

## Short Communication

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### Absolute Rate Constants for the Reaction of O(<sup>3</sup>P) with NO in Ar from 237 to 397 K

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The rate of the reaction



has been studied extensively by various methods. The room temperature rate constant for reaction (1) in Ar has been found to be in the range  $(5.5 - 8.0) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . The early rate data on the temperature dependence of this reaction suggested that the reaction had a negative activation energy of about  $-1900 \text{ cal mol}^{-1}$ . More recent investigations of the temperature dependence of this reaction have reported less negative activation energies. A recent kinetics data survey [1] recommends an activation energy of  $-1160 \text{ cal mol}^{-1}$ . This study uses flash photolysis of NO with NO<sub>2</sub> chemiluminescence detection to investigate the temperature dependence of the termolecular reaction (1) in Ar.

#### 1. Experimental

The technique used is similar to that described by Stuhl and Niki [2] and Atkinson *et al.* [3]. O(<sup>3</sup>P) atoms were produced by the vacuum ultraviolet flash photolysis of NO either at wavelengths longer than the LiF window cutoff (above 105 nm) or by light transmitted by an interference filter (39% T at 180 nm, half-bandwidth 40 nm). The relative O(<sup>3</sup>P) atom concentration was monitored as a function of time after the flash by detection of NO<sub>2</sub> chemiluminescence.

#### 2. Results and discussion

The rate constant for reaction (1) was determined by performing the experiments under pseudo first order conditions,  $[\text{NO}] \gg [\text{O}({}^3\text{P})]$ . The observed pseudo first order rate constant  $k_{\text{obs}}$  is given by

$$k_{\text{obs}} = k_{\text{ter}} [\text{NO}] [\text{Ar}] + k_{\text{d}} \quad (2)$$

where  $k_{\text{ter}}$  is the termolecular rate constant for reaction (1) and  $k_{\text{d}}$  is the first order rate constant for the loss of O(<sup>3</sup>P) atoms by diffusion out of the

reaction viewing zone. The pseudo first order rate constant was determined from a least-squares fit of the logarithm of the NO<sub>2</sub> chemiluminescence signal *versus* time. The termolecular rate constant for reaction (1) was determined by an analysis of the pseudo first order rate constants for different NO and Ar concentrations. An Arrhenius fit of the data for the six temperatures investigated resulted in

$$k_{\text{ter}} = (1.27 \pm 0.20) \times 10^{-32} \exp\{(1010 \pm 100)/1.987 T\} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

where the quoted uncertainties are one standard deviation. Alternatively, the temperature dependent data were fitted to an equation of the form  $k = BT^{-n}$ . This fit resulted in  $B = (1.17 \pm 0.20) \times 10^{-27}$  and  $n = 1.70$ .

Figure 1 shows a comparison of the temperature dependence of the present values of  $k_{\text{ter}}$  with those reported previously for Ar as the third body. The agreement is generally good. The activation energy reported in this work,  $-1010 \pm 100 \text{ cal mol}^{-1}$ , is in good agreement with that recently reported for Ar by Michael *et al.* [4],  $-1180 \pm 70 \text{ cal mol}^{-1}$ , and Atkinson *et al.* [3],  $-940 \pm 200 \text{ cal mol}^{-1}$ . The similarity between these activation energies and those reported for He, Ne, Kr and N<sub>2</sub> by Michael *et al.* [4] and for N<sub>2</sub>O by Atkinson and Pitts [12] and Singleton *et al.* [13] suggests that there is little change in the temperature dependence of this reaction with different third bodies.

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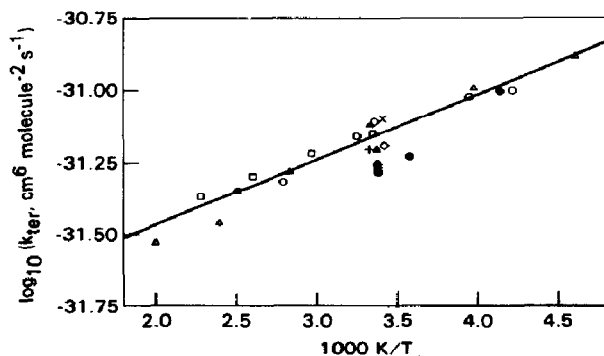


Fig. 1. Comparison of the temperature dependence of  $k_{\text{ter}}$  values:  $\circ$ , this work;  $\Delta$ , ref. 4;  $\square$ , ref. 3;  $\bullet$ , ref. 5;  $\blacksquare$ , ref. 6;  $\blacklozenge$ , ref. 7 (as recalculated [4]);  $\blacktriangle$ , ref. 8;  $\times$ , ref. 9;  $+$ , ref. 10;  $\diamond$ , ref. 11. The line represents a least-squares fit to the data reported in this work.

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