DIRECT KINETIC STUDY OF THE REACTION OF OH RADICALS WITH METHYL-ETHYL-KETONE

Emese Szabó, Gábor L. Zügner, István Szilágyi, Sándor Dóbé*, Tibor Bérces** and Ferenc Márta
Chemical Research Center,
Hungarian Academy of Sciences
Pusztaszeri út 59–67, H-1025 Budapest, Hungary

Received August 19, 2008, in revised form October 9, 2008, accepted October 15, 2008

Abstract
The low-pressure discharge flow technique with resonance fluorescence monitoring of OH has been applied to study the kinetics of the overall reaction:

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

The rate constant of \( k_3 = (1.09 \pm 0.09(1\sigma)) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) has been determined at \( T = 297 \pm 3 \text{ K} \). This value agrees well with the IUPAC recommendation which is based on photolysis kinetic studies.

Keywords: Atmospheric chemistry, hydroxyl radical, butanone

INTRODUCTION

Methyl-ethyl-ketone (CH\(_3\)C(O)CH\(_2\)CH\(_3\)), butanone, MEK) occurs in significant concentration in the global troposphere [1] where it has both direct

* Corresponding author. E-mail: dobe@chemres.hu
** Deceased
anthropogenic and biogenic sources, and it is formed also via the atmospheric photo-oxidation of \( n \)-butane. MEK is removed from the atmosphere primarily by its reaction with OH radicals [2,3].

In this letter we present a room temperature experimental study aimed at determining the rate constant for the overall reaction (1) with the application of the thermal kinetic method of discharge flow and direct monitoring of OH. Several direct and relative-rate kinetic studies have been reported for this reaction, but all of them applied the photolysis method to produce the OH radicals [4].

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

**EXPERIMENTAL**

The kinetics of the reaction between OH radicals and MEK were studied by using the low-pressure discharge flow method (DF). Direct monitoring of OH was achieved by \( \text{A}^2\Sigma^+ \rightarrow \text{X}^3\Pi \) (0,0) resonance fluorescence (RF) centered at around 309 nm. The flow reactor was made of Pyrex and had the dimensions of 40.3 mm internal diameter and 600 mm length. Its internal surface was coated with halocarbon wax to reduce the heterogeneous loss of OH radicals. A coaxially positioned moveable injector was used to vary the reaction time. OH radicals were produced in the injector via \( \text{H} + \text{NO}_2 \), H atoms were generated from \( \text{H}_2 \) in a microwave discharge. The DF-RF apparatus and experimental procedure have been described in detail previously [5,6].

Helium (Messer-Griesheim, 99.996%) was the main carrier gas, which was passed through liquid-nitrogen-cooled silica-gel traps before entering the flow system. \( \text{CH}_3\text{C(O)CH}_2\text{CH}_3 \) was obtained from Merck (>99.7% purity) and it was degassed by freeze-pump-thaw cycles prior to use. \( \text{NO}_2 \) (Messer-Griesheim, 98%) was purified by repeated low-temperature distillation. \( \text{H}_2 \) (Linde-Gas, 99.98%) was used premixed with helium and a few percent of argon. Ar was required to facilitate the dissociation of \( \text{H}_2 \) in the microwave discharge (the degree of dissociation was ~10%).

**RESULTS AND DISCUSSION**

The experiments were conducted at \( T = 297 \pm 3 \text{ K} \) reaction temperature and \( p = 3.17 \pm 0.08 \text{ mbar} \) pressure (the quoted uncertainties throughout the paper refer to one standard deviation precision, if not otherwise noted). The bimolecular rate constant for the overall reaction, \( k_1 \), was determined under pseudo-first-order conditions with \( [\text{CH}_3\text{C(O)CH}_2\text{CH}_3] \gg [\text{OH}]_0 \approx 4 \times 10^{11} \)