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THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF FORMALDEHYDE INVESTIGATED BY LASER FLASH PHOTOLYSIS

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Laser excitation of formaldehyde is used to measure fluorescence lifetimes of individual rovibronic levels of the first excited singlet state. Both collision-free and collision-induced radiationless processes are observed. Intracavity dye laser spectroscopy is used to study the HCO produced by laser photodissociation of H₂CO. Vibrational relaxation rates and both radical-molecule and radical-radical reaction rates are determined. End product analysis of laser-photolyzed formaldehyde mixtures gives absolute quantum yields for radical, H + HCO, and molecular, H₂ + CO, photodissociation for individual vibronic bands. Selective photolysis of single lines in the ¹⁴CH₂O spectrum yields CO enriched by as much as 150 times in ¹⁴C. Significant improvements in ¹⁴C dating may be possible.

Lifetimes of S₁ formaldehyde

The decay of fluorescence from the 4⁰ and 4¹ levels of the S₁ (\tilde{A}^1A_2) state of H₂CO and D₂CO has been monitored as a function of pressure after selective, pulsed laser excitation. For D₂CO, single exponential decays modified by 4⁰ ↔ 4¹ energy transfer were observed over the entire pressure range 4 × 10⁻⁵ - 4 Torr. The zero pressure lifetimes τ₀(4⁰) = 7.8 ± 0.7 μs and τ₀(4¹) = 6.0 ± 0.4 μs are probably the radiative lifetimes. The rate of 4¹ ↔ 4⁰ energy transfer in D₂CO was found to be (9.6 ± 0.4) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, about three times the gas kinetic rate. For H₂CO at pressures above 0.1 Torr, fluorescence decays were also single exponentials modified by 4⁰ ↔ 4¹ energy transfer. However, in the range 2 × 10⁻⁴ - 0.1 Torr, the decays of the individual 4⁰ and 4¹ vibronic levels were multiexponential. Lifetimes of individual rovibronic levels vary

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between 70 ns and 3 μ s. A few approach the radiative lifetime of about 5 μ s. The Stern-Volmer plots of τ^{-1} versus pressure give quenching rates between 2.2×10^{-9} and 6.5×10^{-9} cm³ molecule⁻¹ s⁻¹ for both fast and slow levels below about 20 mTorr. The Stern-Volmer plots are dramatically curved and give quenching rates of only about 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹ above 1 Torr. The low pressure quenching rates and zero pressure lifetimes for H₂CO depend significantly on the *K*' and *J*' rotational quantum number within 4⁰. The large quenching rate constants and the curvature of the Stern-Volmer plots can be qualitatively understood in terms of mixed-state models of collision-induced radiationless decay.

Flash-kinetic spectroscopy of HCO

Formaldehyde vapor was photolyzed with a tunable pulsed UV laser. Flash kinetic absorption spectra of the HCO produced were recorded by intracavity dye laser spectroscopy with a time resolution of 1 μ s. The energy threshold for radical production was confirmed to be at 86 ± 1 kcal mol⁻¹. Photolysis at 294.1 nm produced HCO in its ground vibronic state (about 2/3) and with one quantum of vibrational excitation in either the bending (about 1/3) or CO stretching (10^{-1} - 10^{-2}) vibrations. Observation of the CO stretching hot band absorptions allowed that frequency to be determined as 1868.4 ± 1 cm⁻¹. Quantitative state-resolved measurements of concentration versus time were made in pure H₂CO and in mixtures with O₂, NO or Ar. The vibrational relaxation rate for the bending vibration of HCO in collisions with H₂CO was $(4.3 \pm 1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Reaction rates for HCO + NO \rightarrow HNO + CO and HCO + O₂ \rightarrow HO₂ + CO were measured as $(1.4 \pm 0.2) \times 10^{-11}$ and $(4.0 \pm 0.8) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively. Approximate rates were determined for the radical-radical reactions H + HCO \rightarrow H₂ + CO and 2HCO \rightarrow H₂CO + CO as $10^{-9.26 \pm 0.3}$ and $10^{-10.2 \pm 0.5}$, respectively. Since laser photolysis may be used to produce large accurately known concentrations of free radicals, radical-radical rate constants may be determined with good accuracy. By use of two photolysis lasers reactions between two different radicals or between two excited states may be studied.

THE INFLUENCE OF TEMPERATURE ON UV ABSORPTION CROSS SECTIONS OF HALOCARBONS

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Aeronomic processes are initiated by the photodissociation of atmospheric constituents under the influence of the UV solar radiation. In the particular case of the stratosphere, a complete description of the prevailing chemical scheme has to take into account the numerous components present as traces, either of natural origin or artificially introduced. During the last few years, special attention has been paid to the case of halocarbons: owing to their intensive industrial uses and lack of chemical reactivity at low altitudes, these compounds slowly diffuse up to stratospheric altitudes where their concentrations have proved to retain significant values. Their photodissociation in the 200 nm wavelength range corresponding to the atmospheric optical window is their most important destruction mode and leads to the release of atomic chlorine which in turn initiates a catalytic destruction cycle for ozone. In order to evaluate the chlorine production above 30 km absorption cross sections are needed. When available, measurements have usually been restricted to room temperature conditions, although actual stratospheric temperatures can be as low as 220 K.

In the present work, UV absorption cross sections of chloromethanes (CH₃Cl, CH₂Cl, CHCl₃, CCl₄) and chlorofluoromethanes (CF₃Cl, CF₂Cl₂, CFCl₃) have been deter-