Sulphur anion chemistry in hydrocarbon flames with H_2S, OCS, and SO_2 additives

JOHN M. GOODINGS, DIETHARD K. BOHME, KAMAL ELGUINDI, AND ARNOLD FOX
York University, Department of Chemistry, 4700 Keele Street, Downsview, Ont., Canada M3J 1P3

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A premixed, fuel-rich, methane–oxygen flame at atmospheric pressure was doped separately with 0.2 mol% of H_2S, OCS, and SO_2 to probe the behaviour of fuel sulphur during combustion. These three additives represent compounds occurring early, intermediate, and late in the oxidation sequence of fuel sulphur. They are chemically ionized in the reaction zone of a hydrocarbon flame to give large signals of sulphurous negative ions. Those detected include S^-, SH^-, SO^- (uncertain), SO_2^- (S_2^-), SO_3^-, HSO_3^-, $CH_3O^-\cdot SO_2$, SO_4^- ($S_2O_2^-$, S_3^-), and HSO_4^-. Ion concentration profiles of these ions were measured along the conical flame axis by sampling the flame into a mass spectrometer. The shapes of the profiles are insensitive to the nature of the additive, but their relative magnitudes are indicative of the additive's position in the sulphur oxidation sequence. For each additive, the very large HSO_4^- signal has analytical implications as an indicator for total fuel sulphur. The sulphurous anion chemistry is discussed for each additive in terms of roughly twenty ion (electron)-molecule reactions of six basic types, whose rate constants were known previously, or were measured at room temperature using the York flowing afterglow apparatus.

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Dans le but d'examiner le comportement de combustibles/soufre au cours de combustions, on a ajouté séparément 0,2 mol% de H_2S, de OCS et de SO_2 à des flammes prémélangées de méthane–oxygène, riches en combustibles et qui opéraient à la pression atmosphérique. Ces trois additifs représentent les composés qui se retrouvent respectivement dans les stades préliminaires, intermédiaires et finaux de la séquence d'oxydation de mélanges combustibles/soufre. Ils sont ionisés chimiquement dans la zone de la réaction de la flamme d'hydrocarbure pour donner des signaux importants des ions négatifs des entités sulfurées. Les entités détectées comportent: S^-, SH^-, SO^- (incertain), SO_2^- (S_2^-), SO_3^-, HSO_3^-, $CH_3O^-\cdot SO_2$, SO_4^- ($S_2O_2^-$, S_3^-) et HSO_4^-. On a mesuré les profils des concentrations ioniques de ces ions en fonction de l'axe conique de la flamme en faisant appel à un échantillonage de la flamme dans un spectromètre de masse. Les formes de ces profils ne varient pas avec la nature des additifs; toutefois, leurs amplitudes relatives sont reliées à la position de l'additif dans la séquence de l'oxydation du soufre. Pour chaque additif, le signal très important du HSO_4^- a des implications analytiques comme indicateur de la quantité totale du soufre/combustible. Pour chacun des additifs, on discute de la chimie des anions sulfureux en fonction d'environ vingt réactions ion (électron)/molécule de six types de base dont les constantes de vitesse étaient antérieurement connues ou qui ont été mesurées à la température ambiante en faisant appel à un appareil de phosphorescence continue de York.

[Traduit par la revue]

Introduction

The control of SO_x emissions from the combustion of fossil fuels has become important for reasons of public health and because of the impact on the environment by acid rain. Industry reports (1) indicate that the sulphur content of coal and heavy fuel oil can amount to 1–5% by weight; an average figure for gasoline is 0.03%. Increasing energy costs and problems of supply may necessitate the burning of high-sulphur fuels in the future, a trend which is at odds with an increasingly stringent body of environmental and health regulations.

Other combustion pollutants such as NO_x and soot are, to some extent, amenable to chemical modification during the combustion process. Undesirable products can be converted into less harmful forms by altering the combustion conditions or by means of additives (2). On the other hand, sulphur does not appear to offer the same possibilities for its chemical manipulation into harmless forms. The seemingly inevitable conversion of fuel sulphur into SO_2 has focussed effort in two other directions; namely, sulphur removal from the fuel before combustion, and stack-gas scrubbing of SO_2 from the burnt gas afterwards. However, continued study of the sulphur chemistry occurring in a flame may provide insight into more esoteric approaches to sulphur removal at source during the combustion process. It is also valid because of the analytical implications for the evaluation of sulphur-containing fuels.

An important insight was gained in a previous study (3) in which flame ionization was employed as a probe for sulphurous intermediates leading to SO_x formation in the reaction zone and burnt gas of a premixed, CH_4–O_2 flame doped with 0.2% of OCS. It was found that sulphur species readily form negative ions in the flame, and that these negative ions reveal features of the stepwise oxidation of OCS. These results encouraged us to extend the investigation further to include the addition of 0.2% of H_2S and of SO_2 for comparison with OCS. The three additives represent a progression in the sulphur oxidation chain with H_2S occurring early, OCS being intermediate and SO_2 being late as the final oxidation product.

For each additive, sulphurous negative ions are formed by chemical ionization (CI) processes of the neutral sulphur intermediates with the natural ions which are present in any hydrocarbon flame. The ion chemistry of the source and sink reactions is discussed, and comparisons are drawn amongst the three additives. The advantage of this method is that the sulphurous ions serve as a probe of the neutral sulphur chemistry in the flame reaction zone where it originates.

Experimental

All of the ion concentration measurements were performed on the same CH_4–O_2 flame of fuel-rich composition (equivalence ratio ϕ = 2.15) whose ion chemistry we have studied extensively in the past (4, 5). It was of the laminar premixed type with a conical luminous reaction zone (height $\simeq$ 5 mm, base diameter $\simeq$ 3 mm, thickness $\simeq$ 0.3 mm) to facilitate ionic sampling along the flame axis into a mass spectrometer. The flame has an adiabatic flame temperature of 2460 K and burnt gas velocity of approximately 1 m s^{-1}. It was stabilized at atmospheric pressure on a simple, tubular, quartz burner (2.3 mm id) surrounded by a flowing argon shield to minimize the entrainment of atmospheric air. Provision was made to add 0.2 mol% of H_2S or of SO_2 to the premixed gas in exactly the same way as was done previously for OCS (3). The additives could be introduced or removed without altering the flame. All gases were used straight from the cylinders without further purification ($CH_4 > 99.0\%$, $O_2 > 99.6\%$, $Ar > 99.9\%$, $H_2S > 97.5\%$, $OCS > 97.5\%$, $SO_2 > 99.90\%$). The burner was mounted on a motor-driven carriage with accurate alignment of the flame axis with the sampling orifice of the mass spectrometer. The calibrated burner drive provided spatial resolution of ± 0.02 mm along the flame axis (designated z) for measurements of ion concentration profiles.

The flame–ion mass spectrometer has been described previously in detail (4). The flame burned against a 60°, conical, chromium, sampling nozzle of orifice diameter *ca.* 0.1 mm mounted in a water-cooled flange of the type described by Hayhurst and Telford (6). The sampled ions pass through two stages of differential pumping into a quadrupole mass filter. The mass-analyzed ions are detected with a parallel-plate Faraday cage connected to a vibrating reed electrometer having a grid-leak resistance of 10^{11} ohms. The ion signal magnitudes in the figures are quoted in volts based on the detected ion current passing through 10^{11} ohms. Modifications to the quadrupole power supply have improved the resolution of the mass filter, particularly at high mass numbers. We have adopted the same normalization technique described in the paper with OCS additive (3). The profiles shown in the figures include a correction for mass discrimination in the filter against ions of high m/e measured at high resolving power. The dynamic range of sensitivity of the apparatus is five orders of magnitude. A method has been described (4) for locating a reproducible origin ($z = 0$) in the *flame* (not referred to the burner) corresponding to the downstream edge of the luminous reaction zone on the flame axis. In this way, a family of ion profiles at different mass numbers m/e can be accurately overlaid on the distance scale z.

The shapes of the profiles obtained for the three additives at the same mass number are very similar. However, some of the profiles presented in this work are somewhat different from those reported earlier (3) in that they are not as noticeably double-peaked. This is due to the use of a new chromium sampling nozzle having a larger orifice diameter such that the effect of boundary layer cooling, as discussed in the previous study (3), is less. In the present case, negative ion equilibria shift less in the exothermic direction, and electron attachment to form negative ions is reduced, particularly downstream where the temperature is high. That is, the free electron concentration is enhanced at the expense of the negative ion concentration, and distortion of the profiles due to sampling is reduced.

Results and discussion

Anion profiles

Figure 1 displays the dramatic enhancement observed in the total negative ion profiles with the separate additions of equimolar amounts of H_2S, OCS, and SO_2 into the premixed flame gas. In contrast, the total positive ion profiles showed no change in peak magnitude for these three cases. It is clear from Fig. 1 that SO_2 has the largest effect on the upstream concentration of negative ions and that H_2S and OCS also enhance negative ion formation and do so about equally. The bulk of the observed increases could be accounted for by the anions listed in Table 1. Individual profiles for the ions with m/e equal to 33, 64, 80, and 97 are shown in Figs. 2–5. While differences in the peak magnitudes of these profiles are again noticeable with the three different additives, the shapes of the individual profiles appear to be quite insensitive to the nature of the additive.

The ion assignments of the individual masses are given in Table 1. In making these assignments account has been taken of isotopic contributions as indicated previously (3). Increases in signal are apparent for all the ions in Table 1 with the following exceptions: $m/e = 32$ decreases for all three additives and $m/e = 33$ decreases for the addition of SO_2 only. The former ion is O_2^- in the undoped flame and reacts when the sulphur compounds are added. The $m/e = 33$ ion is HO_2^- in the undoped flame and it reacts when SO_2 is added to the premixed

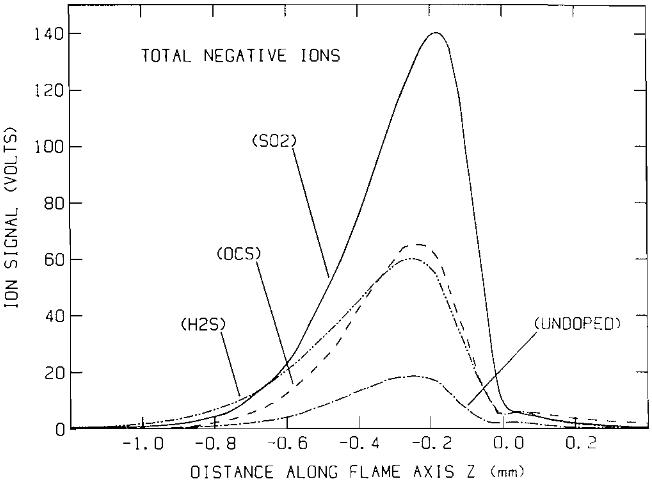

FIG. 1. Total negative ion profiles of the undoped flame and of the flame doped with 0.2 mol% of H_2S, OCS, and SO_2. The flame reaction zone is located upstream of $z = 0$.

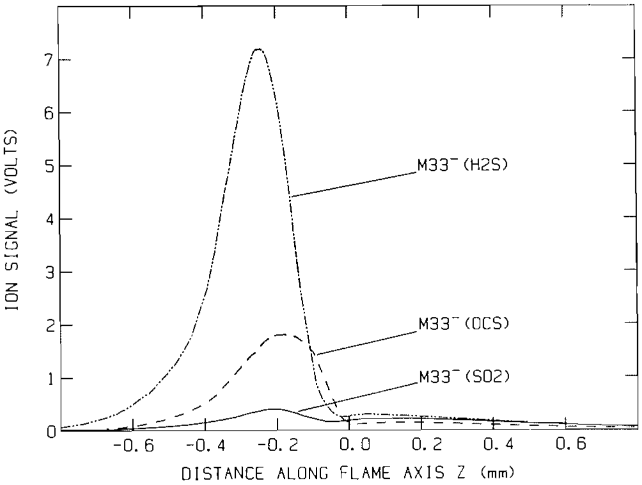

FIG. 2. Profiles of $m/e = 33$ representing SH^- and (or) HO_2^- when the flame is doped with 0.2 mol% of H_2S, OCS, and SO_2. The flame reaction zone is located upstream of $z = 0$.

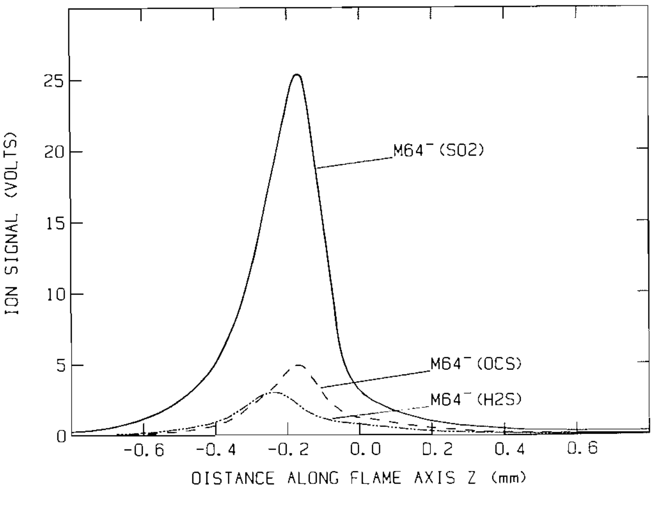

FIG. 3. Profiles at $m/e = 64$ representing SO_2^- (and possibly S_2^-) when the flame is doped with 0.2 mol% of H_2S, OCS, and SO_2. The flame reaction zone is located upstream of $z = 0$.

TABLE 1. Peak intensities of anion signals (in volts) in the reaction zone of the undoped flame, and with the flame doped with 0.2 mol% of H_2S, OCS, and SO_2

Parent ion	Mass number	No additive	H_2S	OCS	SO_2
Total positive		320	320	320	320
Total negative		18.5	60	65	140
S^-	M32$^-$	6.5 (O_2^-)	1.1	0.56	0.57
SH^-	M33$^-$	0.82 (HO_2^-)	7.2	1.8	0.40
SO_2^- (S_2^-)	M64$^-$	0.50	3.0	4.9	25.3
SO_3^-	M80$^-$	0.05	11.7	12.7	20.6
HSO_3^-	M81$^-$	0.01	2.3	3.0	3.1
$CH_3O^-SO_2$	M95$^-$	—	2.9	3.9	10.3
SO_4^- ($S_2O_2^-$, S_3^-)	M96$^-$	—	3.1	4.0	10.0
HSO_4^-	M97$^-$	—	29.5	38.0	88.3
Σ (sulphur anions)		—	60.8	68.9	158.6

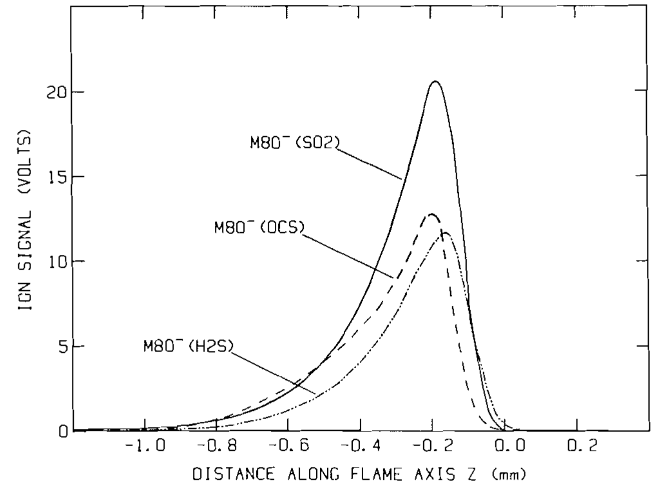

FIG. 4. Profiles at $m/e = 80$ representing SO_3^- when the flame is doped with 0.2 mol% of H_2S, OCS, and SO_2. The flame reaction zone is located upstream of $z = 0$.

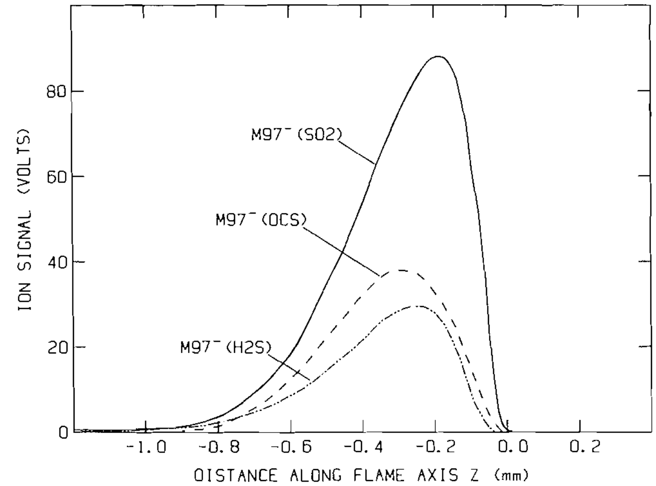

FIG. 5. Profiles at $m/e = 97$ showing the large signals of HSO_4^- obtained when the flame is doped with 0.2 mol% of H_2S, OCS, and SO_2. The flame reaction zone is located upstream of $z = 0$.

flame gas. The sulphur content of the residual peaks at $m/e = 32$ and $m/e = 33$ could not be determined with confidence due to the complications discussed previously (3). All the ions which were observed to increase contained at least one sulphur atom. Several of the sulphurous ions observed contained hydrogen and (or) oxygen and one at $m/e = 95$ must contain carbon.

Inspection of the ion peak intensities in Table 1 reveals that the appearance of sulphurous anions is dominated by HSO_4^- and, to a lesser extent, by SO_3^- in all three doped flames, approximately in proportion to the total negative ion peaks. Distinguishable features for the different additives are manifested with several of the relatively minor ions. The SO_2 flame is characterized by a considerably enhanced abundance of SO_2^- and a shortage of SH^-. The flame doped with H_2S clearly shows an enhanced SH^- peak. In general, the OCS peaks are intermediate between those of the other two additives.

Sulphurous anion chemistry

It is clear from the observed increases in the total negative ion profiles that the additives provide the flame with additional anions. These new anions may arise by attachment or dissociative attachment of electrons with the additive or with molecules derived from the additive by neutral chemistry. The ion assignments indicate that all of the new negative ions are sulphurous so that the sulphur in the additive becomes entrained in the ion directly in the initial formation by attachment or dissociative attachment, or indirectly through secondary ion–molecule reactions. The secondary ion chemistry will be complex but should be dominated by reactions of sulphurous anions with the dominant (non-sulphurous) neutrals in the flame. Secondary reactions with the additive itself or some of its neutral derivatives will have less impact but may still be noticeable.

Dissociative attachment in OCS should proceed in the manner indicated by reaction [1]

$$[1] \quad e^- + OCS \rightarrow S^- + CO$$

since it is by far the least endothermic option of five possible channels (7). The endothermicity of reaction [1] is about 25 kcal mol^{-1}. The two channels given by reaction [2] appear likely with H_2S

$$[2a] \quad e^- + H_2S \rightarrow S^- + H_2$$

$$[2b] \quad e^- + H_2S \rightarrow SH^- + H$$

They are approximately 23 and 38 kcal mol^{-1} endothermic, respectively. Formation of H^- and SH is endothermic by more than 70 kcal mol^{-1} and is thus not expected to be significant. With SO_2, direct exothermic attachment to form SO_2^- is expected (8) according to

[3] $e^- + SO_2 + M \rightarrow SO_2^- + M$

The channels leading to SO^-, S^-, O_2^-, or O^- in this case are all endothermic by more than 80 kcal mol^{-1}. We may therefore conclude that all the new primary ions formed from the three additives by electron attachment are sulphurous: S^- from OCS, S^- and SH^- from H_2S, and SO_2^- from SO_2.

Some of the secondary ion chemistry in OCS has been discussed previously in considerable detail (3). Briefly, with S^- as the primary ion we can expect the following secondary reactions to predominate

[4*a*] $S^- + O_2 \rightarrow SO_2 + e^-$

[4*b*] $S^- + O_2 \rightarrow SO^- + O$

[4*c*] $S^- + O_2 + M \rightarrow SO_2^- + M$

[5] $SO^- + O_2 + M \rightarrow SO_3^- + M$

[6] $SO_2^- + OH \rightleftharpoons SO_3^- + H$

[7] $SO_3^- + XH \rightleftharpoons HSO_3^- + X$

[8] $SO_2^- + O_2 + M \rightarrow SO_4^- + M$

[9] $SO_4^- + XH \rightleftharpoons HSO_4^- + X$

where M is a third body and XH is likely to be OH. Other reactions are possible if secondary sulphurous neutrals are present in sufficient concentration

[10] $S^- + SO_2 + M \rightarrow S_2O_2^- + M$

[11] $CH_3O^- + SO_2 + M \rightarrow CH_3O^- \cdot SO_2 + M$

Reaction [10] could account for the formation of some $S_2O_2^-$ at $m/e = 96$ although SO_4^- predominates from analysis of the ^{34}S isotope contribution at $m/e = 98$. Improved resolving power of the mass filter has led to the unequivocal identification of a sulphurous anion at $m/e = 95$, presumably formed by association of SO_2 with CH_3O^- via reaction [11]. It is noteworthy that the magnitude of this ion peak is approximately equal to that of SO_4^- at $m/e = 96$ for all three additives. This is the first sulphurous anion which must contain carbon that we have been able to detect. It is significant because it indicates the presence of appreciable SO_2 in the reaction zone of the OCS flame. It was also possible to detect the parent CH_3O^- ion at $m/e = 31$ in the undoped flame, which was not resolved previously because it occurs in the asymmetric foot of the very large O_2^- signal at $m/e = 32$. With OCS additive we can expect the following additional reactions to contribute

[12] $O_2^- + OCS \rightarrow SO_2^- + CO$

[13] $OH^- + OCS \rightarrow SH^- + CO_2$

[14] $S^- + OCS \rightarrow S_2^- + CO$

Isotope contributions of ^{34}S at $m/e = 66$ indicate that SO_2^- predominates over S_2^- at $m/e = 64$.

Reactions [10] and [12]–[14] have been examined separately at room temperature with the flowing afterglow technique in the Ion Chemistry Laboratory at York University. Reaction [10] has an effective second-order rate constant of 8.4×10^{-12} cm^3 molecule^{-1} s^{-1} at 294 ± 2 K and a pressure of 1.5 Torr (1 Torr = 133.3 Pa).[1] This is a relatively high value for addition reactions of this type and suggests a stability for $S_2O_2^-$ brought about by covalent bonding. However, the ion has not often been observed in the gas phase although it has been identified previously in sulphur-doped crystals at low temperatures. Reactions [12]–[14] have all been found to occur rapidly with rate constants of (4.1 ± 1.2), (9.5 ± 2.9), and (9.1 ± 2.7) × 10^{-10} cm^{-3} molecule^{-1} s^{-1}, respectively.[1] Also, no further reactions were observed for SO_2^-, SH^-, and S_2^- with OCS; i.e., $k \leq 10^{-12}$ cm^3 molecule^{-1} s^{-1} in each case. Thus, reactions [1] and [4]–[14] together can account qualitatively for all the predominant sulphurous ions observed with the OCS additive; the importance of [10] and [14] is doubtful.

The enhanced abundance of SO_2^- in the flame seeded with SO_2 clearly is to be attributed to the direct attachment of electrons to SO_2. The lack of production of SH^- in this case is not unexpected. OH^- is known to add to SO_2 to produce HSO_3^- (9, 10) according to

[15] $OH^- + SO_2 + M \rightarrow HSO_3^- + M$

Production of SH^- from these reagents is about 20 kcal mol^{-1} endothermic and requires considerable bond redisposition. The ion signal at $m/e = 33$ actually decreases with SO_2 addition, presumably because of the charge transfer reaction

[16] $HO_2^- + SO_2 \rightarrow SO_2^- + HO_2$

The charge transfer is almost thermoneutral according to the known electron affinities of 1.16 eV for HO_2 (11) and 1.1 ± 0.1 eV for SO_2 (12).

The identifying features of the flame doped with H_2S can also be understood in terms of the ion chemistry with the additive. More SH^- can clearly be expected with H_2S than with OCS because of proton transfer reactions of the type

[17] $X^- + H_2S \rightarrow SH^- + XH$

which can be expected to occur between H_2S and a number of the anions present in the undoped flame. Also, some production of SH^- is expected from the dissociative attachment reaction [2*b*]. Starting with reaction [2*a*], the S_2^- and S_3^- ions might be expected to arise from the following two reactions with H_2S and (or) SH

[18] $S^- + H_2S\,(SH) \rightarrow S_2^- + H_2\,(H)$

[19] $S_2^- + H_2S\,(SH) \rightarrow S_3^- + H_2\,(H)$

Sulphur bond formation reactions of this type may be generalized by the reaction

[20] $S_n^- + XS \rightarrow S_{n+1}^- + X$

Their energies may be expressed with equation [21]

[21] $\Delta H^0 = D(\text{X—S}) - D(\text{S}_n\text{—S}) + EA(\text{S}_n) - EA(\text{S}_{n+1})$

where D and EA are the bond dissociation energy and electron affinity, respectively. $D(\text{S}_n\text{—S})$ is approximately 70 kcal mol^{-1} for $n = 2$–7 and 103 kcal mol^{-1} for $n = 1$. $D(\text{X—S})$ for H_2S is 72 kcal mol^{-1} and for SH is 85 kcal mol^{-1}. Values of 2.077, 1.663, and 2.0 eV are available for $EA(S)$, $EA(S_2)$, and $EA(S_3)$, respectively (11, 13). They indicate that reaction [18] is exothermic for both H_2S and SH; reaction [19] is exothermic for H_2S and slightly endothermic for SH. We have investigated the reactions of S^-, S_2^-, and S_3^- with H_2S separately with the flowing afterglow technique near room temperature. S_2^- and S_3^- were found not to react at 473 K while S^- reacted at 317 K primarily according to reaction [22], which may be either proton transfer or hydrogen atom transfer, with a rate constant of (5.2 ± 1.6) × 10^{-10} cm^3 molecule^{-1} s^{-1};[1]

[22] $S^- + H_2S \rightarrow SH^- + SH$

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[1] D. K. Bohme and co-workers. Unpublished results. York University, Downsview, Ont., Canada M3J 1P3.

Reaction channel [22] is only thermoneutral. The observation that it is preferred over the more exothermic reaction channel [18] near room temperature may reflect the kinetic barrier which is likely to be associated with the considerable bond redisposition required to bring about reaction channel [18]. Apparently the same chemistry is operative at flame temperatures; reaction channel [22] is the preferred route rather than the reaction sequence [18] + [19]. This behaviour is borne out by the ^{34}S isotope analysis which indicates the presence of SO_2^-, not S_2^-, at $m/e = 64, 66$ and SO_4^-, not S_3^-, at $m/e = 96, 98$.

Influence of the sulphurous neutral chemistry

It is possible that the discussion to this point underestimates the amounts of secondary sulphurous neutrals formed from the parent additives within the short time scale of the flame reaction zone. Certainly the observation of $CH_3O^- \cdot SO_2$ with all three additives gives pause for thought since neutral SO_2 must be involved in its formation. In this fuel-rich flame where H_2 is the major combustion product, relatively large concentrations of free H atoms will be present in the reaction zone and also upstream of it because of their very large diffusivities (4, 14). Thus, the following sequence of reactions may be near to being balanced

[23] $SO_2 + H \rightleftharpoons SO + OH$

[24] $SO + H \rightleftharpoons S + OH$

[25] $S + H_2 \rightleftharpoons SH + H$

[26] $SH + H_2 \rightleftharpoons H_2S + H$

Overall, the net reaction is

[27] $SO_2 + 2H_2 \rightleftharpoons H_2S + 2OH$

Since the OH concentration exceeds its equilibrium value in the reaction zone (4, 14), then the production of H_2S, and to a lesser extent SH, is suppressed with SO_2 additive. In contrast, the production of SO_2 with H_2S additive is enhanced. The entry and participation of OCS into the above scheme will occur via the reaction

[28] $OCS + H \rightleftharpoons SH + CO$

which has the same H-atom dependence as the reverse of reaction [26]. On the other hand, radical reactions of H and OH with sulphur species may be minimized if SO_2 catalyzes radical recombination according to

[29] $SO_2 + OH(H) + M \rightarrow HSO_3(HSO_2) + M$

[30] $HSO_3(HSO_2) + H \rightarrow SO_2 + H_2O(H_2)$

Other channels akin to reaction [30] might produce neutral SO_3

[31] $HSO_3 + H(OH) \rightarrow SO_3 + H_2(H_2O)$

or even sulphuric acid

[32] $HSO_3 + OH + M \rightarrow H_2SO_4 + M$

Thus, radical attack on the additives in the flame reaction zone may give rise to a variety of species (S, SH, SO, SO_2, HSO_2, SO_3, HSO_3, H_2SO_4) which can attach electrons to form sulphurous negative ions. The degree to which the neutral sulphur chemistry affects the observations of sulphurous anions is difficult to assess quantitatively, but its influence cannot be disregarded.

Conclusions

The present range of additives including H_2S, OCS, and SO_2 is representative of fuel sulphur compounds occurring early, intermediate, and late in the sulphur oxidation sequence. Thus, more general conclusions can be advanced than were possible with OCS in isolation (3).

(*1*) All three additives produce a dramatically increased concentration of sulphur anions in the flame reaction zone, and it is reasonable to assume that any fuel sulphur will do the same. This means that fuel sulphur gives rise to species (e.g., S, SH, SO_2, etc.) having higher stabilities than those of the C—H—O molecules normally present in a hydrocarbon flame.

(*2*) The ambient concentration of negative ions represents a balance between the rates of electron attachment and detachment. Three-body and dissociative attachment have a negative temperature dependence. Associative detachment by radicals and thermal detachment (near $z = 0$ in the profiles) have a positive temperature dependence. Thus, possible attempts to remove sulphur from combustion products as sulphurous anions will benefit from a lower temperature.

(*3*) The profile shape of a given sulphurous anion is remarkably insensitive to the nature of the additive. This will be the case if the rates of production and loss of the sulphurous anion are fast such that its profile essentially replicates that of the reagent C—H—O anion (or free electrons in the case of attachment).

(*4*) The profile magnitudes are not sufficiently distinct to predict the nature of the fuel sulphur from the anion signals. However, some useful qualitative trends are discernible at each end of the oxidation sequence; H_2S enhances SH^- at one end, while at the other end, SO_2 enhances SO_2^- and SH^- is absent.

(*5*) The anions are dominated by HSO_4^- which accounts for roughly half of the total ion signal present for each of the three additives. This has analytical implications for the detection of total sulphur. It does *not* necessarily imply the presence of sulphuric acid in the flame, however.

(*6*) The full range of sulphurous anions detected (in order of increasing m/e) includes S^-, SH^-, SO^- (uncertain), SO_2^- (S_2^-), SO_3^-, HSO_3^-, $CH_3O^- \cdot SO_2$, SO_4^- ($S_2O_2^{-}\cdot$, S_3^-), and HSO_4^-. Thus, S—H and S—O bonds may form, but evidently C—S and S—S bond formations are not favoured.

(*7*) The $CH_3O^- \cdot SO_2$ ion is revealing since its formation via reaction [11] requires the presence of SO_2 as a reagent. For the H_2S and OCS additives, appreciable secondary SO_2 must be present as a combustion product in the flame reaction zone. Evidently the oxidation of sulphurous neutrals (e.g., $H_2S \rightarrow SH \rightarrow SO \rightarrow SO_2$ or $OCS \rightarrow S \rightarrow SO \rightarrow SO_2$) proceeds very rapidly under flame conditions.

(*8*) The sulphurous anion chemistry is explicable in terms of roughly twenty ion (electron) – molecule reactions. The types of reactions are diverse and include attachment and dissociative attachment, association, atom transfer, proton transfer, and charge (electron) transfer.

(*9*) Sufficient time is available in the flame reaction zone for the occurrence of at least four consecutive ion–molecule reactions. This is evident from sequences such as $S^- \rightarrow SO_2^- \rightarrow SO_3^- \rightarrow HSO_3^-$ or $S^- \rightarrow SO_2^- \rightarrow SO_4^- \rightarrow HSO_4^-$ with the H_2S or OCS additives. The sequences might be longer except that we have not been successful in detecting sulphurous anions unambiguously having $m/e > 100$. Fast reaction rates are aided by the high (atmospheric) pressure of the flame (many of the reactions are termolecular) but not necessarily by the high flame temperature (many of the reactions have a negative or zero temperature dependence).

(*10*) These results bear out a general contention of flame-ion chemistry; namely, that the elevated flame temperature is sufficient to overcome reaction endothermicities of at least 25 kcal mol^{-1}. Reactions [1] and [2*a*] are cases in point. This behaviour is in contrast to room-temperature studies, for example, using the flowing afterglow apparatus, in which endothermic reactions generally do not proceed at measurable rates.

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1. E. Robinson. Air quality monographs. Monograph #75-23, American Petroleum Institute, Washington, DC. 1976.
2. C. P. Fenimore. Pollutant formation and destruction in flames. Frontiers of chemistry. *Edited by* K. J. Laidler. Plenary and keynote lectures presented at the 28th IUPAC Congress, Pergamon Press Ltd., Oxford, Great Britain. 1982. p. 41.
3. J. M. Goodings, K. Elguindi, and D. K. Bohme. Can. J. Chem. **61**, 1703 (1983).
4. J. M. Goodings, D. K. Bohme, and C.-W. Ng. Combust. Flame, **36**, 27 (1979).
5. J. M. Goodings, D. K. Bohme, and C.-W. Ng. Combust. Flame, **36**, 45 (1979).
6. A. N. Hayhurst and N. R. Telford. Combust. Flame, **28**, 67 (1977).
7. K. A. G. MacNeil and J. C. J. Thynne. J. Phys. Chem. **73**, 2960 (1969).
8. L. Bouby, F. Fiquet-Fayard, and C. Bodere. Int. J. Mass Spectrom. Ion Phys. **7**, 415 (1971).
9. F. C. Fehsenfeld and E. E. Ferguson. J. Chem. Phys. **61**, 3181 (1974).
10. A. B. Raksit and D. K. Bohme. Can. J. Chem. **61**, 1683 (1983).
11. H. Hotop and W. C. Lineberger. J. Phys. Chem. Ref. Data, **4**, 539 (1975).
12. R. J. Celotta, R. A. Bennett, and J. L. Hall. J. Chem. Phys. **60**, 1740 (1974).
13. P. S. Drzaic, J. Marks, and J. I. Brauman. Gas phase ion chemistry. Vol. 3, *Edited by* M. T. Bowers. Academic Press Inc., New York, NY. 1984. p. 167.
14. J. W. Hastie. Combust. Flame, **21**, 187 (1973).