Rate Constant for the Reaction of OH with n-C_4H_{10}

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The kinetic behavior of OH radicals was studied in the presence of a large excess of *n*-butane. Hydroxyl radicals were produced by pulsed vacuum-uv photolysis of H_2O and were monitored directly by a resonance fluorescence method. The rate constant for the reaction OH + *n*-butane was determined to be 2.35 $(\pm 0.35) \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} at 298 °K.

The photooxidation of n-butane in reaction chambers containing polluted air has been proposed to take place in a chain mechanism involving the chain-carrying reaction of OH with n-C_4H_{10} [1]. This system is of special interest since it can play a role in atmospheric chemistry and, in particular, in the formation of photochemical smog [1].

During the course of an investigation of OH reactions of atmospheric significance [2–4], we have studied the reaction

$$OH + n\text{-}C_4H_{10} \rightarrow H_2O + C_4H_9 \,. \qquad (1)$$

The apparatus used in this study consisted of a vacuum-uv flash lamp (20 joules; $\lambda > 1050$ Å), a reactor vessel, a lamp to generate OH emission, and a detector for OH resonance fluorescence. The experimental technique has been described elsewhere in detail [3]. Briefly, low concentrations of OH radicals ($\sim 3 \times 10^{11}$ cm^{-3}) were generated by the repetitive flash potolysis of H_2O. Decays of OH radicals were monitored in the presence of a large excess of *n*-C_4H_{10} by OH resonance fluorescence ($A^2\Sigma^+$; $v' = 0 \rightarrow X^2\Pi$; $v'' = 0$). Typically, 100 decay curves were averaged by a multichannel analyzer to improve the signal-to-noise ratio. The gases were used without further purification and had the following stated purities: *n*-C_4H_{10}, 99,98% (Phillips) and He, 99,9999% (Matheson). The most probable impurity in the *n*-C_4H_{10} sample was iso-C_4H_{10} as stated by the manufacturer. The H_2O samples were thoroughly degassed prior to use.

The decays of OH radicals were always found to be exponential over a range of OH concentration of more than one order of magnitude. From the lifetime, τ, first order decay rates, τ^{-1}, of OH radicals were determined as a function of pressure of *n*-C_4H_{10} at constant pressures of 0.05 torr H_2O and 20 torr diluent He. The results of this study are presented in Fig, 1 as a plot of τ^{-1} vs. $[n\text{-}C_4H_{10}]$. The pressure of n-butane was varied from 1.8 to 8 mtorr. The filled circles in this figure represent decays of OH at an initial OH concentration of $\sim 2 \times 10^{12}$ cm^{-3}. This concentration was generated in the photolysis of 0.3 torr H_2O. The data of Fig. 1 were analyzed according to Equation (I)

$$\tau^{-1} = \tau_0^{-1} + k_1 [n\text{-}C_4H_{10}] \qquad (I)$$

as described previously [3]. In Eq. (I), τ^{-1} and τ_0^{-1} are the decay rates in the presence and absence of *n*-C_4H_{10}, and k_1 is the rate constant for Reaction (1). According to Eq. (I), the slope of the linear plot in Fig. 1 determines k_1 to be 2.35×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} at 298 °K. The accuracy of this rate constant was estimated from the precision of the pressure and the time measurements to be ±15% [3]. Impurities contained in the sample gas or produced photolytically should have a negligible effect on the decay rates because of the low concentrations of these impurities. Secondary reactions of reaction products with OH radicals are not very likely under the present experimental conditions. This is supported by the experiments at higher initial concentrations of OH (filled data points in Fig. 1), which would favor secondary reactions.

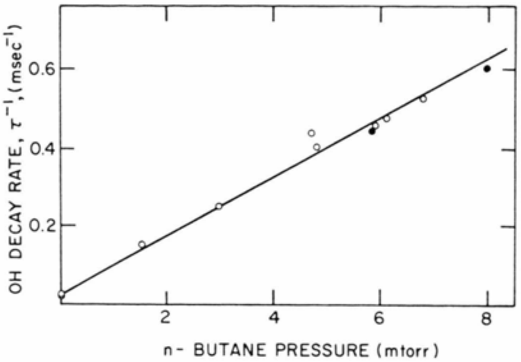

Fig. 1. Decay rates of OH radicals, τ^{-1}, as a function of the pressure of *n*-butane. *n*-Butane was added to a mixture of 0.05 torr H_2O and 20 torr He. In two experiments, (●), 0.3 torr H_2O was added.

The rate constant k_1 has been previously reported by Greiner [5] using flash photolysis (~ 1000 joules; $\lambda > 1600$ Å) combined with kinetic absorption spectroscopy. After a small stoichiometric correction, this author determined a value of 2.57×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} at 298 °K [5]. This value is in

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Table 1. Summary and Comparison of the Rate Constants for $OH = n\text{-}C_4H_{10}$ and $OH + C_3H_6$ at 2989 °K[a].

	Ref. [6, 7]	Ref. [5]	This Work
$n\text{-}C_4H_{10}$	4.1×10^{-12}	2.57×10^{-12}	2.35×10^{-12}
C_3H_6	1.7×10^{-11}		1.45×10^{-11} [b]

[a] Rate constants in units cm^3 molecule^{-1} sec^{-1}.

[b] F. Stuhl, to be published.

very good agreement with the present result. In a tection, Morris and Niki[6] determined relative rate discharge flow study using mass spectrometric de- constants for a number of reactions of OH with hydrocarbons. These relative rate constants have been based on the absolute value for the reaction of OH with propylene which has been reported previously by Morris, Stedman, and Niki[7]. On the basis of these relative[6] and absolute[7] values, one calculates k_1 to be 4.1×10^{-12} cm^3 molecule^{-1} sec^{-1} which is 75% greater than the present value. Table 1 summarizes previous results and the present value. For comparison, rate constants for the reaction of OH with propylene are also included.

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