CHEMICAL REACTION KINETICS AND HEISENBERG SPIN EXCHANGE OF THE ETHYL RADICAL WITH OXYGEN

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The kinetics of the chemical reaction and Heisenberg spin exchange of the ethyl radical with oxygen in the gas phase is investigated using the time differential μSR technique in longitudinal magnetic fields. At a total pressure of 1.5 bar and a temperature of 311 K, rate constants of $k_1 = (9.2 \pm 0.6) \times 10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for chemical reaction and $k_{ex} = (4.2 \pm 2.3) \times 10^{-10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for spin exchange are obtained.

1. Introduction

Free radicals play a key role as intermediates in the photochemical degradation of organic pollutants in the atmosphere and in combustion processes. Although gas phase reactions have received considerable attention over the last decade [1], the mechanisms beyond the initial steps and subsequent products under atmospheric conditions are poorly understood. For model calculations of the detailed balance of the many interrelated reactions, accurate kinetic parameters are necessary.

The ethyl radical was chosen as a model system for the present study. Its reaction with oxygen can be split into the four elementary steps:

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\begin{align*}
\text{CH}_2\text{MuCH}_2 + \text{O}_2 & \rightarrow \text{CH}_2\text{MuCH}_2\text{O}^* \quad (1) \\
\text{CH}_2\text{MuCH}_2\text{O}^* & \rightarrow \text{CH}_2\text{MuCH}_2 + \text{O}_2 \quad (2) \\
\text{CH}_2\text{MuCH}_2\text{O}^* + \text{M} & \rightarrow \text{CH}_2\text{MuCH}_2\text{O}^* + \text{M}^* \quad (3) \\
\text{CH}_2\text{MuCH}_2\text{O}^* & \rightarrow \text{CH}_2\text{CHMu} + \text{HO}_2 \quad (4)
\end{align*}
\]
Addition of oxygen (1) leads to an excited peroxy radical which can dissociate back to the reactants (2) or to new products CH₂CHMu and H₉O₂ (4). Alternatively, it can lose its excess energy by collisions with surrounding molecules (M) to reach the ground state (3). This leads to a pressure-dependent product formation. At low pressures the products of (4) are built up, but in the high pressure limit CH₂MuCH₂O₂ is produced in a high yield. At the high pressure limit the rate constants become pressure independent.

The above reactions, with H substituted for Mu, were described in a detailed theoretical study by Wagner et al. [2], supported by experimental data obtained at pressures of 0.5-15 Torr. Based on RRKM theory, the rate constants were extrapolated to the high pressure limits. \( k_1 \), calculated for a pressure of 1 bar, is 1.5-2 times higher than the experimental value obtained at the same pressure [3].

Standard methods of magnetic resonance are not suitable for the investigation of kinetics in the gas phase because of the numerous and broad lines which lead to low sensitivity. Most of the optical methods yield only relative rate parameters. Product analysis gives reliable measurements of the product distribution but little information about the time scale of product formation.

The first detection of a muonated organic free radical in the gas phase was achieved in ethylene at pressures of 25-50 bar in a transverse magnetic field [4]. Further investigations used longitudinal field techniques at pressures down to 1 bar, to study the temperature dependence of the hyperfine coupling constants [5] and the field and pressure dependence of the muon relaxation in the ethyl radical [6].

In the presence of \( O_2 \), interaction between the unpaired electron of the radical with the paramagnetic \( O_2 \) molecule leads to Heisenberg Spin Exchange (HSE) which may induce a muon spin flip in the radical. This occurs in addition to the above intrinsic relaxation in pure ethylene and to the chemical reactions (1-4).

The influence of electron relaxation together with chemical reaction on the muon spin of bare muonium was studied theoretically with a treatment based on the Wangsness-Bloch equation [7]. In high fields the protons are decoupled from the muon and render the radical muonium-like. This allowed us to adopt the same approach for the analysis of our data.