
General Discussion

Dr Whitaker opened the discussion of Prof. Kohse-Höinghaus's paper: In your paper you describe experiments in which you excite to $v' = 2$ and look at the 0–0 band fluorescence and observe a very high apparent rotational temperature. Similarly for the 1–1 band. Now the $v' = 2$ state exhibits fairly rapid predissociation so I am curious to know if this is what could be responsible for the high apparent rotational temperatures observed—because I don't understand how VET on its own could account for this effect.

Prof. Kohse-Höinghaus responded: Our understanding of this process is that VET and RET are closely coupled, and that an individual VET step does not necessarily end in the same rotational level in the lower vibrational state. High apparent temperatures are observed since high rotational levels are populated by combined VET/RET steps. Additionally, for OH, RET in higher rotational levels is slower than in the lower ones.

Apparent high temperatures are also observed in $v' = 0$ after excitation of $v' = 1$,^{1,2} which is not predissociative. Predissociation is just another loss term, as quenching, in this experiment; it does not influence the population in the lower vibrational levels.

- 1 A. T. Hartlieb, D. Markus, W. Kreutner and K. Kohse-Höinghaus, *Appl. Phys. B*, 1997, **65**, 81.
- 2 D. R. Crosley and G. P. Smith, *Appl. Opt.*, 1983, **22**, 1428.

Prof. Stuhl asked: In your publication you say that you try 'to avoid saturation'. Further, you expect that polarization might affect some results. My question is: why don't you work under saturation conditions? In this case, polarization effects are expected to be negligible.¹

- 1 R. Altkorn and R. N. Zare, *Ann. Rev. Phys. Chem.*, 1984, **35**, 265.

Prof. Kohse-Höinghaus replied: In our contribution, we wish to *study* the effects of polarisation, since not much is known about the temporal decay of these effects; picosecond laser experiments now offer the time resolution to investigate the influence of collisions on the prepared population under defined polarisation conditions in combustion experiments. We expect these effects to contribute significantly to the LIF signals observed in typical experiments for concentration or temperature measurement, where *linear* LIF is most often employed. Saturated LIF experiments are much less suitable for quantitative measurements, since saturation may affect the population distribution in the ground state and lead to population re-circulation, which would complicate the interpretation. Additionally, it is very hard to maintain constant saturation over the complete excitation volume.

Prof. Cheskis asked: Did you check the pressure dependence? How does your model work at different pressures? Does your model take into account the slower rotational relaxation of rotational levels with higher J numbers?

Prof. Kohse-Höinghaus answered: We applied the model at different pressures, ranging mostly from reduced pressure (near 1 mbar) to atmospheric. The model seems to represent most conditions tested so far quite well. Additional examples can be found in ref. 1 and 2. Some tentative modelling experiments with LASKIN have been performed at higher pressures, but reliable experimental data for comparison are still scarce in that regime.

The change in rotational energy transfer rate coefficient with rotational quantum number has been considered in the model, see ref. 1 and 3 for more detail.

- 1 U. Rahmann, W. Kreutner and K. Kohse-Höinghaus, *Appl. Phys. B*, 1999, **69**, 61.
- 2 A. Brockhinke, W. Kreutner, U. Rahmann, K. Kohse-Höinghaus, T. B. Settersten and M. A. Linne, *Appl. Phys. B*, 1999, **69**, 477.
- 3 R. Kienle, M. P. Lee and K. Kohse-Höinghaus, *Appl. Phys. B*, 1996, **63**, 403.

Prof. Greenhalgh asked: (1) How does your system compare with Roger Farrow's distributed feedback dye laser (DFDL) system? (2) Please can you explain what you mean by quench-free measurements, since you seem to indicate that this is a goal rather than a reality? (3) Please recommend the best transition for probing in a practical measurement.

Prof. Kohse-Höinghaus answered: (1) At the time we purchased our regeneratively amplified mode-locked laser (in 1995), it was the only commercially available picosecond laser system which met our specifications (that is, which produced Fourier-limited pulses with a high-enough power to allow two-dimensional wavelength–time imaging even when exciting a multi-photon transition). Recent advances in the DFDL development showed that they can meet these specifications as well. However, they are still more unstable and less flexible than our all-solid-state system and to our knowledge, they still can't be bought off the shelf.

(2) In the paper itself, we explain that rotational and vibrational redistribution may, even on very short time scales, lead to the erroneous assumption that collisions would not influence the result. Thus, experiments using the conventional 'gated-detection' approach are 'quench-insensitive' at most. Only experiments where the complete temporal evolution of the LIF signal is monitored can be truly 'quench-free'. One approach is described in our paper, another can be found in ref. 1.

(3) In our opinion, exciting the OH A–X 1–0 transition and collecting the fluorescence in the 1–1 and 0–0 transitions has several advantages for many practical applications, which have been often exploited and described in previous work. The 0–0 transition is more susceptible to optical density/re-absorption problems. Transitions with $v' \geq 2$ are attractive mainly because they can be pumped with cheap excimer lasers and are predissociated (which alleviates part of the quenching problem). However, due to problems with collisional redistribution in the ground state, these transitions are not recommended for quantitative measurements.

- 1 M. W. Renfro, S. D. Pack, G. B. King and N. M. Laurendeau, *Appl. Phys. B*, 1999, **69**, 137.

Prof. Hippler asked: (1) What are the important colliders for energy transfer (ET) and quenching of OH(A) in a flame? (2) Are there estimates for radicals and atoms doing ET or quenching? (3) For what kind of flames does the LASKIN model work well?

Prof. Kohse-Höinghaus replied: (1) In many flames of hydrocarbons burning in air, water and nitrogen are the two most important colliders. This may not hold for very fuel-rich conditions.

(2) In low-pressure flames with high H-atom or OH radical concentrations, as investigated in ref. 1, H-atom quenching has been estimated to contribute with a rate constant of $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

(3) Typically, the flames described above (hydrocarbon–air) as well as hydrogen–air flames, can be modelled with surprising success. However, LASKIN can also predict the qualitative energy transfer behaviour under quite different conditions, including flow reactor experiments. LASKIN has been tested in the pressure range from a few mbar to several bar.

- 1 J. B. Jeffries, K. Kohse-Höinghaus, G. P. Smith, R. A. Copeland and D. R. Crosley, *Chem. Phys. Lett.*, 1988, **152**, 160.

Prof. Wolfrum opened the discussion of Prof. Griffiths's paper: Are the PLIF images of formaldehyde shown in Fig. 9 and Fig. 10 of your paper corrected for the temperature dependence of the ground state population?

Dr Whitaker responded: The PLIF images of H₂CO shown in the paper are primary data. Of course, you are absolutely right to point out that the formaldehyde fluorescence signal will be a function of the temperature field as well as the concentration field. Klein-Douwel *et al.*¹ have

shown that the effect of the partition function is minimal for 370 nm excitation of the $\tilde{A}^1A_2-\tilde{X}^1A_1$ 4_0^1 vibronic band. However, in our case, *i.e.* excitation at 355 nm, there is a strong dependence of the fluorescence signal from the 4_0^1 band on temperature.² Just as for the acetone PLIF images presented in our paper, at higher temperatures the partition function effects reduce the observed LIF signals. This is simply a reflection of the fact that at higher temperatures a greater number of rotational states are energetically accessible. Collisional quenching, which to a first approximation will scale as $1/\sqrt{T}$, has the opposite effect of enhancing the signal at elevated temperatures. It is known that the relatively strong Raman signal from any methane that might be present can be a source of interference in LIF measurements of formaldehyde (shift ~ 50 nm). Another known problem associated with the determination of formaldehyde concentration fields by LIF is interference from polycyclic aromatic hydrocarbons (PAHs). The combined effects of these phenomena are difficult to quantify (although the latter two are unlikely to be of any significance in our case). Of course, if the temperature field was known *a priori* it would be simple enough to calculate the partition function correction.

The implication of your question with respect to the interpretation of the images presented for n-pentane combustion in Fig. 10 of our paper is interesting. The bottom three images, for $T_c = 765, 790$ and 840 K respectively, are obtained at a time delay where the pressure record indicates that the reacting mixture has attained approximately the same average temperature in all three cases (see Fig. 3 in the paper). The images show approximately uniform fluorescence yield across the chamber in the three cases but that the intensity becomes weaker through the sequence from $T_c = 765$ to 840 K. Our interpretation is that this reflects the decrease in the extent of reaction resulting from the increased ignition delay, and not a decrease of fluorescence quantum yield as a result of increased nominal adiabatic temperature of the compressed charge. The results obtained at earlier times for $T_c = 840$ K, where the heat release is quite slow, are also consistent with this interpretation. The result for $T_c = 790$ K at 3.4 ms is, however, harder to interpret. Under these conditions we expect that the core gas in the centre of the chamber $1-2$ ms after the end of the compression stroke is about 750 K, close to the bottom of the ntc curve (Fig. 1 of our paper), and consequently that the core gas should react (slightly) faster than the periphery. Yet we observe a weaker fluorescence signal in the centre of the chamber. However, as we mention in the paper, the interpretation is clouded by the diverse kinetic origins of formaldehyde. As Fig. 4 e₇ of the paper shows there is a considerable chemiluminescent signal from excited state formaldehyde some 3 ms after the end of the compression at the edge of the chamber, albeit at the compressed temperature of 765 K.

- 1 R. J. H. Klein-Douwel, J. Luque, J. B. Jeffries, G. P. Smith and D. R. Crosley, *Appl. Opt.*, 2000, **39**, 3712.
- 2 J. E. Harrington and K. C. Smyth, *Chem. Phys. Lett.*, 1993, **202**, 196.

Dr Morley said: Rapid compression machines were originally designed to provide an ideal environment and many sets of data, particularly ignition delay as a function of temperature, and have been presented assuming ideality. You have demonstrated, and to some extent quantified the temperature inhomogeneity. Is it possible to develop a methodology based on this understanding to correct these earlier results? I'm thinking of autoignition delays which occur in the colder regions in systems with negative temperature coefficients being erroneously assigned to the peak temperature.

Prof. Griffiths responded: Of course, the experimental results are what they are. The normal procedure is to use the adiabatically compressed gas temperature as the reference temperature, regardless of the thermal development that follows as a result of heat release and heat loss. The important implication of your comment is that modelling, in which a spatially uniform temperature is assumed, cannot be compared directly with these results when seeking validation of the model. Our best estimate is that, within several milliseconds after the piston has stopped, the core gas is about 40 K lower than the adiabatically heated gas surrounding it.

The simplest qualitative interpretation from our observations might be that the longest measured delay in the negative temperature dependent range, and/or the compressed gas temperature range over which the negative temperature dependence of ignition delay exists, is shorter than would be the case for an experiment in ideal conditions. Simulations of ignition delay from a two

zone model, with a core at 40 K lower than the toroidal region surrounding it, might be compared with the predictions from a spatially uniform model as a first step to understanding the quantitative implications.

As you have mentioned [see below], the roll-up vortex can be suppressed by careful design of the piston crown. Also the gas motion that is created must be dependent on piston speed. So different machines will cause different types and extents of departure from ideality. For example, the long compression time (60 ms) at proportionately lower speed, that is used by workers at Lille, will cause a different spatial temperature distribution after the end of compression from that in our machine. Their temperature measurements by Rayleigh scattering and thermocouples indicate that the adiabatic region probably resides in the core, but I would suggest that there may be variations in temperature at the periphery, resulting from heat transfer to the wall. So whatever methodology is developed, it would have to be specific to a particular rapid compression machine.

Prof. Greenhalgh asked: How quiescent is the gas in the rapid compression machine when the piston stops? Also the image at 2 ms later shows some structure. Would stirring help and what role might shear stresses play in the autoignition?

Prof. Griffiths answered: There must certainly be significant gas motion at the moment the piston stops since the piston speed during compression is about 10 m s^{-1} , but it tends to die out within the first 10 ms. The penetration of a colder plug into the core from off the piston face, very soon after the piston has stopped, is consistent with the generation of a roll-up vortex.¹ Our evidence is that this colder gas reaches the central plane of the combustion chamber only after about 2 ms, as you have noted.

Undoubtedly stirring does have an effect on the combustion process. We have shown previously^{2,3} that the development of autoignition is affected by enhancing the gas motion during the post compression period, but the consequence seems to be connected mainly with modification of the heat loss rate to the chamber walls. Those studies predated our ability to investigate the temperature field, so we do not know how the spatial development was affected. It is easiest to enhance or modify the gas motion on the relevant timescale by controlling the gas that is being pushed ahead of the piston, such as by squeezing it through a mesh. I am inclined to think that shear stress might have a part to play in autoignition particularly in turbulent non-premixed gases.

1 R. J. Tabaczinski, D. P. Hault and J. C. Keck, *J. Fluid Mech.*, 1970, **42**, 249.

2 J. F. Griffiths and W. Nimmo, *Nature*, 1986, **322**, 46.

3 J. Franck, J. F. Griffiths and W. Nimmo, *Twenty-first Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1986, p. 447.

Dr Morley said: Rapid compression machines can be made more ideal by suppressing the roll up vortex. Lee and Hochgreb (ref. 4 of the paper by Griffiths *et al.*) have shown that by incorporating a crevice in the piston that swallows the cold boundary layer, the cold gas can be prevented from mixing into the adiabatic core gas in the chamber. They verified the effectiveness of this approach by CFD modelling and showed that, with the modifications, the pressure could be calculated using a thermodynamic model, which was inadequate in the unmodified system.

Prof. Griffiths responded: This is an important experimental development. We have not explored its potential but it would certainly be interesting to demonstrate the response using our non-invasive methods to study the temperature distribution. Part of our interest lies in the behaviour close to the walls of the chamber, because there is evidence that autoignition may originate there in certain circumstances. Consequently, to date we have maintained a flat piston crown extending to the circumference of the cylinder so that optical aberrations in that important region are minimised.

Dr Taatjes said: I notice that your mechanism for autoignition includes a branching step involving O_2 addition to a QOOH species. In this connection I would like to point out that the calculations in our paper (presented here), as shown in the figure for isobutyl + O_2 , confirm that the isomerization from RO_2 to QOOH *via* a six-membered ring proceeds over a relatively small

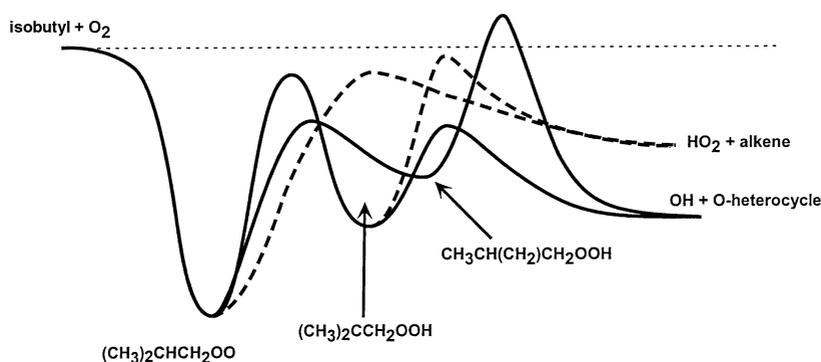


Fig. 1 Reaction paths for the oxidation of isobutane.

barrier. However, the well for QOOH is very shallow, and the barrier in the exit channel to form OH plus an oxetane is above the energy of the R + O₂ reactants (see Fig. 1 here). Therefore, the fate of this QOOH species will be to rapidly return to the more stable RO₂ form, and our calculations indicate that the equilibrium will greatly favor RO₂. I would like to ask what level of stability of QOOH is necessary in order for present models to accurately predict low temperature oxidation and autoignition phenomena? I would also invite general comments on the consequences of the reversibility of the RO₂ ⇌ QOOH isomerization.

Prof. Griffiths responded: It is believed that low temperature autoignition of alkanes evolves through chain branching *via* a small fraction of QOOH forming the O₂QOOH species, coupled to self-heating. Thus the kinetic issue that you have addressed in the context of the 'stability of QOOH' is highly relevant. Your analysis presented here of the elementary reactions of R and RO₂ also includes other interactions that determine the existence of the overall negative temperature dependence of the reaction rate during alkane oxidation, which means that your fundamental studies constitute a very important contribution to the correct interpretation of the global behaviour.

The fraction of QOOH leading to branching (and hence the relative reactivity of different alkanes), must be affected by the ease of the RO₂/QOOH isomerization, the stability of RO₂ preceding it and (in a similar way) the stability of O₂QOOH following it. It would be necessary to turn to numerical studies based on comprehensive kinetic schemes, such as those by Westbrook and co-workers,¹ to quantify the fraction of QOOH involved in chain branching. Reversibility of RO₂ ⇌ QOOH is assumed for all species in the computations, and I believe that the consensus would support that interpretation.

The database for RO₂/QOOH isomerizations obtained from experimental work is still quite limited, being principally that derived by Pilling *et al.*² The activation energies for RO₂ ⇌ QOOH range from 62 to 176 kJ mol⁻¹ (15 to 42 kcal mol⁻¹).

For the *sec*-C₄H₉ in the 1,4p and *tert*-C₄H₉ in the 1,4t transitions, the activation energies for the forward processes are (in your units) 36.6 and 28.2 kcal mol⁻¹, in excellent agreement with and reflect a similar spread for transfer of H from different sites as those predicted from your calculations (37.0 and 29.7 kcal mol⁻¹, respectively). This is very encouraging. For the 1,5s transition in *n*-C₄H₉, the data from Pilling *et al.*² are not quite as close (26.3 *vs.* 22 kcal mol⁻¹).

The *ab initio* calculations should certainly be exploited for more accurate quantitative interpretation of these complex processes within the overall alkane mechanisms and the origins of discrepancies or uncertainties resolved through them. The overall consequence of different values for the activation energies should also be put to numerical test. We could investigate the latter through numerical experiments on *n*-C₄H₁₀ and *i*-C₄H₁₀ combustion using a unified approach to kinetic modelling of alkane ignition in the rapid compression machine.³ Although the reduced form of the kinetic scheme means that there are empirical elements in a number of rate coefficients, there is sufficient detail for us to test variations of parameters, with specific reference to your calculated values and recommendations for the butyl radical reactions.

To be consistent we would have to change the qualitative structure of the scheme to include the independent elimination channel for alkene + HO₂, which is not incorporated in the scheme as it is set up at present. This must have a significant effect, requiring correction of other parameters to give quantitative accord with experiment. Perhaps you can comment on the implications that this alteration might make.

- 1 H. J. Curran, P. Gaffuri, W. J. Pitz and C. K. Westbrook, *Combust. Flame*, 1998, **114**, 149.
- 2 K. J. Hughes, P. A. Halford-Maw, M. J. Pilling and T. Turanyi, *Twenty-fourth Symposium (Int.) on Combust.*, The Combustion Institute, Pittsburgh, 1992, p. 645.
- 3 J. F. Griffiths, K. J. Hughes, M. Schreiber and C. Poppe, *Combust. Flame*, 1994, **99**, 533.

Dr Taatjes replied: If the alkene + HO₂ channel is direct elimination from RO₂ (as appears to be the case), its activation energy no longer need be tied to that of the isomerization step. This would have a couple of advantages. First, the calculated activation energy for elimination seems to be independent of the type of hydrogen eventually taken to form HO₂, as can be seen in Tables 5 and 6 of our paper. This is because the reaction coordinate for the elimination is mostly heavy-atom motion, so the bond energy of the 'abstracted' H atom does not contribute. The isomerization transition state energy does, in fact, depend on the type of C-H bond attacked as you note. So separate activation energies for the QOOH and HO₂ production steps seems like a good idea. Also, then the alkene production comes from the more stable isomer in the RO₂ ⇌ QOOH pair, and is somewhat decoupled from the QOOH stability question.

Our calculations suggest that the QOOH may be less stable than some of the models appear to assume. For example, while the calculated energy for the 1,5s transition state is calculated to be ~22 kcal mol⁻¹ above the n-C₄H₉O₂ well, not significantly different from the activation energy in your model, this transition state is only 8.5 kcal mol⁻¹ above the QOOH well, a little more than half the QOOH → RO₂ activation energy in your model. That may still provide sufficient stability to permit the chain-branching step to occur as modelled. The numerical experiments you propose would be most helpful in determining how sensitive the models are to that reverse activation energy.

Prof. Pilling† commented: A few years ago we studied the reaction between the neopentyl radical and O₂, by following, using LIF, the time dependence of OH formed from dissociation of C₅H₁₀OOH (QOOH).¹ The advantage of this system, as a vehicle for studying the kinetics of the RO₂ → QOOH reaction, arises from the absence of a competing HO₂ channel.

The reaction mechanism is shown in Fig. 2 here. There are three channels for reaction of QOOH, one of which depends on reaction with O₂, while the other two involve dissociation.

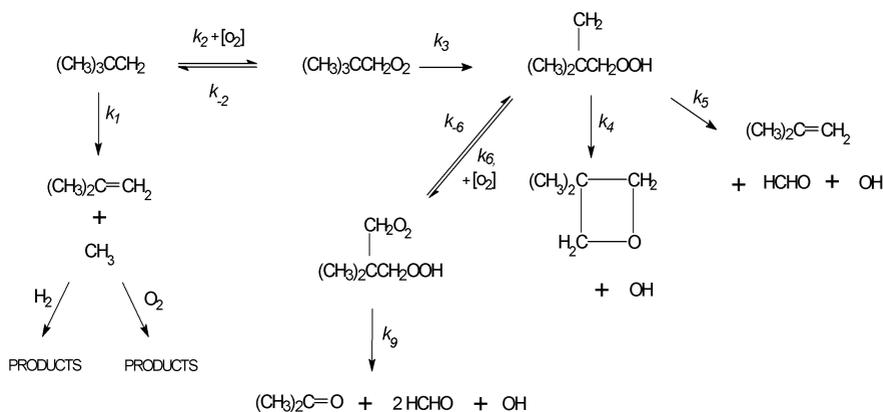


Fig. 2 Mechanism for the oxidation of neopentyl radicals.

† Also Dr A. R. Clague (University of Leeds), Dr S. J. Griffiths (University of Leeds), Dr K. H. Hughes (University of Leeds) and Dr D. W. Stocker (University of Leeds).

While the rate coefficient for the reverse reaction, $\text{QOOH} \rightarrow \text{RO}_2$, k_{-3} , is substantially greater than the rate coefficient for the forward reaction, k_3 , the evidence at the time suggested that the removal of QOOH to form the forward products, *via* reactions 4, 5 and 6, is sufficiently rapid that QOOH is removed irreversibly and the reverse isomerisation *via* reaction (-3) can be neglected. Since then we have re-evaluated the equilibrium constant, K_3 , and found that the ratio, R , of the rates of the forward and reverse reactions of QOOH, lies in the range 3–8, over the range of $[\text{O}_2]$ used experimentally and at a temperature of 700 K. R is defined as $(k_4[\text{O}_2] + k_5 + k_6)/k_{-3}$. The rate coefficients k_5 and k_6 were obtained from measurements of Walker and coworkers,² k_4 was equated to the rate coefficient for neopentyl + O_2 and k_{-3} was equated to k_3/K_3 , with K_3 determined by group additivity³ and k_3 obtained by fitting the experimental data.

The OH LIF profile is biexponential (Fig. 3) with the reciprocal time constant for the rise ($-\lambda_+$) related to the rate coefficients for reactions (1)–(5) and that for the decay to the removal of OH by diffusion and reaction with the neopentyl radical precursor. The profiles were studied over a range of $[\text{O}_2]$, and Fig. 4 shows a plot of $|\lambda_+|$ vs. $[\text{O}_2]$ at 700 K. Two fits are shown, one assuming that reaction (3) is irreversible (*i.e.* $R \gg 1$) and the other using the best estimates for k_{-3} – k_5 . The two

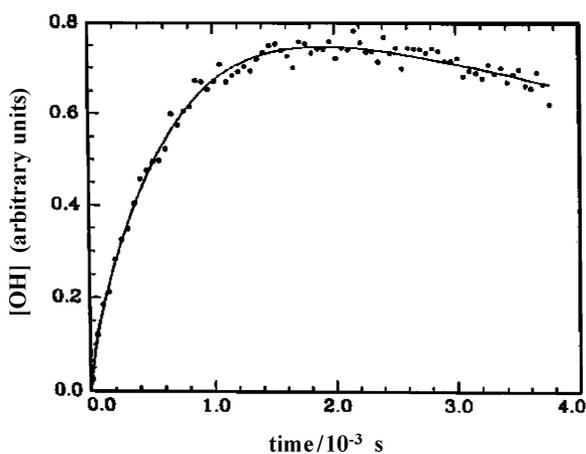


Fig. 3 Time profile of OH fluorescence.

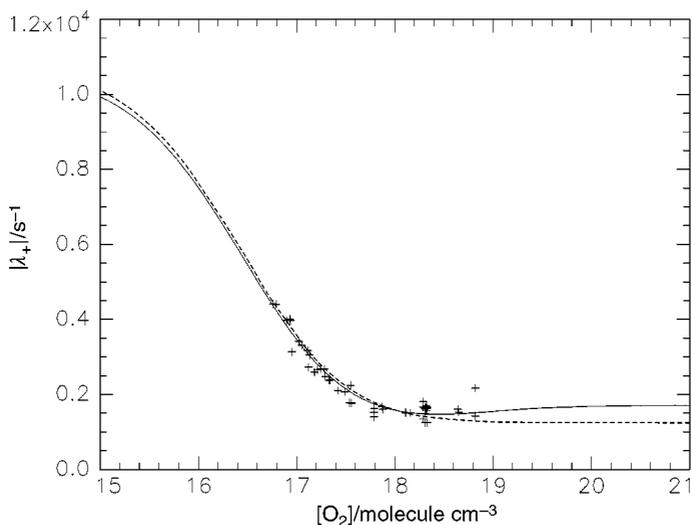


Fig. 4 Comparison of the fits to the experimental data at 700 K with an irreversible model (dashed curve) and a reversible model (solid curve).

Table 1 Comparison of fitted k_3 values obtained from assuming reversible and irreversible kinetics for reaction (3)

T/K	$10^{-3} k_3/s^{-1}$ irreversible model	$10^{-3} k_3/s^{-1}$ reversible model
660	0.30 ± 0.03	0.28 ± 0.03
670	0.33 ± 0.04	0.37 ± 0.04
690	0.85 ± 0.17	1.24 ± 0.24
700	1.23 ± 0.09	1.72 ± 0.14
715	1.64 ± 0.25	2.14 ± 0.20
730	2.05 ± 0.33	3.01 ± 0.50
750	4.12 ± 0.81	3.76 ± 0.76

approaches show a comparable quality of fit and only deviate significantly from one another at higher $[O_2]$ —on the basis of the experimental data alone it is not feasible to establish the value of R .

Table 1 compares the values of k_3 obtained from analysis of the data (i) assuming that reaction (3) is irreversible (*i.e.* $R \gg 1$) and (ii) using the best estimates for k_{-3} – k_5 . The latter values are slightly larger than the former.

- 1 K. J. Hughes, P. A. Halford-Maw, M. J. Pilling and T. Turanyi, *Twenty-fourth Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1992, p. 645.
- 2 R. R. Baldwin, M. W. Hisham and R. W. Walker, *J. Chem. Soc., Faraday Trans.*, 1982, **78**, 1615.
- 3 D. W. Stocker and M. J. Pilling, in preparation.

Dr DeSain commented: You stated that you have previously observed only OH formation from the reaction of neopentyl (C_5H_{11}) + O_2 .¹ As you know the C_5H_{11} + O_2 mechanism is different from that of most $R + O_2$ reactions in that the direct elimination to form the conjugate alkene and HO_2 is impossible. However, the formation of HO_2 in Cl-initiated neopentane oxidation has recently been experimentally observed by Dr Taatjes and myself. The HO_2 time profile in neopentane oxidation is somewhat different from those in other $R + O_2$ studies² in that no prompt HO_2 formation is observed (see Fig. 5 presented here). At 673 K the HO_2 yield is 9.5% (referenced to a 100% signal from the $CH_2OH + O_2$ reaction). This yield is also somewhat smaller than the HO_2

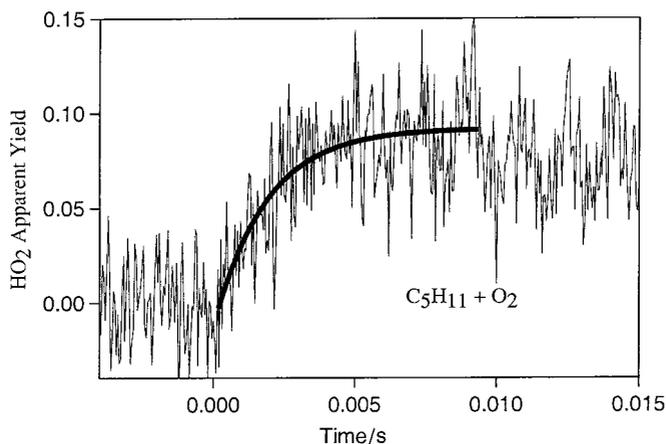


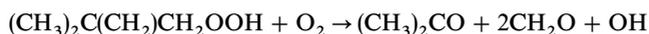
Fig. 5 The time resolved infrared FM signals for HO_2 from neopentane oxidation taken at 673 K and 59.3 Torr. The trace is obtained by an experimental method similar to that in ref. 2. The amplitude has been scaled by the amplitude of the HO_2 signal from the reference reaction $CH_2OH + O_2$ to obtain an apparent yield. The trace has been corrected for $HO_2 + HO_2$ reaction as described in ref. 2. The line through the $C_5H_{11} + O_2$ trace is an exponential fit to the HO_2 formation which corresponds to a rate constant of formation of $540 \pm 100 s^{-1}$.

yields observed in other alkane oxidation studies at this temperature. The observation of HO₂ formation should be of interest for validating neopentane oxidation models at these temperatures.

1 K. J. Hughes, P. D. Lightfoot and M. J. Pilling, *Chem. Phys. Lett.*, 1992, **191**(6), 581.

2 J. D. DeSain, C. A. Taatjes, J. A. Miller and S. J. Klippenstein, *Faraday Discuss.*, 2001, **119**, 101.

Dr Taatjes added: I would add that one interpretation of the HO₂ production in this system is that it results from the oxidation of formaldehyde produced in reactions of the QOOH species, *e.g.*,



Reactions of OH or other radicals with formaldehyde will produce HCO, which will rapidly react with excess O₂ to make HO₂. If this mechanism is correct, modelling of the HO₂ formation in neopentane oxidation could provide data on the RO₂ ⇌ QOOH isomerization complementary to the direct measurements of OH production in neopentyl + O₂ from Pilling and co-workers. This analysis is presently underway in our laboratories.

Prof. Greenhalgh addressed Prof. Griffiths: Would filtered Rayleigh scattering assist the interpretation of the acetone images since this would give some temperature information?

Dr Whitaker and **Prof. Griffiths** responded: We have recently reported elsewhere some results obtained by filtered Rayleigh scattering under both non-reactive and reactive conditions in our RCM and compared these to acetone LIF measurements.¹ We found that even in non-reactive mixtures Rayleigh scattering was not sufficiently sensitive to detect the slightly colder core gas, the roll-up vortex, that is present just after the end of the compression stroke. However, when acetone was seeded at 1% into the non-reactive mixture the existence of the colder core was clearly visible in the PLIF images. By comparison with data from Hanson and co-workers^{2,3} we were able to estimate a temperature difference of approximately 40–50 K between the core gas and the surrounding gas from the LIF images when the mixture was compressed to a notional adiabatic temperature of 717 K. In other experiments on the exothermic decomposition of di-*tert*-butyl peroxide vapour, Rayleigh measurements were able to clearly observe the effects of the presence of the roll-up vortex. In this case, the gas mixture towards the periphery of the chamber reacts faster than the gas in the core and, since the reaction is exothermic, locally heats it, and we were able to observe the Rayleigh signal reducing as a function of time in the surrounding gas as a consequence. From these measurements we concluded that, although a useful technique, filtered Rayleigh scattering was rather less sensitive for thermal imaging than acetone tracer LIF measurements.

There are two additional comments that we would like to add. Firstly, our filtered Rayleigh measurements were made using an I₂ filter at ~532 nm by tuning the output of an injection seeded frequency doubled Nd : YAG laser into coincidence with a strong molecular absorption. Iodine vapour is easy to handle and 532 nm is a convenient wavelength, but it would obviously be better to perform Rayleigh scattering measurements at a shorter wavelength because the signal scales as λ⁻⁴. Unfortunately, there seems to have been little work to date in identifying suitably narrow atomic or molecular transitions at the higher harmonics of the Nd : YAG laser that could be used as filters⁴ (although, recently, Hg vapour has been used to filter the output of a frequency tripled Ti : sapphire laser⁵). Secondly, the interpretation of Rayleigh scattering measurements is complicated in reactive mixtures because the scattering cross-section depends on the (changing) molecular polarisability as well as the temperature.

1 J. Clarkson, J. F. Griffiths, J. P. MacNamara and B. J. Whitaker, *Combust. Flame*, 2001, **125**, 1162.

2 M. C. Thurber, F. Grisch and R. K. Hanson, *Opt. Lett.*, 1997, **22**, 251.

3 M. C. Thurber, F. Grisch, B. J. Kirby, M. Votmeier and R. K. Hanson, *Appl. Opt.*, 1998, **37**, 4963.

4 R. B. Miles, W. R. Lempert and J. N. Forkey, *Meas. Sci. Technol.*, 2001, **12**, R33.

5 A. P. Yalin and R. B. Miles, *J. Thermophys. Heat Transfer*, 2000, **14**, 210.

Prof. Lindstedt commented: There are two issues that come to the fore. (i) In the flame under consideration the CH + O₂ channel is of key importance and is responsible for 30–60% of the oxidation of CH. The good agreement shown between the current experimental study and that of

Juchmann *et al.*¹ for this species coupled with the apparent success of the high temperature determinations by Rohrig *et al.*² and Markus *et al.*³ in the context of flame modelling raises an interesting inconsistency with room temperature determinations for this channel.⁴ (ii) It may be pointed out that the measured peak CN mole fraction of 3.2 ppm also agrees comparatively well with the predictions of 4.7 ppm (GRI Mech. 2.11) 2.8 ppm (Lindstedt) and 10 ppm (Warnatz) presented by Juchmann *et al.*¹

- 1 W. Juchmann, H. Latzel, D. L. Shin, G. Peiter, T. Dreier, H. R. Volpp, J. Wolfrum, R. P. Lindstedt and K. M. Leung, *Twenty-seventh Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1998, p. 469.
- 2 M. Rohrig, E. L. Petersen, D. F. Davidson, R. K. Hanson and C. T. Bowman, *Int. J. Chem. Kinet.*, 1997, **29**, 781.
- 3 M. W. Markus, P. Roth and T. Just, *Int. J. Chem. Kinet.*, 1996, **28**, 171.
- 4 A. Bergeat, T. Calvo, F. Caralp, J.-H. Fillion, G. Dorthe and J. C. Loison, *Faraday Discuss.*, 2001, **119**, 67.

Prof. Kohse-Höinghaus commented: I would like to acquaint the audience with recent results of Burak Atakan and Tobias Hartlieb¹ with respect to NO reburning in fuel-rich propene flames. In these flames at three different stoichiometries, the NO measurements agree quite well with model simulations. The reaction flow analysis reveals that under these conditions, CH + NO reaction plays only a minor role while both NO and HCN are more sensitive to HCCO + NO reactions. Among radicals to be monitored, it might thus be useful to consider HCCO.

- 1 B. Atakan and T. Hartlieb, *Appl. Phys. B*, 2000, **71**, 697.

Prof. Kohse-Höinghaus opened the discussion of Dr Desgroux's paper: (1) Your flame is almost stoichiometric (actually even slightly leaner because of the admixed NO). For study of (fuel-rich) reburning chemistry, would you not rather investigate richer flames? Have you done so?

(2) With respect to your CH measurement and the disagreement with the model, you attribute this potentially to the temperature dependence of the CH + O₂ reaction at high temperatures. With your temperature uncertainty of ± 120 K, would this affect the CH profile enough so that model and measurement would be in better agreement?

Dr Desgroux responded: (1) The validation of reburning chemistry is also an important task in stoichiometric flames. But you are right that more extensive studies are required in richer flames. We believe that the CRDS-LIF coupling will also be well suited in such flames.

(2) Tests have been performed by imposing different temperature profiles within the uncertainty range (± 120 K in the burnt gases). An important effect on the CH mole fraction profile (peak value and position) is effectively observed. But the difference with the experimental mole fraction (also affected by the temperature change due to the conversion of the concentration into a mole fraction) is still outside the experimental error. The smallest difference (28% with respect to the experimental value) is obtained for the coldest temperature profile. But in that case the peak position of the CH mole fraction (4.05 mm) is 0.65 mm downstream of the experimental peak.

Prof. Kohse-Höinghaus asked: Your temperature profile needs high accuracy in the gradient where you observe the NO 'dip'. Could you comment on the superiority of using OH LIF rather than LIF of your seeded NO for this purpose?

Dr Desgroux replied: At the location of the NO dip (around 4 mm) the OH concentration is sufficient to make accurate OH LIF temperature measurements. Near the burner the temperature measurements are less accurate due to the cumulative effects of a weak OH concentration and of an important temperature gradient. NO-LIF measurements would not have been affected by sensitivity problems in the vicinity of the burner surface. However we believe that NO excitation spectra would have been perturbed by self-absorption from the cold NO surrounding the burner, which was not isolated by a coflow. Strong absorption from the cold NO was shown in our burner enclosure using the CRDS technique.

Dr Whitaker asked: I would like to follow up on this problem of the temperature gradient. In CRDS in an open cavity containing a flame and therefore refractive index gradients, I imagine

there will be an effect on the cavity hold time due to beam walk. Can you characterise these effects and more importantly correct them?

Dr Desgroux answered: The presence of refractive index gradients might effectively modify the beam walk. As long as the perturbation is weak, such an effect acts like supplementary off-resonance losses and the time decay of the CRD signal is still exponential. Under these conditions the net losses due to the absorbing species are obtained after subtraction of the off-resonance losses including the thermal effects but also broadband absorption (or scattering) from the flame and losses due to the mirrors.

Prof. Cheskis asked: Why did you not use CRDS for the OH calibration? It is possible if the weaker lines are used.

Dr Desgroux replied: CRDS on OH weak lines (S_{21} lines for example) would have been possible. But with our laser bandwidth, the exponential behavior would have been obtained only for high rotational levels (*i.e.* corresponding to a weak Boltzmann fraction and thus to a weak absorbance) leading to a temperature-sensitive measurement.¹ We have found that it is more accurate to work with the single-pass absorption technique performed on a weak-temperature dependent transition in the specific case of the abundant OH species.

¹ X. Mercier, E. Therssen, J. F. Pauwels and P. Desgroux, *Combust. Flame*, 2001, **125**, 656.

Mr Zsély opened the discussion of Prof. Cheskis's paper: You used GRI-Mech version 2.11. Why didn't you use version 3.0 instead of 2.11?

Prof. Cheskis responded: Both versions of the GRI-Mech demonstrate similar qualitative behaviour for HNO and NH_2 . Both versions predict two maxima in the HNO profile and do not predict NH_2 at high locations above the burner. Fig. 6 shows the concentration profiles of HNO and NH_2 calculated using both versions of the mechanism. Absolute concentration of HNO in the

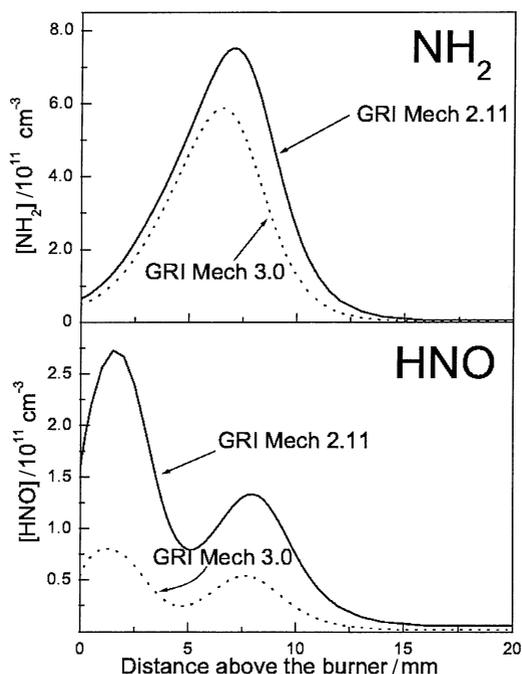


Fig. 6 The HNO and NH_2 concentration profiles calculated using versions 2.11 and 3.0 of GRI-Mech. The calculations were performed for stoichiometric ($\phi = 1.0$) doped with 7.2 cm^3 of NO.

first maximum is lower in version 3.0 because of two times higher value for H + HNO reaction and 50% lower value for H + NO + M reaction used in this version. Thus, the discrepancy with our experimental results is higher for version 3.0.

Prof. Kohse-Höinghaus commented: (1) I would like to express some concern about the build up of radicals in the burner housing, *i.e.* in the zone surrounding the flame. The assumption of a homogenous 60 mm absorption length and ‘top-hat’ temperature profile will not be appropriate in regions as high as 50–60 mm above the burner. Outer zones with ‘cold’ radicals will potentially distort spectra and affect the concentration measurement, mixing of the hot combustion gases with the N₂ shroud flow may add to these uncertainties. Did you change the shroud flow too? A one-dimensional model will probably not represent your measurement condition.

(2) Also, I would like to ask about the uncertainty of the HNO absorption cross section which was based on an HCO calibration using the reaction of HCO + NO → HNO + CO. As a total impression, it seems premature from these measurements to state that models may or may not be in agreement, unless the effects of absorption path length and temperature as well as absorption coefficient were properly quantified.

Prof. Cheskis replied: (1) I agree with your comment that a one-dimensional model does not represent the experiment correctly. For HNO we were able to improve this situation using the nitrogen flow through the window holders preventing accumulation of HNO in the vicinity of the windows. On the other hand, the NH₂ concentration is not affected by this flow substantially. It demonstrates that NH₂ is located closer to the center of our vacuum chamber. We changed the shroud flow over a wide range and did not observe any influence of the shroud flow on the HNO and NH₂ concentrations.

(2) The cross section of HNO was measured in only one study and that was more than 20 years ago. In this work the concentration of HNO was measured on the basis of the HCO concentration, assuming that all HCO formed as a result of the acetaldehyde photolysis, converts to HNO *via* the reaction HCO + NO → HNO + CO. I think that the possible error is less than 100%, taking into account that the rate constant of the reaction of HCO + HCO, which is directly related to the HCO concentration, was obtained in this work in reasonable agreement with literature data. The uncertainties in the optical length and in the temperature increase the total error in the measured HNO concentration. On the other hand the discrepancy found, which is of the order of magnitude, probably could not be explained by these errors alone, and some corrections in the mechanism will be needed. I agree that in order to correct the mechanism we will need a more accurate value of the HNO cross section as well as three dimensional measurements in flames. I believe that the direct measurement of the H + HNO rate constant will also be very useful.

Prof. Lindstedt said: The rate for the reaction $\text{H} + \text{HNO} \rightleftharpoons \text{NO} + \text{H}_2$ is uncertain and the determination by Soto and Page¹ ($4.5 \times 10^{11} T^{0.72} e^{330/T}$) used in GRI-Mech 2.11 may be somewhat fast. However, it has been shown² that for a range of flames the early estimate by Bulewicz and Sugden³ (5×10^{12}) results in persistent over-predictions of HNO in cases where the channel matters. There are obvious multiple uncertainties and it would be good to see the sensitivity to the (arguably) lower limit rate.³

1 M. R. Soto and M. J. Page, *Chem. Phys.*, 1992, **97**, 7287.

2 R. P. Lindstedt, F. C. Lockwood and M. A. Selim, *Combust. Sci. Technol.*, 1994, **99**, 253.

3 E. M. Bulewicz and T. M. Sugden, *Proc. R. Soc. London, Ser. A*, 1962, **277**, 143.

Prof. Cheskis responded: Unfortunately there is no reliable measurement of the rate constant for the H + HNO reaction. The sensitivity of the calculated profile of HNO to the value of that rate constant is illustrated in Fig. 7, (presented here) where calculations were carried out for the same system with the only difference being the H + HNO rate constant. The over-prediction of HNO which was mentioned by Lindstedt *et al.*¹ varied from 40% to three times that for flames where HNO concentrations have been measured and can be caused by different reasons. It should be noted that experimental values of the HNO concentration were obtained by mass spectroscopy.^{2,3} In order to obtain absolute concentrations the authors calibrated the signal using the

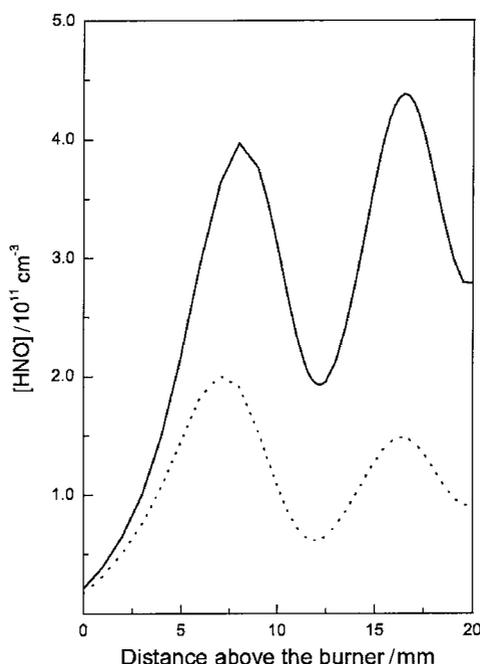


Fig. 7 The HNO concentration profile calculated for two different expressions for the rate constant of the reaction of H + HNO. Solid line is the result of calculation with $k = 5 \times 10^{12}$. The dotted line is for $k = 4.5 \times 10^{11} T^{0.72} \exp(330/T)$ as adopted in GRI-Mech 2.11. The calculations were performed for methane-air flame with equivalence ratio $\phi = 1.2$ doped with 7.2 cm^3 of NO.

ionization cross section of stable compounds having a molecular weight close to the investigated species. The accuracy of that procedure is questionable and this uncertainty can be also involved in the over-prediction reported by Linstedt *et al.*¹

- 1 R. P. Lindstedt, F. C. Lockwood and M. A. Selim, *Combust. Sci. Technol.*, 1994, **99**, 253.
- 2 J. Bian, J. Vandoreen and P. J. Van Tiggelen, *Twenty-first Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1986, p. 953.
- 3 J. Bian, J. Vandoreen and P. J. Van Tiggelen, *Twenty-third Symp. (Int.) Combust.*, The Combustion Institute, 1990, p. 379.

Dr Miller asked: (1) What is the source of the rate constant for $\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M}$ in GRI-Mech? Peter Glarborg *et al.* measured the rate constant a couple of years ago¹ for $1000 < T/\text{K} < 1170$, and my impression at the time was that the rate constant from 300 K up to these temperatures was not uncertain by more than a factor of two. Such an uncertainty would not be consistent with this rate constant being the cause of the discrepancy between the model predictions and your measurements.

(2) How do you calculate transport properties in the flame model? Do you include thermal diffusion? One might expect the HNO predictions early in the flame to be quite sensitive to the transport model.

- 1 P. Glarborg, M. Østberg, M. U. Alzueta, K. Dam-Johansen and J. A. Miller, *Twenty-seventh Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1998, p.219.

Prof. Cheskis replied: (1) The GRI-Mech 2.11 used $k = 9 \times 10^{19} T^{-1.32} \exp(-370/T)$ from ref. 1. This value was halved in version 3.0. This change, along with a twofold increase in the rate constant of the reaction of $\text{H} + \text{HNO} \rightarrow \text{H}_2 + \text{NO}$, results in the lower HNO concentration predicted by version 3.0. For lower temperatures ($\sim 300 \text{ K}$) the recommendation of Glarborg *et al.*² is close to that used in GRI-Mech 2.11, at higher temperatures this work gives a value that is three times lower than that adopted in the GRI-Mech 2.11. The uncertainty of the rate constant of the

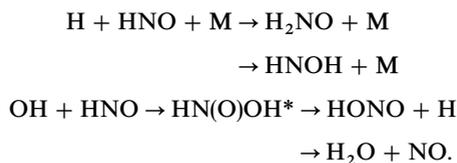
reaction of $\text{H} + \text{HNO}$ is higher than that of $\text{H} + \text{NO} + \text{M}$ and the discrepancy between the measurements and predictions depends on the ratio of these constants which uncertainty is obviously higher than those of both constants.

(2) We used the PREMIX code, which allows one to take into account thermal diffusion. Thermal diffusion increases substantially the concentration of H atoms in the preflame zone, but the HNO concentration increases only by several percent. The reason is the concurrent acceleration of the reactions of $\text{H} + \text{NO}$ and $\text{H} + \text{HNO}$ which form and consume HNO respectively.

1 W. Tsang and R. Herron, *J. Phys. Chem. Ref. Data*, 1991, **20**, 623.

2 P. Glarborg, M. Østberg, M. U. Alzueta, K. Dam-Johansen and J. A. Miller, *Twenty-seventh Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1998, p. 219.

Prof. Lin said: The rate constants for both $\text{H} + \text{HNO}$ and $\text{OH} + \text{HNO}$ have been calculated by Page and co-workers.^{1,2} In addition to the commonly assumed exchange processes, other facile indirect product channels should perhaps be included in kinetic modeling of HNO concentration profiles. For example:



1 M. R. Soto, M. Page and M. L. McKee, *Chem. Phys.*, 1991, **153**, 415.

2 M. Page and M. R. Soto, *J. Chem. Phys.*, 1993, **99**, 7709.

Prof. Cheskis replied: I agree with you that more detailed kinetic modelling including different channels of the HNO reactions is needed.

Prof. Wolfrum asked: Could you perform some tomography experiments with your set up to measure deviations from the 1D-flame behaviour? In your broadband absorption you should also be able to discriminate groups of absorption lines originating from cooler and hotter parts of your absorption path to correct for contribution outside the flame.

Prof. Cheskis replied: We are planning such tomographic experiments now. In our opinion it is the best way to overcome the disadvantages of the line of sight techniques. Simultaneous measurements of the absorption originated from the levels with different energy might help to solve this task.

Prof. Kohse-Höinghaus said: Certainly it would be advisable in your measurements to specify your actual absorption path. In following the suggestion of using tomographical reconstruction, you know that it is also done to monitor laser-induced fluorescence at the same time for an independent observation of the absorption path. It is certainly difficult for some radicals, but you could maybe comment for your own system.

Also, would the use of two-photon absorption techniques in CRD assist in placing the actual zone of measurement more into the center of the flame where your (one-dimensional) model calculates the concentrations?

Prof. Cheskis replied: It was demonstrated that the combination of CRDS and LIF provides very important information and offers in several cases an alternative to the tomographic measurements. Unfortunately, the sensitivity of LIF is not sufficient in order to use this technique for CH_2 , NH_2 , etc. On the other hand, the space profiles can vary for different species, as was demonstrated in this work for HNO and NH_2 . Thus, the measurements of radial profiles of one radical cannot be used for another radical directly. Your idea of using two-photon absorption is very interesting. However, one must keep in mind that the use of two beams in order to localize the monitoring zone will decrease the optical length, and therefore the sensitivity of the line of sight method.

Dr Miller asked: At what distance above the burner does the HNO mole fraction peak?

Prof. Cheskis responded: The first maximum of HNO is located at ~ 3 mm above the burner.

Prof. Wolfrum asked: The first HNO-maximum should be located before the flame front due to the counter diffusion of H-atoms towards the cold NO. Did you observe this?

Prof. Cheskis responded: Yes, we do observe it. And its location is in good agreement with predictions of the GRI-Mech.

Dr Miller said: It is known that jetting of the gases through the porous-plug burner can cause the flow near the burner not to be one-dimensional. Could this be the cause of the discrepancy between the model predictions and experiments for HNO? Also, the boundary condition at the burner surface in the PREMIX code is a continuity of mass fluxes, which implies a discontinuity of the mole fractions at the surface. Obviously, this is an idealization and, for highly stabilized flames, could produce errors near the surface. However, this problem is easily alleviated by turning up the flow rates in the experiment and pushing the flame zone away from the burner as far as possible.

Prof. Cheskis responded: The position of the flame zone was different for flames with different equivalence ratios. However, in all flames studied we observed good agreement in the location of the first HNO peak, and the same disagreement in absolute value. In our opinion the main two reasons for this disagreement could be the uncertainties in the HNO absorption cross section and in the HNO rate constants.

Prof. Pilling opened the discussion of Dr Hughes's paper: Hughes *et al.* have emphasized the importance of $\text{H} + \text{SO}_2$ in removing SO_2 under flame conditions. We have examined this reaction using a master equation model,¹ with the potential energy profile shown as Fig. 19 in Hughes *et al.* and the transition state parameters calculated by Marshall *et al.*² We also used our direct measurements of $\text{OH} + \text{SO}$, over the temperature range 300–700 K,³ to characterize the loose transition state between $\text{OH} + \text{SO}$ and HOSO.

At low temperatures (~ 300 K), the reaction is limited to the formation of HSO_2 , with a pressure dependent rate coefficient of $\sim 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 atm. At ~ 400 K, HSO_2 dissociates to regenerate the reactants and the overall rate coefficient falls.

At higher temperatures (~ 1000 K), formation of HOSO becomes the major channel, with, at low pressures, some direct formation of $\text{OH} + \text{SO}$ via energized HOSO^* , without stabilization. As the temperature is increased further, HOSO becomes unstable, again regenerating reactants. Finally, and at the limiting temperatures established in the flames reported by Hughes *et al.*, the reaction forms $\text{OH} + \text{SO}$ directly, via the final loose transition state, with a rate constant that is independent of pressure and that is related to the rate coefficient for $\text{OH} + \text{SO}$, via the equilibrium constant. The intermediates HSO_2 and HOSO play no role in the reaction under these conditions.

We are currently determining rate coefficients for the individual steps in the mechanism, from the results of the master equation calculations.¹

1 M. A. Blitz, K. J. Hughes and M. J. Pilling, in preparation.

2 A. Goumri, J. D. R. Rocha, D. Laakso, C. E. Smith and P. Marshall, *J. Phys. Chem. A*, 1999, **103**, 11328.

3 M. A. Blitz, K. W. McKee and M. J. Pilling, *Proc. Combust. Inst.*, 2000, **28**, 2491.

Dr Tomlin responded: It is possible from your calculations to establish the relative contributions from the reactions $\text{SO}_2 + \text{H} \rightarrow \text{products}$ and the third body reaction $\text{H} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO} + \text{M}$? This may be important since our sensitivity studies show that for a lean methane flame $\text{SO}_2 + \text{H} \rightleftharpoons \text{SO} + \text{OH}$ has a positive sensitivity with respect to NO whereas $\text{H} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO} + \text{M}$ has a negative one which also varies significantly with distance from the burner.

Prof. Pilling said: As the temperature increases, over the first 5 mm above the burner, the formation of HOSO will be important and the rate coefficient will be pressure dependent. At the

highest temperatures, where OH + SO are formed directly, the rate coefficient is independent of pressure. The results of the master equation calculations can be analysed to produce temperature and pressure dependent rate coefficients for the individual steps which will allow a detailed assessment of the relative rates to be made.

Dr Desgroux asked: Could you tell me the precise initial (relative) values of the NO concentrations that you measured in the different flames before the injection of SO₂?

Could you also comment on how accurate the prediction of NO was compared to your measurements without SO₂ in the different flames?

What is the accuracy of your NO (relative) measurements?

Dr Hughes replied: We have measured the relative LIF signals in the different flames at a height of 25 mm above the burner. Table 2 presented here. However these may not directly provide the relative NO concentrations, as surface, the results being summarised in corrections for the different flame temperatures on the rotational population distribution of NO need to be made, and different quenching rates of excited NO in the different flames may have to be accounted for. These measurements were made by adjusting the detection system to give a large signal at $\phi = 0.7$, then in a single run, in order to minimise the effect of any drift in laser output power, data were collected for the different flame stoichiometries, both with and without NH₃ doping of the flame. The NO LIF signal was averaged over typically 100 laser shots, and corrected for the baseline signal observed in the absence of NH₃, which was collected in a subsequent run. The quoted errors represent one standard deviation obtained from the averaging of the NO signal and the background signal. Without further experiments, it is important to note that the numbers from one table cannot be compared with the other table.

For comparison, predicted relative NO values for each flame at 25 mm above the burner surface have been calculated from the simulations and are shown in the final column of Table 2. For flames 4, 5 and 6 containing 66% of argon, the agreement is very good, but less so for flames 7–10 containing 33% of argon. Currently the origin of this discrepancy is unknown. One possible contributory factor is that flames 7–10 exhibit a greater temperature difference, and having less argon will have a greater contribution from different quenching rates for excited NO, therefore larger corrections to convert the LIF signals to relative concentrations for flames 7–10 will be required.

Prof. Plane said: The LIF intensity is assumed to be proportional to the radical concentration. Did you establish that the species were thermally equilibrated in the rotational levels that you probed? How reliable is the temperature measurement using the thermocouple, and were you able to compare this with OH LIF thermometry, for example?

Dr Hughes replied: We were not able to establish whether the species were thermally equilibrated in the rotational levels that we probed. In the case of NS and SO₂ we did not have a sufficiently detailed assignment and analysis of the spectra to enable us to do so. For NO it was

Table 2 Relative LIF signals in different flames

Flame	ϕ	Relative NO LIF signal	Predicted relative [NO]
66% Argon			
4	0.7	1 ± 0.134	1
5	1.0	0.84 ± 0.122	0.864
6	1.4	0.58 ± 0.12	0.53
33% Argon			
7	0.7	1 ± 0.2	1
8	1.0	0.853 ± 0.189	0.736
9	1.3	0.621 ± 0.155	0.337
10	1.6	0.214 ± 0.124	0.071

not necessary, as we were not trying to measure a concentration profile in the flame, but only the effect on NO at a fixed point in the flame of the addition of small quantities of SO₂.

The temperature measurement using the thermocouple has some uncertainty due to the fact that the thermocouple needs to be coated with silica to minimise catalytic surface reactions, and temperature corrections for radiation loss made. These corrections depend on assumptions regarding the diameter of the coated thermocouple and its emissivity. Additionally under some of the flame conditions the coating was not totally stable, and needed to be periodically replaced. Ideally we would have liked to compare it with OH LIF thermometry, but time constraints prevented us from performing these measurements.

Prof. Wolfrum asked: Did you perform fluorescence lifetime measurements for the sulfur containing radicals?

Dr Hughes answered: No explicit measurement of the fluorescence lifetime of NS was made, the only observation being that there was no obvious change as a function of position in the flame.

Dr Seakins said: You mentioned in your talk that you looked for SO but did not observe any characteristic fluorescence. Does this allow you to put any limiting values on the concentration of SO. If so, is this limiting value consistent with the model calculations? In the paper, a number of the reactions that you identify as being important involve SO, would future SO observations be a good test of your model?

Dr Hughes replied: Theoretically, it may be possible to infer a limiting value of SO, but this would require a detailed investigation of the detector efficiency, laser power and linewidth, knowledge of the SO spectrum and quenching rates of excited SO in the flame conditions. We were not in a position to perform all of this, and even so, we would still have the problem of overlapping fluorescence observed from SO₂ when interpreting the maximum SO level. Future SO observations would be a useful test of the model, and may be possible at a different wavelength.

Dr Kaiser said: Although not many C₂ molecules exist in hydrogen rich, sulfur containing fuel flames, it could be important to investigate the role of dicarbon reactions with H₂S in hydrogen and oxygen poor combustion flames. Our recent crossed beam study on the C₂-H₂S system found three reaction pathways, *i.e.* formation of HCCS, HSCC and CCS.¹ In particular, the HCCS radical could be of potential importance to form—upon multi-step reactions with acetylene and vinyl—sulfur heteroaromatic molecules (see Fig. 8 presented here).

1 R. I. Kaiser, Y. T. Lee and Y. Osamura, *J. Phys. Chem. A*, submitted.

Dr Hughes responded: Given the current state of knowledge of the kinetics and product channels of elementary reactions involving sulfur species, it is difficult to comment on the importance of species such as HCCS and their reactions. A search of the NIST chemical kinetic database¹ shows no entries for HCCS. It is unlikely however that C₂ molecules exist in large quantities in methane flames as opposed to higher hydrocarbon flames and therefore we do not believe that such reactions are the major source of error in our simulations.

1 *Standard Reference Database 17*, Version 7.0 (Web Version), <http://kinetics.nist.gov/index.php>.

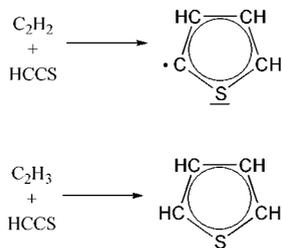


Fig. 8 Possible reactions of the HCCS radical in sulfur-rich hydrocarbon flames.

Prof. Troe asked: Do you find any evidence for the formation of S_2 ? Would S_2 be a kinetically relevant species?

Prof. Cheskis also asked: Did you observe the presence of S_2 molecules in your flame, in particular did you observe light emission of electronically excited sulfur molecules? The presence of sulfur in the flame usually produces a blue-violet light emission.

Dr Hughes responded: A fluorescence signal consistent with S_2 was observed by LIF in experiments that were designed to detect SH although detailed experiments were not carried out. A violet light emission from the flame was observed when it was doped with sulfur. In the current model and for the conditions simulated however, reactions of S_2 did not show high sensitivities and so are not likely to be of importance.

Prof. Wolfrum asked: Could you observe the formation of solid products during the experiment in your burner?

Dr Hughes replied: When the flame was doped with SO_2 , there was a slow build up of a solid deposit on the surface of the burner.