

# RATE CONSTANT FOR THE REACTION OF OH WITH CH<sub>3</sub>CCl<sub>2</sub>F (HCFC-141b) DETERMINED BY RELATIVE RATE MEASUREMENTS WITH CH<sub>4</sub> AND CH<sub>3</sub>CCl<sub>3</sub>

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**Abstract,** Determination of accurate rate constants for OH abstraction is of great importance for the calculation of lifetimes for HCFCs and their impact on the atmosphere. For HCFC-141b there has been some disagreement in the literature for absolute measurements of this rate constant. In the present work rate constant ratios for HCFC-141b were measured at atmospheric pressure in the temperature range of 298-358K, with CH<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> as reference gases. Ozone was photolyzed at 254 nm in the presence of water vapor to produce OH radicals, Relative depletions of 141b and the reference gases were measured by FTIR. Arrhenius expressions for 141b were derived from each reference gas and found to be in good agreement with each other. The combined expression for HCFC-141b which we recommend is  $1.4 \times 10^{-12} \exp(-1630)$  with k at 298 K being  $5.9 \times 10^{-15}$  cm<sup>3</sup>/molec-s. This value is in excellent agreement with the JPL 92-20 recommendation.

## Introduction

Reported kinetics parameters for the OH reaction with 141b have been until recently in poor agreement [Talukdar et al., 1991; Liu et al., 1990; Brown et al., 1990, and Zhang et al., 1992]. The proposed rate constants resulted in calculated lifetimes which differed by a factor of about 2.5. These kinetics parameters were obtained directly by measuring the disappearance of OH in the presence of HCFC-141b. As discussed by Wayne [1992] and others, errors are possible due to impurities, secondary reactions and heterogeneous processes. The relative rate method, in which losses of the reacting molecules are measured, is independent of secondary effects which affect OH concentrations, and therefore serves as a useful check on the consistency of absolute rate constants. In the present work we have measured the rate of OH reaction with HCFC-141b relative to that of two

reference reactants, CH<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub>. Each of these reference compounds has rate constants that are believed to be well established [JPL-92-20].

### Experimental

The method for measuring the relative rate constant for 141 b against reference substances was the same as that previously used by DeMore [1992]. The reactant pairs, 141 b/CH<sub>4</sub> and 141 b/CH<sub>3</sub>CCl<sub>3</sub>, were prepared at pressures of 10 Torr each in a 10 liter storage bulb, and were diluted with Ar to 1000 Torr. Argon, flowing (100 seem/min) through a water bubbler at room temperature, was saturated with water and mixed with a flow (0.8 seem/min) from the storage bulb and with a flow of oxygen (30 seem/min) containing about 1% ozone. Upon entering the temperature-controlled quartz reactor the mixture was irradiated at 254 nm. At this wavelength only the ozone was photolyzed, producing O(<sup>1</sup>D) atoms which react with the water vapor to produce the OH radicals. FTIR spectroscopy was used to monitor the reactant concentrations with and without the reaction with OH. For the experiment of 141b with CH<sub>4</sub> the 141 b C-Cl band at 754 cm<sup>-1</sup> was used for analysis, whereas in the experiments with CH<sub>3</sub>CCl<sub>3</sub> the 141b C-F band at 927 cm<sup>-1</sup> was used, due to interference with the CH<sub>3</sub>CCl<sub>3</sub> C-Cl band at 727 cm<sup>-1</sup>. For CH<sub>4</sub> the C-H stretch at 3016 cm<sup>-1</sup> was used. Products, which included formaldehyde and phosgene, did not interfere with the parent spectra.

The measured absorbance ratio of 141 b with and without the reaction is called the depletion factor (DF), and is defined as the concentration ratio for the given reactant with and without the OH reaction. The rate constant ratio is then given by:

$$\frac{k_{\text{reactant}}}{k_{\text{reference}}} = \frac{\ln(\text{DF})_{\text{reactant}}}{\ln(\text{DF})_{\text{reference}}} \quad (1)$$

### Results

For the experiments with CH<sub>4</sub> as the reference the results for the rate constant ratio are shown in Arrhenius form in Figure 1. Least squares analysis gives

$$k_{141b}/k_{CH_4} = (0.49 \pm 0.16) \exp(189 \pm 105)/T \quad (1)$$

With the recommended kinetic parameters from JPL 92-20 [1992] for CH<sub>4</sub>,

$$k(CH_4) = 2.9 \times 10^{-12} \exp(-1820/T) \quad (2)$$

we obtain for 141b:

$$k_{141b} = 1.4 \times 10^{-12} \exp(-1631/T) \quad (3)$$

$$k(298 \text{ K}) = 5.9 \times 10^{-15} \text{ cm}^3/\text{molec}\cdot\text{s}.$$

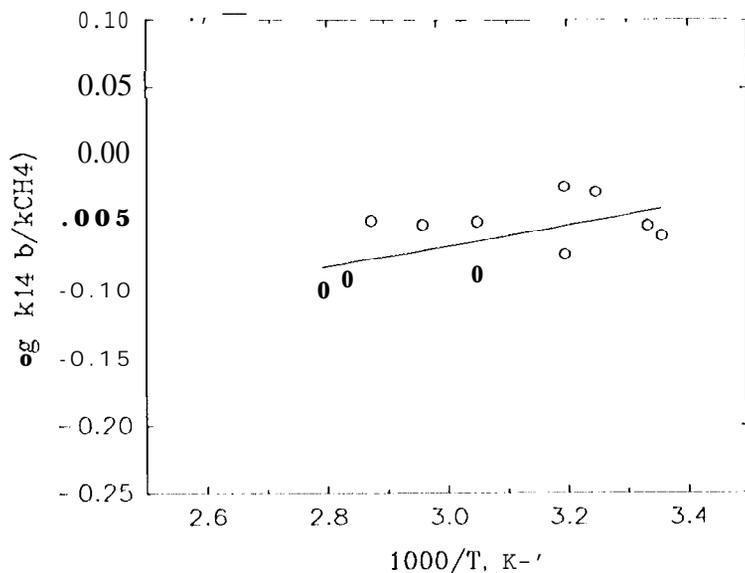


Figure 1. Arrhenius plot for the rate constant ratio of HCFC-141b to CH<sub>4</sub>.

Figure 2 shows the data for the rate constant ratio with CH<sub>3</sub>CCl<sub>3</sub> as the reference gas. The derived Arrhenius for the rate constant ratio is

$$k_{141b}/k_{CH_3CCl_3} = (0.79 \pm 0.07) \exp((-74 \pm 28)/T) \quad (4)$$

With the Arrhenius expression for CH<sub>3</sub>CCl<sub>3</sub> from JPL 92-20 [1992],

$$k_{\text{CH}_3\text{CCl}_3} = 1.8 \times 10^{-12} \exp(-1550/T) \quad (5)$$

the resulting expression for 141 b is:

$$k_{141b} = 1.4 \times 10^{-12} \exp(-1624/T) \quad (6)$$

$$k(298 \text{ K}) = 6.0 \times 10^{-15} \text{ cm}^3/\text{molec}\cdot\text{s}.$$

Thus the derived expressions (equations 3 and 6) for  $k_{141b}$  from the two reference gases,  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ , are in excellent agreement.

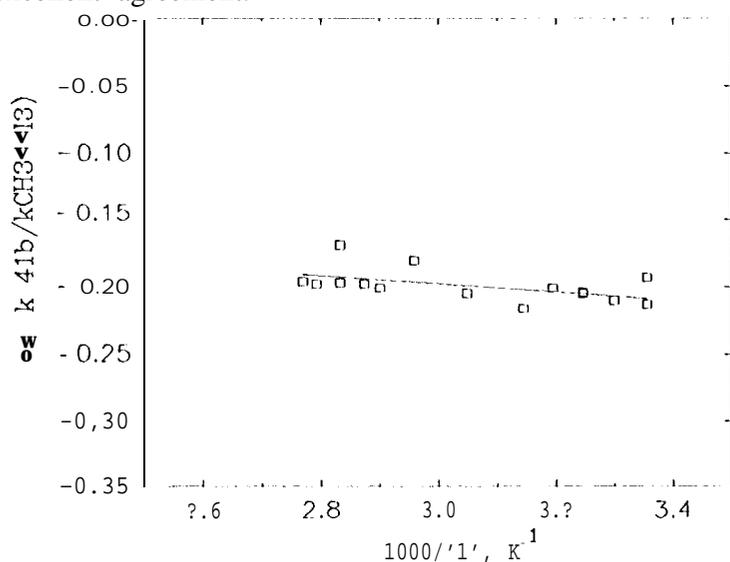


Figure 2. Arrhenius plot for the rate constant ratio for HCFC-141b and  $\text{CH}_3\text{CCl}_3$ .

### Discussion

Figure 3 compares the present results to recent literature data. Our derived rate constants with both  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  as reference gases are in excellent agreement with the data of Talukdar et al. [1991] and Zhang et al. [1992]. A combined value for  $k_{141b}$  from our results (equations 3 and 6) can be represented satisfactorily as

$$k_{141b} = 1.4 \times 10^{-12} \exp(-1630/T) \quad (7)$$

$$k(298) = 5.9 \times 10^{-15} \text{ cm}^3/\text{molec}\cdot\text{s}.$$

The absolute uncertainty at 298 K is probably 10% or less, and the uncertainty in the E/R value is estimated to be  $\pm 150$  K. This expression is very similar to the current JPL 92-20 recommendation,  $k_{41b} = 1.3 \times 10^{-12} \exp(-1600/T)$ , which is based largely on the Talukdar et al. [1991] and Zhang et al. [1992] data.

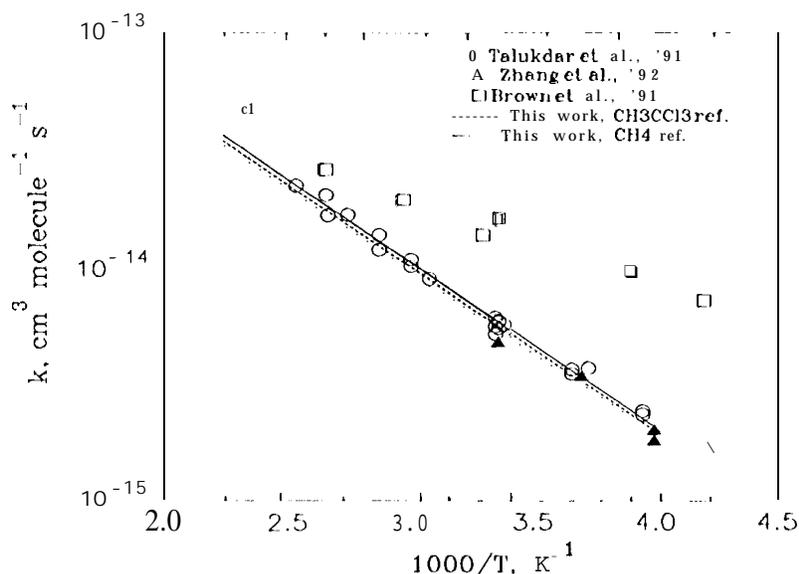


Figure 3. Comparison of present results with recent literature data for  $k_{41b}$ . Our data were taken in the temperature range 298-358 K, but are extrapolated here to a wider range for comparison with the other data.

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