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Reactions of O-atoms and O_2 With Small Carbonaceous Free Radicals

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The interactions of carbonaceous combustion species in rocket plumes with the atmosphere are thought to play an important role in the production of ultraviolet, visible, and infrared radiation signatures at high altitudes. A detailed understanding of the pertinent chemical reactions that produce the electronically excited species, and of the competing quenching reactions that remove the internal energy in radiation-less processes is needed to accurately calculate plume spectral signatures and absolute radiances (in the short wavelength region), and their temporal/spatial evolution in the high atmosphere. To facilitate these efforts, we have carried out laboratory investigations to elucidate the reaction mechanism(s) in the oxidation of CH, CH_2, C_2H, and C_2O with O-atoms and O_2. Sufficient exothermicity in CH, CH_2, and C_2H reactions (except C_2H + O) is available to produce CO in one or more of the triplet states (a, a', and d). Even more reaction enthalpy is available in C_2O reaction(s) to produce higher excited states of CO (e, A, I, and D). Other excited species such as $CH(A^2\Delta)$ in C_2H plus O or O_2, and $OH(A^2\Sigma^+)$ in CH + O_2 reactions are also possible. CO-uv chemiluminescence has previously been identified in C_2H + O_2 reaction and both CO-uv and CO-vuv in the C_2O + O reaction. However, no information is available on the product branching ratios of the excited CO states responsible for the emission. Estimates of the branching ratio of $CH(A^2\Delta)$ formation in the reactions of C_2H with O and O_2 can be found in the literature. To our knowledge, triplet CO formation in CH and CH_2 reactions has not yet been positively identified. Fast discharge-flow tube and pulsed-laser photolysis methods have been employed in this work to study the reaction kinetics and chemiluminesence in these reactions. The experimental approach and results of these studies will be presented.