FINAL TECHNICAL REPORT
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INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL KINETICS OF FREE RADICALS

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PROGRAM SCOPE

This research was directed at the detection, monitoring, and study of the chemical kinetic behavior by infrared absorption spectroscopy of small free radical species thought to be important intermediates in combustion. Work on the reaction of OH with acetaldehyde has been completed and published and work on the reaction of $O(^1D)$ with CH_4 has been completed and submitted for publication. In the course of our investigation of branching ratios of the reactions of $O(^1D)$ with acetaldehyde and methane, we discovered that hot atom chemistry effects are not negligible at the gas pressures (13 Torr) initially used. Branching ratios of the reaction of $O(^1D)$ with CH_4 have been measured at a tenfold higher He flow and fivefold higher pressure.

PRODUCT YIELDS IN THE REACTION OF OH WITH ACETALDEHYDE

The reaction of OH with acetaldehyde in the gas phase has been studied by tunable infrared laser kinetic spectroscopy. As expected the main channel is the production of water (~100%). An upper bound of 5% was placed on the yield of CH_3, and the yield of H is estimated as 5±5%. A rate constant of $1.67(10)\times10^{-11}$ molecules^{-1} cm^3 s^{-1} is obtained for the title reaction in good agreement with previous measurements. The major product of the reaction, CH_3CO, reacts with O_3 producing CH_3, CO_2 and O_2 in one channel with a rate constant of $1.4(5)\times10^{-11}$ molecules^{-1}cm^3 s^{-1} and producing CH_3CO_2 and O_2 in the other channel with a rate constant of $3.3(5)\times10^{-11}$ molecules^{-1} cm^3 s^{-1}. Thus the reaction between OH and acetaldehyde is primarily an H atom abstraction. Any contribution at room temperature from addition channels is small.

HOT ATOM EFFECTS IN $O(^1D)$ REACTIONS

After beginning work with $O(^1D)$ in its reaction with acetaldehyde, we decided that we needed to develop our understanding of the application of our infrared kinetic spectroscopy approach to $O(^1D)$ reactions. Our primary interest is in the determination of branching ratios, but we do have the capability of measuring relative rates by competition for $O(^1D)$. A good test for our procedures was to measure the rate constant of $O(^1D) + H_2$ (reaction 1) relative to $O(^1D) + N_2O$ (reaction 2). The expected OH absorbance (base e) upon photolysis of a mixture of H_2 and N_2O with a small amount of NO added to relax vibrationally excited OH can be expressed as

$$A(OH) = \sigma L \frac{k_1[H_2]}{k_1[H_2] + k_2[N_2O] + k_3[NO]}[O(^1D)]_0$$

where σ is the OH absorption cross-section, L is the pathlength, and the other quantities are rate constants and concentrations. This can be rearranged to

$$\frac{1}{A(OH)} = \frac{1}{\sigma L[\,O(^1D)]_0}\left(1 + \frac{k_2[N_2O] + k_3[NO]}{k_1}[H_2]^{-1}\right)$$

Thus if 1/A(OH) is plotted vs $1/[H_2]$, a straight line is expected with the ratio of the slope to intercept being $k_2[N_2O]/k_1$. Figure 1a shows such a Stern-Volmer plot in a system where the partial pressure of N_2O is 362.8 mTorr and the partial pressure of the helium buffer gas is 12 Torr. The straight line on this graph is the best fit to the data adjusting only the quantity $\sigma L[O(^1D)]_0$ with k_1 and k_2 fixed to the literature values of $1.1\text{x}10^{-10}$ and $1.15\text{x}10^{-10}$ cm^3sec^{-1} respectively. Clearly the data of Fig. 1a strongly disagrees with the ratio of the accepted rate constants.

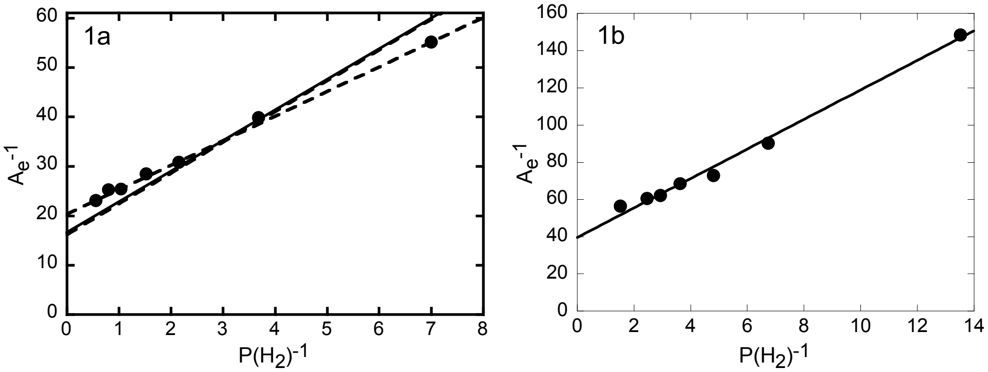

Fig. 1. In Fig. 1a, F(He)=1000 sccm; P(He)=12 torr; $F(N_2O)$=30 sccm; F(NO)=6 sccm; $F(H_2)$~10; 20; 35;50;75;100;150 sccm. The solid straight line assumes $k(H_2)=1.1\text{x}10^{-10}$, $k(N_2O)=1.15\text{x}10^{-10}$, $k(NO)=0.6\text{x}10^{-10}$ cm^3s^{-1}. The dashed line is the best linear fit of the points. In Fig. 1b, F(He)=10000 sccm; P(He)=63.22 torr; the other flows are essentially the same. The solid straight line assumes the rate constants above. The best straight line through the points is indistinguishable from the model line.

It occurred to us that the disagreement might be the result of hot atom chemistry. The photolysis of N_2O at 193 nm can produce $O(^1D)$ with a maximum translational energy of 166 kJ/mol. We estimate using a hard sphere collision model a fractional translational energy loss per collision with He of about 1/3. As many as one in ten collisions will be with H_2 at the highest H_2 pressures used so that some effects caused by translationally hot $O(^1D)$ seem quite possible. Fig 1b shows a Stern-Volmer plot of the same system with the helium flow rate raised tenfold with the flow rates of the reagents fixed. The agreement with the literature results is excellent.

BRANCHING IN THE REACTION OF $O(^1D)$ WITH METHANE

Since our methodology had not been previously tested, we decided to study a reaction system, $O(^1D) + CH_4$, which had been studied by several previous investigators using different methods. Even this simple reaction has several open channels:

$O(^1D) + CH_4 \rightarrow CH_3 + OH$ $\Delta H=-179\text{kJ/mol}$ (1a)
$\rightarrow CH_2OH + H$ $\Delta H=-172\text{kJ/mol}$ (1b)
$\rightarrow CH_3O + H$ $\Delta H=-128\text{kJ/mol}$ (1c)
$\rightarrow H_2CO + H_2$ $\Delta H=-473\text{kJ/mol}$ (1d)
$\rightarrow H_2CO + 2H$ $\Delta H=-37\text{kJ/mol}$ (1e)
$\rightarrow {}^1CH_2 + H_2O$ $\Delta H=-176\text{kJ/mol}$ (1f)

$$\rightarrow O(^3P) + CH_4 \qquad \Delta H=-439 kJ/mol \tag{1g}$$

With regard to the branching ratios, the recent JPL compilation[1] summarizes previous work and lists channel (1a) as 75±15%, (1b)+(1c) as 20±7% and (1d) as 5±5% and is silent concerning channels (1e) and (1f).

To measure the branching into channel (1a), we divide the intercept of the Stern-Volmer plot of the OH absorbance from $O(^1D) + H_2$ by the intercept of the Stern-Volmer plot of the OH absorbance from $O(^1D) + CH_4$ and obtain 67±5% for channel 1a. To measure the sum of channels (1d)+(1e), we compare the formaldehyde absorbance to the OH absorbance under the same conditions

$$\frac{(1d)+(1e)}{(1a)} = \frac{\sigma(H_2CO)}{\sigma(OH)} \quad \frac{S(H_2CO)}{S(OH)}$$

using the HITRAN integrated absorption cross-section and the measured linewidths at the elevated He pressure of 66 Torr to calculate the σ's. The resulting total fraction into (1d)+(1e) is 5%.

To our knowledge, channel (1f) has never been observed previously. We observed that when N_2O is photolyzed in the presence of a mixture of CH_4 and CD_4 infrared absorptions of H_2O and D_2O, but not of HDO appear. This is compelling evidence for channel (1f). Because of H_2O background absorptions, measuring this yield for the normal system does not seem feasible. We measure the branching ratio into (1f) by dividing the D_2O signal in the N_2O and CD_4 system (at high pressures of CD_4) by the D_2O signal obtained with the same partial pressure of N_2O in a system flooded with D_2 containing sufficient CD_3CDO to convert all the OD produced by $O(^1D) + D_2 \rightarrow OD + D$ is converted into D_2O through reaction with CD_3CDO (see the first section). This gives the branching into (1f) for the D system of 8±2%.

To measure the sum (1c) + (1d) + 2(1e), we determine the total OH yield with NO_2 as the source of $O(^1D)$ using the same Stern-Volmer intercept approach making use of the reactions

$$O(^1D) + H_2 \rightarrow OH + H \tag{2}$$

$$H + NO_2 \rightarrow OH + NO \tag{3}$$

to obtain

$$(1a) + (1b) + (1c) + 2(1e) = \frac{2*(\text{SV intercept of OH from } H_2)}{\text{SV intercept from } CH_4}$$

The sum (1a) + (1b) + (1c) + 2(1e) resulting is about 97±10%.

Summarizing all our measurements, we have (1a)+(1d)+(1e)+(1f) = 80% from direct measurements assuming that the D_2O yield of 8% for (1f) is applicable to the H_2O system. Assuming no other channels are present, (1b)+(1c)=20%. Substituting this last result together with (1a)=67%, we have 2(1e)=(97-67-20)%=10% or (1e)=5%. Since (1d)+(1e) = 6%, we conclude that we can account for all the observations without a need for (1d), i.e. the production of H_2, but (1e) is definitely needed. Because the uncertainties are large, whether (1d) is actually absent is unclear.

An interesting observation is that the yield of CH_2O when NO_2 is photolyzed to produce $O(^1D)$ is three times higher than obtained when N_2O is photolyzed with the extra CH_2O being produced at longer reaction times (10-100 μsec). CH_3O reacts with NO_2 primarily by a three body reaction that forms an adduct, with less than 3% of the reaction occurring via a bimolecular reaction to form CH_2O,[2] and no other carbon-containing radicals are formed in 12% yield. We believe most of the additional CH_2O results from the reaction of CH_2OH with NO_2 suggesting that (1b)>>(1c).

The ratio of the overall rate constant of the CD_4 reaction to the overall rate constant of the $O(^1D) + N_2O$ reaction was determined to be $1.2_5 \pm 0.1$. A measurement of the reaction of $O(^1D)$ with NO_2 gave 1.3×10^{-10} molecule^{-1}cm^{3}sec^{-1} relative to the literature values for the rates of $O(^1D)$ with H_2 and CH_4.

PRODUCT YIELDS IN THE REACTION OF $O(^1D)$ WITH ACETALDEHYDE

We were involved in measuring the yields into the following reaction channels:

$O(^1D) + CH_3CHO \rightarrow CH_3 + CO_2 + H$ $\Delta H = -262.6$ kJ/mol (2a)
$\rightarrow CH_3 + HCO_2$ $\Delta H = -281.2$ kJ/mol (2b)
$\rightarrow CH_3 + HOCO$ $\Delta H = -350.1$ kJ/mol (2c)
$\rightarrow CH_2OH + HCO$ $\Delta H = -261.8$ kJ/mol (2d)
$\rightarrow CH_3O + HCO$ $\Delta H = -213.7$ kJ/mol (2e)
$\rightarrow OH + CH_3CO$ $\Delta H = -258.4$ kJ/mol (2f)
$\rightarrow CH_4 + CO_2$ $\Delta H = -741.4$ kJ/mol (2g)
$\rightarrow H + CH_2OHCO$ $\Delta H = ?$ (2h)

At pressures of 13 Torr (mostly He buffer), we observed infrared absorption lines of CH_3, HCO, OH, CH_4 and CO_2 from this reaction, but were unable to observe any transient absorption signals at the known frequencies of the strongest lines of the HOCO OH stretch fundamental. We observed H indirectly through the NO_2 precursor method described above. Our qualitative observations were that H is a major product and HCO, OH, CH_4 and CO_2 are relatively minor products.

Reference

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Publications

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