtures of C_2H_2/O_2, $C_2H_2/C_2H_6/O_2$, and C_2H_6/O_2 diluted in Ar were observed and the mixture dependences of the emissions were obtained. OH($^2\Sigma$) production, depending on the test gas mixture, could be in accordance with the view-point that the two oxidations of C_2H_2 and C_2H_6 progress by influencing each other.

The reaction on OH($^2\Sigma$), hereafter abbreviated as OH*, at high temperatures (above 1000 K) has been studied for many reaction systems using shock-tube techniques.[1,2] As for OH* in hydrocarbon oxidation, only single hydrocarbon/O_2 systems, excepting multi-hydrocarbon/O_2 systems, have been investigated.[3]

The temperature reached by hydrocarbon combustion is high due to their large exothermicity. The hydrocarbons used for fuels therefore decay to smaller species, thermally, as well as by oxidation processes. Acetylene is one of the primary products given by such thermal decay. Thus, at high temperatures acetylene could be present from the beginning of combustion; hydrocarbon combustion seems to proceed by self decay, as mentioned above, influenced by acetylene combustion.

We paid attention to the OH* produced in a $C_2H_2+C_2H_6$ systems, studying it in comparison with those in the C_2H_2 and C_2H_6 systems. The time parameters and intensities of OH* emission were investigated in relation to the test gas compositions used. The production of OH* could be understood by considering that the two oxidations of C_2H_2 and C_2H_6 progress by influencing each other.

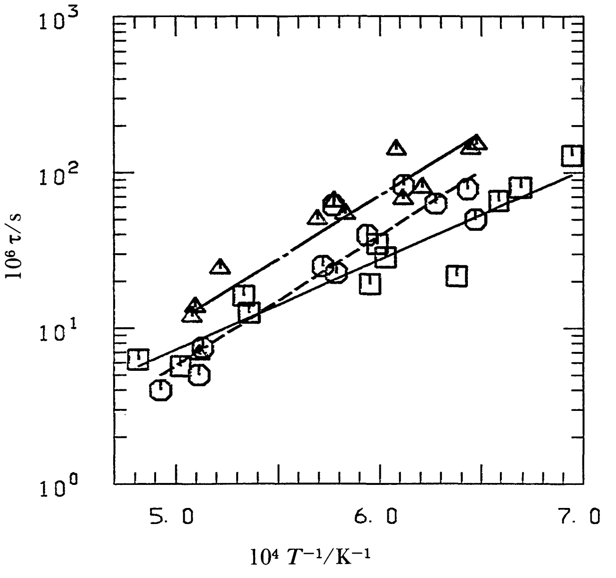

Fig. 1. Induction times, τ, vs. $10^4/T$. Symbols used are; □: $C_2H_2/O_2/Ar=1/2.5/96.5$, ○: $C_2H_2/C_2H_6/O_2/Ar=1/1/6/92$, △: $C_2H_6/O_2/Ar=1/3.5/95.5$. Lines through each data point show least squares fit.

Experimental

The rectangular shock tube used in the present study for incident shock waves was detailed in previous papers.[3,4]

OH* emission at 306.4 nm was observed using a monochromator (Jarrell-Ash, JE-25) and a photomultiplier (Hamamatsu, R-208). The output signal of the photomultiplier was fed into an operational amplifier and then recorded on a digital-oscilloscope (Iwatsu, DS-6121).

The purities of the element gases used for the test gas were; C_2H_2, 99.5% pure; C_2H_6, 99.3% pure; O_2, 99.999% pure; and Ar, 99.999% pure. The compositions of the test gas mixture are shown in the footnote of Fig. 1.

Results and Discussion

The obtained oscillograms show that after shock arrival at the observation window of the shock tube, OH* emission can not be observed for a reaction period (induction time), but increases abruptly to a maximum value and finally decays. Although the time profile and intensity of OH* emission changes depending on the temperature and the test gas mixture examined (as shown below), such profiles of OH* emission are common for the three mixtures, as well as for other hydrocarbons.[1,3]

We evaluated three parameters from these oscillograms: (1) induction time(τ),[3] (2) reaction time at which the emission intensity reaches a maximum (t_m), (3) the maximum emission intensity (I_m).[3] The time parameters, τ and t_m, were evaluated on the laboratory time base. The I_m values are proportional to [OH*].

Figure 1 shows the relation between τ and $10^4/T$. Except for high temperatures (around 2000 K), the dependence of τ on the test gas mixture was found to be $\tau(C_2H_6)>\tau(C_2H_2+C_2H_6)>\tau(C_2H_2)$, where the species in parenthes identifies the hydrocarbons contained in the test gas mixtures used. Such a mixture dependence on τ is in accord with the experimental results reported for both C_2H_2 and CH_4 oxidation:[3,5] that $\tau(CH_4)>\tau(C_2H_2+CH_4)>\tau(C_2H_2)$. Since C_2H_2 and CH_4 oxidation was confirmed to progress by influencing each other in a $C_2H_2+CH_4$ mixture,[5] in a $C_2H_2+C_2H_6$ mixture the C_2H_2 and C_2H_6 oxidation are also expected to proceed similarly and to affect the production of OH*.

It should be pointed out here that the values of τ evaluated at high temperatures are not accurate as those evaluated at lower temperatures, since τ at high temperatures becomes small and is hard to estimate from each oscillogram with sufficient precision. In contrast to such a time parameter as τ, both the t_m and

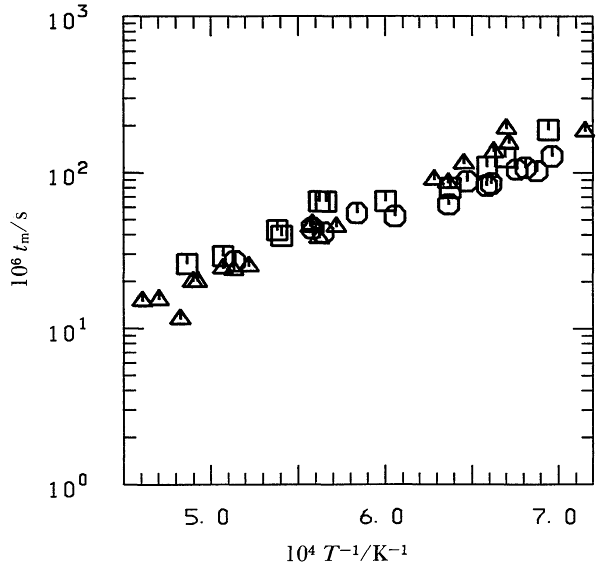

Fig. 2. Reaction times, t_m, vs. $10^4/T$. Symbols used are the same as those in Fig. 1.

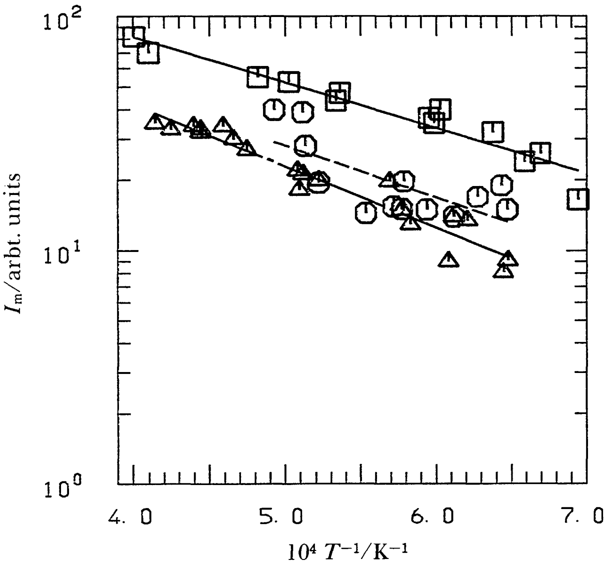

Fig. 3. Maximum emission intensity, I_m, vs. $10^4/T$. Symbols used are the same as those in Fig. 1.

I_m values could be evaluated precisely even at high temperature.

Figure 2 shows the relation between t_m and $10^4/T$. The difference of the t_m values between the three mixtures is not so clear and, thus, the influential relation between C_2H_2 and C_2H_6 oxidation to produce OH* seems to proceed much more.

Figure 3 shows the relation between I_m vs. $10^4/T$. In accordance with the former experimental results regarding I_m for C_2H_2 and CH_4 oxidation,[3] that $I_m(C_2H_2) > I_m(CH_4)$, the mixture dependence $I_m(C_2H_2) > I_m(C_2H_6)$ can be seen. If C_2H_2 and C_2H_6 oxidation could progress independently in a $C_2H_2+C_2H_6$ mixture, the relation $I_m(C_2H_2+C_2H_6) \approx I_m(C_2H_2)+I_m(C_2H_6)$ would be expected, since t_m is almost same for all three mixtures. The result is that the $I_m(C_2H_2+C_2H_6)$ values lie between those in the other two mixtures.

Taking into account the temperature dependences of the time parameters, τ and t_m, and the I_m values, the production of OH* can be seen to proceed rapidly and violently at high temperature. Such results may support the viewpoint that the difference in the heat of combustion between the two oxidations affects the production of OH* much more than does the difference of the generated radicals between them. As for the reaction temperature in the $C_2H_2+C_2H_6$ mixture, it must reach the highest value among the three mixtures, and the observed I_m values in the mixture could be largest. The result shown in Fig. 3 does not seem to be in accord with these hypotheses. Therefore, it can be concluded that in OH* production the two oxidations of C_2H_2 and C_2H_6 in the $C_2H_2+C_2H_6$ mixture proceed with any influence other than the thermal effect.[5] Such influences could arise due to chemical coupling of the generated radicals in each oxidation.

It is also informative regarding the existence of chemical coupling that the time variation of OH* emission is also very smooth in a test gas mixture of $C_2H_2+C_2H_6$. If C_2H_2 and C_2H_6 oxidation could proceed independently, two peaks of maximum emission, attributed to the two oxidations, should appear.

Although the producing step of OH* in hydrocarbon oxidation is still controversial, the fate of OH* is mentioned here briefly. If OH* is produced by the process $CH+O_2=OH^*+CO$, as proposed by Gaydon,[6] the I_m values should be proportional to the concentration product of $[CH][O_2]$.[1,3] It was, however, found that the I_m does not increase simply with increasing $[O_2]$ in the mixture used. We can thus say that the producing step of OH* depends greatly on the value of [CH].

Shock tube studies concerning the production of OH* in other hydrocarbon mixtures are in progress and the results may appear elsewhere.

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