THE SIGNIFICANCE OF EMISSION FROM EXCITED FORMALDEHYDE IN PREMIXED FLAMES OF SOME HYDROCARBONS AND PERCHLORIC ACID

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Abstract

Measurement of the rate of emission of light quanta in the cool flame bands of these flames indicates that the reaction concerned is not a step in the main combustion mechanism.

The cool flame spectrum is given in the combustion of ammonium perchlorate in methane.

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SUMMARY

The "cool flame" emission from excited formaldehyde in premixed flames of perchloric acid (72%) and methane, or a fuel which produces methane in the flame, is attributed to a reaction between the CH_3 radical and ClO_3, ClO_2 or ClO.

The yield of light quanta emitted by HCHO* per molecule of methane consumed has been measured. Although this reaction does not constitute a step in the main mechanism of the combustion the emission could, in principle, be used to indicate the proportion of fuel in a composite propellant based on ammonium perchlorate and polyisobutene which reacts with chlorine-oxygen compounds.

CONTENTS

1 INTRODUCTION

An unexpected characteristic of the spectra of premixed flames of perchloric acid (72 per cent) with methane or hydrocarbons which produce methane in their flame reactions is the emission of "cool flame" bands. The emission is very strong with methane at both atmospheric and reduced pressures[1], but much weaker with ethane and isobutene; with ethylene and propane the combined effect of the hydrocarbon bands and a continuum makes detection of "cool flame" bands impossible.

The spectrum of a "cool flame" is shown in Ref. 2 to be identical with that of the resonance fluorescence of the formaldehyde molecule, the bands arising from the polyatomic emitter HCHO. Much energy, i.e. ~340 kJ mol^{-1}, is required for the electronic excitation.

There is no unanimous view of the reaction step which produces excited formaldehyde in "cool flames" but there is general support for the theory that it involves an alkoxy group (produced in the decomposition of a hydroperoxide) and an unspecified radical

$$RCH_2O + R^1 = RR^1 + HCHO^* \qquad (1)$$

where R^1 may be an alkyl radical, O, H, OH or another alkoxy group, all the reactions being sufficiently exothermic to provide the excitation energy. HCHO* emission occurs in the autoignition of methane[3] but the only 'hot' flames with oxygen in which it occurs are those with methyl alcohol[4] and methyl nitrite[5]. The restriction of the bands to these spectra supports their assignment to a reaction of an alkoxy (in these latter cases a methoxy) group with OH .

No reaction scheme proposed for the combustion of methane in flames involves the production of the methoxy radical, but it is generally accepted that formaldehyde is formed as an intermediate after the initial reaction with methane has given rise to the methyl radical:

$$(CH_4 + OH, \text{ or } H \longrightarrow CH_3 + H_2O, \text{ or } H_2 .)$$

The possible reactions are:

$$CH_3 + O_2 \longrightarrow HCHO + OH; \Delta H = -210.5 \text{ kJ mol}^{-1} \qquad (2)$$

$$CH_3 + O \longrightarrow HCHO + H; \Delta H = -281 \text{ kJ mol}^{-1} \qquad (3)$$

Neither of these reactions releases sufficient energy to excite the formaldehyde.

In flames perchloric acid does not act merely as a carrier of molecular oxygen and chlorine but exerts a specific action of its own. "Cool flame" bands are not formed with flames of perchloric acid and formaldehyde so their occurrence with other perchloric acid flames arises from a reaction step which both forms and excites the formaldehyde. There may be more methoxy radicals formed in some side reaction in flames with perchloric acid (e.g. between CH_3 and ClO) than with oxygen. HCHO*, however, seems more likely to be produced in a reaction between CH_3 and some chlorine oxygen entity derived from perchloric acid:

$$CH_3 + ClO_3 \longrightarrow HCHO + HCl + O_2; \quad \Delta H = -495.5 \text{ kJ mol}^{-1} \qquad (4)$$

$$CH_3 + ClO_2 \longrightarrow HCHO + HClO; \quad \Delta H = -447 \text{ kJ mol}^{-1} \qquad (5)$$

$$CH_3 + ClO \longrightarrow HCHO + HCl; \quad \Delta H = -443 \text{ kJ mol}^{-1} \; . \qquad (6)$$

All these reactions release more energy than is required to produce HCHO*. The initial reaction of perchloric acid is expected to release ClO_3 (or ClO_2 if catalyst is present) but this is expected to break down rapidly to form ClO :

$$HOClO_3 \; (+ H) \longrightarrow ClO_3 + OH \; (H_2O) \qquad (7)$$

$$ClO_3 \longrightarrow ClO + O_2 \qquad (8)$$

In the methane-perchloric acid flame the CH_4 molecule must react to give a CH_3 radical which, apart from secondary reactions, is then oxidized in one, or more, of the reactions (2) to (6). The importance of reactions (4), (5) and (6) has been tested by measuring the light quanta emitted in the "cool flame" band for every CH_4 molecule consumed. It is concluded that this type of reaction is not an important step in the combustion mechanism of perchloric acid flames with methane (or other hydrocarbons which break down to yield methane).

2 EXPERIMENTAL METHOD

The absolute light emission of the flames in photons/sec over the wavelength range 330 nm to 485 nm, i.e. the "cool flame" band, was measured by comparison of the light output with that of a lamp of known optical characteristics.

2.1 Perchloric acid flames

Premixed flames of methane with 72 per cent perchloric acid and nitrogen at atmospheric pressure were produced as described earlier[1] and stabilized on a Pyrex burner of 1.5 mm id.

The perchloric acid was of Analytical Reagent grade having the constant boiling point composition (bp 476 K at atmospheric pressure) corresponding to $HClO_4$, 2.17 H_2O. The methane and nitrogen were of commercial grade with purities of 97 and 99 per cent respectively.

The gas mixtures used had compositions which may be expressed as

$$x\ CH_4 + HClO_4,\ 2.17\ H_2O + 5\ N_2 \qquad (9)$$

where x was varied between 0.83 and 1.45, the corresponding length of the flame varying between 4 mm and 2 mm. Nitrogen was added to reduce the flame temperature and avoid melting the port of the burner. The flame was surrounded with a flow of nitrogen to preclude secondary combustion with ambient air.

2.2 Optical system and procedure

A tungsten strip lamp was calibrated at the National Physical Laboratory for use as a standard light source. A Jarrell-Ash-Eberhardt scanning monochromator recorded the light emitted. The variation of light intensity with wavelength for the lamp naturally differed from that of the flame. It was therefore necessary to ensure that the signal output remained directly proportional to the intensity of the light received over the wavelength range used. The curve of sensitivity versus wavelength with the EMI photomultiplier tube 9529B appeared to be flat enough for the desired measurements.

To allow for the low light intensity of the flames a monochromator slit width of 0.15 mm was adopted and the flame was placed as near to the slit (63 mm) as possible without overfilling the grating. The lamp was placed 300 mm from the slit and stops were sited so that the area of the strip filament exposed to the slit was accurately known.

The lamp was used at a series of known brightness temperatures and the areas of chart between the baseline and the spectral curve of light intensity versus wavelength were measured for the range 330 nm to 485 nm. The area was directly proportional to the corresponding theoretical light output of the lamp. The spectra of the flames were then recorded under the same conditions.

Knowledge of the photon emission rate from the lamp (see Section 3) permitted calibration of the recording system and thus measurement of the photon flux of the flame.

3 CALCULATION OF LIGHT YIELD FROM HCHO*

Planck's radiation formula giving the spectral radiant exitance, M_λ, may be expressed in the form

$$M_\lambda \, d\lambda = AE_\lambda \, c_1 \, d\lambda/\lambda^5 \left[\exp(c_2/_\lambda T) - 1\right] \qquad (10)$$

where M_λ is the rate of energy release over a hemisphere over the wavelength interval λ to $\lambda + d\lambda$

A is the area of the radiator

E_λ is the emissivity of the radiator at wavelength λ

c_1 is the first radiation constant, $c_1 = 2\pi hc$, or 3.7418×10^{-16} Jm^2s^{-1}
where h is Planck's constant
and c is the speed of light in a vacuum

c_2 is the second radiation constant, $c_2 = hc/k$, or 1.4388×10^{-2} m K
where k is Boltzmann's constant (ratio of gas constant to Avogadro constant)

T is the temperature of the radiator, K .

The rate of energy release per unit solid angle normal to the surface of the radiator is given by dividing expression (10) by π (not 2π). For the corresponding rate of photon emission, N, the expression is further divided by the energy per photon, hc/λ, giving

$$N d\lambda = AE \, c_1 \, d\lambda/hc\lambda^4 \left[\exp(c_2/\lambda T) - 1\right] . \qquad (11)$$

The lamp was calibrated in brightness temperature (against current). The true temperatures were calculated as indicated in Appendix 1. The emissivity of tungsten varies with both temperature and wavelength. Using mean values for E_λ expression (11) was integrated over the wavelength range concerned, to obtain the photon flux from the lamp, for the calibration of the monochromator. The photon flux from the HCHO* in the flame was then obtained (making allowance for the different distances of lamp and flame from the monochromator slit).

Knowledge of the rate of flow of methane in each flame then gave the photon emission from HCHO* in terms of methane molecules consumed.

The recorded spectra contained bands attributable to emission from C_2 (473.7 nm) and CH (431.5 and 388.9 nm)but there was no difficulty in excluding the sections under these peaks from the remainder of the spectrum. There was also an apparent continuum underlying the "cool flame" bands but there was no reason to attribute it to anything but formaldehyde band overlap.

4 RESULTS

The number of molecules of methane consumed in the flame for each photon emitted by HCHO* is shown in the following table for a range of values of x in expression (9), i.e. moles of methane per mole of perchloric acid.

Mixture composition mol CH_4 per mol $HClO_4$	CH_4 molecules consumed per photon emitted from HCHO*
0.83	30×10^6
0.92	32.5×10^6
1.01	34.5×10^6
1.09	36×10^6
1.18	37.5×10^6
1.27	40×10^6
1.45	44.5×10^6

5 DISCUSSION AND CONCLUSIONS

Only a proportion of the molecules formed in an excited state has time to radiate before either de-excitation by collision or other means, or further chemical reaction. The processes which may remove excited formaldehyde before it radiates are considered more fully in Appendix 2. It is sufficient here to note, as argued below, that even if HCHO* became de-excited at the first collision (at least 10 are probably required - see Appendix 2) the photon yield per methane molecule consumed indicates that the reaction step which produces the HCHO* is not important in the kinetics of the flames concerned.

In the absence of reaction or de-excitation other than by emission, the radiative decay with time of an excited species conforms to the rate relationship

$$N_t = N_o \exp(-kt) = N_o \exp(-t/\tau) \qquad (12)$$

where N_t is the number of excited molecules after time t

N_o is the original number of excited molecules

t is the lapse of time

k is a reaction coefficient which is the inverse of the average lifetime, τ of the excited species.

The number of collisions which a molecule undergoes per second, Z, is given approximately by

$$Z = 4\sigma^2 n \sqrt{\pi RT/M} \qquad (13)$$

where σ is the mean collision diameter of the colliding molecules

n is the number of molecules per unit volume

R is the gas constant

T is the temperature (taken here as 2000 K)

M is the mean molecular weight (taken here as 30)

Z is then 3×10^9 s^{-1} for HCHO in the present flames. As shown in Refs 2 and 6 the average lifetime of HCHO* is generally accepted to be 10^{-5} to 10^{-6} sec. Substitution of this value for τ in expression (12) reveals that the HCHO* formed which radiates in the time interval before the first collision, viz. $\sim 3 \times 10^{-10}$ sec, amounts to only about 3 molecules in every 10^4 to 10^5. The figures obtained for the numbers of methane molecules consumed for every photon emitted from HCHO* (see table, in Section 4) may now be expressed as the numbers consumed for every HCHO* molecule formed, and these are about 10^2 to 10^3. This figure is proportionately higher if the deactivation of HCHO* necessitates more than one collision.

Some of the energy of reaction which produces HCHO must appear as relative translational velocity of the products, so the proportion of HCHO formed which is energised to radiate in the "cool flame" band system is not known. However, pending evidence to the contrary, it is reasonable to suppose that it is much greater than 1 in 10^2 or 1 in 10^3 in reactions (4), (5) or (6), particularly considering that much more energy is produced than is required for the excitation. It is concluded that the process responsible for the formation of HCHO* is not a step in the main reaction but a secondary process.

The occurrence of "cool flame" bands is, nevertheless, a useful indication of reaction between perchloric acid products and, for instance, polyisobutene (which pyrolyzes to give isobutene), and could possible be used to indicate

the presence, and even the extent, of such reaction in the combustion of a propellant based on ammonium perchlorate and polyisobutene (see Appendix 3). Selzer, in his spectrum of such a solid propellant, shown in Ref. 7, tentatively identified some bands as "cool flame" emission possibly arising from formaldehyde formed in the initial reaction of the polyisobutene. However, it is apparent that any such bands would have resulted from reaction between perchloric acid, produced by vaporization of ammonium perchlorate, and pyrolysis products of polyisobutene. Unfortunately, there is reason to doubt the assignment of the bands; they are more likely to be hydrocarbon flame bands.

Acknowledgement

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Appendix 1

True temperature of pyrometer lamp filament

From the approximation

$$1/\left[\exp\ (c_2/\lambda T)-1\right] \approx \exp\ (-c_2/\lambda T) \qquad (14)$$

Wien's law is obtained from Planck's radiation law (see expression 10):

$$M_\lambda = 2E_\lambda\ Ac_1\ \lambda^{-5}\ \exp\ (-c_2/\lambda T) \qquad (15)$$

which holds quite accurately as long as λT is less than 5 mm K.

The pyrometer (strip) lamp was calibrated at the National Physical Laboratory for brightness temperature, T_{Br}, against current at 660 nm.

As in Ref. 8, it may be shown from Wien's law that the true temperature, T, of the lamp is given by the following equation:

$$T = 1/\left[\lambda \ln E_\lambda / c_2 + 1/T_{Br}\right] \ . \qquad (16)$$

Appendix 2

Processes removing HCHO* in flames

In addition to collisional deactivation some internal quenching of HCHO* may result from radiationless transition to the ground state. As it is expected to be of only secondary importance here it has been ignored.

In methane-oxygen flames of all but the most fuel-rich compositions the most likely reaction for the removal of formaldehyde is the step

$$HCHO + OH \longrightarrow HCO + H_2O \quad , \tag{17}$$

(see Ref. 9). The corresponding reaction with O atoms is ruled out because it violates the spin conservation rules. As so little HCHO accumulates in these flames the step which removes it appears to be rapid. Until recently the only data for reaction (17) were those of Avramenko and Lorentso in discharge tube experiments, quoted in Ref. 10. These gave:

$$k = 2.4 \times 10^{11} \exp(-1000/RT) \text{ ml mol}^{-1} \text{ sec}^{-1} \quad . \tag{18}$$

The pre-exponential factor is so low that the step seems unlikely as the main route for the removal of HCHO . However, a more probable value has since been deduced by Schofield[11] from an evaluation of the literature:

$$k = 3.12 \times 10^{14} \exp(-4240/RT) \quad . \tag{19}$$

The pre-exponential factor here implies a steric factor of unity, indicating that in the present flames 1 in 2 collisions between HCHO and OH should result in reaction. The reactivity of HCHO* may also be enhanced by the excitation, but little if any useful data exist on the effect of electronic, vibrational or rotational excitation in a reactant on its rate of reaction.

The efficiency of collisional deactivation of HCHO* by other molecules is generally low and it has been proposed (in Ref. 2) that 1 in 100 or 1 in 1000 collisions are required for deactivation.

However, oxygen and other paramagnetic molecules quench the triplet state of aromatic molecules with nearly unit encounter efficiency[12], and (from Refs. 6 and 13) oxygen appears also to have this effect with HCHO* . The present conception of the reaction mechanism of flames supported by perchloric acid

involves the production of one molecule of O_2 for each molecule of perchloric acid, in the early stages, and its consumption in later stages[14].

The equilibrium concentration of OH in the flames is only about 10^{-3} mole per mole of gas, but studies with fuel-rich hydrogen or hydrocarbon-oxygen-diluent flames suggest that the actual concentration may be several orders of magnitude higher, at least in the burnt gas, and thus at the reaction zone boundary.

The combined effect of OH and O_2, therefore, is that approximately 1 in every 10 collisions of HCHO* cause it either to react or to become deactivated.

Appendix 3

Spectra of flames of (a) composite propellants, and (b) ammonium perchlorate in methane

Records of the flame spectra (visible and UV) of composite propellants based on ammonium perchlorate and polyisobutene were examined for the presence of "cool flame" bands. The spectra were obtained from propellant strands of 3 mm diameter x 50 mm length, inserted into a closely fitting quartz tube open at both ends and mounted horizontally on the optical axis of a Hilger F/4 spectrograph. The strands were burnt cigarette-wise and secondary combustion of the products in ambient air was prevented with a stream of nitrogen. As the strands burnt away the tube was moved so as to maintain the burning zone at the same location and keep it in focus on the spectrograph slit. A series of strands was burnt for each propellant, to obtain spectra of adequate density.

Spectra of propellants RD 2311, E 3176 and E 3610 were obtained in this way, at atmospheric pressure. (These formulations were selected because they are free from metal catalysts which might have added too many unwanted lines to the spectra.) Attempts to burn the strands at one fifth of an atmosphere succeeded with E 3176, and with RD 2403, the spectrum of which was also obtained at this pressure.

Each spectrum was composed predominantly of a continuum extending from the red end towards shorter wavelength, to a degree dependent on the exposure, combined with band emission from CH , CN , NH and OH ; NO bands were recorded with longer exposures. These emissions left "windows" through which only the HCHO* bands at 370.6 nm, 405.3 nm, 412.9 nm and (sometimes) 424.2 nm could be recorded.

As no bands attributable to HCHO* were evident in any of these spectra, the spectrum of ammonium perchlorate burning in methane was investigated at both atmospheric and reduced pressure, to see whether "cool bands" were emitted.

For work at atmospheric pressure ammonium perchlorate was sieved through 60 mesh BSS (i.e. $\leq$ 0.25 mm). The particles were agglomerated into a stable bed in a Pyrex tube of 10 mm diameter by passing moist air through the powder. The bed could be ignited on one face, which then burnt back in a reasonably planar fashion if methane were passed through the bed from the other face. The methane was diluted with twice its volume of nitrogen to reduce the burning rate. The spectrum was obtained in the same way as with the propellant strands.

The band emitters were the same as those listed above for the propellants. Only in one of six recordings of the spectrum were bands noted which could be confidently attributed to HCHO* . It is presumed that the exposures of the other spectra were either too short or too long for these bands to be recorded clearly.

To obtain the spectrum at reduced pressure (26 kN/m^2, or 35 mm Hg) a bed of ammonium perchlorate particles in the size range of 1 mm to 2 mm was formed in a quartz tube of 30 mm diameter mounted vertically in a low pressure burner housing with quartz windows. Oxygen was added to the methane and nitrogen flowing up through the bed until a premixed flame could be ignited by a discharge at the port of the tube. This flame was lowered onto the surface of the bed until the latter ignited, whereupon the oxygen supply was discontinued.

The bed burnt with a narrow blue flame zone immediately above its surface, followed by a thicker and more diffuse yellow zone. The flame was focused on the spectrograph slit directly through the wall of the quartz tube, and during the combustion the spectrograph table was racked steadily down so that the flame image on the slit was kept in a constant position. In this way the spectra from the two regions of the flame were recorded individually.

HCHO* bands, seen in two out of four recordings of the spectrum, were confined to the emission from the blue zone. Most, if not all, of the other bands reached their maximum intensity downstream of the HCHO* region.

As emission from HCHO* on combustion of methane with solid ammonium perchlorate is so much weaker than from other emitters that it is not easily recorded, it is not surprising that the bands were not apparent in the spectra obtained from burning composite propellants. However, it is probable that these latter spectra will also reveal the bands if (a) the optimum exposure is sought and (b) the burning surface is viewed from the side so as to avoid overlap of emission from successive stages of the combustion zone.