



A Kinetic and Mechanistic Study of the Atmospheric Oxidation of β -diketones.

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Oxygenated volatile organic compounds constitute a major component of tropospheric trace gases, ketones in particular, are of significant atmospheric importance. Ketones are emitted by a variety of anthropogenic and biogenic sources. Ketones are used widely as solvents and vegetation have been shown to emit certain ketones, they may also result from the atmospheric oxidation of hydrocarbons. Unsaturated carbonyls may be formed during the atmospheric transformations of conjugated dienes, unsaturated carbonyls and some monoterpenes.

Reaction with the hydroxyl radical represents a major loss process for ketones, however in the marine boundary layer, removal by reaction with Cl atoms may also be an important loss process. Photodissociation provides another loss process for ketones, the carbonyl group being a chromophore allows absorption of long wavelength radiation with the main absorption band occurring at ~ 280 nm. Photolysis rates depend on the absorption cross-section of the ketone in question. Unsaturated ketones may be removed by reaction with ozone.

Investigation of the atmospheric oxidation of the β -diketone 2,4-pentanedione has been carried out. Rate coefficients for the reaction of 2,4-pentanedione with OH, O₃ and Cl were measured. It is well established that in the gas-phase this compound exists predominantly in the enol form. As a result it was expected that oxidation would involve addition of OH/Cl/O₃ to the carbon-carbon double bond system. It has been shown that when 2,4-pentanedione is irradiated at 248 nm, the molecule undergoes a $\Pi - \Pi^*$ transition resulting in the production of OH. The rate coefficient for reaction of 2,4-pentanedione with OH was measured using an absolute rate, laser photolysis-laser induced fluorescence, and a relative rate method. In the case of the absolute rate

study the parent compound was used as the OH precursor.

The concentration-time profiles from experiments on the OH radical initiated oxidation of 2,4-pentanedione in the presence of NO_x carried out at the European outdoor simulation chamber (EUPHORE) identified primary products of the reaction: acetic acid ($\sim 10\%$) and methyl glyoxal ($\sim 20\%$). Small yields of formaldehyde and PAN were also evident. The major products of the reaction were not characterized fully although product FTIR spectra suggest the presence of a polycarbonyl compound ($\sim 70\%$).