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KINETICS AND MECHANISM OF COMBUSTION-RELATED REACTIONS  
OF METHOXY RADICALS(U) CATHOLIC UNIV OF AMERICA  
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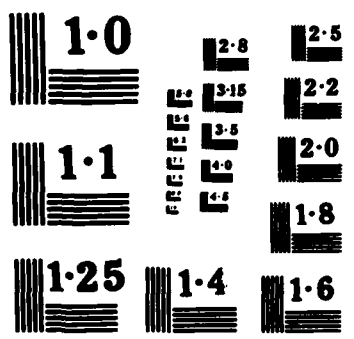
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KINETICS AND MECHANISM OF COMBUSTION-RELATED REACTIONS  
OF METHOXY RADICALS

Final Report

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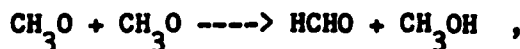
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Reactions of methoxy ( $\text{CH}_3\text{O}$ ) radicals prepared by the reaction of ground state fluorine atoms ( $\text{F}(^2\text{P})$ ) with methanol ( $\text{CH}_3\text{OH}$ ) were studied. The intensity of laser-induced fluorescence (LIF) at 298 nm was used as a measure of methoxy concentration. The presence of various excited molecular products was proven by the analysis of chemiluminescence (CL) spectra.

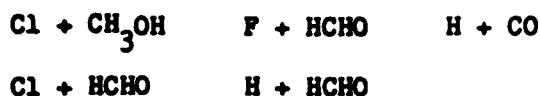
The CL spectra were very complicated and became significantly different when the operating conditions were varied slightly. It was learned that trace amounts of oxygen or air were primarily responsible for these observations. When these gases were present the following excited molecules and states were observed:  $\text{OH}(A^2\Pi)$ ,  $\text{CO}(a^3\Pi)$ ,  $\text{CN}(B^2\Sigma)$ , possibly  $\text{CH}(B^2\Sigma)$ ,  $\text{C}_2(A^3\Pi)$ , glyoxal ( $A^1A_u$  and probably a  $^3A_u$ ),  $\text{HCHO}(A^1A_2)$  and  $\text{HF}(X^1\Sigma, v=4-9)$ . When all  $\text{O}_2$  and air were removed, a new banded CL was present along with the previously observed HF high- $v$  levels. This new emission, which had not been reported in the literature, strongly resembled  $\text{HCHO}(A^1A_2)$ , and we were able to assign it to  $\text{HCHO}(a^3A_2)$ . The emission spectrum of this state has been sought for some 40 years using excitation of the ground state by ultraviolet light. The failure of the earlier methods was due to the very small Einstein B coefficients for absorption of radiation near the electronic origin and to the large probability of dissociation of the excited states at higher energies. The success of CL in producing an observable spectrum is due to the lifting of both of the above restrictions when the excited state is prepared directly by chemical reaction. The source reaction is:



which is exothermic by 82 kcal/mole (for ground state products). The source reaction was assigned on the basis of the known thermochemistry and the observation of a quadratic dependence of the CL intensity on the methoxy concentration. A manuscript describing this work is in preparation.

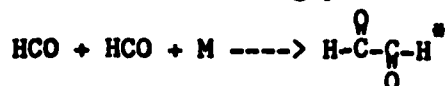
The presence of  $\text{O}_2$  in the F + methanol system quenches the  $\text{HCHO}(a)$  state by spin-allowed energy transfer, a well-known property of  $\text{O}_2$ . In addition,  $\text{O}_2$  excites virtually all of the CL band systems (corresponding to one or zero carbon atoms) which are known in combustion. The use of 99.99% pure helium as the discharge carrier gas did not remove the problem. However, it was solved by passing the carrier gas through a trap containing #80 mesh molecular sieve 5A and activated charcoal which was thermostatted at 77 K during experiments and baked at 650 K under vacuum at all other times.

Several important conclusions about the mechanisms of the CL reactions were reached by running CL spectra of the following chemically similar systems and subsystems:



These reactions were run both with and without added  $\text{O}_2$  and  $\text{F}_2$  (in separate experiments). The general conclusions are:

1. Added  $\text{F}_2$  or  $\text{O}_2$  quenches all of the free radical reactions by converting carbon-centered free radicals to C-F bonds or peroxy radicals, respectively.
2. The high vibrational states of HF are formed directly by F reacting with free radicals. Under our conditions, there is no significant HF( $v > 4$ ) formed by energy-pooling reactions of HF( $v < 4$ ).
3. A 1967 report that the glyoxal (A) state is formed by the reaction



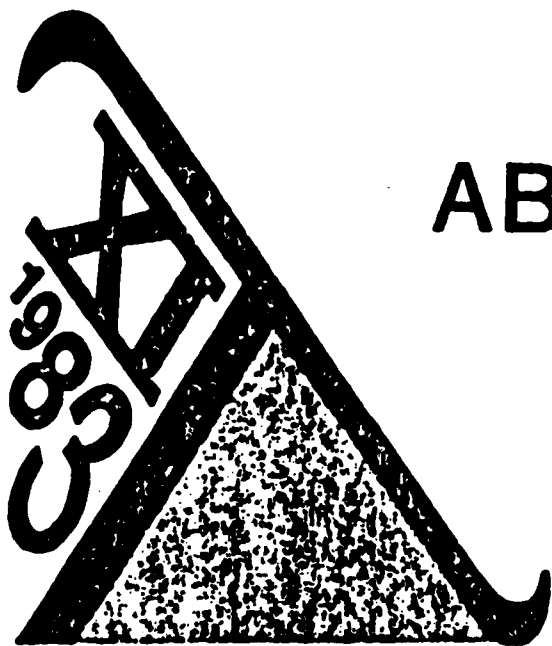
is wrong. The glyoxal (A) and (a) states are formed in our reactions only when  $\text{O}_2$  is present in the discharge. Thus they are due to "flame-like" reactions, and this was probably true for the 1967 study as well.

Our results, together with earlier work of NRL Code 6180, serve to establish that

1. Formaldehyde ( $\text{A } ^1\text{A}_2 \text{ ----> X } ^1\text{A}_1$ ) CL in flames is almost certainly due to the reaction  $\text{CH}_3\text{O} + \text{CH}_3\text{O}$ .
2. In the absence of  $\text{O}_2$ , the reaction  $\text{CH}_3\text{O} + \text{CH}_3\text{O}$  yields  $\geq 2000$  excited triplet HCHO molecules for every excited singlet. However, the ground state products predominate.

At least one additional manuscript will be prepared from our CL studies. Two abstracts of conference presentations based on the work are appended to this report.

In addition to the reportable scientific progress made under this contract, a great deal of important work has been done in support of Code 6180's fast flow reactor facility. A principal contribution was the construction of an electronic integrator which greatly improved the signal-to-noise ratio of laser-induced fluorescence and chemiluminescence signals. In addition, control circuitry and software were designed and fabricated for a versatile system which now makes it possible to position and scan a monochromator and collect spectral data under complete computer control.



# ABSTRACTS

## XI<sup>th</sup>

## International Conference

### on

## Photochemistry

The University of Maryland  
College Park, Maryland, U.S.A.

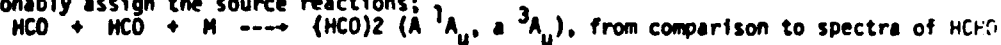
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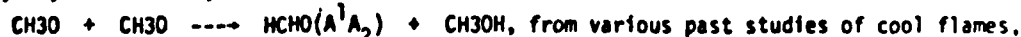


M8 Detailed Study of Visible-UV Chemiluminescence in the F(<sup>2</sup>P) plus Methanol System D. J. Bogan, H-t. Wang, C. W. Hand, M. J. Kaufman, and W. A. Sanders Naval Research Laboratory, Code 6180, Washington, D. C. 20375

We have observed visible-UV chemiluminescence (CL) in a 2 Torr flow discharge study of the F plus CH<sub>3</sub>OH system. Initial concentrations were ca. 10<sup>11</sup> to 10<sup>12</sup> cm<sup>-3</sup> for both F and CH<sub>3</sub>OH; the balance of the gas was He. Analysis of the CL is informative of the overall kinetics. In the absence of F<sub>2</sub>, we observed spectra from the states; CO(a<sup>3</sup>π), OH(A<sup>2</sup>π), CN(B<sup>2</sup>Σ), possibly CH(B<sup>2</sup>Σ), C<sub>2</sub>(A<sup>3</sup>π), and glyoxal (A<sup>1</sup>A<sub>1</sub> and probably a<sup>3</sup>A<sub>1</sub>). In the presence of either F<sub>2</sub> or O<sub>2</sub>, added after the discharge, we observed very similar spectra from the states; OH(A<sup>2</sup>π), C<sub>2</sub>(A<sup>3</sup>π), HCHO(A<sup>1</sup>A<sub>2</sub>), and HF(X<sup>1</sup>Σ, v=4-9). We can reasonably assign the source reactions;



+ F, Cl, and H atoms,



and,  $\text{RH} + \text{F} \rightarrow \text{HF}(\text{X}^1\Sigma_0, v > 0)$  followed by vibrational relaxation. The remaining CL is at least partly due to discharge impurities. A very sensitive CL titration for F atom was found, with a sharp intensity maximum at  $\lambda = 675 \pm 10$  nm. occurring at  $4.0 \pm 0.1$  F atoms per CH<sub>3</sub>OH. With added F<sub>2</sub> the overall stoichiometry and the titration endpoint change due to chain reactions allowing measurement of the chain length and of the branching fraction for CH<sub>3</sub>O,  $\Gamma_{\text{CH}_3\text{O}} = 0.36 \pm 0.05$ .

M1 PHOTOCHEMICAL STUDIES WITH TUNABLE NARROW-BAND VUV LASER LIGHT  
Karl H. WELGE, Fakultät Physik, University Bielefeld, D-4800 Bielefeld 1, FRG

Considerable progress has recently been made in producing tunable narrowband laser radiation in the vacuum ultraviolet down to, and below, the LiF cut-off wavelength at 1050 Å. In this paper we report in two parts some recent applications of tunable vuv laser radiation in spectroscopic and photochemical studies. One kind of application has been concerned with the kinetics and dynamics of photochemical primary processes, such as photodissociation, studied by time resolved photoionization with pulsed vuv laser light. This technique allows to probe photochemically complex photochemical systems in gas phase in real-time with nanosecond time resolution. First applications to (1) photodissociation of neutral and ionic molecules with uv and vuv laser radiation and (2) to infrared multiple photon dissociation of polyatomic molecules, also isotopically labeled ones, will be presented. The second part is concerned with tunable vuv laser spectroscopy experiments with atomic and molecular hydrogen by resonant two-photon excitation - ionization. Aspects have been the state-selective and sensitive detection of these fundamentally important species in gas phase reactions and state-selective pumping of hydrogen molecules in the electronic ground and excited states.

# **CHEMICAL AND PHYSICAL PROCESSES IN COMBUSTION**

**1983 FALL TECHNICAL MEETING**

**Eastern Section: The Combustion Institute  
8-10 November, Providence, Rhode Island**

***Co-Hosted by:***

***AeroChem Research Laboratories, Inc.***

***Princeton University***

***Brown University***

MECHANISM OF EXCITED FORMALDEHYDE  
FORMATION IN COOL FLAMES

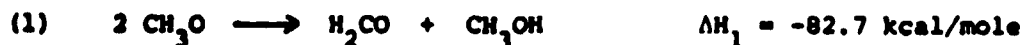
D. J. Bogan, W. A. Sanders, H.-t. Wang, and R. S. Sheinson  
Combustion & Fuels Branch, Code 6180, Naval Research Laboratory,  
Washington, D. C. 20375

Cool flames remain one of the most captivating and stubborn intellectual challenges in combustion, a field rich in such phenomena.<sup>1-8</sup> The fascinating observed features of cool flames include the following:

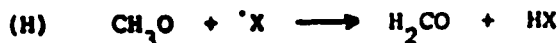
- 1.) They are the lowest temperature luminous flame stage, occurring at temperatures as low as 200 C, yet they emit high energy near-UV and blue radiation.
- 2.) Under some conditions they can be spatially separated from hotter, more violent flame stages.
- 3.) They exhibit a negative temperature coefficient. If the temperature of the environment is raised, the cool flame will weaken or extinguish, or re-establish itself at a different position having the same temperature and chemical composition that existed at the previous location, before it was perturbed.
- 4.) Under some conditions multiple cool flames occur, separated by dark periods, with repetition frequencies on the order of seconds.
- 5.) Spectroscopic observation of cool flames has confirmed the presence of electronic excited formaldehyde in the  $^1A_2$  ( $= ^1n\pi^*$ ) state.<sup>2,5-8</sup> No other excited states are known to be present in cool flames regardless of the fuel.<sup>8</sup>

In this paper we address the question of the mechanism of excited formaldehyde formation in cool flames.

The excitation energy of formaldehyde ( $^1A_2$ ), hereafter  $H_2CO^*$ , is 80.6 kcal/mole.<sup>9</sup> The reaction forming  $H_2CO^*$  must be at least this exothermic. Thus the candidates are restricted to a few radical-radical reactions giving non-radical products;



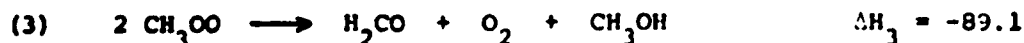
where the thermochemistry is taken from Benson.<sup>10</sup> Hydrogen abstraction from methoxy by any free radical, 'X, is a candidate, if it is sufficiently exothermic,



where reactions (1) and (2) are members of the set (H). Taking into consideration the energetic species known to be present in cool flames and thermochemistry, the reactions (H) and (R) are the only reasonable  $\text{H}_2\text{CO}^*$  sources.



The most important member of the class (R) for the present discussion is:



The approximate order of relative concentration of radical species, appearing in the above reactions, in cool flames is  $\text{CH}_3\text{OO} \sim \text{CH}_3\text{O} \gg \text{OH} > \text{CH}_3$ .

Reactions (1) and (2) have been the favored candidates as the  $\text{H}_2\text{CO}^*$  source.<sup>4-8</sup> Reaction (1) is known to give  $\text{H}_2\text{CO}^*$ , based upon chemiluminescence (CL) studies of the thermal decomposition of methyl nitrite<sup>11</sup> and dimethyl peroxide<sup>12</sup>. Reaction (2) might also give  $\text{H}_2\text{CO}^*$ , however no one has yet reported the kind of very careful study of CL intensity as a function of methoxy and hydroxyl concentrations, needed as proof. It has been proposed<sup>4</sup>, and extensive arguments have been advanced,<sup>13</sup> that OH is the major chain propagating free radical in cool flames. The chemical complexity of cool flames and the need to explain the excited state quantum yields have prevented knowledge of the relative importance of reactions in the class (H).

Weak CL also occurs in the low temperature oxidation of liquid hydrocarbons (HC). Vassil'ev proposed reactions (R) as the sources of excited states in these systems.<sup>14</sup> Indritz has proposed that reactions (R) are responsible for CL in cool flames based upon the observation of only a very weak  $\text{D}_2\text{CO}^*$  component when dimethyl peroxide- $d_6$  was introduced into a di-tert-butyl peroxide cool flame.<sup>15</sup> The difficulty in proving this mechanism is that reaction (R) is always accompanied by disproportionation to give alkoxy radicals



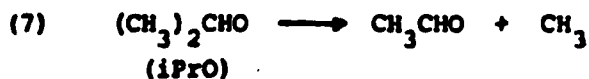
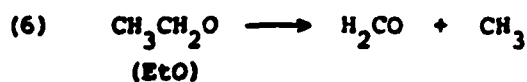
Reactions (R) are very interesting. They are believed to take place via the mechanism proposed by Russell<sup>16</sup> involving a dialkyl tetraoxide intermediate and a cyclic transition state leading to the products. There are extensive data in support of this mechanism giving ground state products in both solution<sup>17,18</sup> and gas<sup>19</sup> phases.

In summary, this problem is very complex. We find ourselves unable to offer an explanation which is not in conflict with some experiments (as reported and interpreted by the original investigators). We believe that the way out of this dilemma is by comparison and contrast of CL spectra from cool flames and liquid HC oxidation.

Among many other studies, Vassil'ev reported CL spectra from oxidation of

liquid ethylbenzene, cyclohexane, n-decane, and methyl ethyl ketone (MEK) at 60 - 65 C.<sup>14</sup> The spectra of the first three systems were different from one another although they were without distinctive structure. The spectrum of MEK oxidation was distinctive, different from the other three, and was identified as biacetyl ( $^1n\pi^*$ ) CL by matching it to a biacetyl photoluminescence spectrum.<sup>14</sup> The major difference between HC cool flame and HC liquid oxidations are temperature and phase. The lower temperature in liquid HC oxidation will affect reaction rates through the Arrhenius  $E_a$ , and will thus lower all radical concentrations. However the relative order of the radical concentrations is expected to remain the same as in cool flames. In every case where rate constants have been reliably measured for reactions of these species they are the same, within experimental error for both gas and liquid phases.<sup>18</sup> We consider the question: Can either class of reactions (H) or (R) consistently explain the chemiluminescence observed in both cool flames and liquid HC oxidations?

Both RO and ROO radicals are subject to competitive consumption by processes other than reactions (H) and (R). For RO radicals the most important processes are hydrogen abstraction by  $O_2$ , forming a carbonyl product, and the unimolecular decompositions exemplified below.



Experimental Arrhenius rate parameters for reactions (5) - (8) have been reported by Batt,<sup>20</sup> These parameters and derived values of  $k(T)$  for the T range of interest are:

RO	log A (sec) <sup>-1</sup>	E (kcal/mole)	k(T, °K) (sec) <sup>-1</sup>				
			k(300)	k(350)	k(400)	k(450)	k(500)
MeO	14.2	27.5	1.5(-6)	1.6(-3)	1.5(-1)	7.0	1.5(2)
EtO	15.0	21.6	1.8(-1)	3.2(1)	1.6(3)	3.2(4)	3.6(5)
iPrO	14.6	17.2	1.2(2)	7.2(3)	1.6(5)	1.8(6)	1.2(7)
tBuO	15.5	17.0	1.3(3)	7.7(4)	1.6(6)	1.7(7)	1.2(8)

where 1.5(-6) =  $1.5 \times 10^{-6}$ , etc.

When  $k(T)$  exceeds approximately  $10^5 \text{ sec}^{-1}$ , unimolecular decomposition will dominate the loss processes for a given RO and thus prevent its involvement in CL reactions. Thus RO radicals, other than MeO, cannot be responsible for CL under typical cool flame conditions, and only  $\text{H}_2\text{CO}^*$  can be produced.

Although ROO radicals are also subject to several loss processes, experimental data show that ground state carbonyl products arising from reactions (R), at  $T < 700 \text{ K}$ , are the major products in 2 Torr studies of ROO radicals derived from n-butane and other HC's,<sup>19</sup> and were observed in a 1 Atm. n-butane cool flame.<sup>21</sup> If the ground state products can be formed in cool flames, then the excited state products ought to be observed as well. Since they are not observed, we conclude that hydrogen abstraction from methoxy, primarily by methoxy and hydroxyl radicals, is responsible for  $\text{H}_2\text{CO}^*$  formation in cool flames.

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