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MEMORANDUM FOR PRS (In-House Contractor Publication)

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-AB-2002-062** Ghanshyam L. Vaghjiani (ERC), "Kinetics of CH Radicals With O_2: Evidence for CO-Chemiluminescence in the Gas Phase Reaction"

XXV Informal Conference on Photochemistry **(Statement A)**
(Univ. of Miami, FL, 2-7 June 2002) **(Deadline: 08 April 2002)**

Kinetics of CH Radicals With O_2: Evidence for CO-Chemiluminescence in the Gas Phase Reaction

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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 Air Force Research Laboratory is interested in the methylidyne and the methylene (CH_2) radical reactions with O_2 and O-atoms since they are thought to play an important role in the production of ultraviolet/visible chemiluminescence when rocket plumes interact with the earth's ambient atmosphere.[4]

Production of CO vis-uv-chemiluminescence has been observed for the first time in the gas phase reaction of the methylidyne radicals with molecular oxygen. A trace amount of $CHBr_3$ vapor was photo-decomposed in a pulsed-photolysis reactor using a 248-nm laser under multi-photon-dissociation conditions to produce the $CH(X^2\Pi)$ radicals in an excess of O_2 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 $[O_2]$ was studied to obtain the rate coefficient(s) for the chemiluminescent reaction(s). The data is best interpreted by postulating that $CH(v''\geq 0)$ reactions with O_2 lead to the observed CO-emissions as well as the well-known[5-7] OH-chemiluminescence.

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