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ESR Studies of Bunsen-type Methane-Air Flames. II. The Effects of the Addition of Halogenated Compounds to the Secondary Air on the Hadrogen Atoms in the Flame

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Hydrogen atoms in a methane-air Bunsen-type flame were detected by the flame-in-cavity ESR method. The addition of a halogenated compound to the secondary air was found to reduce the H-atom concentration linearly with an increase in the additive concentration. The eight halogenated compounds examined showed an increased effectiveness in scavenging H atoms in this order; $HCl < CF_2Cl_2 < CHCl_3 < CH_3Cl < CH_2Cl_2 < CFCl_3 < CCl_4 < CH_3Br$. This chemical effect of the halogenated compounds on the combustion reactions agrees well with the inhibitor index for these compounds.

Extensive studies have been carried out on the effects of additives such as halogenated compounds on the inhibition of premixed flames.[1-6] The relative effectiveness of a flame inhibitor has been evaluated from the change in the burning velocity of the flame upon the addition of the inhibitor, according to this equation:

$$\phi_\nu = ([O_2]/[In])(\delta V/V_0), \qquad (1)$$

where $[O_2]$ and [In] are the initial concentrations of O_2 and the inhibitor respectively, where V_0 is the burning velocity in the absence of the inhibitor, and where δV is the decrease in the burning velocity due to the presence of the inhibitor.[1,7] There has been few reports on the inhibition of diffusion flames.[8,9] The addition of hydrogen halides to the surrounding air has been found to quench diffusion flames more effectively than direct addition to the fuel.[8] It has been suggested that CH_3Br quenches diffusion flames chemically, though no mechanism for this has been discussed.[9]

Flame inhibition is a combination of the chemical and physical effects of an inhibitor. The chemical effects are mostly the scavenging of the carriers of the chain reactions in the combustion, like H, O, and OH. There have, however, been no reports showing the correlation between flame inhibition and radical scavenging.

In a preceeding paper (Part I of this study)[10] we found, by using the flame-in-cavity electron-spin-resonance (ESR) method, that the concentration of H atoms in the Bunsen-type methane-air flame is reduced when the O_2 content in the secondary air is increased. This indicates that O_2 diffuses from the secondary air into the inner zone of the flame, as the H atoms are most abundant in the fuel-rich inner reaction zone.[11] This also shows that the flame-inhibition effect can be studied by adding inhibitors to the secondary air around Bunsen-type flames and by detecting the H atoms in the flame by means of ESR. Because of the collisional broadening of the resonance lines, the reaction intermediates observable by the flame-in-cavity ESR method from a flame at atmospheric pressure are atoms whose electronic ground state is a S-state like $H(^2S)$ or $N(^4S)$. In spite of this limitation, the flame-in-cavity ESR method is a useful method for studying H atoms under a variety of burning conditions.

Experimental

The Bunsen-type burner used consisted of three concentric quartz tubes and was the same as that reported previously.[10] The premixed combustible gas consisted of a mixture of methane (99.0% purity), 88 cm^3/min, and air, 380 cm^3/min. The flow rate of the secondary air was 430 cm^3/min. These flow rates were chosen to maximize the ESR signal of the H atoms. The added inhibitor was injected into the secondary air using a 200-cm^3 glass syringe and a microfeeder. Five different flow rates of an added inhibitor, ranging from 0.067 to 0.33 cm^3/min, could be attained by using different combinations of driving gears on the microfeeder. The halogenated compounds used as inhibitors were HCl (purity 99%, Takachiho), CH_3Cl (99%, Takachiho), CH_2Cl_2 (Spectrograde, Eastman Kodak), $CHCl_3$, CCl_4, CF_2Cl_2, $CFCl_3$, and CH_3Br (all reagent grade, Tokyo Kasei). As they were liquid at room temperature, they were evaporated in a heated chamber, while the syringe and secondary air were preheated to keep them from condensing.

The H atoms in the flame were detected by ESR using a flam-in-cavity method which has been described elsewhere.[10,12] The spectrometer (Varian, Model E-109) was operated in the X-band with a magnetic-field modulation of 100 kHz.

Results

ESR Spectra of the Flame Gases. H atoms were detected in both the presence and absence of a halogenated compound in the secondary air. The H-atom spectrum showed two lines with a hyperfine separation of 51.0 mT, the same as has been reported previously.[10-12] O_2 molecules have been demonstrated to cause a broadening of the H-atom lines in the ESR spectrum from a flame.[12] We found that the spectral linewidth of the H-atom signal was independent of the concentration of all the halogenated compounds added except for the case of CH_3Br. On the addition of CH_3Br, the linewidth increases with an increase in the CH_3Br concentration in the secondary air, as can be seen in Fig. 1.

An ESR linewidth is inversely proportional to the

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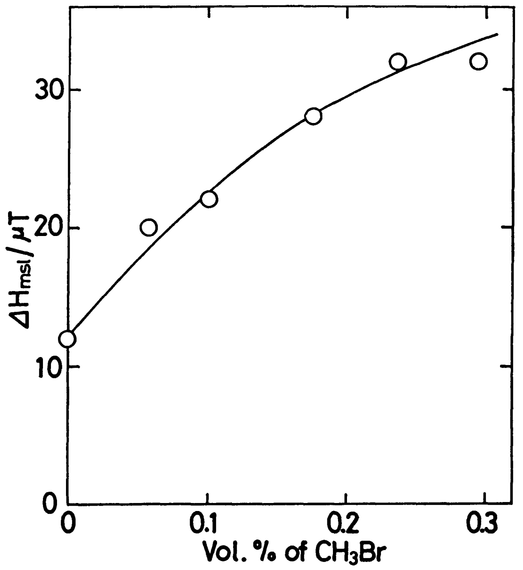

Fig. 1. Dependence of the peak-to-peak width of the derivative ESR spectrum of H atoms in a Bunsen-type methane-air flame on the concentration of CH_3Br added into the secondary air. 1 G=0.1 mT.

spin-spin relaxation time, T_2, which can be expressed as:

$$\frac{1}{T_2}=\frac{1}{T_2'}+\frac{1}{2T_1}, \qquad (2)$$

where T_2' is the spin-dephasing time and where T_1 is the spin-lattice relaxation time. The latter is related to the lifetime of the spin sublevels.[13] The most important intermolecular process in the gas phase is collision broadening; on each collision, the phase memory of the spin precession is lost. This will make the first term on the right-hand side of Eq. 2 comparatively important and will determine the ESR linewidth. The presence of halogenated compounds is expected to produce paramagnetic halogen atoms, like Cl and Br.[4,7] The Br atoms have a rapid spin-lattice relaxation which makes them an efficient sink of the spin energy of the H atoms. The presence of Br atoms will thus shorten the T_1 of the H atoms and cause a line-broadening due to the second term. The H-atom concentration in the flame as deduced from ESR was corrected for this variation in linewidth.

Effect of Inhibitors on H-atom Concentration. The amount of H atoms in a Bunsen flame has been found to depend on the concentration of O_2 in the secondary air.[10] It has also been demonstrated that H atoms react with O_2 molecules which diffuse into the flame from the surrounding air.[11]

The introduction of halogenated compounds into the secondary air reduced the amount of H atoms in the flame to a varying extent, depending on the inhibitor. The observed results are shown in Fig. 2 for some of the inhibitors. As a blank test, excess air was added to the secondary air in place of an inhibitor, but no appreciable reduction in the amount of the H atoms was observed. This indicates that the change in the H-atom concentration arises from the chemical reactions of the added inhibitors, and not from any physical modification of the flame caused by the addition of the inhibitors.

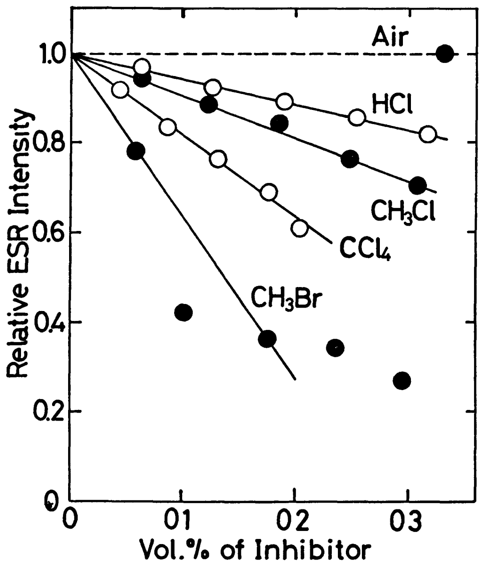

Fig. 2. Dependence of the ESR intensity of the H atoms in a Bunsen-type methane-air flame on the concentration of halogenated compounds added into the secondary air. For simplicity, the data for CH_2Cl_2, $CHCl_3$, CF_2Cl_2, and $CFCl_3$ were omitted.

The observed ESR signal intensity of the H atoms decreases linearly with the concentration of the halogenated compound added, as is shown in Fig. 2. This linearity comes fortuitously through the complex combustion reactions in the flame. However, the negative slope of the straight lines in Fig. 2 serves to determine the chemical effectiveness of the inhibitors, as

$$\phi_r = \frac{[H]_0-[H]}{[H]_0}\cdot\frac{1}{[In]}, \qquad (3)$$

where [H] and $[H]_0$ are the amounts of H atoms in the presence and in the absence of an inhibitor respectively. The ϕ_r values thus obtained are shown in Fig. 3 for all the halogenated compounds examined.

Discussion

For halogenated compounds, Fristrom and Van Tiggelen[1] derived an inhibitor index, ϕ_ν, as:

$$\phi_\nu = n_C\phi_C + n_H\phi_H + \sum n_X\phi_X, \qquad (4)$$

where n_C, n_H, and n_X are the numbers of carbon, hydrogen, and halogen atoms in a halogenated compound and where ϕ_C, ϕ_H, and ϕ_X are the atomic-inhibitor indices for the corresponding atoms. The atomic-inhibitor indices have been derived from the observed change in the burning velocity of a premixed flame caused by the inhibitors based on kinetic considerations of combustion reactions.[1] They have also been shown to depend on the fuel and also on equivalence ratio, though not strongly. Although the equivalence ratio can not be defined for a Bunsen-type flame, one can obtain a good linear relationship between ϕ_r and ϕ_ν, as can be seen in Fig. 3, by using a typical set of values:[1] $\phi_C=1.0$, $\phi_H=0.25$, $\phi_F=1.0$, $\phi_{Cl}=1.5$, and $\phi_{Br}=12.3$. The general trend is that

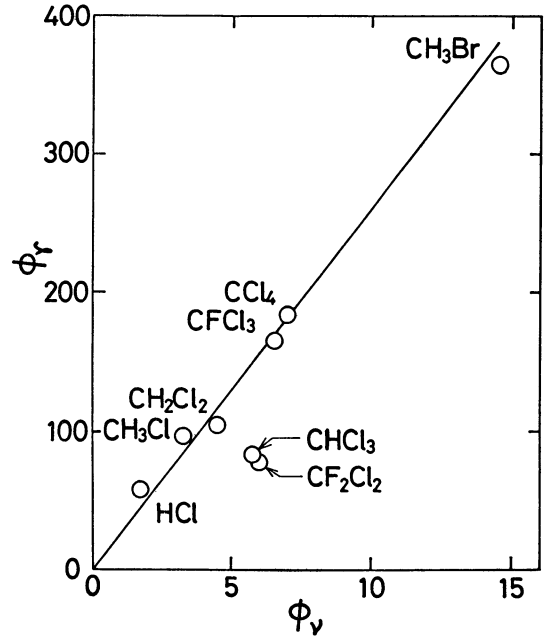

Fig. 3. Correlation between the effectiveness, ϕ_r, of halogenated compounds in scavenging H atoms in a methane-air flame determined by the ESR method and the inhibitor index, ϕ_ν, determined from their effect on the burning velocity.[1]

an increase in the number of Cl atoms in the inhibitor molecule results in a more pronounced reduction in the amount of H atoms in the flame. The halogen atoms reduce the amount of H atoms in this increasing order: F<Cl<Br.

A halogenated compound inhibits flame reactions by scavenging H atoms, which are the principal reactive intermediates in hydrocarbon combustion. The reduction in the amount of H atoms observed above is not necessarily due to the direct scavenging of H atoms by the inhibitors; it can also be an indirect result of the scavenging of other reactive intermediates, like O atoms and OH radicals. However, because, in a fuel-rich hydrocarbon flame, H atoms are the most abundant reactive intermediates,[7] we will focus our discussion on the scavenging of H atoms.

Halogenated compounds can scavenge H atoms and convert them into stable molecules and unreactive radicals by reactions like:

$$H + RX = HX + R, \tag{5}$$

$$H + HX = H_2 + X. \tag{6}$$

In addition, halogen atoms can assist the cyclic recombination of H atoms in reaction sequences where the halogen atom is rapidly regenerated:[1]

$$H + X + M \rightarrow HX + M, \tag{7}$$

followed by Reaction 6. The equilibrium of Reaction 6 tends to be shifted far to the right in a high-temperature flame when X is Br and I.[5,6] As a matter of fact, about 70% of the bromine has been shown to exist in the atomic form in a HBr-inhibited methane-air flame.[14] From the ϕ_ν data, the rate constant of the forward reaction, 7, for Br (and I) has been evaluated to be about nine times larger than that for Cl.[1] Thus, the efficient decrease in the amount of H atoms caused by CH_3Br compared to the chlorinated and fluorinated methane found in this study is consistent.

An inhibitor molecule containing more than one halogen atom (*e.g.*, CCl_4) can be stripped of its halogen atoms by successive reactions with H atoms:

$$CCl_4 + H \rightarrow CCl_3 + HCl, \tag{8}$$

$$CCl_3 + H \rightarrow CCl_2 + HCl, \tag{9}$$

and so forth.[5] Therefore, HCl can be expected to scavenge one H atom by means of Reaction 6, while CH_3Cl scavenges two H atoms by the combined reactions of 5 and 6, and CCl_4 even more by successive reactions of the 9 type. The observed ϕ_r values agree qualitatively with what can be expected, except for the cases of $CHCl_3$ and CF_2Cl_2.

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