Studying the methyl reorientation process in further detail,[3] we repeated the line shape measurement on heptane (purity >99%) at 133 and 93°K (Figure 1). The signal-to-noise ratio was improved by means of a spectrum accumulator.

Only one broad peak at 93°K, with a line width (δH) of 15.2 G, was observed, which suggests that the entire molecule can be considered rigid at this temperature. Contrary to the results of Anderson and Slichter, the line shape at 133°K consists of three rather than two peaks, the line width of the narrowest peak being 0.57 G. The intensity increases with increasing temperature. A repetition of the solidifying procedure, however, showed that the reproducibility of this peak is poor, which will be clear from a comparison of our results with those of Anderson and Slichter. The peak must be due to lattice defects, which give sufficient motional freedom to the surrounding molecules to narrow the line as observed.

The line widths of the two broader peaks are 13.2 and 6.7 G and differ by only a factor of 2. The peak with line width 6.7 G corresponds with the reorienting methyl groups. The narrowing factor agrees reasonably well with that found in solid methyl ketones.[3]

Absolute Rate Constants for the Reaction of Atomic Oxygen with 1-Butene over the Temperature Range of 259-493°K

by Robert E. Huie,[1]

University of Maryland, College Park, Maryland, and National Bureau of Standards, Washington, D. C.

John T. Herron,

National Bureau of Standards, Washington, D. C.

and Douglas D. Davis*[2]

University of Maryland, College Park, Maryland
(Received May 26, 1971)

Several studies have been made of the reaction of atomic oxygen in its ground electronic state with 1-butene.[3-5] Typically, these investigations have involved the production of atomic oxygen in a mixture of two reactive species, with the relative rates of reaction determined by following the rate of production of characteristic reaction products. In only one study, using a discharge flow system, has an absolute rate measurement been made.[6] Because there is disagreement among the rate measurements with regard to the reaction's temperature dependence,[7] we have applied the technique of flash photolysis-resonance fluorescence to this system in an effort to better define its kinetic rate parameters.

The apparatus and technique used in this study have been previously described[8-10] and will be discussed here only briefly. In these experiments, a mixture of oxygen, 1-butene, and a large excess of argon is flash-photolyzed, producing between 10^{11} and 10^{12} oxygen atoms per cm³ (3×10^{-3} to 3×10^{-2} mTorr). The oxygen atoms are excited by the absorption of oxygen resonance radiation from an oxygen resonance lamp and fluoresce in a time on the order of 10^{-8} to 10^{-9} sec. The fluorescence is monitored at right angles to the resonance and flash lamps using an electron magnetic multiplier detector, and the temporal history of the oxygen atoms is then followed by feeding the signal from the detector into a multichannel analyzer. Since single photon counting techniques are employed here, statistical fluctuations in the signal are reduced by taking many flashes (>50) to produce one kinetic curve. The gas mixture in these experiments is changed several times during the development of a kinetic curve to ensure that the total consumption of the 1-butene never exceeds 5%. The experiments are performed with an excess of 1-butene, so that first-order loss of atomic oxygen prevails. The pseudo-first-order rate constant for the loss of atomic oxygen, corrected for both diffusion of oxygen atoms from the reaction zone and reaction of O atoms with O_2, can then be used to derive the second-order rate constant for the reaction. The diffusion and O plus O_2 reaction correction is typically 15% or less of the rate of reaction of O atoms with 1-butene.

The reaction has been studied over a pressure range of 20 to 200 Torr, using argon as a diluent gas, over a concentration range of 1-butene of 1.29 to 12.9 mTorr, and over an approximate initial oxygen atom concentration range of 2×10^{11} to 8×10^{11} atoms cm⁻³ (6×10^{-3} to 2.5×10^{-2} mTorr). The results given in Table I demonstrate that over these ranges the rate constant for this reaction is both independent of the total pressure and the concentration of either reactant.

(1) This research, carried out at the University of Maryland, is part of a thesis to be submitted to the Faculty of the University of Maryland in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

(2) Acknowledgment is made by this author to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(3) R. J. Cvetanović, *J. Chem. Phys.*, 23, 1063 (1960).

(4) I. M. W. Smith, *Trans. Faraday Soc.*, 64, 378 (1968).

(5) D. Saunders and J. Heicklen, *J. Phys. Chem.*, 70, 1950 (1966).

(6) L. Elias, *J. Chem. Phys.*, 38, 989 (1960).

(7) R. J. Cvetanović, *Advan. Photochem.*, I, 115 (1963).

(8) W. Braun and M. Lenzi, *Discuss. Faraday Soc.*, 44, 252 (1969).

(9) D. D. Davis, W. Braun, and A. M. Bass, *Int. J. Chem. Kinet.*, 2, 101 (1970).

(10) D. D. Davis, R. E. Huie, J. T. Herron, M. J. Kurylo, and W. Braun, *J. Chem. Phys.*, in press.

Table I: Absolute Rate Constants for the
Reaction $O(^3P)$ + 1-butene → products[a]

T, °K	[1-C$_4$H$_8$], mTorr	[O$_2$], Torr	Total pressure, Torr, Ar	Flash energy,[b] J	k, cm^3 molecule^{-1} sec^{-1} × 10^{12}
298	5.26	1	20	32	3.84
298	5.26	1	20	18	4.10
298	5.26	1	20	8	4.20
298	5.26	1	200	26	3.86
298	2.63	0.5	10	20	4.10
298	1.29	1	200	18	3.73
298	12.9	1	200	18	4.20
259	2.53	0.5	100	42	3.38
274	2.77	1	40	45	3.76
343	2.63	1	200	20	4.69
403	2.63	1	200	20	5.27
493	4.25	1	200	45	7.16

[a] Products from this reaction would include α-butene oxide, n-butanal, carbon monoxide, and methyl ethyl ketone.[7] [b] A flash energy of 45 J in this system corresponds to an incident light intensity at the reaction cell of $\sim 8 \times 10^{12}$ photons/cm^2.

A linear least-squares fit of the data to the Arrhenius expression yields

$$k = (1.46 \pm 0.15) \times 10^{-11} \exp\left(\frac{-760 \pm 60 \text{ cal mol}^{-1}}{RT}\right)$$

cm^3 molecule^{-1} sec^{-1}

where 1 cal mol^{-1} = 4.18 J mol^{-1}. The quoted error limits are the standard errors of the reported values based upon the least-squares treatment of all the data. Figure 1 shows the data in the Arrhenius form, along with the data of previous workers. The relative rate data of Saunders and Heicklen[5] and Cvetanović[3] were converted into absolute rate constants using the rate expression for the reaction of atomic oxygen with ethylene obtained in this laboratory[10]

$$k(O + C_2H_4) = 5.42 \times 10^{-12} \exp\left(\frac{-1130 \text{ cal mol}^{-1}}{RT}\right)$$

cm^3 molecule^{-1} sec^{-1}

The absolute values from Smith's data depend on the results of Klein and Herron[11] for the reaction of atomic oxygen with nitrogen dioxide.

The data points of the other workers all fall within about 25% of our computed Arrhenius line. With the exception of the activation energy derived from the relative rate data of Cvetanović ($E \sim -70$ cal mol^{-1}), the
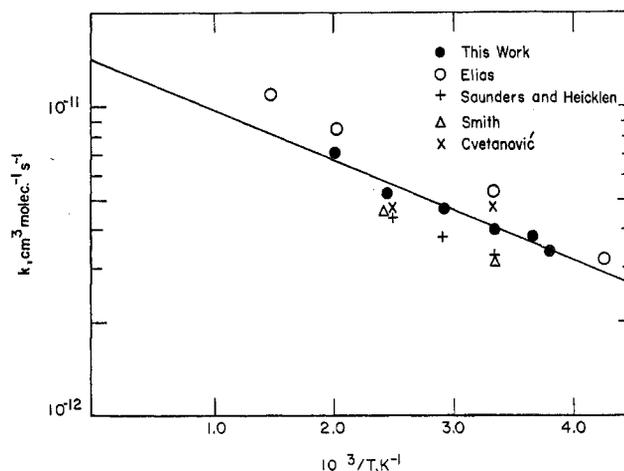

Figure 1. Arrhenius plot of the reaction of atomic oxygen with 1-butene.

activation energies predicted by these other data agree quite well with ours (within 15%). A comparison of our data for ethylene and 1-butene with the relative data of Cvetanović shows that for the ratio of 1-butene to ethylene at 298°K Cvetanović's results are 16% higher than ours (5.7 to 4.9). However, at 398°K we are 30% higher than Cvetanović (4.0 to 3.0). Thus, although the absolute discrepancy is not extremely large at either temperature, the combined deviations at the two temperatures result in a very significant difference in the calculated Arrhenius activation energy for 1-butene. The reason that the relative rate data of Cvetanović give such a large activation energy difference between ethylene and 1-butene is not, at present, obvious.

(11) F. S. Klein and J. T. Herron, *J. Chem. Phys.*, **41**, 1285 (1964).