

xenon as an internal standard we find the result: $I_2(\text{C}_2\text{H}_5\text{NO}) = 10.1 \pm 0.2$ eV. Also shown for comparison is an ionization efficiency curve for formation of $\text{C}_2\text{H}_5\text{N}=\text{NC}_2\text{H}_5^+$ which leads to a value of $I_2(\text{C}_2\text{H}_5\text{N}=\text{NC}_2\text{H}_5) = 8.7 \pm 0.1$ eV. This value may be compared with the value of 8.65 ± 0.2 eV for the ionization potential of azomethane reported by Prasil and Forst;³⁷ the agreement suggests that the lowest ionization potential of azoalkanes involves removal of a non-bonding electron on one of the nitrogen atoms.

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Absolute Rate Constants for the Addition and Abstraction Reactions of Atomic Oxygen with 1-Butene over the Temperature Range 190–491 K¹

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Using the technique of flash photolysis-resonance fluorescence, absolute rate constants have been measured for the reaction of ground-state atomic oxygen with 1-butene over the temperature range 190–491 K. With a measured precision of 3–5% at each temperature, it was found that the data could not be fit by a single straight line. It was concluded that the curvature in the Arrhenius plot was due to concurrent abstraction and addition reactions, the former process representing approximately 15% of the total reaction at 300 K and 39% at 500 K. The rate expressions derived were $k_{\text{addition}} = (3.7 \pm 1.8) \times 10^{-12} \exp(-50 \pm 210 \text{ cal mol}^{-1}/RT)$ cm³ molecule⁻¹ sec⁻¹ and $k_{\text{abstraction}} = (1.6 \pm 0.9) \times 10^{-11} \exp(-1970 \pm 430 \text{ cal mol}^{-1}/RT)$ cm³ molecule⁻¹ sec⁻¹.

In a recent paper,³ absolute rate constants were reported for the reaction of atomic oxygen, O(³P), with 1-butene over the temperature range 259–493 K. An activation energy for this reaction of 760 cal mol⁻¹ was derived. More recently, Kurylo⁴ has studied the reaction of atomic oxygen with propene, also a terminal olefin, and found an activation energy of 73 cal mol⁻¹. Since O(³P) addition to propene and 1-butene might be expected to have similar activation energies (both being terminal olefins), we have extended our previous measurements to lower temperatures to investigate the possibility that abstraction of the internal α -hydrogens in 1-butene might have been important at the higher temperatures.

The apparatus and technique used in this work have been described previously^{3,5} and will not be discussed here. For the 1-butene reaction, rate constants have been determined from 190 to 491 K with the results

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Table I: Rate Constants for the Reaction of Atomic Oxygen with Propene and 1-Butene

<i>T</i> , K	Olefin, mTorr	O ₂ , Torr	Total pres- sure, Torr, Ar	Flash energy, ^a J	First- order <i>k</i> , (s ⁻¹)	<i>k</i> × 10 ¹² , cm ³ mole- cule ⁻¹ sec ⁻¹	<i>T</i> , K	Olefin, mTorr	O ₂ , Torr,	Total pres- sure, Torr, Ar	Flash energy, ^a J	First- order <i>k</i> , (s ⁻¹)	<i>k</i> × 10 ¹² , cm ³ mole- cule ⁻¹ sec ⁻¹
Propene							272	12.6	1	20	45	1670	3.61
215	5.47	1	20	31	892	3.43	274	...	1	40	30	64	...
257	5.30	1	20	26	801	3.77	274	2.77	1	40	30	455	3.62
298	5.30	1	20	18	730	3.99	298	...	0.5	10	40	81	...
							298	...	1	20	45	44	...
							298	...	1	200	40	130	...
							298	1.29	1	200	18	282	3.73
							298	2.63	0.5	10	20	424	4.10
190	6.65	1	20	45	1168	3.23	298	2.71	1	20	18	444	4.57
200	...	1	20	31	66	...	298	5.26	1	20	32	689	3.84
200	1.81	1	20	45	394	3.73	298	5.26	1	20	18	730	4.10
200	2.67	1	20	31	467	3.12	298	5.26	1	20	8	747	4.20
200	6.65	1	20	20	1155	3.40	298	5.26	1	200	26	777	3.86
200	6.65	1	20	130	1100	3.24	298	8.20	1	20	18	1156	4.20
200	7.98	1	20	31	1272	3.13	298	8.25	1	20	28	1110	3.99
215	...	1	20	31	51	...	298	12.9	1	200	18	1895	4.20
215	2.68	1	20	31	467	3.47	343	...	1	200	20	59	...
215	7.93	1	20	31	1316	3.56	343	2.63	1	200	20	396	4.69
226	...	1	20	29	51	...	370	...	1	20	45	60	...
226	...	1	200	29	296	...	370	3.3	1	20	39	437	4.38
226	1.84	1	20	26	311	3.31	370	6.38	1	20	39	810	4.52
226	3.10	1	200	29	996	3.10	370	13.7	1	20	39	1670	4.51
226	5.31	1	20	10	820	3.47	403	...	1	200	20	44	...
226	5.31	1	20	80	757	3.19	403	2.63	1	200	20	366	5.27
226	10.7	1	20	26	1530	3.24	472	...	1	20	29	196	...
248	...	1	40	45	41	...	472	3.26	1	20	29	556	5.41
248	2.77	1	40	45	397	3.62	472	6.18	1	20	29	891	5.51
259	...	0.5	100	45	46	...	472	11.1	1	20	29	1350	5.14
259	2.53	0.5	100	45	364	3.38	484	...	1	20	36	187	...
272	...	1	20	45	51	...	484	3.26	1	20	36	566	5.74
272	...	2	200	45	191	...	484	6.61	1	20	18	950	5.79
272	2.21	1	20	45	357	3.91	484	6.61	1	20	100	928	5.62
272	5.37	1	200	45	934	3.90	484	13.3	1	20	36	1613	5.38
272	7.10	1	20	22	972	3.68	491	...	1	200	45	111	...
272	7.10	1	20	100	919	3.45	491	7.3	1	200	45	961	5.92

^a A flash energy of 45 J corresponds to an incident light intensity of about 8×10^{12} photons/cm² at the reaction cell at wavelengths <1800 Å.

presented in Table I. Excluded is the data point at 493 K reported previously³ and now thought to have been in error. At several temperatures, reactant concentration, total pressure, and flash intensity were varied to ascertain that no secondary reactions were taking place, as has been described previously.⁵ In Figure 1, the data are presented in Arrhenius form. The points shown are average values at temperatures where three or more measurements were made. It can be seen that these data can only be fit by a curved line. This curve, however, can be approximated by the sum of two straight lines—one of which can be assumed to correspond to the addition of atomic oxygen to the double bond and the other to the abstraction of the internal α -hydrogens. Thus, the following two rate expressions may be derived.

$$k_{\text{addition}} = (3.7 \pm 1.8) \times 10^{-12} \times \exp\left(\frac{-50 \pm 210 \text{ cal mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_{\text{abstraction}} = (1.6 \pm 0.9) \times 10^{-11} \times \exp\left(\frac{-1970 \pm 430 \text{ cal mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

The expression for the addition reaction was obtained by a straight line fit to the lower temperature data (<260 K). The expression for the abstraction reaction was determined by subtracting the values predicted for the addition reaction from the higher temperature data and fitting this difference to a straight line. The stated uncertainties in the Arrhenius expressions were derived from a consideration of the lines with the max-

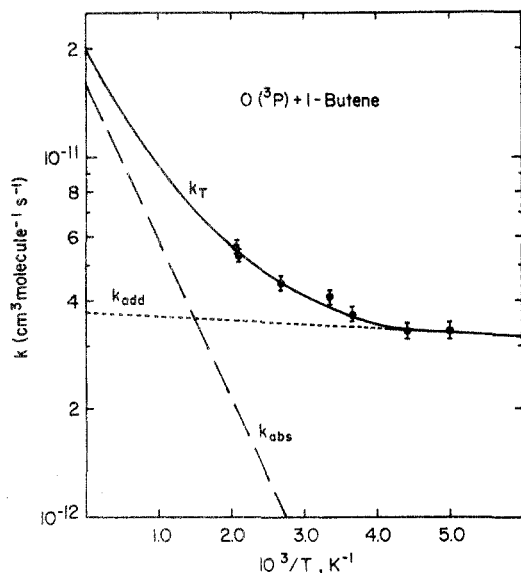


Figure 1. Arrhenius plot for the reaction of atomic oxygen with 1-butene.

imum and minimum slopes drawn through the attached error bars (3–5%). In addition to the measurements reported here, Kurylo has also made several measurements of the rate constant for reaction of $O(^3P)$ with 1-butene and found the values to be in good agreement ($\pm 5\%$) with ours.⁶

In the case of the reaction of $O(^3P)$ with propene, single measurements were made in this study at 216, 257, and 298 K. These results are also given in Table I and are within 6% of those rate constants reported by Kurylo at comparable temperatures.⁴ Although these data do not establish that both addition and abstraction reactions are taking place in the 1-butene reaction, the derived Arrhenius parameters are consistent with this interpretation. A comparison of the activation energy for reaction of $O(^3P)$ with propene and 1-butene shows that for the addition reaction very similar values are obtained, 76 vs. 50 cal/mol. The reasonableness of these values has recently been demonstrated in a related study by Klemm and Davis⁷ in

which the activation energies for addition of $S(^3P)$ to propene and 1-butene were both found to be 360 cal/mol. It is also noteworthy that in the study by Klemm and Davis⁷ no curvature was observed in the Arrhenius plot for the $S(^3P)$ –1-butene system over the temperature range 216–475 K. This result is in keeping with the known higher activation energy required for H atom abstraction from hydrocarbons by $S(^3P)$ vs. $O(^3P)$.

For the $O(^3P)$ –1-butene abstraction reaction, it is observed that the preexponential factor is in good agreement with those observed for atomic oxygen–alkane reactions ($1\text{--}3 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹) in which hydrogen abstraction is the most probable reaction.^{8,9} The activation energy for this process is lower than the activation energies measured for most alkane reaction,^{8,9} but is consistent with the very low C–H bond strength for internal α -hydrogens (82 kcal/mol) recently reported by Tsang.¹⁰

The conclusion that the curvature in the Arrhenius plot is due to concurrent abstraction and addition reactions is supported further by comparison with the equivalent situation involving atomic hydrogen. From an analysis of the reaction products, Falconer and Sunder¹¹ concluded that 1.6% of the $H + 1\text{-C}_4\text{H}_8$ reaction proceeded by the abstraction of the α -hydrogen at room temperature. The addition and abstraction component lines presented in Figure 1 indicate that for atomic oxygen, 15% of the reaction proceeds by abstraction at 298 K and 39% at 500 K. However, the lower error limit given in the Arrhenius expression for abstraction predicts $\sim 1\%$ of the total reaction is due to abstraction at 298 K and 20% at 500 K. The correct value at each temperature undoubtedly lies somewhere between these two sets of numbers.

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