Tunneling in the reaction of acetone with OH†

Françoise Caralp,*a Wendell Forst,a Eric Hénon,b Astrid Bergeata and Frederic Bohr b

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Based on recent detailed quantum mechanical computations of the mechanism of the title reaction (Phys. Chem. Chem. Phys., 2003, 5, 333) and (J. Chem. Phys., 2003, 119, 10 600), this paper presents kinetics analysis of the overall rate constant and its temperature dependence, for which ample experimental data are available for comparison. The analysis confirms that the principal channel is the formation of acetonyl radical + H2O, while the channel leading to acetic acid is of negligible importance. It is shown that the unusual temperature dependence of the overall rate constant, as observed experimentally, is well accounted for by standard RRKM treatment that includes tunneling. This treatment is applied at the microcanonical level, with chemically activated distribution of entrance species, i.e. using a stationary rather than a thermal distribution that incorporates collisional energy transfer and competition between the redissociation and exit channel. A similar procedure is applied to the isotopic reaction acetone-d6 + OH with equally satisfying results, so that the experimental temperature dependence of the KIE (kinetic isotope effect) is perfectly reproduced. This very good agreement between calculation and experiment is obtained without any fitting to experimental values and without any adjustment of the parameters of calculation.

Introduction

Acetone is one of the most important trace organic compounds in the atmosphere, providing an important source of HOx radicals, in particular in the upper troposphere and lower stratosphere. The two major pathways for atmospheric degradation of acetone are photolysis and reaction with OH radical. The overall rate constant for the latter reaction, along with its temperature dependence, has been the subject of much experimental work.¹–⁸ There is good agreement among all the results as shown in Fig. 1 where symbols are experimental results. The rate exhibits unusual temperature dependence, with the rate constant decreasing with decreasing temperature, first rapidly, but much more slowly below room temperature, becoming quasi-constant at and below ca. 250 K. It is nowadays well-established that this unusual temperature dependence is often observed in these types of reactions.⁹

There are essentially two possible exothermic channels for the title reaction: H-atom abstraction leading to water and acetonyl radical

\[
\text{OH} + \text{CH}_3\text{C(O)}\text{CH}_3 \rightarrow \text{CH}_3\text{C(O)}\text{CH}_2 + \text{H}_2\text{O} \quad (1)
\]

and OH-addition to the carbonyl C-atom followed by methyl elimination leading to acetic acid

\[
\text{OH} + \text{CH}_3\text{C(O)}\text{CH}_3 \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3 \quad (2)
\]

It is now experimentally well established that the yield of acetic acid is negligible,¹⁰–¹³ the major channel being the production of acetonyl radicals. The kinetic isotope effect in the title reaction was also thoroughly explored⁵–⁸ demonstrating a large primary effect. Experimental Arrhenius plots for both OH + acetone and OH + acetone-d6 reactions are shown in Fig. 2.

Extensive theoretical work was performed by several groups⁴,⁵,¹²,¹⁴–¹⁶ and the main features of the molecular mechanism have been clarified, disagreement among the different groups concerning only minor details. A detailed quantum chemical calculation of the mechanism of the reaction of OH with acetone was previously published by some of us¹⁵ and the main points of this study are summarised here. The reaction proceeds chiefly by OH hydrogen-atom abstraction producing acetonyl radical. This route takes place via a complex mechanism involving hydrogen-bonded (“pre-reactive”) complexes MC prior to formation of transition states TS. The transition states then evolve via other complexes into acetonyl + H2O. Two channels are characterised:

\[
\text{OH} + \text{acetone} \rightarrow \text{MC1a} \rightarrow \text{TS1a} \rightarrow \text{MC4a} \rightarrow \text{acetonyl} + \text{H}_2\text{O} \quad (1a)
\]

\[
\text{OH} + \text{acetone} \rightarrow \text{MC1b} \rightarrow \text{TS1b} \rightarrow \text{MC4b} \rightarrow \text{acetonyl} + \text{H}_2\text{O} \quad (1b)
\]

Another possible channel involves the OH-addition to the carbonyl C-atom followed by methyl elimination