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The ESR Detection of N Atoms in Methane–Air Combustion Flames Doped with Nitrogen Compounds

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Synopsis. The ESR spectra of nitrogen atoms were detected for the first time in the combustion flames of methane doped with ammonia. The dependence of the N-atom concentration on the flame conditions was examined. The results were then discussed with reference to the models of the reduction of NH_3, leading to the NO formation.

The elucidation of the mechanism of NO formation in combustion flames is currently one of the most important subjects in combustion-chemical studies. NO is now believed to be formed by three different mechanisms: Thermal NO (from a reaction between N_2 and O_2, the Zeldovich mechanism), prompt NO (originating from reactions between labile intermediates, such as CH or C_2 and N_2), and fuel NO (originating from fuel-bound nitrogen).[1] Nitrogen atoms have been suggested to be of essential importance as the reaction intermediates in the prompt and fuel NO formation. However, there has been very little direct observation of N atoms in combustion flames. Although the paramagnetic intermediates in flames, such as the H and O atoms and the OH radicals, have recently been studied extensively by means of the electron-spin-resonance (ESR) method,[2–4] the ESR detection of N atoms in flames has, as far as the present authors know, not yet been reported.

This note aims to report the first successful ESR detection of N atoms in Bunsen-type flames of methane doped with ammonia under atmospheric pressure. It will also compare the observed dependence of the N-atom yield on the flame conditions with the models of the fuel NO formation reported previously.

Experimental

The Bunsen-type flame was obtained by using a burner composed of three concentric quartz tubes, as has been described in detail previously.[5] Premixed combustible gases, mixtures of methane and air with or without ammonia, were flowed through the innermost tube (4 mm in diameter). The secondary air was supplied through the second tube to support the flame. The outermost tube was used for the flowing of the coolant nitrogen gas, so that the flame was isolated from the surroundings. The flame temperature was measured by using a fine (0.1 mm in diameter) Pt/Pt-Rh thermocouple coated with SiO_2.

The paramagnetic entities were detected by means of the flame-in-cavity method[6] using an X-band spectrometer (Varian, Model E-109) equipped with a TE_{011} large-access cavity (Model E-235). The spectrometer was operated with a 100-kHz field modulation. Because the paramagnetic entities were subjected to ESR measurements under the atmospheric pressure, neither non-S-state atoms nor free radicals could be observed because of the collision broadening. Only H and N atoms with a S-state as the ground electronic state were observed. Another limitation of the flame-in-cavity method is that the paramagnetic entities in a flame are observed as a whole, so that their locations in the flame cannot be determined. This means that neither the concentration distribution in the flame nor the absolute concentration at particular positions in the flame can be determined. Therefore, we are mainly concerned with the relative change in the total amount of the paramagnetic entities dependent on the flame conditions. Occasionally, however, the absolute concentrations of H and N atoms in the flames were estimated from the integrated intensity of the ESR spectra.

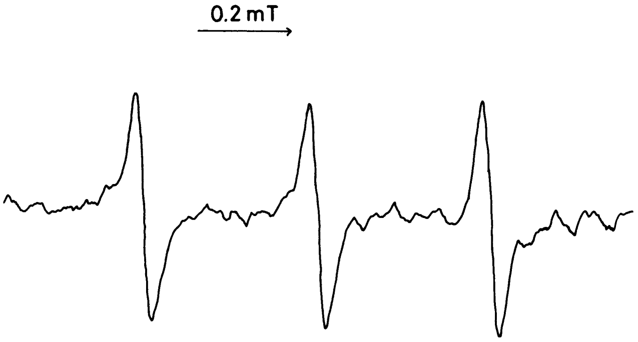

Fig. 1. ESR spectrum of N atoms observed from a Bunsen-type flame of methane–air premixed gas doped with ammonia under atmospheric pressure by the flame-in-cavity method. The flow of premixed gas was 200 cm^{3}min^{-1} of air, 33 cm^{3}min^{-1} of methane, and 8 cm^{3}min^{-1} of ammonia. The flow rate of secondary air was 220 cm^{3}min^{-1}.

Results and Discussion

The ESR signals observed from the flames of methane–air mixtures doped with ammonia were composed of an intense two-line spectrum with the hyperfine separation of 51.0 mT due to H atoms and a weak three-line spectrum with the hyperfine separation of 0.38 mT at $g=2.002$. An example of the latter is shown in Fig. 1. This spectrum is attributed to N atoms on the basis of the ESR parameters, which are identical with those of the N atoms studied by the flow-discharge method.[7] The only difference in the spectral features is the much larger linewidth of each hyperfine line in the present study, but this can be attributed to the collision broadening, very probably due to collisions with paramagnetic molecular oxygen[6,8] at high pressures.

When triethylamine was added to the premixed gas instead of ammonia, the ESR spectrum of N atoms was also observed. The premixed gas without nitrogen compounds gave no N-atom spectrum. These observations indicate that the N atoms in the flames come from the added nitrogen compounds and are involved

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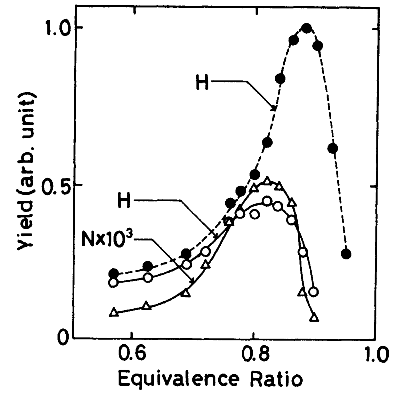

Fig. 2. Dependence of the yield of (circles) H and (triangles) N atoms in Bunsen-type flames of methane–air premixed gas (solid curves) with and (dashed curve) without ammonia on the equivalence ratio of the flame. The equivalence ratio of the flame (calculated by assuming complete mixing of the premixed gas and the secondary air) was changed by changing the flow rate of the secondary air, while the equivalence ratio of the premixed gas was kept constant, 1.71, both in the presence and absence of the added ammonia.

in the fuel-NO mechanism of the NO formation. The yields of N atoms due to the other mechanisms, thermal and prompt NO, are too low to be detected under the present experimental conditions.

The dependence of the ESR intensities of the H- and N-atom spectra on the equivalence ratio (stoichiometric oxygen concentration/actual oxygen concentration) was examined for methane–air flames doped with ammonia by keeping the flow rate of the premixed gas unchanged (33 $cm^3\,min^{-1}$ of methane, 200 $cm^3\,min^{-1}$ of air, and 8 $cm^3\,min^{-1}$ of ammonia) and by changing the flow rate of the secondary air. The composition of the premixed gas corresponds to the equivalence ratio of 1.71, if the combustion of ammonia is expressed as $NH_3+(3/4)O_2\rightarrow(1/2)N_2+(3/2)H_2O$. The observed dependence is shown in Fig. 2. Both the H and N atoms show their maximum yield at the equivalence ratio of 0.82. The variation in the N-atom yield is found to be parallel with that of the H atom.

For purpose of comparison, the dependence of the H-atom yield for the undoped flame on the equivalence ratio is also shown in Fig. 2. The observed trend of the H-atom yield is essentially the same as has previously been reported and been attributed to the effect of the diffusion of the secondary air (oxygen) into the flame.[5] The composition of the premixed gas was unchanged at the corresponding equivalence ratio of 1.71 here, also. For the undoped flame, the H-atom yield reaches its maximum at the equivalence ratio of 0.88. It should be noted that the H-atom yield is higher in the undoped flame than in the ammonia-doped flame throughout the region of equivalence ratios examined.

The effect of the concentration of added ammonia was also examined at a constant equivalence ratio, 0.88. Qualitatively, the H-atom yield decreases, while the N atom yield increases, with an increase in the concentration of ammonia in the range of the flow rate of ammonia, 0—8 $cm^3\,min^{-1}$. The maximum yield of both the H and N atoms appears at a lower equivalence ratio with a higher concentration of added ammonia.

The ESR intensities changed depending on the position of the burner when it was moved along the center axis of the ESR cavity. This is because the H and N atoms are confined in a comparatively narrow region of the flame and because the ESR sensitivity depends on the location of the paramagnetic entities in the cavity (the sensitivity is expressed by the squared sinesoidal function). When the luminous inner cone was at the center of cavity (the position of the highest sensitivity), both the H and N atom signals showed the largest intensity. This indicates that the H and N atoms are located mostly in the inner cone, the height of which is less than 10 mm.

Assuming a uniform distribution of the H atoms in the region within 10 mm from the burner mouth, an assumption based on the concentration profile observed by the probe-sampling-ESR method,[2] the absolute concentration of the H atoms was estimated from the integrated ESR intensity to be 1×10^{15} atoms cm^{-3} (1×10^{-4} mole fraction) for the undoped flame at the concentration maximum shown in Fig. 2. The absolute concentration of N atoms was estimated in the same way to be 5×10^{11} atoms cm^{-3} (5×10^{-8} mole fraction) in the doped flame, also at the concentration maximum in Fig. 2. These estimations were made by calibrating the ESR intensities with reference to the ESR signals of molecular oxygen of known concentrations, and by correcting the temperature effect (the effect of the Boltzman distribution between spin states and of the gas density)[9] on ESR intensities using the highest temperatures actually measured in the luminous cone, 1660 and 1700 K for the doped and undoped flame, respectively.

It has been commonly accepted that the N atoms are generated in the ammonia-doped flame by the successive oxidation of NH_3 with H atoms or OH radicals as $NH_3\rightarrow NH_2\rightarrow NH\rightarrow N$. However, the detailed mechanism of the oxidation of ammonia has not been fully elucidated, though it is thought to be dependent on the flame conditions. Miller et al.[10] have studied the reaction mechanism of the ammonia oxidation in one-dimensional flames based on numerical-model calculations. Their conclusion is that NH_i species are oxidized mostly by H atoms or OH radicals, that the increase in the equivalence ratio results in the increase in the mole-fraction ratio of H to O and also in the increase in the N-atom concentration, and that NO is generated not only from N, but also directly from NH_2 by the reaction with the O atom, especially in fuel-lean flames.

The present experimental results may be summarized as: (1) the H and N atoms are observed concomitantly, and (2) the formation of N atoms in the presence of NH_3 accompanies the decrease in the H-atom concentration. Although the present results are still insufficient for the comprehension of the complex reaction mechanism of fuel-NO formation, they seem to be consistent with the view that the N-atom formation by the fuel-NO mechanism is assisted by the existence of H atoms.[10] The present success in detecting the ESR spectrum of N atoms in combustion flames will encourage the further application of the ESR method to studies of combustion chemistry.

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