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(Statement A)

Kinetics of CH Radicals With O₂: Evidence for CO-Chemiluminescence in the Gas Phase Reaction

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ABSTRACT

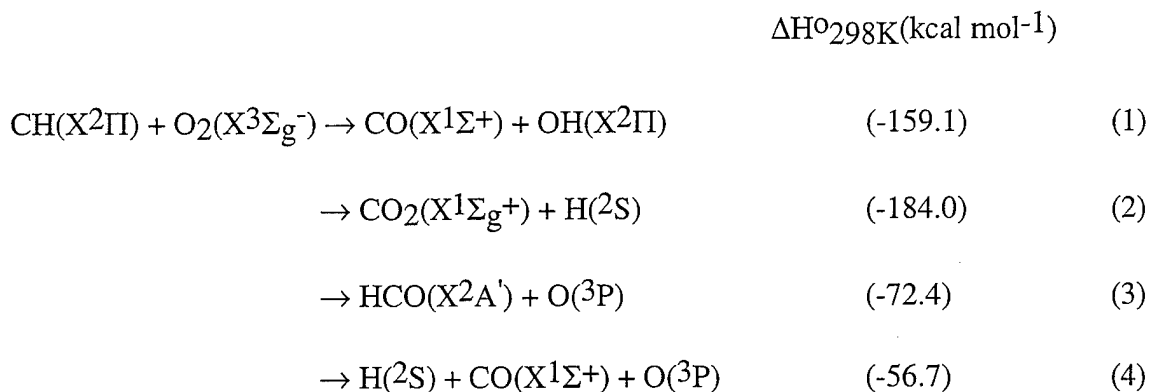
Production of CO vis-uv-chemiluminescence has been observed for the first time in the gas phase reaction of photolytic-methylidyne radicals with molecular oxygen. A trace amount of CHBr₃ vapor was photo-decomposed in a pulsed-photolysis reactor using a 248-nm laser under multi-photon-dissociation conditions to produce the CH(X²Π) radicals in an excess of O₂ in diluent helium carrier gas at 2.0 torr and 298 K. The time resolved chemiluminescent traces due to characteristic CO(A-X), CO(a-X) and CO(d-a) vibronic emissions were recorded at several band positions. 147.8 nm was the shortest wavelength at which CO emission was recordable. The integrated intensities of the CO emissions showed a quadratic dependence on the photolysis fluence employed as did the OH(A-X) emission in the (1-0) band. The dependence of the OH and CO chemiluminescence on [O₂] was studied to obtain the rate coefficient(s) for the

chemiluminescent reaction(s). The data is best interpreted by postulating that $\text{CH}(v'' \geq 0)$ reactions with O_2 lead to the observed CO-emissions as well as the well-known OH-chemiluminescence.

INTRODUCTION

The methylidyne (CH) radical is known to be an important reaction intermediate during the oxidation of hydrocarbon fuels. Its reactivity with combustion species such as O_2 , O-atoms, CO_2 , N_2 , N_2O , NO, NO_2 , NH_3 and numerous other hydrogenous, carbonaceous and sulfurous species is well reviewed^{1,2} and compiled in the literature.³ However, the nature of product branching, energy disposal and its theoretical treatment has been examined in only a few of these reactions; (CH + NO) and (CH + N_2) reactions by far being the most studied systems. Particularly lacking in the literature is information on the production of electronically excited state species. The methylidyne and the methylene (CH_2) radical reactions with O_2 and O-atoms are thought to play an important role in the production of ultraviolet/visible chemiluminescence when the Space Shuttle plume interacts with the earth's ambient atmosphere.⁴ Our results on the (CH + O-atoms), (CH_2 + O-atoms) and (CH_2 + O_2) reaction systems will be the subject of detailed discussions in future publications.

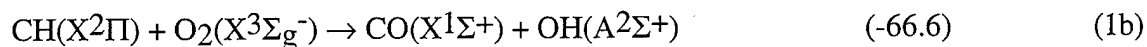
For the O₂ reaction with ground state CH, a number of exothermic channels (with ground state products) are possible:



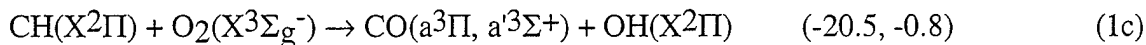
Overall bimolecular rate coefficient measurements have previously been reported over a wide range of temperature ($T = 13\text{-}3500\text{ K}$) and Ar or He pressure ($P = 2\text{-}350\text{ torr}$).⁵⁻¹⁸ No pressure dependence of the rate coefficient has been found in this range, and for ($700\text{ K} \leq T \leq 300\text{ K}$), the rate coefficient has a constant value, as it does in the 2200-3500 K range, though here it is a factor of 3-4 higher¹¹⁻¹² than the room temperature value. The room temperature value lies in the range $(2.3\text{-}5.9) \times 10^{-11}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$ amid the various reported works, except that of Duncanson and Guillory⁹ who reported a much smaller value of $2.1 \times 10^{-12}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$. In the $T = 13\text{-}300\text{ K}$ range, however, the rate coefficient shows a strong negative temperature dependence of $(3.8 \pm 0.7) \times 10^{-11}(T/298)^{-0.48}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$.¹⁰ The non-Arrhenius behavior exhibited by the rate coefficient, over the extended 13-3500 K range, may be as a result of a change in the reaction mechanism and/or changes in the branching ratios into different product channels, as determined by the influence of the temperature on the transition state properties of the reaction. Recently, Okada and co-workers¹³ reported a small OH(X²Π)

product yield of ~ 0.20 in the reaction at 297 K. Their theoretical calculations on the potential energy surface for this reaction suggests that a $[\text{HCO}_2]^*$ reaction intermediate is most likely involved and it dissociates into products, principally, via channels (1) and (2). During the tenure of this work, we became aware of Bergeat and co-workers¹⁸ estimates for the branching ratios of 20%, 30%, 20%, and 30% for channels (1), (2), (3), and (4), respectively determined by direct observations of O-atom and H-atom yields, and statistical calculations on the corresponding reaction intermediates identified by *ab initio* methods. Previously, Lin⁸ had observed strong CO_2 and CO ir-emissions, as a result of vibrational excitation, presumably through their direct formation in channels (2) and (1), respectively.

The availability of $159.1 \text{ kcal mol}^{-1}$ of enthalpy in channel (1) can provide a means of exciting one of the reaction products into a higher electronic state. Previously,^{5,7,8,14,18,19,20} ultraviolet chemiluminescence attributable to the formation of electronically excited hydroxyl radicals has been reported in this reaction:



The reaction is thought, in part, to be responsible for the strong characteristic $\text{OH}(A \rightarrow X)$ emissions in hydrocarbon flames.²⁰ Grebe and Homann,¹⁴ and Porter et al.¹⁹ have provided estimates for the 298 K yield of $\text{OH}(A^2\Sigma^+)$ to be ~ 0.0048 and ~ 0.0060 , respectively. Electronically excited carbon monoxide may form in channel (1c):



Depending on the extent of vibrational excitation in the methylidyne radicals used, higher electronic states of CO such as ($d^3\Delta$) and ($A^1\Pi$) might also be possible. These CO states should experimentally be readily observable through their ultraviolet emissions in the ($a^3\Pi \rightarrow X^1\Sigma^+$) Cameron system, ir/visible emissions in the ($a'^3\Sigma^+ \rightarrow a^3\Pi$) Asundi and ($d^3\Delta \rightarrow a^3\Pi$) Triplet systems, and vuv emissions in the ($A^1\Pi \rightarrow X^1\Sigma^+$) 4th Positive system. Similarly, in channel (3) the excess enthalpy could be available to produce electronically excited formyl radicals in the (\tilde{A}^2A'') state. However, the strongly predissociative nature of this state might preclude one from seeing emissions in its 460-860 nm band system. The other possibilities of O(1D) formation in this channel or of CO₂(A^1B_2) formation in channel (2) remain to be verified experimentally.

In this paper we present first ever measurements of the time-resolved CO vis-uv-emission profiles observed when CHBr₃ vapor is photo-dissociated at 248 nm in the presence of O₂ in helium bath gas at 2.0 torr and 298 K. The observations are discussed in terms of the ($\text{CH}(v'' \geq 0) + \text{O}_2$) reaction as the likely source of the chemiluminescence. It is to be noted that Bergeat et al.¹⁸ recently mentioned seeing CO($a^3\Pi, v' \leq 4 \rightarrow X^1\Sigma^+$) chemiluminescence in their flow-tube work on the CH + O₂ reaction. However, no actual data was reported in their paper and they could not rule out the possible contribution to the signal from secondary reaction chemistry of O-atoms with the CH.

EXPERIMENTAL TECHNIQUE

The pulsed-photolysis apparatus used in this work has previously been described in detail elsewhere.^{21,22} Here we only give the experimental procedures used to record the chemiluminescence data. A minute amount of CHBr_3 (bromoform) vapor entrained in a small flow of He was sent into an ultraviolet photometric cell to determine its gas phase concentration before diluting it further in a larger flow of He carrier gas containing a known excess of O_2 . An uv-absorption cross-section, $\sigma_{213.9\text{-nm}}$, of $524 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ for the CHBr_3 was used.²³ Previously calibrated electronic mass flow transducers, chromel-alumel thermocouples and capacitance manometers were used to introduce the gases into the photolysis reactor and monitor the system's temperature (typically 298 ± 2 K) and pressure (2.0 ± 0.1 torr). A collimated 248-nm beam from a pulsed excimer laser (width ~ 20 ns, full-width at half-maximum, FWHM) operating at 10 Hz was gently focused into the photolysis reactor and its fluence determined at a disc colorimeter positioned at the exit window of the reactor. Typically $(1-2) \times 10^{12} \text{ molec cm}^{-3}$ of CHBr_3 was subjected to 5-40 mJ/pulse of laser energy to produce transient levels of CH concentrations via multi-photon dissociation of the bromoform.²⁴⁻²⁸ The photolysis reactor was operated under quasi-static gas flow conditions. That is, the He flow was sufficiently rapid to ensure that the reaction zone was replenished with a fresh mixture of the photolyte upon each laser pulse, but was slow enough to be considered static when compared to the time scale of the chemical reaction of the CH radicals with the O_2 ($(7-100) \times 10^{13} \text{ molec cm}^{-3}$), plus with the undissociated CHBr_3 , and also to a lesser extent with any other species produced in the photolysis. The vis-uv-chemiluminescence that ensued from the detection zone was monitored perpendicular to the photolyzing beam by imaging the radiation onto the entrance

slits of two different scanning spectrometers positioned opposite to each other. The operating ranges of the spectrometers were 110-360 nm and 200-900 nm, and had, respectively, band-passes set to 1.9 and 2.2 nm, FWHM. Appropriate long-pass glass filters were placed in front of the spectrometer when recording visible emissions to block the strong uv-radiation from entering the instrument and thus prevent any coincidental detection of its *higher-order* diffracted signal. The photomultipliers used to detect the radiation were configured for single-photon counting detection, the outputs of which were sent for recording at two separate multi-channel scalers controlled by a microcomputer. Time-resolved temporal profiles of the chemiluminescence, at several discrete CO and OH vibronic band positions, were recorded using dwell-time resolutions in the range of 2 to 10 μ s. 50000 chemiluminescent traces were typically co-added at the computer to improve the signal-to-noise ratio of each of the data sets. Chemiluminescence data was also recorded in the presence of O-atoms generated through O₂/He or N₂O/He microwave discharges.²¹

Materials

He (> 99.9997%) from Air Products, N₂O (99.99%) from Matheson Gas Products and O₂ (99.991%) from Big Three Industry were used as received. CHBr₃ (> 99.5%) from Aldrich Chemicals was subjected to several freeze-thaw purification cycles at a grease-less vacuum line and stored in a darkened liquid bubbler. NO₂ (99.9%) from M. G. Scientific Gas was mixed with excess O₂ to react away any NO present and the mixture collected in a trap over silica gel at 213 K. The excess O₂ and any other volatiles were pumped off and the condensate subjected to

several freeze-thaw purification cycles. A standard 10% NO₂ in He titration mixture was prepared for use when the [O-atom] in reactor needed quantifying.²¹

RESULTS AND DISCUSSION

OH(A-X) Chemiluminescence

Since the bromoform photolyte concentration, [CHBr₃]₀ employed was typically ~ 2 x 10¹² molec cm⁻³ or less, the maximum initial methylidyne concentration, [CH]₀, possible in the photolysis will be set by this limit if one assumes complete beaching of the photolyte under sufficiently intense laser field conditions. However, our experimental conditions are far from this limit as evident from the observed quadratic variation in the OH chemiluminescence intensity with the 248-nm laser fluence, E₂₄₈(photons/cm²/pulse) employed. Despite the frequent use of CHBr₃ as the preferred photolyte for CH production,²⁴⁻²⁷ the details of how the 'molecule' undergoes dissociation remains unclear. The continuous absorption spectrum in the 190-362 nm range suggests that, like other simple halides, CHBr₃ should undergo unit dissociation at conditions for *single-photon* absorption in the long-wavelength-tail of the spectrum to give (HCBBr₂ + Br) as the principle products,²⁹ which we expect to be present in our 248-nm photolysis with relatively high concentrations in the range of ~ [CHBr₃]₀/10. However, the relative contributions from (Br₂ + HCBBr)³⁰ or (CBr₂ + HBr)⁸ or (CBr₃ + H) if any (especially when short-wavelength photolysis is employed) remain to be determined. In the non-

linear absorption regime, $\sigma_{248} E_{248} \geq 1$, which is easily attained when a focused laser beam of moderate fluence is used, the '*CHBr₃-photolyte*' exhibits a strong tendency to undergo *2-photon* and *3-photon* dissociation. In the most recent work by Lindner and co-workers,²⁸ a three-step *sequential-absorption* mechanism for the production of electronically excited methylidyne radicals, CH(A) was proposed through successive photo-fragmentations of the HCB_r2 and HCB_r intermediates at 248 nm. They observed a $(E_{248})^3$ dependence of the total spontaneous emission due to CH(A→X) in their photolysis experiments. Upon second-photon absorption, the HCB_r2 intermediate may also very likely yield ground state CH plus Br₂ as alternate products to (Br + HCB_r). Thus, one can expect the absolute yields of [CH(X)] to be of the order of $\sim [CHBr_3]_0/100$ and [CH(A)] of the order of $\sim [CHBr_3]_0/1000$ if the second-step and third-step absorptions are comparable to that for the first photon. Any CH(A) formed in the photolysis will be expected to rapidly relax to the ground X state, through (A→X) diagonal emissions at ~ 431 nm. The ($v'=0$) level in the A state has a *collision-free* radiative lifetime of ~ 526 ns.³¹ Similarly, the higher electronic B and C states, which form at even more minuscule levels compared to the A state,^{7,32} will also rapidly radiate to the ground X state.³³

Hence, if we neglect the small contribution from (A→X) relaxation to the total CH(X) yield in our experiments, the observed variation of $[CH(X, v'' \geq 0)]_0$ with the laser fluence is expected to be quadratic in the photolysis. We have confirmed this by measuring the variation in the OH(A→X) chemiluminescence intensity at ~ 282 nm in the (1-0) band with the laser fluence employed when a small excess of O₂ was present in the reactor. (This wavelength is chosen since there is minimum inference in the OH(A) measurements from other sources of radiation

such as that possible from CO(a→X) emissions.) Since $[\text{CH}]_0$ is very low compared to $[\text{O}_2]$ and $[\text{CHBr}_3]_0$, the methylidyne is expected to react away under pseudo-first-order conditions with these species as the contribution from its self-reaction^{34,35} will be negligible in our photolysis. It can be shown that:

$$[\text{OH}(\text{A}, v'=1)] = k_{1b(v'=1)}[\text{CH}]_0[\text{O}_2]\{\exp(-k_{\text{CH}}t) - \exp(-k_{\text{OH}(\text{A}, v'=1)}t)\}/(k_{\text{OH}(\text{A}, v'=1)} - k_{\text{CH}}) \quad (5)$$

Where $k_{\text{CH}} = k_{\text{O}_2}[\text{O}_2] + k_{\text{CHBr}_3}[\text{CHBr}_3] + k_{\text{loss}}$ is the pseudo-first-order rate coefficient for $[\text{CH}]$ decay in the system, with k_{O_2} and k_{CHBr_3} as the second-order bimolecular rate coefficients for reaction of ground state CH with O_2 and CHBr_3 , respectively. k_{loss} is the sum of first-order loss rate terms for diffusion of CH out of the reaction volume and for reaction with any background species that may be present in the photolysis mixture. $k_{1b(v'=1)}$ is the specific branching rate coefficient for the channel that gives $\text{OH}(\text{A}, v'=1)$ as the product in the $(\text{CH} + \text{O}_2)$ reaction. As a first approximation, energy transfer processes such as $\text{OH}(\text{A}, v' > 1) \rightarrow v'=1$ via collisional quenching or via radiative-cascading are ignored in Equation (5), since pre-dissociation will essentially be the dominant loss mechanism for $v' \geq 2$ states. (Bergeat and co-workers¹⁸ simulated their OH emission spectrum to arrive at the values of 32% and 68% for the relative vibrational population, respectively, in the $v'=1$ and 2 levels for the $\text{OH}(\text{A})$ product in this reaction.) $k_{\text{OH}(\text{A}, v'=1)} = k_{\text{rad}(v'=1)} + k_{q, \text{O}_2}[\text{O}_2] + k_{q, \text{CHBr}_3}[\text{CHBr}_3] + k_{\text{OH}(\text{A}, v'=1)\text{loss}}$ is the pseudo-first-order rate coefficient for $[\text{OH}(\text{A}, v'=1)]$ decay in the system, with k_{q, O_2} and k_{q, CHBr_3} as the second-order bimolecular rate coefficients for quenching (vibrational and electronic) of $[\text{OH}(\text{A}, v'=1)]$ by O_2 and CHBr_3 , respectively. $k_{\text{rad}(v'=1)}$ and $k_{\text{OH}(\text{A}, v'=1)\text{loss}}$ are, respectively, the $[\text{OH}(\text{A}, v'=1)]$ first-

order rate coefficients for radiative decay to the ground electronic state and the sum of loss rate terms for diffusion of $\text{OH}(A, v'=1)$ out of the detection volume and for reaction with any background impurities.

The 282-nm OH chemiluminescence intensity, I_{282} in the experiment will thus be expected have a time profile governed by equation (5), where immediately after the laser photolysis, there will be a fast exponential rise in the signal followed by a slower exponential decay determined by the values of $k_{\text{OH}(A, v'=1)}$ and the k_{CH} , respectively. Since the value of $k_{\text{OH}(A, v'=1)}$ is very large (which is dominated by the short radiative lifetime of the $\text{OH}(A, v'=1)$ state) and our shortest time resolution is 2 μs , experimentally we expect to see an instantaneous rise (within $\leq 4 \mu\text{s}$) in the I_{282} signal followed by its single-exponential decay. The integrated I_{282} intensity over this decay time (or even the initial I_{282} height) will be directly proportional to the initial yield of $[\text{CH}]_0$ in the photolysis, and therefore to $(E_{248})^2$ employed for fixed conditions in $[\text{CHBr}_3]_0$ and $[\text{O}_2]$. In Figure 1, $\ln[\text{integrated } I_{282} \text{ intensity}]$ of the chemiluminescence curve like the one shown in Figure 2 is plotted as a function of $\ln[E_{248}]$. A linear-least-squares fit to the data points yields a value of (1.96 ± 0.22) for the slope thus confirming the *2-photon* production of CH in the photolysis. The decay curve of Figure 2 represents the net chemiluminescence signal after having subtracted the scattered background radiation due to the phosphorescence induced in the quartz windows and walls of our reactor by the laser pulse. The above result is consistent with the recently reported (2.1 ± 0.2) photon dependence of the methylidyne radical yield, measured directly by its LIF detection, during 248-nm bromoform photolysis.³⁶

The chemiluminescence trace of Figure 2 shows a slightly faster decay component at early times (20~150 μ s) than that at longer reaction times. This could arise as a result of contribution to the [CH] decay from the methylidyne self-reaction. However, the [CH]₀ is too low in our experiments for this reaction^{34,35} to significantly compete with other first-order loss processes for CH. Also, a variation in the E₂₄₈ employed by a factor of 4 to create the CH radicals had no effect on the observed 'degree of curvature' of the decays thus indicating that (CH + radical) reactions are not important in the photolysis. A possible explanation for the observed faster initial decay in the chemiluminescence trace is that the data represents chemiluminescence arising from an ensemble of CH(X) radicals in different vibrational levels reacting with the O₂ at slightly different rates. Many previous studies^{13,16,27,37} have confirmed the production of CH(X, v'' \geq 0) in CHBr₃ photolysis by direct laser-induced fluorescence detection. Estimates of the initial vibrational population, P_{v''=i} in the ratio 1.0:0.26:0.07 for P_{v''=0}:P_{v''=1}:P_{v''=2} at 193 nm¹³ and 1.0:0.17 for P_{v''=0}:P_{v''=1} at 248 nm¹⁶ have been reported. To our knowledge, the relative yields for vibrational excitation in v''=3 and higher levels have not been measured. In 2 torr of He, complete thermalization of rotational levels in any given v''-level of the X state is expected to be achieved in \leq 4 μ s via rotational energy transfer (RET) collisions. (Very large RET rate coefficients, comparable to the *Gas-Kinetic-Limit*, for He have previously been reported for CH(A, v'=0) and CH(B, v'=0).³⁸) However, vibrational energy transfer (VET) in the ground X state is known to occur relatively slowly in room temperature helium, with rate coefficients of 1.0 x 10⁻¹⁴ and 2.2 x 10⁻¹⁴ cm³ molec⁻¹ s⁻¹, respectively, for v''=1 and v''=2 recently being reported by Blitz et al.³⁷ Hence in our experiments, the chemical reactions of O₂ and CHBr₃^{15,37,39} can effectively compete with

VET by He in removing $\text{CH}(X, v'' > 0)$. The $(\text{CH}(v''=1) + \text{O}_2)$ rate coefficient has previously been measured. Duncanson and Guillory⁹ reported a room temperature value of $4.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ which is \sim twice their value for the corresponding ground state $(\text{CH}(v''=0) + \text{O}_2)$ reaction. However, Mehlmann and co-workers¹⁶ reported a 298 K value of $(4.1 \pm 0.5) \times 10^{-11}$ for the $\text{CH}(v''=1)$ reaction and $(3.3 \pm 0.2) \times 10^{-11}$ for the $\text{CH}(v''=0)$ reaction, i.e. a difference of only $\sim 25\%$, while Okada and co-workers¹³ saw no difference and reported the values, $(3.4 \pm 0.8) \times 10^{-11}$ and $(3.5 \pm 0.3) \times 10^{-11}$, respectively, at 297 K.

Our computer simulations for the production of $\text{OH}(A, v'=1)$ with an assumed initial $\text{CH}(v'')$ pollution ratio, $P_{v''=0}:P_{v''=1}:P_{v''=2}$ in the range from 1:0.1:0.05 to 1.0:0.2:0.1, and reactivity ratio, $k_{\text{CH}(v''=0)}:k_{\text{CH}(v''=1)}:k_{\text{CH}(v''=2)}$ of $3.0 \times 10^{-11}:4.5 \times 10^{-11}:6.0 \times 10^{-11}$ produced curvatures in the $\text{OH}(A)$ profiles that were in qualitative agreement with the observed OH -chemiluminescence. An alternative explanation for the curvature which would also equally be valid is one in which there is fast $\text{OH}(A)$ production from O_2 reaction with a hot radical species other than $\text{CH}(v'' \geq 1)$ produced in the bromoform dissociation. The most likely candidate might be the bromomethylene radical. We are not aware of any reported rate coefficient or product distribution data for the $\text{CHBr} + \text{O}_2$ reaction, though CHBr^* produced in 2-photon bromoform photolysis could have sufficient internal excitation to produce $\text{OH}(A)$. The yield of $\text{OH}(A)$ would be determined by any competition from helium in quenching CHBr^* to the ground state. However, further evidence that $\text{CH}(v'' > 0)$ has a higher reactivity towards O_2 compared to $\text{CH}(v''=0)$ comes from our examination of the observed CO -chemiluminescence data as explained in the next section.

CO vis-uv-Chemiluminescence

Reaction (1) is $159.1 \text{ kcal mol}^{-1}$ exothermic for ground state reactants and products ($\text{CH} + \text{O}_2 \rightarrow \text{OH} + \text{CO}$). Therefore, if a reactive channel is available to electronically excite the carbon monoxide, vibrational excitations of up to $v'=4$ in the $\text{CO}(a)$ state could be achievable. Hence only Cameron band emissions with wavelengths longer than $\sim 179.7 \text{ nm}$ would be possible from the photolysis mixture. However, in our experiments band emissions were discernable for wavelengths as short as $\sim 147.8 \text{ nm}$. The observed band spectrum in the vacuum-ultraviolet was reminiscent of the $\text{CO}(A, v' \leq 2 \rightarrow X)$ 4th Positive system. The signal-to-noise ratio of the data (for $\frac{1}{2}$ -second integration) to the blue of this wavelength limit was too poor to conclusively identify any higher vibrational excitations in the $\text{CO}(A)$ state. Hence the data implies that up to $\sim 34.3 \text{ kcal mol}^{-1}$ of extra energy in the reaction co-ordinate is involved, which could be provided by having excited methylidyne radicals $\text{CH}(v'' \geq 5)$ available for reaction with the O_2 .

Alternatively, the CO-chemiluminescence in the present experiments could arise from the reaction of O-atoms with the methylidyne radicals (or any other suitable bromoform-photofragment). In separate experiments, where we have produced a known excess of O-atoms in the absence of O_2 , we have seen strong CO vis-uv-emissions in the $(\text{CH} + \text{O})$ reaction.⁴⁰ Since the 248-nm photon energy ($\sim 115.3 \text{ kcal mol}^{-1}$) is less than the convergence limit of $\sim 119.2 \text{ kcal mol}^{-1}$ for the forbidden (and therefore weak) Herzberg I, II, and III bands, no photolytic O^3P formation is expected from ground state $\text{O}_2(X^3\Sigma_g^-)$ due to excitations into any

of these three ($A^3\Sigma_u^+$, $A^3\Delta_u$, and $c^1\Sigma_u^-$) Herzberg states. However, dissociation can be achieved from vibrationally excited O_2 .^{41,42} At 298 K, a population ratio, $P_{v''=1}:P_{v''=0}$, of $\sim 5 \times 10^{-4}$ is to be expected, thus $\sim (3.5-50) \times 10^{10}$ molec cm^{-3} of $O_2(v''=1)$ would nominally be available in our experiments for *hot-band* dissociation. We estimate⁴³ this can lead to only $\sim (4-60) \times 10^5$ molec cm^{-3} of O^3P under the typical laser fluences used in this work, and thus would be a negligible source for detecting any CO vis-uv-emissions. Another potentially stronger source of O^3P might be via *multi-photon* absorption by the O_2 . Although (2+1) REMPI of $O_2(X^3\Sigma_g^-)$, via *2-photon* ($3s\sigma$) $^3\Pi_g$ and ($3s\sigma$) $^1\Pi_g$ Rydberg state excitations followed by their ionization with the *third-photon*, using a tunable *narrowband* dye laser radiation in the 275-306 nm range, has been observed by direct O_2^+ ion detection,^{44,45} we are not aware of any REMPI data near 248 nm, or of any quantitative measurements addressing how the relative yield for ionization compared to atomic fragmentation varies upon the laser intensity employed once the Rydberg states have been prepared in the *2-photon* adsorption by $O_2(X^3\Sigma_g^-)$. We expect our use of the *broadband* 248-nm excimer laser radiation to be a very inefficient source for O_2 REMPI processes or O-atom generation as explained below. If significant photolytic atomic oxygen production (i.e. $[O]_0 \gg [CH]_0$) was taking place, we would expect the integrated CO-chemiluminescence signal to show a $(f_{(CO^*,O_2)}k_{O_2}[O_2] + f_{(CO^*,O)}k_O[O])_0[CH]_0$ dependence, where k_O is the second-order rate coefficient for reaction of methylidyne radicals with O-atoms, and $f_{(CO^*,O_2)}$ and $f_{(CO^*,O)}$ are the phenomenological branching fractions, respectively, in (CH + O_2) and (CH + O) reaction channels that produce the electronically excited carbon monoxide. If $f_{(CO^*,O_2)}k_{O_2}[O_2] \ll f_{(CO^*,O)}k_O[O]_0$ (i.e. negligible CO-chemiluminescence production in reaction

(1c)), an $(E_{248})^{(2+n)}$ laser fluence dependence for CO-chemiluminescence signal would be expected, with $n=1$ for *hot-band* O₂ photolysis only, and $n \geq 2$ for *multi-photon* O₂ dissociation only, since $[CH]_0$ has been shown to be proportional to $(E_{248})^2$ in our experiments. On the other hand if $f(\text{CO}^*,\text{O})k_{\text{O}}[\text{O}]_0 \ll f(\text{CO}^*,\text{O}_2)k_{\text{O}_2}[\text{O}_2]$, an $(E_{248})^2$ laser fluence dependence would be expected.

Experimentally, the Cameron band (215.8-nm) and the 4th Positive system (159.7, 165.3 and 171.2-nm) emissions were all observed to have quadratic laser fluence dependences as shown in Figure 3. Since we have shown elsewhere the production of CO* to be relatively much more efficient in the (CH + O) system compared to that in (CH + O₂), with $(f(\text{CO}^*,\text{O})k_{\text{O}}/f(\text{CO}^*,\text{O}_2)k_{\text{O}_2})$ to be at least ~ 70 ,⁴⁰ the data of Figure 3 implies negligible O-atom production in the present experiments. Similarly, an analysis for the ($d^3\Delta, v'=3 \rightarrow a^3\Pi, v''=0$) Triplet emission intensity at ~ 643.6 nm gave an $(E_{248})(1.88 \pm 0.17)$ photolysis fluence dependence.

Besides the vibrationally excited methylidyne radicals, other vibrationally excited carbonaceous species such as CBr₃^{*}, CHBr₂^{*}, CBr₂^{*}, CHBr^{*} and CBr^{*} could also be present in our photolysis reactor. Even if all of the excess 248-nm photon energy were available as internal energy in the tribromomethyl radical during its *one-photon* formation from CHBr₃, its reaction with O₂ would be endothermic by $\geq \sim 80.5$ kcal mol⁻¹ for (CO(a) + BrO + Br₂) formation, and therefore not important in our experiments for any electronically excited CO. Similarly, the O₂ reaction with CHBr₂^{*} can be ruled out since it would be $\geq \sim 25.2$ kcal mol⁻¹ endothermic for

(CO(a) + HOBr + Br) formation, and the $\text{CBr}_2^* + \text{O}_2 \rightarrow \text{CO(a)} + \text{BrO} + \text{Br}$ reaction $\geq \sim 38.7$ kcal mol⁻¹ endothermic if CBr_2^* was produced in *one-photon* CHBr_3 photolysis, and $\geq \sim 20.4$ kcal mol⁻¹ endothermic if formed in a *2-photon* process via CBr_3^* or CHBr_2^* fragmentation. However, the $\text{CHBr}^* + \text{O}_2 \rightarrow \text{CO(a)} + \text{HOBr}$ reaction would be $\leq \sim 20.8$ kcal mol⁻¹ exothermic for internally excited bromomethylene produced directly from CHBr_3 and $\leq \sim 75.6$ kcal mol⁻¹ exothermic when produced from subsequent CHBr_2^* photo-fragmentation. Since the former CHBr^* source can only give $\text{CO(a}, v' \leq 4 \rightarrow \text{X})$ emissions (and would show a linear photolysis fluence dependence), our observations of the $\text{CO(A}, v' \leq 2 \rightarrow \text{X})$ 4th Positive system (with quadratic photolysis fluence dependence), requires that copious amounts of bromomethylene radical be formed in very high v'' -levels from the latter source. We are not aware of any measurements reporting the relative yield of CHBr (or its internal state distribution) compared to CH formation in the photodissociation of bromoform. Also, the $\text{CBr}^* + \text{O}_2 \rightarrow \text{CO} + \text{BrO}$ reaction could be up to ~ 193.9 kcal mol⁻¹ exothermic to excite the CO up to $v'=2$ in the A-state. However, based on reactivity trends³ of ground-state halo-methyenes and halo-carbenes the reactions of CHBr and CBr ⁴⁶ with O_2 are expected to be too slow under our experimental conditions to be of any significance as explained in the next section.

CH($v'' \geq 0$) + O₂ Rate Coefficients

The strong 4th Positive CO-chemiluminescence was seen to decay exponentially in this work (see Figure 4). An expression analogous to equation 5 can be derived to describe the temporal behavior of $[\text{CO}^*]$. When the first-order decay rate coefficients are plotted as a

function of O₂ used, the second-order bimolecular rate coefficient for the methylidyne + O₂ reaction is determined (see Figure 5). The values obtained when monitoring the 165.3-nm and 159.7-nm bands were, respectively, $(6.27 \pm 0.60) \times 10^{-11}$ and $(6.63 \pm 0.64) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹. When the much weaker Triplet emission at 601.6 nm was examined, again exponential decays were seen and this gave a rate coefficient value of $(5.23 \pm 0.87) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹. The 171.1 kcal mol⁻¹ enthalpy of the CH(X,v''=4) radical, which could form in the 2-photon photolysis of CHBr₃, would be sufficient to produce the CO* in (A¹Π,v'=0) and (d³Δ,v'=4) electronically excited states that radiate, respectively, in the above vuv and visible bands. The fact that the decays were exponential suggests that there is little CH(X,v''>4) produced in the photolysis to cause interference or that the reactivity of CH(X,v''>4) is comparable to that of CH(X,v''=4) for the O₂ reaction. Our detection of a chemiluminescent band at ~ 147.8 nm suggests that there is some CH(X,v''=5) formed in the CHBr₃ photolysis. Thus the measured average value of $(6.04 \pm 0.59) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹ for the CH(X,v''=4) radical is much larger than that for CH(X,v''=0) which we can estimate from the observed phenomenological decay rates of the CO(a³Π,v'=0 → X¹Σ⁺,v''=1) Cameron band emission at 215.8 nm and the OH(A²Σ⁺,v'=1 → X²Π,v''=0) band emission at 282.2 nm. As discussed earlier, since reaction of all methylidyne radicals, CH(X,v''≥0) with O₂ can lead to CO(a³Π,v'=0) and OH(A²Σ⁺,v'=1) formation, the decay data was fitted at the longest reaction times possible in order to get limiting values for the first-order decay coefficients. This is shown in Figure 5 for the 282.2-nm chemiluminescence (open squares), which yields a value of $(2.70 \pm 0.49) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹ for the (CH(v''→0) + O₂) bimolecular reaction rate coefficient. When the early portion of the chemiluminescence decay is fitted, the phenomenological bimolecular rate coefficient was

slightly and consistently higher with a value of $(3.41 \pm 0.61) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (dotted line). The phenomenological bimolecular rate coefficient in the case of the 215.8 nm CO-emission was $(4.00 \pm 0.72) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ which, within our experimental uncertainties, can be regarded to be the same as that determined when monitoring OH(A) chemiluminescence.

Previously, room temperature OH(A) chemiluminescence decay rates have been measured in three studies where the methylidyne radical was produced photolytically. The values of the rate coefficient reported were $(3.3 \pm 0.4) \times 10^{-11}$,⁵ $(8 \pm 3) \times 10^{-11}$,⁷ and $(4.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.⁴⁷ In the flow-tube work, where presumably only the ground state methylidyne is responsible for the observed OH(A) chemiluminescence, Bergeat et al.¹⁸ reported a room temperature value of $(3.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. An average value of $(3.9 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ can be deduced from all previous rate coefficient determinations in which CH decays were directly monitored (with the exception of that in Ref. 9).^{5,6,10,13,15,16,17,18,24} The present OH(A) and CO(a) data is consistent with this number, and with the previous OH(A) values of Bergeat et al.,¹⁸ Messing and co-workers,⁵ and Taatjes.⁴⁷ However, Lichtin and co-worker's⁷ value is the highest room temperature number reported in the literature.

CONCLUSIONS

The quadratic laser fluence dependence of the integrated chemiluminescence signals measured in the photolysis of CHBr_3/O_2 mixtures, and the close similarity of $\text{OH}(\text{A})$ and $\text{CO}(\text{a})$ decay rates suggests a common *2-photon* photolysis fragment from CHBr_3 to be the chief O_2 reactant responsible for the observed transient radiation. The absolute values of the bimolecular rate coefficients derived from the chemiluminescence traces in this work can best be interpreted as due to the reaction of the methylidyne radical with O_2 . The observation of the $\text{CO } 4^{\text{th}}$ Positive and CO Triplet chemiluminences in this work requires the presence of excited methylidyne radicals. Most likely vibrationally hot methylidyne, $\text{CH}(\text{X}^2\Pi, v'' \leq 5)$, radicals are involved. Their deduced reactivity towards O_2 (i.e. that of $\text{CH}(\text{X}^2\Pi, v'' = 4)$) is significantly higher than that of ground state CH radicals measured in this work, or of $\text{CH}(\text{X}^2\Pi, v'' = 1)$ reported earlier. However, these doublet species may not be the only reactants responsible for the chemiluminescence. Bromoform photolysis can produce the methylidyne radical in the, *low-lying*, electronically excited $\text{CH}(\text{a}^4\Sigma^-)$ quartet state, which lies $\sim 17.5 \text{ kcal mol}^{-1}$ above the $\text{CH}(\text{X}^2\Pi)$ ground state and its reaction with O_2 could lead to $\text{OH}(\text{A})$ and $\text{CO}(\text{a}, \text{a}' \text{ or } \text{d})$ formation, and if sufficiently vibrationally excited, to $\text{CO}(\text{A})$ formation also. Its rate coefficient with O_2 has previously been determined to be $(2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.⁴⁸ This could well be another reason why our $\text{OH}(\text{A})$ chemiluminescence decays were non-exponential. No attempt was made in this work to determine the relative yields of the $\text{OH}(\text{A})$ and CO^* chemiluminences because the present photolytic method apparently gives rise to an array of excited methylidyne radical species, whose distribution needs to be accurately quantified first. A

flow-tube experiment that can provide a cleaner source for $\text{CH}(X^2\Pi, v''=0)$ would be a better choice to perform such emission measurements.⁴⁰

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FIGURE CAPTIONS

Figure 1 A plot of ln[Integrated I₂₈₂ intensity] as a function of ln[E₂₄₈ laser fluence]. The area underneath the time resolved 282-nm, OH(A²Σ⁺, v'=1 → X²Π, v''=0) chemiluminescence trace like the one shown in Figure 2 was calculated to determine the (Integrated I₂₈₂ intensity) value.

Figure 2 Time resolved 282-nm $\text{OH}(A^2\Sigma^+, v'=1 \rightarrow X^2\Pi, v''=0)$ chemiluminescence trace observed immediately after the 248-nm photolysis of a CHBr_3/O_2 mixture at 298 K in 2.0 torr of He. The time resolution for recording the signal was 10 μsec . Typically 10000 temporal profiles were co-added to improve the signal-to-noise ratio of the chemiluminescence trace.

Figure 3 Plots of $\ln[\text{Integrated CO-uv intensity}]$ as a function of $\ln[E_{248} \text{ laser fluence}]$. The data is shown for chemiluminescence observed at 215.8 nm (open circles), 171.2 nm (solid squares), 165.3 nm (solid circles), and 159.7 nm (open squares). The slopes of the plots at these wavelengths were determined by linear-least-squares analysis to be (2.06 ± 0.05) , (2.39 ± 0.35) , (1.92 ± 0.09) , and (2.04 ± 0.09) , respectively.

Figure 4 Time resolved 165.3-nm $\text{CO}(A^1\Pi, v'=0 \rightarrow X^1\Sigma^+, v''=2)$ chemiluminescence traces observed immediately after the 248-nm photolysis of CHBr_3/O_2 mixtures at 298 K in 2.0 torr of He. The spectrometer band-pass was ~ 1.9 nm, FWHM. The time resolution for recording the signal was 10 μsec . Typically 10000 temporal profiles were co-added to improve the signal-to-noise ratio of the chemiluminescence traces. The $[\text{CHBr}_3]$ was 1.5×10^{12} molec cm^{-3} , and $[\text{O}_2]$ was 8.03×10^{13} (circles) and 17.2×10^{13} molec cm^{-3} (squares).

Figure 5 Second-order plots of CO-chemiluminescence and OH-chemiluminescence decay rates as a function of $[\text{O}_2]$ at 298 K and in 2.0 torr of He. Open circles is for the $\text{CO}(A^1\Pi, v'=0 \rightarrow X^1\Sigma^+, v''=2)$ band at 165.3 nm, and open squares is for the $\text{OH}(A^2\Sigma^+, v'=1 \rightarrow X^2\Pi, v''=0)$

band at 282.2 nm. The respective slopes determined by linear-least-squares fit to the data points yield the bimolecular rate coefficient values for $\text{CH}(X, v''=4) + \text{O}_2$ and $\text{CH}(X, v''=0) + \text{O}_2$. The dotted line represents the phenomenological rate coefficient value for $\text{CH}(X, v''\geq 0) + \text{O}_2$.

Figure 1

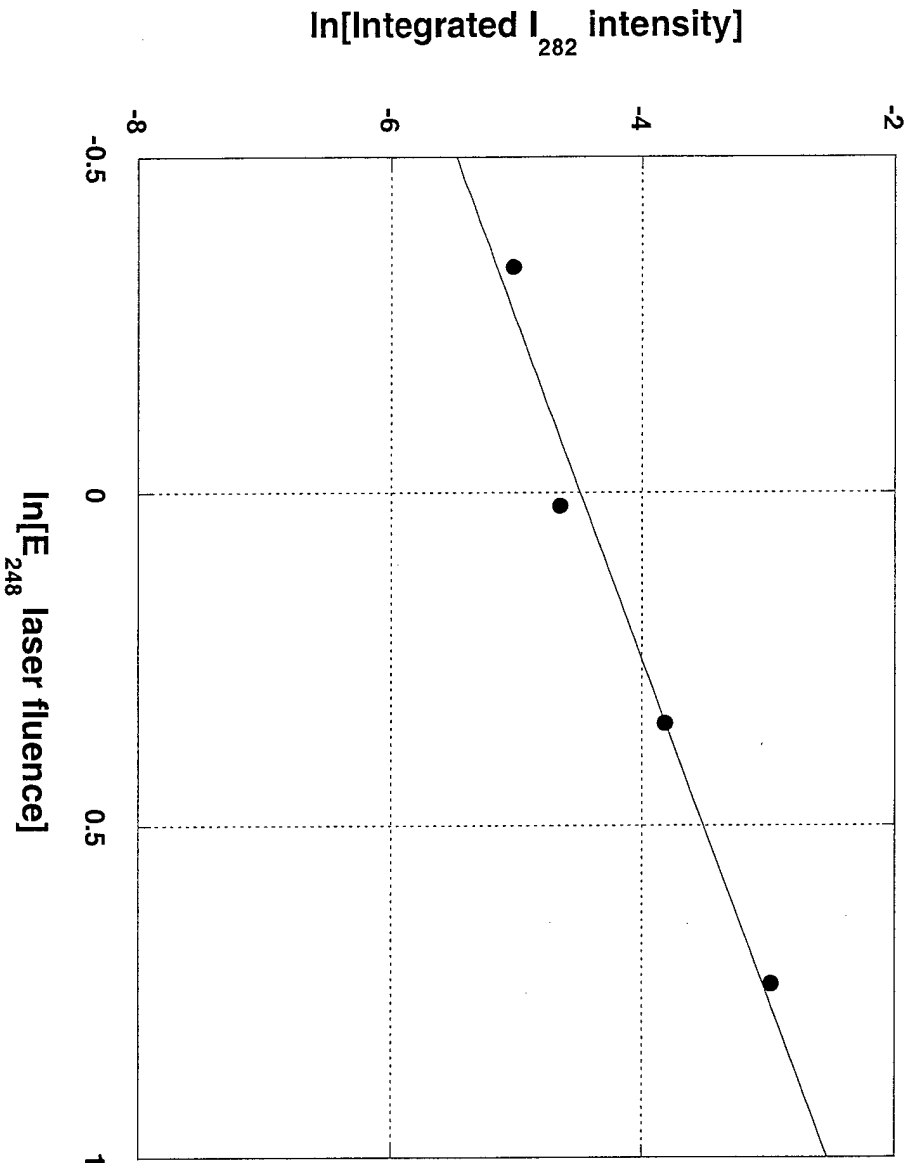


Figure 2

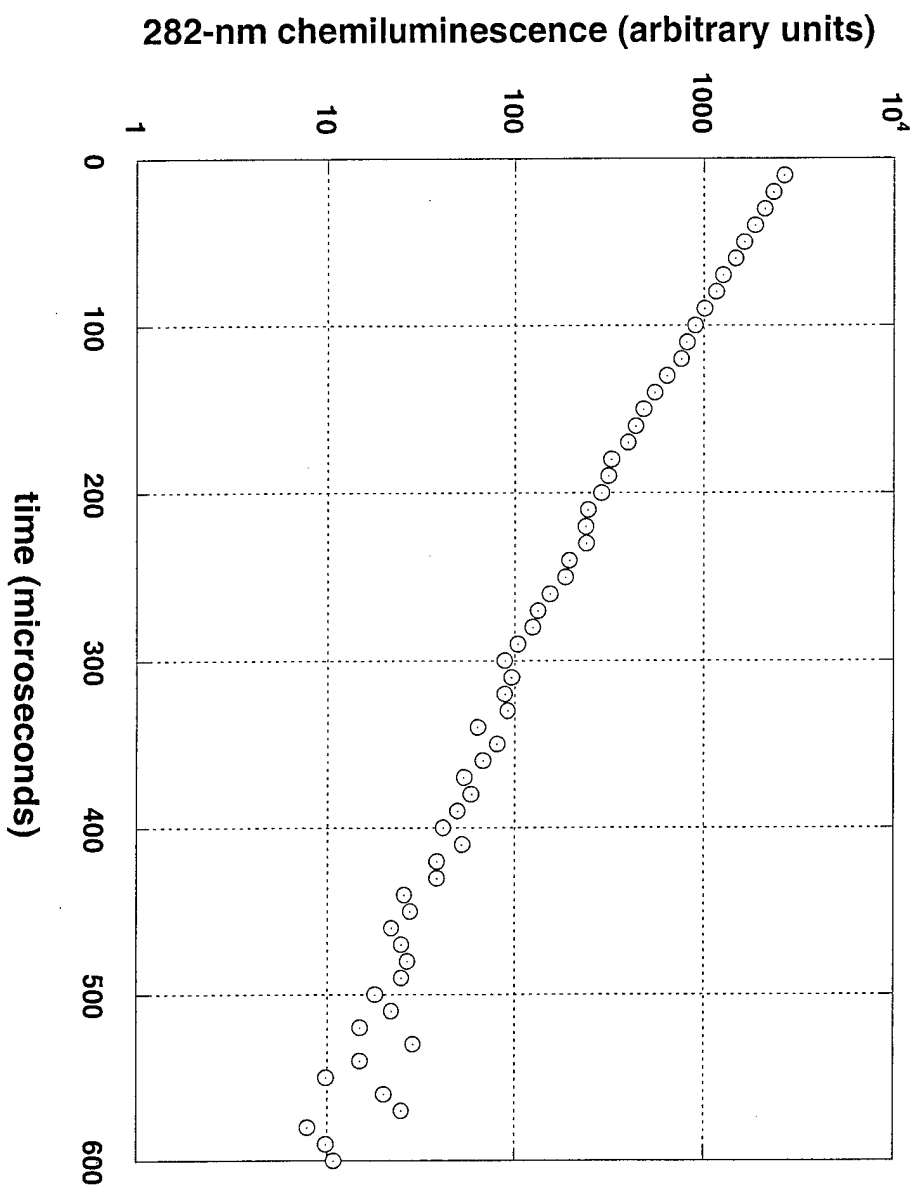


Figure 3

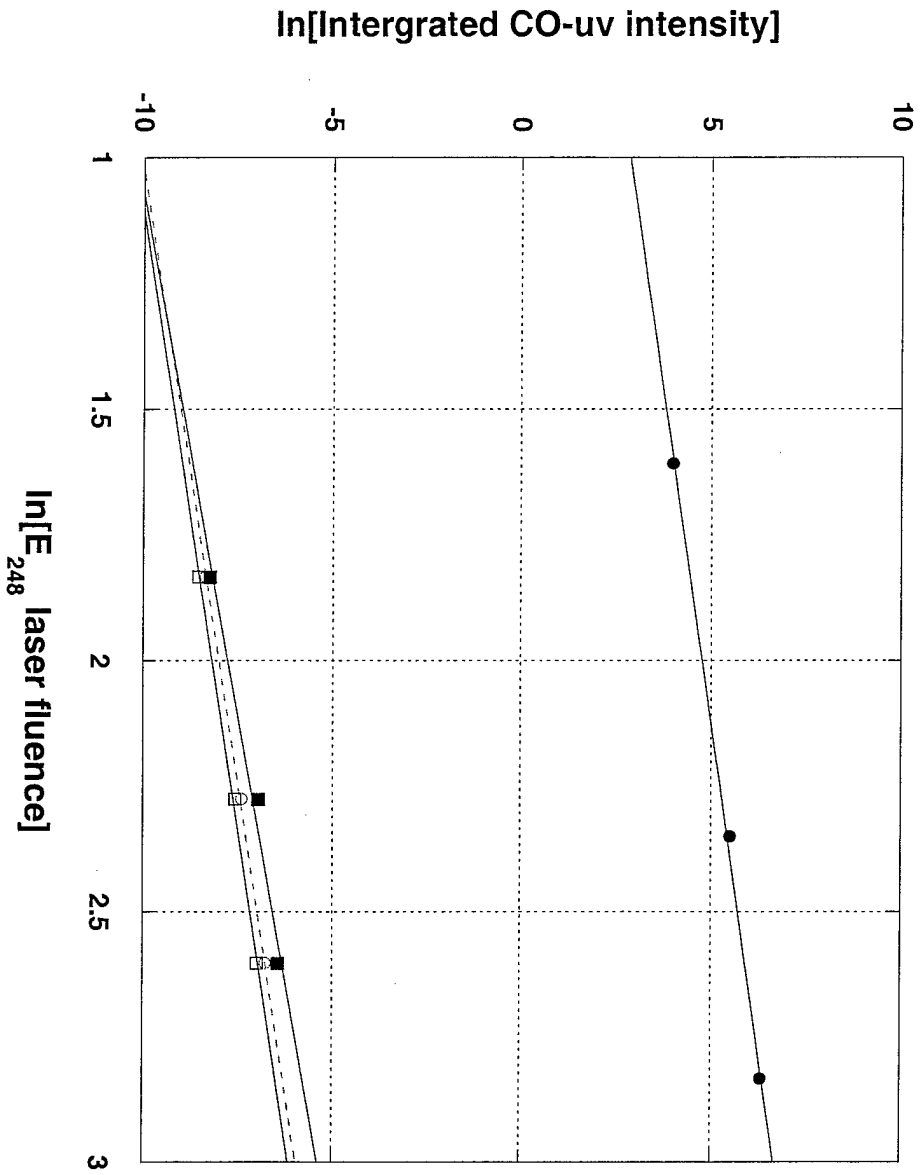


Figure 4

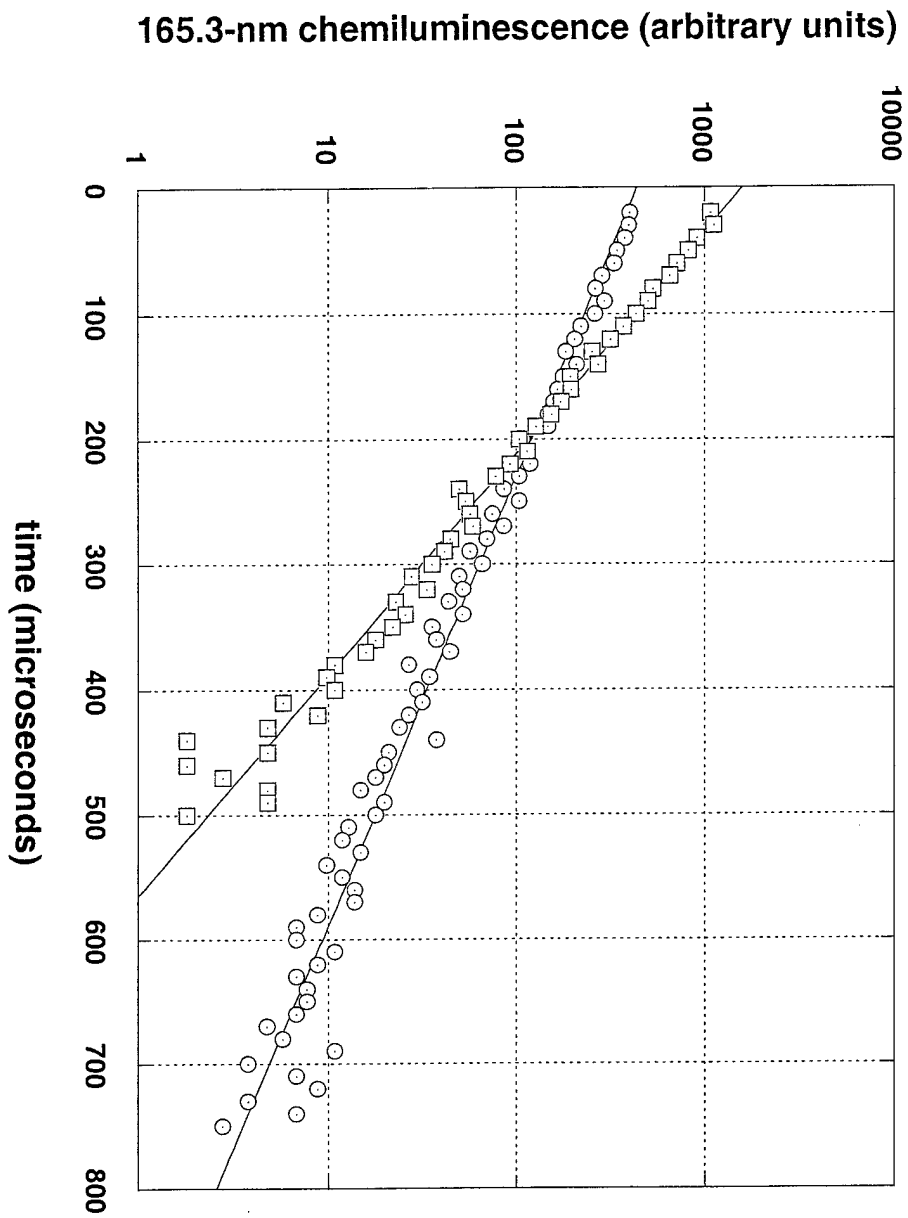


Figure 5

