

**KINETICS OF THE GAS-PHASE REACTIONS OF OH RADICALS WITH  
VOLATILE ORGANIC COMPOUNDS**

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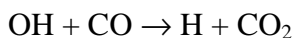
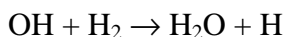
## Introduction

Large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic sources, and a large number of VOCs are present in ambient air (including those formed *in situ* from the atmospheric reactions of other VOCs). In the troposphere, VOCs can be transformed by photolysis (at wavelengths  $\geq 290$  nm), reaction with hydroxyl (OH) radicals (mainly during daylight hours), reaction with nitrate ( $\text{NO}_3$ ) radicals (during nighttime hours), and reaction with ozone ( $\text{O}_3$ ).<sup>1</sup>

Rate constants have been measured for the gas-phase reaction of OH radicals with a large number of VOCs, and the available literature data-base concerning these rate constants has been periodically reviewed and evaluated.<sup>2-5</sup> The reactions of OH radical with  $\leq \text{C}_4$  VOCs are also included in the ongoing NASA<sup>6</sup> and IUPAC<sup>7,8</sup> data evaluations (note that these NASA and IUPAC evaluations are now solely available on the World Wide Web, at the locations given in references 6 and 8). This review and evaluation continues the previous reviews and evaluations of Atkinson,<sup>2-5</sup> and employs the same general format. In each section, for each of the VOCs for which experimental data are available the measured rate constants are reviewed and evaluated. In the table associated with each reaction, under the column labeled “*Technique*” the experimental techniques used are denoted by abbreviations, and the Introduction to each section (alkanes and cycloalkanes, alkenes, aromatic compounds, oxygen-containing compounds, *etc.*) contains a comprehensive list of abbreviations used in that section. For example, use of a flash photolysis system to generate OH radicals with resonance fluorescence monitoring of OH radicals is denoted by PF-RF.

When relative rate methods (denoted in the "*Technique*" column by "RR") were used, the rate constant for the reference compound from the most recent review and evaluation is used to re-evaluate the rate constant for the VOC in question (which therefore may be different from that cited in the original publication). The Introduction to each section also discusses how temperature-dependent data are dealt with in the recommendations.

There are a number of VOCs for which the OH radical reaction rate constants have been measured relative to those for the reactions of OH radicals with H<sub>2</sub> or CO, often at elevated temperatures.



The available rate constant data for these two reactions have been reviewed and evaluated to obtain temperature, and in the case of the CO reaction, pressure dependent rate expressions in order to place the measured rate constant ratios on an absolute basis. For the reaction of OH radicals with H<sub>2</sub>, the absolute rate constants measured by Tully and Ravishankara,<sup>9</sup> Ravishankara *et al.*,<sup>10</sup> Bott and Cohen,<sup>11</sup> Oldenberg *et al.*<sup>12</sup> and Talukdar *et al.*<sup>13</sup> have been fitted to the three-parameter expression  $k = C T^2 e^{-D/T}$  to obtain

$$k(\text{H}_2) = 9.61 \times 10^{-18} T^2 e^{-1457/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 238-1548 K.

The rate constant for the reaction of OH radicals with CO is temperature and pressure dependent (and with the pressure dependence depending on the specific diluent gas used), with the effect of pressure decreasing as the temperature increases. The kinetics of this reaction have been investigated and evaluated by Golden *et al.*,<sup>14</sup> with the recommended rate constant being derived from the experimental data using an RRKM model. In this review and evaluation, a simpler (and somewhat more approximate) rate expression analogous to that used previously<sup>3</sup> has been derived from the recommended experimental rate constants tabulated by Golden *et al.*,<sup>14</sup> of

$$k(\text{CO}) = 9.1 \times 10^{-19} T^{1.77} e^{580/T} [1 + 2.4 \times 10^{-20} [\text{M}](T/298)^{-1}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~290-3000 K and for the pressures encountered in this review article.

Because of the greater uncertainties in the rate constants for this reaction (which are a function of temperature, pressure and diluent gas), rate constants obtained from experimental studies using the reaction of OH radicals with CO as the reference reaction are given relatively low weight in the evaluations, or are not used if other rate data are available.

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