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Additive Effect of CF_3Cl on an Oxidation Reaction in Shock Waves. I. Study with H_2-O_2

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Sample gases, H_2–O_2, H_2–O_2–CF_3Cl, and CF_3Cl, highly diluted with Ar were heated behind reflected shock waves over the temperature range 1400—2200 K and an additive effect of CF_3Cl at various concentrations (0—0.5%) was studied by monitoring ultraviolet and visible emissions. At a temperature below 2200 K, C_2^* and CH^* species were found to be formed in the oxidation reaction of H_2 together with CF_3Cl, but hardly formed in the thermal decomposition of CF_3Cl. The addition of small and large amounts of CF_3Cl increased and decreased, respectively, the intensity of OH^* emission from the H_2–O_2 mixture heated to a constant temperature. An ignition delay time at a fixed temperature above 1400 K was found to shorten with an increase in the concentration of CF_3Cl. A brief discussion is given of the mechanism for the formation of the chemiluminescent species.

The additive effect of an organic halogen compound (*e.g.*, CH_3I, CH_3Br, CH_3F, CF_3Br, CF_3Cl, or CCl_4) on a combustion reaction has been studied by measuring flammability limit,[1)] burning velocity,[2–3)] flame structure,[4)] induction period,[5)] *etc.*, and the compound has been found to generally lower the concentration of active species such as H, OH, and O, thereby inhibiting the combustion reaction. According to a study of the burning velocity in a methane oxidation,[3)] however, CF_3Cl acts as an inhibitor under some conditions but as a promoter under others. This reversible action of CF_3Cl is particularly interesting, and a detailed investigation of the action seems helpful in elucidating an effect of organic halogen compounds on an oxidation reaction.

A visible emission from reaction mixtures including halogen compounds has been studied by using discharges[6,7)] counterflow diffusion flame,[8)] shock waves,[9,10)] *etc.*, and both C_2^* ($A\,^3\Pi_g$) and CH^* ($A^2\Delta$) were observed in the reaction of H with CCl_4, $CHCl_3$, or CH_3Br.[6)] In addition, C_2^* was observed when halomethanes $CH_{2-n}X_{2+n}$ (X=Cl, Br, or I) were introduced into a stream of H produced by passing a H_2–He mixture through a 2450 MHz microwave discharge[7)] and also when a decomposition reaction of CF_4 or CCl_4 occurred in a shock tube at a temperature above 4000 K.[10)] At a relatively low temperature below 2200 K, however, such a C_2^* formation from organic halogen compounds has not yet been reported.

From the viewpoints described above, we have examined the additive effect of CF_3Cl on the light emission from chemiluminescent species produced in the oxidation reaction of CH_4 over the temperature range 1600—2200 K by using a shock tube, and have found that the addition of CF_3Cl increases the C_2^* and CH^* emission intensities.[11)] This previous result is not interpreted reasonably by a mechanism proposed by Gaydon,[12)] and hence suggests that another mechanism should be taken into consideration. Namely, C_2^* and CH^* may be formed from some species produced by the decomposition of CF_3Cl in the oxidation reaction. A mixture of H_2–O_2–CF_3Cl–Ar seems most suited to check this mechanism experimentally, because no emissions of CH^* and C_2^* are observed in the oxidation reaction of H_2.

Our purpose of this work is to clarify the CH^* and C_2^* formation in H_2–O_2–CF_3Cl–Ar, and also to investigate the additive effect of CF_3Cl on the oxidation reaction of H_2.

Experimental

The apparatus and procedures employed in this work are essentially the same as in previous work.[13,14)] Therefore, only a brief description will be given here. In order to record an emission spectrum, a high sensitive film (Kodak 2475) was exposed as many as 15 times by repeating runs with a reaction mixture heated at 2100±50 K, but this trial was fruitless because all of the resultant emissions were extremely weak. Therefore, the spectral distribution was measurod with a system consisting of a monochromator with the half-width 25 Å (Rico-MC-20) and of a photomultiplier (Hamamatsu R-306). Wavelength dependence of the relative detection sensitivity (β) of the system was determined according to NBS data (lamp input voltage 96 V and PM H. V. 1220 V, EMI 9635QA), and the result thus obtained is shown in Fig. 1, on the basis of which the emission intensities measured at various wavelengths were corrected. The emissions at 3055, 4330, 5150, and 2400 Å were monitored with four filters, the half-widths of which were 150, 120, 110, and 200 Å, respectively. After passing through one of the interference filters located behind a quartz window of the shock tube and through two slits with widths 0.2 and 0.4 mm, three kinds of emission among the four were simultaneously monitored at various temperatures by using three photomultipliers (Hamamatsu R-306).

The computer routine used Gear-type integration of the set of differential equations describing the chemical kinetics under constant density conditions for reflected shock waves. Thermochemical properties were computed as functions of temperature using accurate polynomial representations of

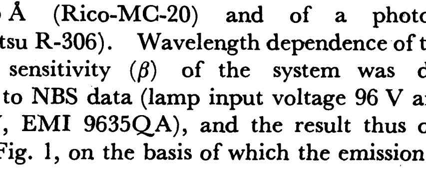

Fig. 1. The relative sensitivity (β) at different wavelengths (W) observed with the measurement system in this work.

JANAF data.[15] Reverse reactions were automatically included with rate constants calculated from the forward rate constants and equilibrium constants. All temperatures referred to in connection with data were calculated from the incident shock velocity assuming full vibrational relaxation but no chemical reaction. The computer programs used previously[16] were modified to match the Facom 230-28 system.

The gases of CF_3Cl, H_2, O_2, and Ar specified to be 99.0, 99.9, 99.9, and 99.99% pure, respectively, were obtained from commercial cylinders and were used without further purification. Table 1 summarizes the composition of the reaction gas mixtures used, each of which had the initial pressure 100±0.1 Torr (1 Torr≈133. 322 Pa).

TABLE 1. MIXTURE COMPOSITION

Mixture	H_2 (%)	O_2 (%)	CF_3Cl (%)	Ar (%)
(A)	0.50	0.25		99.25
(B)	0.50	0.25	0.05	99.20
(C)	0.50	0.25	0.10	99.15
(D)	0.50	0.25	0.17	99.08
(E)	0.50	0.25	0.25	99.00
(F)	0.50	0.25	0.35	98.90
(G)	0.50	0.25	0.50	98.75
(H)			0.50	99.50
(I)	0.50		0.50	99.00
(J)		0 25	0.50	99.25

Results and Discussion

An emission spectrum recorded with the mixture (G) at intervals of about 100 Å is illustrated in Fig. 2, which shows that strong emissions appear at 3900, 4315, 4700, 5165, and 5600 Å. According to Gaydon,[17] (1) the Swan bands of C_2* lie in the wavelength region 4365—6762 Å, (2) the outstanding heads of C_2* exist at 4737, 5165, and 5635 Å, (3) the emission bands of CH* are situated in the region 3144—4941 Å, and (4) the strong peaks of CH* appear at 3871 and 4315 Å. Therefore, the two groups (A_1 and A_2) of the strong heads at 4700, 5165, and 5600 Å and at 3900 and 4315 Å shown in Fig. 2 correspond to spectra of the electronically excited species C_2* and CH*, respectively. As may be known well, C_2* and CH* bands are characteristic of hydrocarbon-flames. To our particular interest, such bands are observed in the oxidation reaction of the H_2–O_2–CF_3Cl–Ar mixtures, too, as shown in Fig. 2, where the spectral distribution is quite similar to that in the oxidation reaction of CH_4.[11] With the mixtures of CF_3Cl–Ar (H), H_2–CF_3Cl–Ar (I), and O_2–CF_3Cl–Ar (J) heated to 1400—2200 K, on the other hand, neither CH* nor C_2* was observed. Hence, it is concluded that, even at the temperature below 2200 K, CH* and C_2* are formed in the oxidation reaction of H_2 together with CF_3Cl, but are produced in neither the thermal decomposition of CF_3Cl nor the reaction of CF_3Cl with O_2 or with H_2. This makes us infer that H, O, or OH which is the active species formed in the oxidation reaction of H_2 helps to form CH* and C_2*.

Since the intensities of emissions at 4315 Å (CH*) and 5165 Å (C_2*) are very strong and also since the emissions other than the CH* and C_2* do not exist in the vicinity of 4315 Å and 5165 Å, the emissions observed at 4330 and 5150 Å by using the interference filters are concluded to come from CH* and C_2*, respectively.

The OH* emission at 3064 Å which is generally observed in the oxidation reaction of H_2 doesn't appear in Fig. 2. This may be due to both the weak emission of OH* observed with the mixture (G) (see Fig. 3) and the low sensitivity near 3064 Å in our measurement system, as shown in Fig. 1. The emission at 3055 Å found with the filter probably comes from the electronically excited species OH* because the strong band of OH* has a main head at 3064 Å.[17] In addition, we observed the emission at 2400 Å, which may be concluded to come from the electronically excited species CF* because the CF*($A^2\Sigma^+$—$X^2\Pi$) bands extend from 2240 to 2560 Å, among which the emission at 2404 Å is particularly strong.[17]

By using one of the filters mentioned above, the emission intensities at 3055, 4330, 5150, and 2400 Å corresponding to OH*, CH*, C_2*, and CF*, respectively, were measured with the mixtures (A)—(G) in the range 1600—2200 K, and their respective maximum intensities are plotted against the concentration (C) of CF_3Cl in Figs. 3—6. In contrast to OH*, neither CH*, C_2*, nor CF* emission at any temperatures is

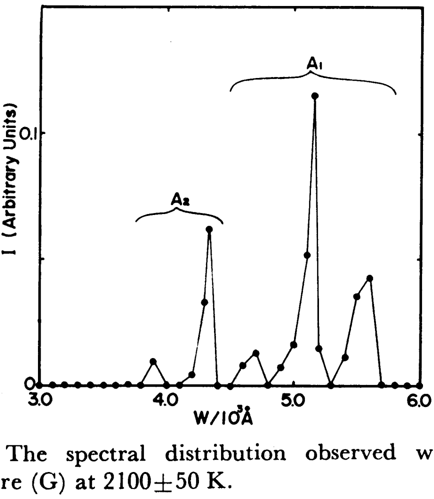

Fig. 2. The spectral distribution observed with the mixture (G) at 2100±50 K.

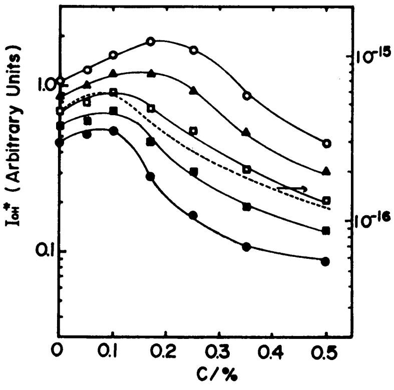

Fig. 3. A plot of the maximum intensity (I_{OH}*) of OH* emission vs. CF_3Cl concentration (C). ●: 1600 K, ■: 1700 K, □: 1800 K, ▲: 1900 K, ○: 2000 K, ------: computed curve.

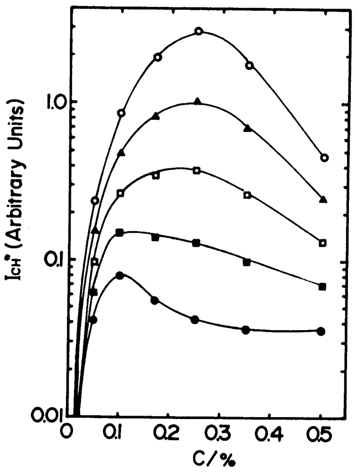

Fig. 4. A plot of the maximum intensity (I_{CH}*) of CH* emission *vs.* CF_3Cl concentration (C). ●: 1600 K, ■: 1700 K, □: 1800 K, ▲: 1900 K, ○: 2000 K.

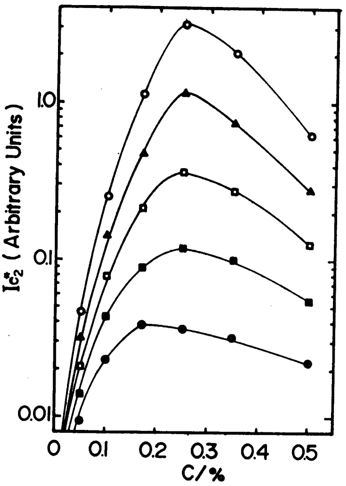

Fig. 5. A plot of the maximum intensity (I_{C_2}*) of C_2* emission *vs.* CF_3Cl concentration (C). ●: 1600 K, ■: 1700 K, □: 1800 K, ▲: 1900 K, ○: 2000 K.

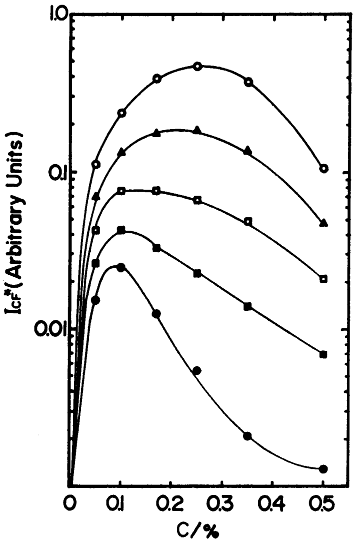

Fig. 6. A plot of the maximum intensity (I_{CF}*) of CF* emission *vs.* CF_3Cl concentration (C). ●: 1600 K, ■: 1700 K, □: 1800 K, ▲: 1900 K, ○: 2000 K.

naturally observed at $C=0$ %. At $C>0$ %, however, any of the four emission intensities at a fixed temperature increases and reaches a maximum at $C=0.1$—0.3 %, above which each emission intensity decreases gradually. This pattern is quite similar among the five curves at different temperatures. Especially CH* and CF* among the four species have a quite similar pattern at each temperature.

Table 2. ΔH_0° value of elementary reactions

Number	Reaction	ΔH_0°/kcal
1	$CF_3Cl+(M)=CF_3+Cl+(M)$	85
2	$Cl+H_2=HCl+H$	−1
3	$CF_3+H_2=CF_3H+H$	−1
4	$CF_3Cl+H=CF_3+HCl$	−18
5	$CF_3+H=CF_2+HF$	−49
6	$CF_2+H=CF+HF$	−14
7	$CF+H=C+HF$	−7
8	$C+CH=C_2+H$	−61
9	$CH+CH=C_2+H_2$	−85
10	$CH_2+C=C_2+H_2$	−63
11	$CF+CH=C_2+HF$	−68
12	$C+CF=C_2+F$	−14
13	$CF+CF=C_2+F_2$	79
14	$C+CF_2=C_2+F_2$	72
15	$C_2+OH=CH+CO$	−93
16	$CF+HF=CH+F_2$	147
17	$C+H_2=CH+H$	24
18	$CF+H_2=CH+HF$	17
19	$C+OH=CH+O$	21
20	$CH+F_2=CF+HF$	−147
21	$C+F_2=CF+F$	−93
22	$C+HF=CF+H$	6
23	$O+H+M=OH+M$	−102
24	$CH+O_2=OH+CO$	−160

Some of the elementary reactions that may be helpful to find a formation mechanism for the chemiluminescent species in this work are summarized in Table 2 together with respective enthalpy changes ΔH. As mentioned above, fair amounts of C_2*, CF*, and CH* are formed under our experimental condition. When the values of ΔH in Table 2 are taken into consideration, the existence of the above electronically excited species makes us infer that both C_2 and CH species must be formed in the reaction process.

Some of typical oscillograms obtained at a middle temperature (about 1850 K) are shown in Fig. 7. The emission curve of C_2* observed with each mixture was similar in shape to that of CH* or CF* emission.

The OH* emission curves thus recorded with the five mixtures heated to high temperature (2150 K) are shown in Fig. 8. The emission intensity of OH* measured with the CF_3Cl-free mixture (A) increases rather slowly up to a maximum after the ignition delay time (τ) which is the time lag between the reflected shock arrival and the onset of the rapid increase of the emission signal, and then decreases more slowly toward the base line. When a small amount of CF_3Cl is added, the emission of OH* rises rapidly to a maximum, falls quickly to some intensity, and then declines slowly

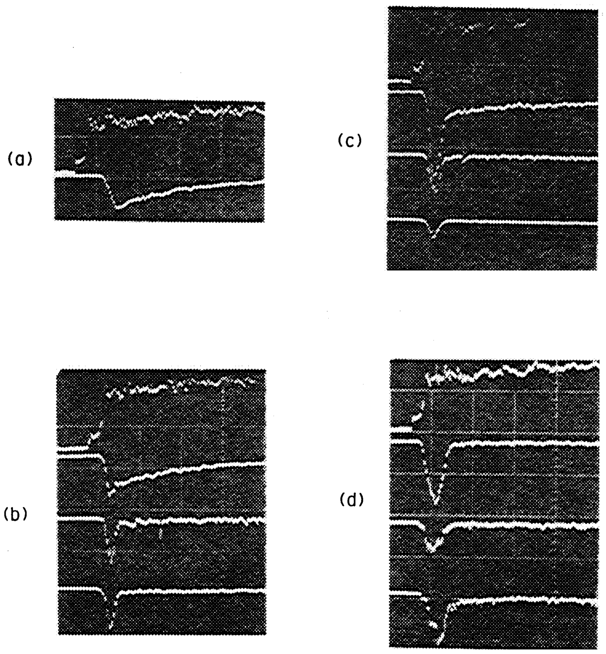

Fig. 7. Time history curves of pressure and emissions. Sweep time = 100 μs/div.
Uppermost trace : pressure. Second trace : OH* emission. Third trace : CF* emission. Lowest trace : CH* emission.
(a) Mixture (A), $T_5 = 1860$ K, $P_5 = 4.3$ atm. (b) Mixture (B), $T_5 = 1885$ K, $P_5 = 4.6$ atm. (c) Mixture(C), $T_5 = 1828$ K, $P_5 = 4.1$ atm. (d) Mixture (G), $T_5 = 1853$ K, $P_5 = 4.2$ atm.

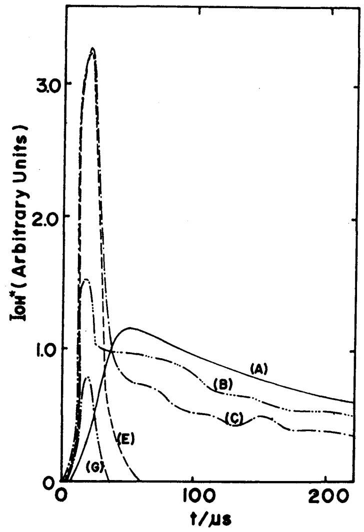

Fig. 8. Time variation of the OH* emissions at 2150 ± 20 K observed with the five mixtures.

toward the base line, thereby showing a spike with a shoulder, as may be seen in Figs. 7b, 7c, and 8. When CF_3Cl is added abundantly, on the other hand, OH* shows a spike with no shoulder (see Figs. 7d and 8).

OH* may be formed through the reactions (23′) and (24′) in the oxidation of hydrogen[18–21] and of hydrocarbon,[22–23] respectively.

$$O + H + M = OH^* + M \tag{23′}$$

$$CH + O_2 = OH^* + CO \tag{24′}$$

Compared with chemical excitation, thermal excitation below 2000 K seems to have little contribution to the OH* formation.[18] Even at a high temperature the emission intensity of OH* (I_{OH}*) observed in the hydrogen oxidation slowly decreases with time from a maximum intensity as shown in Figs. 7a and 8, and this slow decrease of OH* is considered to be a characteristic of the OH* formation through the reaction(23′). These OH* emission curves shown in Figs. 7a and 8 have a striking contrast to those previously obtained with the hydrocarbon oxidation, where I_{OH}* rapidly decreased from a maximum intensity.[11,13] This rapid decrease of OH* may be a characteristic of the OH* formation through the reaction (24′). As already described above, the addition of CF_3Cl has a strong effect upon the emission pattern and intensity of OH*. As may be seen in Figs. 7 and 8, the spike of OH* (rapid decrease of OH* emission from a maximum) appears when CF_3Cl is added. Therefore, this spike suggests that some OH* species are formed through the reaction (24′). For the OH* formation under our experimental condition, the existence of CH needs, in analogy with the C_2* formation mentioned below. Therefore, we consider the reactions for the CH formation, as mentioned below.

It is known well that the reaction $C_2H_6 + M = 2CH_3 + M$ occurs at the temperature above 1300 K.[24] Quite similarly the dissociation reaction (1) may occur readily to produce CF_3[25] because both of the reactions are nearly identical in ΔH. In the present experiment with H_2–O_2–CF_3Cl–Ar mixture, therefore, a fairly large amount of CF_3 may be produced during the reaction process. Since the reactions (5)—(7) are exothermic, the intermediate products CF and C also may be produced quite easily. There exists a large amount of H_2 at the initial stage in the present experiment, and the ΔH values of the reactions (17), (18), and (19) are 24, 17, and 21 kcal/mol, respectively. Hence, it may be possible through the reactions, (17), (18), and (19) that CH is produced in the present experiment. By considering the reactions, as mentioned above, we have repeated computations and finally completed the mechanism and the rate-constant expressions, as shown in Table 3, which are employed in order to obtain the concentration-time relations of all the species at 1800 K. The rate constants for the OH* formation in the H_2–O_2 reaction shown in Table 3 are cited from other paper.[21] The curve calculated with it fits the experimental data best, as may be seen in Fig. 3. When the CH formation reactions (15), (17), and (19), without the reaction (18), were used for the computation, the experimental finding shown in Fig. 3 can not reasonably be explained. Therefore, CH seems to be produced through the reaction (18) in the present experiment. In the computation except the reaction (23′) or (24′) from the mechanism in Table 3, we also were capable to substantiate the characteristic time-variation for the OH* emission, as mentioned above, and found that much existence of CF_3Cl makes it difficult to form OH* through the reaction (23′). The OH* concentration variation computed at 1800 K is shown in Fig. 9. This figure interprets well the relationship, as shown in Figs. 7 and 8. Provided that CH is produced in our

TABLE 3. ELEMENTARY REACTIONS AND RATE CONSTANT EXPRESSIONS[a)]

Reaction	A	n	E	Reference
$H_2+O_2=OH+OH$	1.7×10^{13}	0.0	48100	29
$H_2+M=H+H+M$	2.2×10^{12}	0.5	92600	30
$O_2+M=O+O+M$	1.8×10^{11}	0.5	95700	31
$O+H_2=OH+H$	2.2×10^{14}	0.0	13700	32
$OH+H_2=H_2O+H$	5.2×10^{13}	0.0	6500	33
$H_2+HO_2=H_2O+OH$	7.3×10^{11}	0.0	18700	34
$H+O_2=OH+O$	1.2×10^{17}	-0.91	16630	35
$H+O_2+M=HO_2+M$	2.5×10^{15}	0.0	0	36
$H+OH+M=H_2O+M$	7.5×10^{23}	-2.6	0	37
$H+HO_2=OH+OH$	2.5×10^{14}	0.0	1900	34
$H+HO_2=H_2+O_2$	2.5×10^{13}	0.0	700	34
$O+HO_2=OH+O_2$	5.0×10^{13}	0.0	1000	34
$OH+OH=H_2O+O$	5.5×10^{13}	0.0	7000	38
$OH+HO_2=H_2O+O_2$	5.0×10^{13}	0.0	1000	34
$CF_3Cl+M=CF_3+Cl+M$	2.1×10^{17}	0.0	75000	39
$CF_3Cl+H=CF_3+HCl$	4.4×10^{13}	0.0	10200	39
$H_2+Cl=HCl+H$	7.9×10^{13}	0.0	5500	40
$CF_3+H_2=CF_3H+H$	4.0×10^{11}	0.0	8800	41
$CF_3Cl+Cl=CF_3+Cl_2$	2.0×10^{14}	0.0	31300	42
$CF_3+OH=CF_2O+HF$	1.0×10^{12}	0.0	0	39
$CF_3+O=CF_2O+F$	1.0×10^{12}	0.0	0	39
$CF_3+H=CF_2+HF$	6.0×10^{12}	0.0	0	39
$H+CF_3+M=CF_3H+M$	1.2×10^{20}	-1.0	0	39
$CF_3+CF_3+M=C_2F_6+M$	7.1×10^{17}	0.5	0	43
$CF+CF_3+M=C_2F_4+M$	3.0×10^{18}	0.0	0	Assumed[b)]
$HCl+M=H+Cl+M$	6.8×10^{21}	-2.0	102000	44
$CF_2+H=CF+HF$	4.0×10^{12}	0.0	0	Assumed[b)]
$CF+H=C+HF$	1.0×10^{12}	0.0	0	Assumed[b)]
$C+CF=C_2+F$	1.0×10^{12}	0.0	0	Assumed[b)]
$CF+O=CO+F$	1.0×10^{13}	0.0	0	Assumed[b)]
$CF+H_2=CH+HF$	1.5×10^{11}	0.0	0	Assumed[b)]
$C+O_2=CO+O$	1.0×10^{13}	0.0	0	Assumed[b)]
$C_2+O_2=CO_2+C$	1.0×10^{11}	0.0	0	Assumed[b)]
$H_2+F=HF+H$	1.2×10^{14}	0.0	1700	41
$CH+O=CO+H$	1.0×10^{13}	0.0	0	Assumed[b)]
$O+H+M=OH^*+M$	5.0×10^{13}	0.0	6940	21
$CH+O_2=CO+OH^*$	6.0×10^{10}	0.0	0	45
$OH^*+M=OH+M$	2.5×10^{11}	0.5	0	46
$OH^*+H_2O=OH+H_2O$	4.1×10^{13}	0.5	0	46
$OH^*=OH+h\nu$	1.4×10^{6}	0.0	0	21

a) Rate constants in the form, $AT^n \exp(-E/RT)$, in cm, mol, cal, and K units. b) Rate constants assumed for the reaction at 1800 K.

experiment, then C_2^* is probably formed by some of the following reactions:

$$C + CH = C_2^* + H, \tag{8'}$$

$$CH + CH = C_2^* + H_2, \tag{9'}$$

$$CH_2 + C = C_2^* + H_2, \tag{10'}$$

$$CF + CH = C_2^* + HF. \tag{11'}$$

The reactions (8′)—(10′) have already been reported for the C_2^* formation in the hydrocarbon oxidation.[26-28)]

The concentration of CH thus produced is less than that of CF, as shown in Fig. 10. Accordingly, assumed that the rate constants of these reactions are nearly equal, it appeared that the reaction (11′) was most important for the C_2^* formation under our experimental condition. The CH and CF concentrations calculated with mixture (G) were smaller than those calculated with mixtures (C) and (D), respectively. Hence, it may be possible to explain the relationship between maximum C_2^* intensity and CF_3Cl concentration, as shown in Fig. 5.

As already mentioned above, the endothermic reaction (18) among reactions (17)—(19) contributed to the formation of not CH* but CH in this work because none of the ΔH values (17—24 kcal/mol) is small enough to form CH*. However, the reaction (15) is strongly exothermic, and C_2 and C exist during the reaction process, as shown in Fig. 10. Consequently, it is concluded that CH* is mainly formed by

$$C_2 + OH = CH^* + CO. \tag{15'}$$

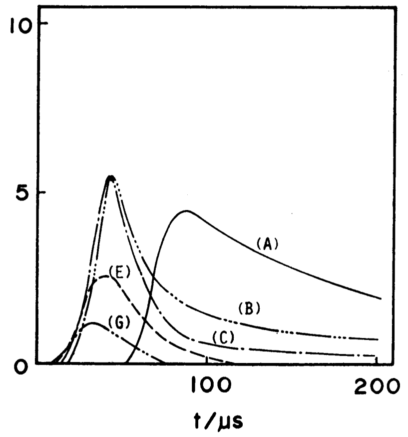

Fig. 9. OH* concentration profiles computed with mixtures (A), (B), (C), (E), and (G) using the mechanism and rate constants in Table 3.

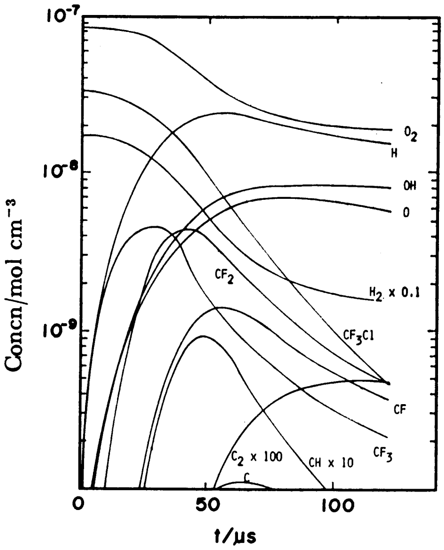

Fig. 10. Concentration profiles computed for mixture (C) at 1800 K using the mechanism and rate constants shown in Table 3.

The OH concentration calculated with mixture (G) is almost the same as that calculated with mixtures (C) and (D), but the C_2 concentration with mixture (G) is extremely smaller than that calculated with mixture (C) or (D). The relationship between maximum CH* intensity and CF_3Cl concentration, as shown in Fig. 4 may be easily interpreted. According to our computation, the increase and decrease of OH*, CH*, and C_2* concentrations owing to the addition of a small and large amounts of CF_3Cl, respectively, were also concluded to mainly come from the competition of the reactions $CF+CF_3+M=C_2F_4+M$ and $CF+H_2=CH+HF$.

Since the reaction (21) is greatly exothermic and since C and F_2 exist abundantly enough to cause the reaction (21′), the reaction (21′) is concluded to be a main process for the CF* formation.

$$C + F_2 = CF^* + F. \tag{21'}$$

Temperature dependence of the ignition delay time τ observed with OH* is shown in Fig. 11, which reveals that τ at a temperature above 1500 K decreases with an increase in *C*. Fig. 11 also shows the value τ computed with mixtures (A), (B), (C), (E), and (G) at 1800 K. τ observed is in fair agreement with that simulated.

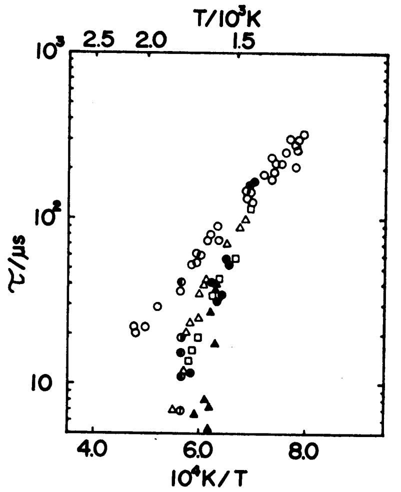

Fig. 11. Temperature dependence of the ignition delay time τ measured with the OH* emission for the mixtures (A)—(G), ○: (A), △: (B), □: (C), ●: (E), ▲: (G), and calculated at 1800 K for the mixtures (A)—(G), ◐: (A), ◑: (B), ◎: (C), ⊙: (E), ⦶: (G).

Under our experimental condition employed with the H_2–O_2–CF_3Cl–Ar mixtures, a fair amount of CF_3 and Cl may be produced through the reaction (1), as shown in Fig. 10. These intermediate products CF_3 and Cl easily generate the active species H through the reactions (2) and (3). In the oxidation reaction of the H_2–O_2–CF_3Cl–Ar mixtures, an occurrance of the reactions (1)—(3) increases the H concentration at the initial stage, thereby promoting the overall reaction rate, as shown in Fig. 11. In the H_2 oxidation over the range 1500—2200 K, therefore, CF_3Cl is concluded to act as a promoter.

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