Temperature Dependence of the Reactions of Oxygen Atoms with Olefins[1]

D. L. Singleton* and R. J. Cvetanović*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received February 25, 1976

Abstract: Modulated photosensitized decomposition of nitrous oxide was used to generate ground state oxygen atoms, $O(^3P)$, and to determine by the phase shift method the temperature dependence of the rate constants for their reactions with ethylene, propylene, 1-butene, 3-methyl-1-butene, isobutene, and *cis*-2-butene over the temperature interval 298–480 K. The Arrhenius parameters obtained are compared with the available values in the literature. An excellent agreement is found particularly with the (normalized) relative data obtained previously in this laboratory by product analysis in competitive experiments. The results are also in very good general agreement with the $O(^3P)$ rate data in the literature obtained by the resonance fluorescence method. Relatively high precision of the present phase shift measurements makes it possible to probe into some finer details of the effect of temperature on the rates of these very fast reactions. A negative value of the Arrhenius energy parameter for the *cis*-2-butene reaction has been confirmed. The negative Arrhenius energy parameters in this and some other reactions are discussed and a potential interpretation of the curvatures of the Arrhenius plots observed for some of the reactions is outlined. The rate constants and Arrhenius parameters determined for propylene, 1-butene, and 3-methyl-1-butene are very similar, despite the decreasing strength of the allylic C–H bonds in this series of olefins. These results, therefore, do not support the postulate that abstraction by $O(^3P)$ atoms of the labile allylic hydrogen atoms in 1-butene competes extensively, in the temperature range employed, with addition of $O(^3P)$ atoms to the double bond.

Since the determination of relative values of the rate constants of the reactions of ground state oxygen atoms, $O(^3P)$, with a series of olefins[2] several new techniques have made possible precise determinations of their absolute values. These include a flash photolysis technique with detection of oxygen atoms by resonance fluorescence[3] and two techniques which use the chemiluminescence from the $O(^3P)$ + NO reaction to monitor oxygen atom concentration. In one technique the atoms are generated by vacuum uv flash photolysis (of NO or O_2)[4] and in the other by modulated mercury photosensitized decomposition of nitrous oxide.[5] The latter technique, the phase shift technique for oxygen atom reactions, was developed in this laboratory. It is particularly well suited for measurements of rate constants of very fast reactions and is potentially very accurate. Although the rate constants of $O(^3P)$ reactions with several olefins reported in the original two papers[5,6] contained a systematic error due to a faulty flow meter calibration, the error was soon recognized and corrected.[7] The room temperature values of the rate constants were redetermined[7] and found to be in very good agreement with the values obtained by the other two techniques. Since a determination of the temperature dependence of such extremely fast reactions requires very high experimental precision, the Arrhenius parameters were not redetermined at that time because work was in progress on further refinements of the phase shift technique. Substantial improvements in the experimental control and precision have resulted in the reduction of the average standard deviation of the room temperature rate constants from 12% in the previous experiments[7] to about 3% in the present work. The Arrhenius parameters for the reactions of $O(^3P)$ with tetramethylethylene[8] and with benzene and toluene[9] have been recently determined with the present degree of precision. The results confirmed the substantial negative value[10] of the Arrhenius activation energy for the tetramethylethylene reaction, but the Arrhenius expression obtained ($k_{2(TME)} = 1.4 \times 10^{10}$ exp(774 cal mol^{-1}/RT) l. mol^{-1} s^{-1}) was significantly different from the resonance fluorescence result ($k_{2(TME)} = 3.36 \times 10^9$ exp(1570 cal mol^{-1}/RT) l. mol^{-1} s^{-1}).[10]
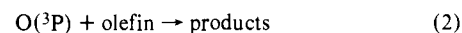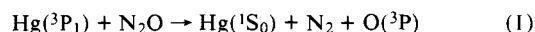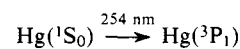
The temperature dependence of the rate constants of several other oxygen atom reactions with olefins determined by the resonance fluorescence technique has been reported recently.[10-12] A slight negative activation energy has been reported for the *cis*-2-butene reaction.[10] Also, considerable attention is focused on the curvature observed in the Arrhenius plot for the 1-butene reaction,[12] with the postulate that it indicates the concurrence of two reactions of oxygen atoms with this olefin: addition to the double bond and extensive abstraction of a labile allylic hydrogen atom.

The main object of the present work has been to measure precisely by the phase shift technique the temperature dependence of the $O(^3P)$ atom reactions with several simple alkenes (ethylene, propylene, 1-butene, 3-methyl-1-butene, isobutene, and *cis*-2-butene). The negative temperature dependence of the *cis*-2-butene reaction has been verified, and the observation of negative Arrhenius activation energies in some of these reactions is discussed. The validity of the postulate of extensive abstraction of the labile allylic hydrogen atoms in the 1-butene reaction has been explored further through a comparative study of the rate constants and their temperature dependence in the series propylene, 1-butene, and 3-methyl-1-butene. In this series the allylic hydrogen atoms, in changing from primary to secondary to tertiary, become significantly more labile. The rate parameters should therefore be quite different for the three olefins if the allylic hydrogen atoms are indeed extensively involved in the reactions.

Experimental Section

Details of the apparatus and procedure have been given previously.[5,7,8] The following sequence of reactions is initiated by a sinusoidally modulated low pressure mercury lamp:

$$Hg(^1S_0) \xrightarrow{254\ nm} Hg(^3P_1)$$

$$Hg(^3P_1) + N_2O \rightarrow Hg(^1S_0) + N_2 + O(^3P) \qquad (1)$$

$$O(^3P) + olefin \rightarrow products \qquad (2)$$

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (3)$$

The measured phase difference, ϕ, between the 254-nm light (modulated at frequency ν) and the chemiluminescence from reaction 3 is related to the rate constants for reactions 2 and 3 by the equation

$$\tan \phi = 2\pi\nu(k_2[olefin] + k_3[NO][M])^{-1}$$

The flow rates of nitric oxide and the olefins were determined with calibrated capillary flow meters. For the more reactive olefins, isobutene and *cis*-2-butene, which required smaller olefin flow rates, capillaries were calibrated for accurately known mixtures of the olefins

and nitrous oxide. The flow rate of nitrous oxide was measured with a rotameter which was calibrated daily.

The rate of formation of oxygen atoms was measured by gas chromatographic analysis of the products of the $O(^3P)$ + 1-butene reaction. The rate was between 1×10^{12} and 1.4×10^{13} atoms cm^{-3} s^{-1} over the period of time it took to do all the experiments. The flow rates were such that there was less than 1% conversion of isobutene and cis-2-butene and less than 0.3% conversion of the other olefins.

The gases had the following stated purities: ethylene, 99.98%; propylene, 99.7%; 1-butene, 99.87%; 3-methyl-1-butene, 99.9%; isobutene, 99.8%; cis-2-butene, 99.9%; nitrous oxide, 98.0%; nitric oxide, 99.0%. The nitric oxide was passed through activated Linde 13X molecular sieve to remove traces of nitrogen dioxide.

Results

Rate constants were obtained from the intercepts (k_2) and slopes (k_3) determined by weighted least-squares analyses of plots of $2\pi\nu/$[olefin] tan ϕ vs. [NO][M]/[olefin] as described previously.[8] At each temperature the flow rates of the olefins were varied by a factor of 4 or 5, the flow rate of NO by about 2, the total pressure by about 2, and the modulation frequency usually by 2. The total pressures were in the range 30–90 Torr and the modulation frequencies were between 2 and 8 kHz. At least 11 points were obtained for each reaction at each temperature. The rate constants are given in Table I. The indicated uncertainties are the least-squares standard deviations. For all olefins except ethylene, the data include two sets of measurements separated by time intervals of several months. The mutual consistency of the sets is shown by the excellent agreement between the two values determined at 298 K.

A previously suggested mechanism[7] has been used to estimate the upper limits of the extent of secondary reactions of oxygen atoms with primary reaction products. It is assumed that two radicals are formed each time an oxygen atom reacts with either an olefin or a radical and that radicals are lost by recombination (to form an unreactive species). According to this mechanism, for all of the present experiments, less than 1% of the oxygen atom loss is due to reaction with free radicals.

The maximum possible influence of the impurities present in the olefins (as indicated in the Experimental Section) was assessed by assuming that the total impurity in each case reacted with oxygen atoms with a rate constant of 1×10^{10} l. mol^{-1} s^{-1} (i.e., the rate constants for $O(^3P)$ + isobutene or 1,3-butadiene). On this basis, calculations show that the rate constants for isobutene and cis-2-butene would not be affected. For ethylene, 1-butene, and 3-methyl-1-butene, the measured room temperature rate constants would be affected less than 0.5% and for propylene less than 1%. Rate constants obtained with 1-butene having a stated purity of 99.0% were slightly larger than the values obtained with research grade 1-butene (99.87%) and therefore are not included in Table I.

The estimated overall experimental uncertainty, including errors in the flow rate, pressure, and phase shift measurements, is about 10% for each value of $2\pi\nu/$[olefin] tan ϕ.

The Arrhenius parameters obtained from the least-squares treatment of the k_2 values in Table I, weighted according to the indicated uncertainties, are given in Table II along with their least-squares standard deviations. The results obtained for individual olefins are outlined briefly in the following. They are compared with the data in the literature in Table III.

O + Ethylene. The present room temperature value of the rate constant is in excellent agreement with the other determinations by the phase shift technique[7,13] and is between the values determined by the flash photolysis chemiluminescence[4] and resonance fluorescence[3] techniques. Although the slope obtained by Atkinson and Pitts[13] is different from ours, their points are within 20% of the present Arrhenius line, as shown in Figure 1. This is within the combined estimated experi-

Table I. Rate Constants for Reactions of Oxygen Atoms with Olefins[a]

Olefin	T, K	$k_2 \times 10^{-9}$, l. mol^{-1} s^{-1}	$k_3 \times 10^{-10}$, l.^{2} mol^{-2} s^{-1}
Ethylene	298	0.423 ± 0.010	4.84 ± 0.11
	361	0.651 ± 0.010	3.70 ± 0.06
	422	0.967 ± 0.022	2.57 ± 0.08
	486	1.24 ± 0.03	2.28 ± 0.07
Propylene	298	2.29 ± 0.04	5.04 ± 0.12
	298	2.27 ± 0.07	4.86 ± 0.19
	337	2.52 ± 0.04	3.84 ± 0.09
	389	2.92 ± 0.07	3.19 ± 0.14
	429	3.23 ± 0.07	2.48 ± 0.20
	479	3.72 ± 0.09	2.23 ± 0.14
	483	3.54 ± 0.09	2.21 ± 0.15
1-Butene	298	2.38 ± 0.06	4.98 ± 0.19
	298	2.45 ± 0.07	4.85 ± 0.21
	339	2.60 ± 0.06	4.26 ± 0.17
	389	3.10 ± 0.06	3.01 ± 0.15
	430	3.32 ± 0.05	2.72 ± 0.13
	484	3.69 ± 0.09	2.22 ± 0.15
3-Methyl-1-butene	298	2.53 ± 0.04	4.68 ± 0.12
	298	2.61 ± 0.08	4.55 ± 0.21
	307	2.63 ± 0.08	4.49 ± 0.24
	316	2.61 ± 0.05	4.23 ± 0.14
	327	2.70 ± 0.04	4.17 ± 0.12
	337	2.51 ± 0.04	4.09 ± 0.12
	342	2.78 ± 0.05	3.82 ± 0.13
	361	2.79 ± 0.09	3.21 ± 0.26
	389	2.91 ± 0.10	3.03 ± 0.15
	430	3.21 ± 0.06	2.71 ± 0.16
	454	3.36 ± 0.05	2.68 ± 0.07
	477	3.77 ± 0.11	2.30 ± 0.18
	484	3.51 ± 0.08	2.38 ± 0.12
Isobutene	298	10.4 ± 0.3	4.86 ± 0.13
	298	10.5 ± 0.2	4.78 ± 0.08
	320	10.6 ± 0.3	4.08 ± 0.13
	348	9.88 ± 0.22	3.85 ± 0.10
	382	9.50 ± 0.30	3.22 ± 0.11
	421	9.74 ± 0.16	2.76 ± 0.05
	481	10.3 ± 0.3	2.20 ± 0.15
	484	9.79 ± 0.2	2.29 ± 0.09
cis-2-Butene	298	10.8 ± 0.5	5.07 ± 0.22
	298	10.5 ± 0.4	4.80 ± 0.18
	320	10.0 ± 0.2	4.39 ± 0.06
	348	10.0 ± 0.2	3.61 ± 0.08
	389	9.56 ± 0.28	2.96 ± 0.13
	421	9.20 ± 0.20	2.71 ± 0.06
	482	8.90 ± 0.25	2.16 ± 0.09
	484	8.71 ± 0.24	2.23 ± 0.08

[a] Two determinations at 298 K (for all olefins except ethylene) represent independent measurements separated by time intervals of several months.

mental uncertainties. The slope of the resonance fluorescence points appears somewhat less than that of the present results. Over the common temperature interval our results are in good agreement with those of Westenberg and de Haas.[14] Their points curve away from the present linear logarithmic Arrhenius plot at both temperature extremes, as will be discussed in a later section.

O + Propylene. The present results give a significantly larger activation energy (722 cal mol^{-1}) than other reported values shown in Figure 2 and Table III. The resonance fluorescence measurements of Huie, Herron, and Davis,[12] although based on fewer experiments and a smaller temperature range, suggest a larger activation energy (235 cal mol^{-1}) than Kurylo's[11] resonance fluorescence results (76 cal mol^{-1}). The phase shift results of Atkinson and Pitts[13] are significantly different from ours, but the reason for the difference is not clear.

O + 1-Butene. There is good agreement between the present

Table II. Arrhenius Parameters for the Reactions of $O(^3P)$ Atoms with Olefins

Olefin	$A \times 10^{-9}$, l. mol^{-1} s^{-1}	E, cal mol^{-1}
Ethylene	6.98 ± 0.89	1679 ± 94
Propylene	7.58 ± 0.42	722 ± 40
1-Butene	7.21 ± 0.44	659 ± 45
3-Methyl-1-butene	6.02 ± 0.44	529 ± 51
Isobutene	8.74 ± 0.53	-102 ± 44
cis-2-Butene	6.68 ± 0.23	-269 ± 26

Table III. Comparison of Arrhenius Parameters for Reactions of $O(^3P)$ with Olefins

Olefin	$A \times 10^{-9}$, l. mol^{-1} s^{-1}	E, kcal mol^{-1}	Ref
Ethylene	6.98	1.68	This work
	3.37	1.27	AP[a]
	3.26	1.13	DHHKB[b]
	5.0	1.5	WdH[c] (226 < T < 380)
	8.4	1.6	Elias[d]
Propylene	7.58	0.722	This work
	2.08	0.0	AP[a]
	2.51	0.076	Kurylo[e]
1-Butene	7.21	0.659	This work
	5.78	0.509	HHD[f] (T ≥ 226 K)
	7.3	0.8	Smith[g]
	12.6	0.85	Elias[d]
Isobutene	8.74	-0.102	This work
	9.0	0.1	Smith[g]
cis-2-Butene	6.68	-0.269	This work
	5.84	-0.319	DHH[h]
	22.9	+0.36	Elias[d]

[a] Atkinson and Pitts.[13] [b] Davis, Huie, Herron, Kurylo, and Braun.[3] [c] Westenberg and de Haas.[14] [d] Reference 17. [e] Reference 11. [f] Huie, Herron, and Davis.[12] [g] Reference 18. [h] Davis, Huie, and Herron.[10]

results and the resonance fluorescence results[12] over the temperature range of our experiments, as shown in the upper part of Figure 3. Both techniques seem to indicate a slight curvature of the Arrhenius plot, although higher precision of the data and larger temperature intervals would be desirable. If a linear Arrhenius plot is imposed on the resonance fluorescence data for $T \geq 226$ K, an activation energy in good agreement with the present value is obtained. The comparison is made in Table III and the potential curvatures of the Arrhenius plots are discussed further below.

O + 3-Methyl-1-butene. The Arrhenius plot for 3-methyl-1-butene is shown in the lower part of Figure 3. There are no data in the literature for comparison with the present results for this olefin.

O + Isobutene. It is seen from Figure 4 that the present room temperature value of the rate constant is in good agreement with the previous phase shift value[7] and with the results of Elias,[17] although the latter results give a larger activation energy. Smith's values[18] are consistently lower than the present results by 20–40% for both isobutene and 1-butene.

O + cis-2-Butene. The present results are compared in Figure 4 and Table III with literature values. The resonance fluorescence values[10] are in very good agreement with the present values, and in fact the sets of points are within 5% of each other. The values of Elias[17] are somewhat higher and show a positive temperature dependence.

Comparison of the Phase Shift, Resonance Fluorescence, and Competitive Data. The Arrhenius parameters determined by the phase shift, resonance fluorescence,[3,10–12] and competitive
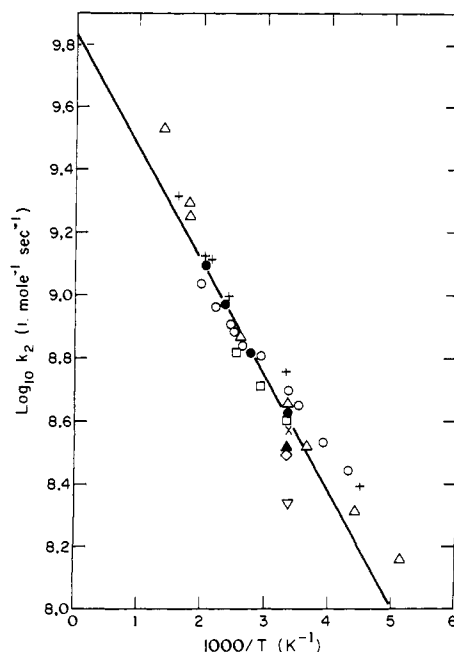
Figure 1. Arrhenius plot for the reaction of $O(^3P)$ atoms with ethylene: (●) this work; (○) Davis, Huie, Herron, Kurylo, and Braun;[3] (□) Atkinson and Pitts;[13] (△) Westenberg and de Haas;[14] (×) Stuhl and Niki;[20] (◇) Niki, Daby, and Weinstock;[22] (+) Elias;[17] (▽) Tanaka, Tsuchiya, and Hikita;[23] (▲) Brown and Thrush.[21]
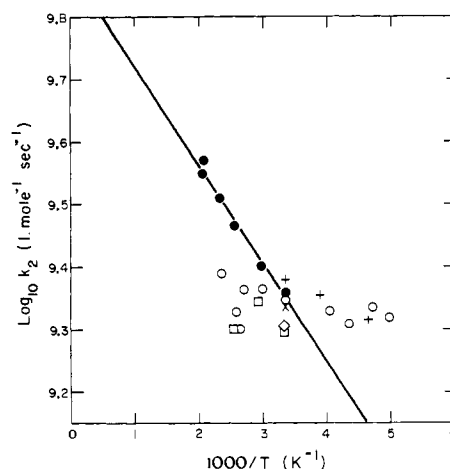
Figure 2. Arrhenius plot for the reaction of $O(^3P)$ atoms with propylene: (●) this work; (◇) Furuyama, Atkinson, Colussi, and Cvetanović;[7] (○) Kurylo;[11] (□) Atkinson and Pitts;[13] (+) Huie, Herron, and Davis;[12] (×) Stuhl and Niki.[20]

techniques[2] are compared in Table IV. The relative values from the competitive experiments were placed on an absolute scale based on the present results for ethylene. It is evident that the present results and the competitive results are in good agreement.

The negative Arrhenius activation energy determined for cis-2-butene in this work is in excellent agreement with the resonance fluorescence value.[10] However, the activation energy for the O + tetramethylethylene reaction determined by the phase shift method[8] is only 50% of the resonance fluorescence value[10] (-774 and -1570 cal mol^{-1}, respectively). Of significance, however, is that two very different techniques for determining absolute values of rate constants both give negative Arrhenius activation energy parameters for these reactions. Possible interpretations of the negative activation energies have been outlined previously[6,8,10] and will be briefly discussed in the following sections.
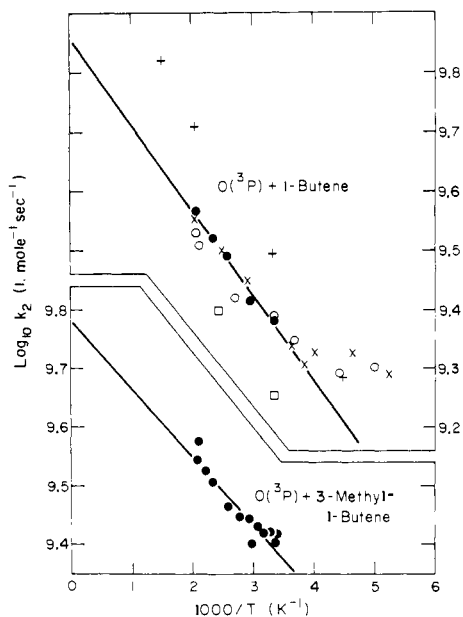
Figure 3. Arrhenius plots for the reactions of $O(^3P)$ atoms with 1-butene and 3-methyl-1-butene: (●) this work; (O) Huie, Herron, and Davis[12] (three or more measurements at each temperature); (X) Huie, Herron, and Davis[12] (less than three measurements at each temperature); (+) Elias;[17] (□) Smith.[18]
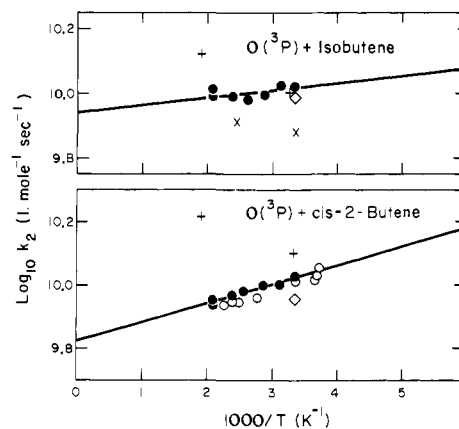

Figure 4. Arrhenius plots for the reactions of $O(^3P)$ atoms with isobutene and cis-2-butene: (●) this work; (◊) Furuyama, Atkinson, Colussi, and Cvetanović;[7] (O) Davis, Huie, and Herron;[10] (+) Elias;[17] (X) Smith.[18]
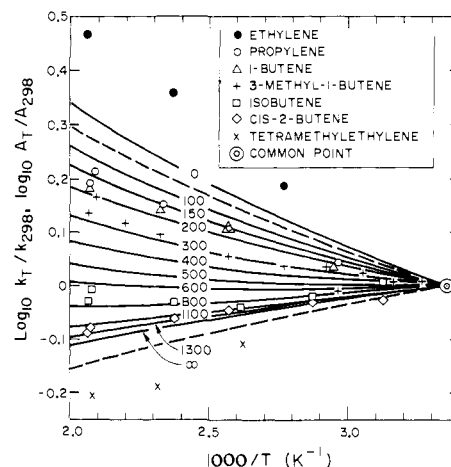

Figure 5. The temperature dependence of the ratios of rate constants (k_T/k_{298}). The points are the experimental values of log k_T/k_{298} obtained in the present work. The solid and dashed lines are the log values of the ratios of the preexponential terms (A_T) calculated from the transition state theory for the indicated values of the frequency parameter ω (cm^{-1}) as explained in the text (eq I and II).

With the exception of 1-butene and cis-2-butene, the resonance fluorescence activation energies are 600–700 cal mol^{-1} lower and the preexponential factors 2 to 4 times smaller than in the other two sets of results in Table IV. There has also been some disagreement previously on the value of the room temperature O + ethylene rate constant as determined by the resonance fluorescence[3,19] and the NO chemiluminescence[4,20] techniques. The cause of the 30% difference has not been determined, despite repetition of measurements by both techniques and careful reexamination of the kinetics.[19,20] It appears now that there are also some significant differences between the resonance fluorescence and the phase shift results for the O + propylene and perhaps the O + tetramethylethylene reactions at elevated temperatures. For the other olefins, the results agree within the combined experimental uncertainties where the temperature intervals of the two techniques overlap. On the whole, the agreement between the results obtained by such vastly different techniques is very gratifying, although further work will evidently be required to resolve the minor differences observed in some instances.

Discussion

In Figures 1–4 linear logarithmic Arrhenius plots (solid lines) have been imposed on the experimental points obtained in the present work and the least-squares values of the Arrhenius parameters thus obtained are listed in Table II. However, visual inspection of Figure 5 shows that slightly curved plots actually provide a better correlation, even after allowance for some unavoidable experimental scatter. To bring this point out more clearly, log values of the ratios of rate constants relative to the mean value at 25 °C taken as unity are plotted in Figure 5 against $1000/T$. The previously published[8] results for tetramethylethylene are also included, for completeness. The plots clearly show the negative temperature dependence of the rate constants for the $O(^3P)$ reactions with tetramethylethylene, cis-2-butene, and also, to a smaller extent, with isobutene. The implications of these results will be discussed in the following and the meaning of the solid and dashed lines in Figure 5 will be evident from the discussion.

Discussion of the Postulated Abstraction of Allylic Hydrogen

Atoms. A curvature in the Arrhenius plot for 1-butene was first observed by Huie, Herron, and Davis,[12] who ascribed it to two concurrent reactions of $O(^3P)$ atoms: addition to the double bond and abstraction of hydrogen. These authors resolved the curved Arrhenius plot into two linear Arrhenius expressions, one with an activation energy of 50 cal mol^{-1} and the other 1970 cal mol^{-1}. The former value was compatible with the value of 76 cal mol^{-1} reported[11] for the addition of oxygen atoms to propylene and the latter (1970 cal mol^{-1}) was assigned to hydrogen abstraction.

The suggestion[12] that abstraction of hydrogen by $O(^3P)$ atoms would be more likely from 1-butene than from propylene, in which the bond dissociation energy of the allylic hydrogen atoms is about 3 kcal mol^{-1} larger, appeared reasonable and was consistent with the much lower activation energy measured at that time for propylene (i.e., for $O(^3P)$ addition only) than for 1-butene, for which both addition and abstraction were assumed. However, the present results give an Arrhenius activition energy of 722 cal mol^{-1} for the $O(^3P)$ + propylene reaction, about 200 cal mol^{-1} *larger* than for 1-butene. Also, as shown in Table II, very similar apparent Arrhenius parameters were obtained for 1-butene as for 3-methyl-1-butene, despite the expectation that the bond dissociation energy of the allylic hydrogen in the latter olefin is even smaller (probably by a further 2 to 3 kcal mol^{-1}) than in 1-butene. It appears therefore from the present results that the

Table IV. Comparison of the Presently Determined Arrhenius Parameters for Reactions of Oxygen Atoms with Olefins with the Competitive and Resonance Fluorescence Results

Olefin	E, kcal mol^{-1}			$A \times 10^{-9}$, l. mol^{-1} s^{-1}		
	Competitive[a]	Phase shift[b]	Resonance fluorescence[c]	Competitive[a]	Phase shift[b]	Resonance fluorescence[c]
Ethylene	(1.7)	1.7	1.1	(6.98)	6.98	3.26
Propylene		0.72	0.076		7.58	2.51
1-Butene	0.47	0.66	0.51[d]	5.1	7.21	5.78[d]
Isobutene	−0.46	−0.10		4.6	8.74	
cis-2-Butene		−0.27	−0.32		6.68	5.84
Tetramethylethylene	−0.92	−0.77[e]	−1.6	8.6	12.4[e]	3.36

[a] The results of the competitive experiments[2] were placed on an absolute scale based on the present Arrhenius parameters for ethylene. [b] Present results. [c] Data taken from ref 3, 10, 11, and 12. [d] Calculated from the resonance fluorescence results in ref 12 for $T \geq 226$ K. [e] Reference 8.

lability of the allylic hydrogen atoms does not have a significant effect on the O(^{3}P) + olefin rate constants in the temperature interval of the present experiments. This is in keeping with other experiments, designed to measure reaction products, which place upper limits on hydrogen abstraction considerably lower than the resonance fluorescence results might suggest.[15,16]

It could perhaps be thought that the difficulties with the suggested explanation involving two competing reactions could be avoided by assuming that the two reactions are not double bond addition and hydrogen abstraction but are in fact additions to the terminal and the internal doubly bonded C atom, respectively, with the terminal addition of considerably lower activation energy. However, this explanation appears also to be unacceptable since the composition of the adducts formed, for example in the case of 3-methyl-1-butene,[16] remains approximately the same at different temperatures. (Moreover, the likelihood[2] that the transition state determining the rate of the reaction reflects interaction of O(^{3}P) with the olefinic double bond as a whole rather than its direct interaction with one of the two doubly bonded C atoms individually is probably also incompatible with this suggestion although this may depend on the finer mechanistic details.)

Curvatures of the Arrhenius Plots. Superposition of the Arrhenius equation on a set of experimental rate constants at different temperatures is frequently a very convenient way of expressing empirically the temperature dependence of the rate constants. In most instances this is an entirely adequate procedure and any deviations from the empirical expression are generally imperceptible. However, for reactions of low activation energies, equal or close to zero, the temperature dependence of the rate constants would be expected, in terms of the transition state theory, to be largely or entirely governed by the temperature dependence of the entropy of activation. Since this dependence generally deviates from exponential, curvatures of the formal logarithmic Arrhenius plots would not be unusual and in fact would be expected in many such instances. A prediction of the magnitude and the sign of the expected curvatures requires information about the transition state which is generally not available. We have nevertheless calculated possible curvatures of Arrhenius plots using some common simplifying assumptions and a range of plausible values of the required constants. The main object has been to show that the observed curvatures of the Arrhenius plots in Figure 5 can be readily explained without having to postulate concurrent involvement of two distinct competing reactions of O(^{3}P) atoms with the individual olefins.

An expression for the rate constant can be formulated in terms of transition state theory as follows. In the addition of an O(^{3}P) atom to an olefinic double bond three translational degrees of freedom are lost with simultaneous formation of

three vibrational degrees of freedom, one of which may be identified with the reaction coordinate. The other two may be associated with the two bending vibrations of the new O-olefin bond, the exact nature of which does not have to be immediately specified. It may be assumed approximately that the two vibrations are harmonic and have equal frequencies and that the partition functions for all other vibrations in the transition state and the olefin cancel.[24] The electronic partition functions for the olefins are essentially independent of temperature, but the electronic partition function of the O(^{3}P) atoms is affected by the small separations of the $J = 2, 1, 0$ states. The $J = 1$ and 0 states lie 158.5 and 226.5 cm^{-1} above the $J = 2$ level. The electronic structure of the transition state is uncertain. Two limiting situations may be visualized. First, if the electronic energy level separations remain the same in the transition state as in the separated reactants, then the electronic partition functions cancel and do not contribute to the temperature dependence of the rate constant. Since the temperature dependence of the rate constants is of primary interest, it is convenient to deal with ratios of rate constants at different temperatures (k_T) relative to, say, the rate constant at 25 °C (k_{298}), as was done in Figure 5. The ratios k_T/k_{298} can then be approximated by

$$k_T/k_{298} = A_T \exp\left\{ -E/R \left(\frac{1}{T} - \frac{1}{298} \right) \right\} \qquad \text{(I)}$$

where

$$A_T = \left(\frac{298}{T} \right)^{0.5} \left\{ \frac{1 - \exp(-h\nu/298k)}{1 - \exp(-h\nu/kT)} \right\}^2 \qquad \text{(II)}$$

The solid lines in Figure 5 are the plots of the computed values of log A_T for the values of ω ($\omega = \nu/c$) indicated on the curves, for the temperature range of interest in the present work (500 K $\geq T \geq$ 298 K). The upper and lower bounds for the family of curves correspond to the limiting values of A_T at $\omega = 0$ ($A_T = (T/298)^{1.5}$) and at $\omega = \infty$ ($A_T = (T/298)^{0.5}$).

On the other hand if in the transition state the J states of the O(^{3}P) atom become degenerate or if they separate sufficiently so that essentially only the lowest state is populated, then the preexponential term in eq I is modified to

$$A_T' = A_T\{5 + 3 \exp(-158.5b/T) + \exp(-266.5b/T)\}^{-1} \qquad \text{(III)}$$
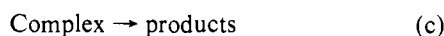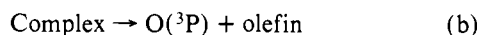
where A_T is defined in eq II, and $b = 1.439$.
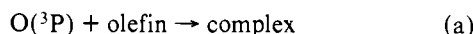
The effect of inclusion of the O(^{3}P) electronic partition function is to lower the values of log A_T for a given ω, as shown in Figure 5 where the limiting values of A_T' at $\omega = 0$ and $\omega = \infty$ are plotted as dashed lines. The discussion that follows will mainly make use of A_T' in eq III, but the nature of the arguments remains the same for A_T in eq II.

It can be seen from Figure 5 that the log A_T curves show very similar curvatures to those displayed by the Arrhenius plots in Figures 1-4. To show this more clearly, the experimental points from Figures 1-4 are also plotted in Figure 5. The curvatures of the Arrhenius plots observed experimentally, for example for propylene, 1-butene, and 3-methyl-1-butene, are evidently very well reproduced by the curvatures of the log A_T plots for ω values anywhere between zero and, say, 300 to 400 cm^{-1}. The magnitudes of curvatures of the log A_T plots change only relatively slowly with ω and the exact values of frequencies required to reproduce the observed trends are not critical, especially in view of some unavoidable scatter of experimental points with experimental precisions currently available.

Figure 5 shows also that trends in A_T alone, i.e., the temperature dependences of entropies of activation, are not sufficient to explain the observed trends in the rate constants. Thus the data for isobutene appear to show a considerably greater curvature than the log A_T curves in the same region in Figure 5, and the experimental points both for ethylene and tetramethylethylene lie well outside the region of the log A_T and log A_T' families of curves. Finite contributions from the exponential term in eq I, i.e., activation energies different from zero, must therefore be invoked. A positive E is required to explain the data for ethylene and a negative E for tetramethylethylene, in agreement with previous conclusions.[6,8,10] In particular it is evident that for tetramethylethylene the trend in the rate constants cannot be explained by the transition state theory alone if the reaction is a simple bimolecular process since the activation energy must then have a negative value.

Negative Values of the Arrhenius Activation Energy Parameters. In a previous publication[8] we have commented briefly on several explanations suggested so far in the literature for the negative Arrhenius activation energy parameters observed in some atom-olefin reactions[8,10,25,26] and there is no need to repeat here these earlier comments. At the same time, one of these suggestions, postulating reversible formation of an intermediate olefin-oxygen atom complex, appears to provide a particularly simple explanation consistent with all the experimental information currently available and we feel that it should be further discussed in the light of the results obtained in the present study.

Potential involvement of intermediate complexes in O(^{3}P) atom-olefin reactions was first postulated in 1959 by Cvetanović[2a] and has been emphasized in subsequent publications from this laboratory.[2c,6,8] The postulated mechanism is

$$O(^3P) + \text{olefin} \rightarrow \text{complex} \qquad (a)$$

$$\text{Complex} \rightarrow O(^3P) + \text{olefin} \qquad (b)$$

$$\text{Complex} \rightarrow \text{products} \qquad (c)$$

(At the pressures generally used, the high pressure limiting rates can be assumed for these reactions, i.e., the three-body reaction a is in the second-order region and the unimolecular reactions b and c are in their first-order regions. A more explicit reaction scheme is given in a footnote further below.)

A knowledge of the exact nature of the intermediate complex is not essential from a kinetic point of view. However, some requirements are obvious. For example, the dissociation energy of the O(^{3}P)-olefin bond in the complex should be relatively small, probably not more than a few kilocalories per mole, and the bond should become stronger with increasing alkyl substitution in the olefin (i.e., in going from ethylene to tetramethylethylene). A molecular complex or, more specifically, an electron-donor-acceptor (EDA) complex[27] with the olefinic π bond as the electron donor (D) and O(^{3}P) as electron acceptor (A) would fulfill these requirements. The ground state of such a complex could be described[27] by a wave function,

ψ_N(DA), which is a linear combination of a no-bond wave function (ψ_0) and a dative bond wave function (ψ_1), i.e., ψ_N(DA) $= a\psi_0$(DA) $+ b\psi_1$(D$^+$A$^-$).

In earlier publications[2,6,8] we have referred to the postulated intermediate as the "π complex" in view of the π electron donation by the olefin. However, there may be some ambiguity regarding the nomenclature in current use.[28] The intermediates considered here should not be identified with the relatively very strong "π complexes" formulated originally by Dewar, in which *both* π electrons are donated to acceptor with an available suitable vacant orbital to form a strong "dative" bond. Since intermediate molecular complexes might be kinetically involved in many other addition reactions, it is clear that different types of polar interactions may be responsible for their formation in different cases.

For steady state conditions applied to reactions a-c, the effective reaction rate (r) is

$$r = r_c = k[\text{olefin}][O(^3P)] \qquad (IV)$$

where

$$k = k_c k_a/(k_b + k_c)$$

i.e., the rate constant (k) observed in the reaction is a composite quantity. When k_b is appreciably larger than k_c, as may be anticipated most frequently to be the case,

$$k = k_c k_a/k_b = k_c K_{a,b} \qquad (V)$$

where $K_{a,b}$ is the equilibrium constant of the intermediate complex formation.[29]

The intermediate complex is the initial reactant for both reactions b and c and its contributions to the ratio of the partition functions (Z) in k as defined in eq V cancel so that

$$k = \text{constant} \times T \frac{Z_c^{\ddagger}}{Z_{O\ atom}Z_{olefin}} \exp\{-(\Delta H^{\circ}_{a,b} + E_c)/RT\}$$

or, with the simplifying assumptions indicated earlier and writing $-\Delta H^{\circ}_{a,b} = E_b - E_a$,

$$k = \text{constant} \times T^{-0.5}[1 - \exp(-h\nu/kT)]^{-2}$$
$$\times \exp\{-(E_a - E_b + E_c)/RT\} \qquad (VI)$$

For ratios of rate constants at two temperatures, say at T and 298 K, eq VI reduces to eq I with $E = E_a + E_c - E_b$. An apparent negative activation energy arises therefore when $E_b > (E_a + E_c)$ or, since E_a is generally close to or equal to zero, when $E_b > E_c$. This situation may be expected when stronger complexes are formed, as for example in the case of tetramethylethylene.

Comparison of the Theoretical and Experimental Temperature Trends. Use of eq I to reproduce the experimental trends in Figure 5 requires the values of two parameters, ω (or ν) and E. The two are coupled since when a value is assigned to one the value of the other is determined (within rather narrow limits) by the general level of the values of k_T/k_{298} for individual olefins. However, a fairly broad range of sets of ω, E values may be used to reproduce essentially equally well the experimental trends in Figure 5 because of the slow variation of the curvature of the log A_T' plots as ω is varied. For the purpose of illustration we have selected for each olefin a particular ω, E set (as indicated in the caption) to calculate from eq 1 the solid lines plotted in Figure 6. The choice has been such to assure good fit of the calculated curves to most of the experimental points and to maintain at the same time plausible trends in ω and E as the postulated intermediate complexes become stronger in going from ethylene to tetramethylethylene. The trend in the selected E values parallels qualitatively the trend in the ionization potentials of the olefins. The solid curves in Figure 6 thus calculated from eq I evidently reproduce well the experimental Arrhenius plots.
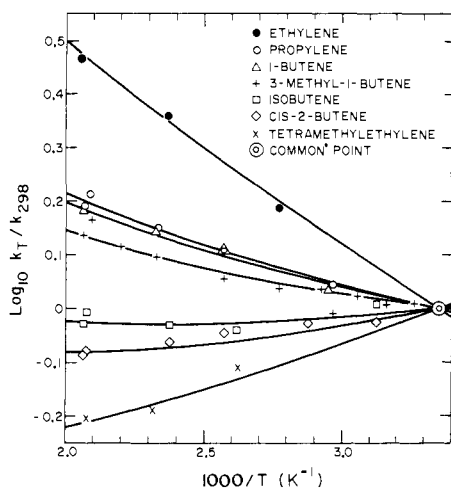
Singleton, Cvetanović / Reactions of Oxygen Atoms with Olefins

Figure 6. Temperature dependence of the rates of $O(^3P)$ + olefin reactions. The points are the experimental values of log k_T/k_{298} obtained in the present work. The lines are calculated from transition state theory (using eq I and III) as described in the text, with the following values of E (cal mol^{-1}) and ω (cm^{-1}): ethylene 1200, 200; propylene 427, 300; 1-butene 372, 300; 3-methyl-1-butene 195, 300; isobutene -208, 400; cis-2-butene -406, 400; tetramethylethylene -733, 500.

Figure 7. Temperature dependence of the rate constants for the $O(^3P)$ + ethylene reaction. The line is calculated from transition state theory (eq I and III): ($\bullet$) this work; ($\triangle$) Westenberg and de Haas.[14]

The choices of the two vibrational frequencies in eq II for the transition state may need some elaboration. For the molecular complex R_3N-I_2, the N-I stretching vibration[30] is 145 cm^{-1}, and the two bending vibrations are expected[27] at lower frequencies, between 50 and 100 cm^{-1}. The $O(^3P)$ + olefin complex may not be as strong, and this would tend to lower the vibrational force constants. The lower mass of the oxygen atom relative to I_2 would likely produce about a fourfold net increase in the vibrational frequencies. Also, since the frequencies of the transition state, and not of the molecular complex, are required, the frequencies could be larger than those estimated for the complex. On the other hand, the frequencies are expected to be less than those of ethylene oxide, for which two of the three C_2O vibrations occur at 808 and 865 cm^{-1} (the third C_2O vibration at 1263 cm^{-1} can be associated with the reaction coordinate). Hence bending vibrations in the transition state between 100 and 600 cm^{-1} seem plausible.

A test of the reality of the suggested curvatures of the logarithmic Arrhenius plots will ultimately have to be based on rate constant measurements over temperature intervals as broad as possible. The data of Westenberg and de Haas[14] for reaction O + C_2H_4 are therefore of particular interest since they cover the interval from 195 to 715 K, i.e., a much larger temperature range than any other measurements for this reaction. These authors have observed a pronounced curvature of the logarithmic Arrhenius plot and have attempted to rationalize it by assuming a transition state with an ethylene oxide-like structure and oxygen bending frequencies of 600 cm^{-1} (200 cm^{-1} lower than in ethylene oxide). The present mechanism suggests the transition state could occur at a greater interatomic distance, so that lower vibrational frequencies would be expected, and hence greater curvature would be obtained from eq I and II than obtained by Westenberg and de Haas. The computed curve in Figure 7 for $O(^3P)$ + C_2H_4 (E = 1200 cal mol^{-1}, ω = 200 cm^{-1}) for the 195-715 K interval gives a reasonable fit for the present results and for the data of Westenberg and de Haas within the experimental error except, perhaps, at the highest temperature where their rate constant is 26% higher than the calculated line.

There are two points to be made concerning the curved Arrhenius line in Figure 7. First, the resonance fluorescence results, shown in Figure 1 but not in Figure 7, can be accom-
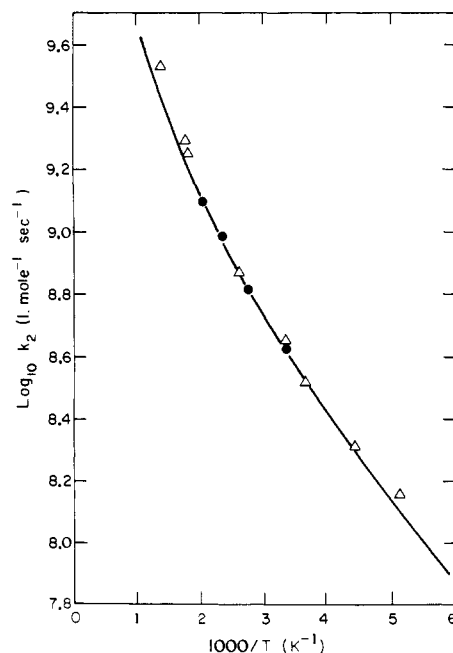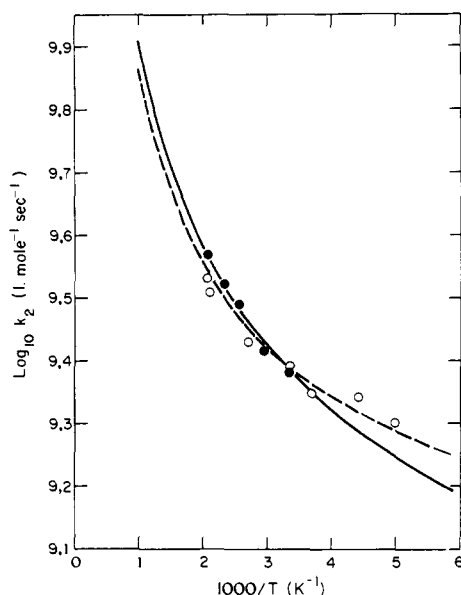
modated by a straight line. At the same time, they do not rule out (within a possible random error of $\pm$10%) a curvature of the magnitude shown in Figure 7. Second, the present results for ethylene are compatible, within the experimental error, with a straight line. Nevertheless, although the present results do not necessarily confirm the curvature reported by Westenberg and de Haas, the suggestion of curvature is there, and seems to fit the general pattern observed in the Arrhenius plots for the present series of olefins. The data of Westenberg and de Haas on the other hand are compatible only with a curved logarithmic Arrhenius plot.

The line calculated for 1-butene shown in Figure 6 is replotted over a wider temperature range as the solid line in Figure 8. The low-temperature results of Huie, Herron, and Davis[12] are significantly above this curve. A better representation of the combined results of the present work and those of Huie, Herron, and Davis is obtained if, instead of letting E = 372 cal mol^{-1}, we let E = 276 cal mol^{-1} (with ω remaining at 300 cm^{-1}) as shown by the dashed line in Figure 8. It appears therefore that transition state theory can account satisfactorily for the curvature in the Arrhenius plot of the $O(^3P)$ + 1-butene reaction, and there is no need to postulate two concurrent reactions of oxygen atoms with the olefin.

Extrapolations of the other curves in Figure 6 to 1000 and 200 K give rise to a range of curvatures, and in some instances, minima occur. The curves for isobutene, cis-2-butene, and tetramethylethylene have minimum values at 420, 500, and 715 K, respectively. Accurate determinations of the rate constants for these more reactive olefins over a larger temperature interval would be useful for examining the validity of this mechanism.

Implications for Other Addition Reactions. A similar mechanism involving reversible formation of intermediate complexes could perhaps explain also the negative Arrhenius energy parameters and Arrhenius plot curvatures for addition of $O(^3P)$ atoms to some sulfur containing compounds (dimethyl sulfide and ethylene sulfide).[31] Negative Arrhenius activation energy parameters for additions of other group 6 atoms to olefins[25,26] are perhaps also explainable in a similar manner. It has been argued[25] that an equilibrium between

Figure 8. Temperature dependence of the rate constants for the $O(^3P)$ + 1-butene reaction. The lines are calculated from transition state theory (eq I and II): solid line, $E = 372$ cal mol^{-1}, $\omega = 300$ cm^{-1}; dashed line; $E = 276$ cal mol^{-1}, $\omega = 300$ cm^{-1}; (●) this work; (O) Huie, Herron, and Davis.[12]

dependence of the transmission coefficient has been neglected in this discussion and any future information on this point could substantially alter the views expressed here. A more quantitative treatment of the curvatures of the Arrhenius plots would require rate determinations over a considerably broader temperature interval than was possible in the present work, and much greater experimental precision than is currently attainable.

References and Notes

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(24) In general, this assumption may not be valid when internal rotations become more or less restricted in the transition state. However, calculations based on transitions from propylene to 1,2-epoxypropane and from *cis*-2-butene to *cis*-2,3-epoxybutane (the epoxides being taken as extreme models of the respective transition states) show that increasing restrictions of the internal rotations of the methyl groups in going from the olefins to the epoxides make only minor contributions to the overall temperature dependence of the calculated rate constants. It is likely that in the actual transition states the internal rotations would be even less restricted than in the epoxides, and thus the effect would be smaller. Similar considerations would be expected to apply to isobutene and tetramethylethylene.
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(29) If the complex formation is a three-body process, the more explicit reaction scheme is

$$O(^3P) + \text{olefin} \rightleftharpoons C^* \qquad (1, -1)$$

$$C^* + M \rightleftharpoons C + M \qquad (2, -2)$$

$$C + M \rightleftharpoons C^{**} + M \qquad (3, -3)$$

$$C^{**} \rightarrow \text{products} \qquad (4)$$

C stands for complex; C^* and C^{**} are the energized complex molecules for reactions −1 and 4. With the steady state assumption for these transients the high-pressure limit of k is $k^\infty = k_1(k_4 k_3/k_{-3})/(k_{-1}k_{-2}/k_2)$, i.e., it is equal to $k_c^\infty k_a^\infty/k_b^\infty$ and is therefore identical with the corresponding expression based on the simplified reaction scheme (reactions a–c). The low-pressure limiting value of k is then expected to be pressure dependent although it is unknown how low the pressure has to be before this can be observed. There are no low-pressure measurements which would indicate a pressure dependence of the rate constants.
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$S(^3P)$, an olefin, and an "excited adduct" could not exist for two reasons. First, the experimental evidence indicated that $S(^3P)$ atoms were not the chain carriers in the isomerization of olefins in the photolysis of mixtures of COS and *cis*-2-butene. Second, the absence of a pressure effect on the bimolecular rate constant for the addition of $S(^3P)$ to olefins suggested that there could not be an excited S-olefin adduct, since its unimolecular back decomposition was expected to be pressure dependent. While the evidence for the first of these two arguments provides support for the suggestion that $S(^3P)$ does not act as the chain carrier in the isomerization of olefins, it does not preclude $S(^3P)$ from forming intermediate molecular complexes with olefins. Transition metals, for example, are known to form π complexes with olefins, and yet isomerization does not occur when the olefin is displaced from the metal. (Nor does isomerization of *cis*-2-butene or *trans*-2-butene occur[16] during the addition reaction of $O(^3P)$.) As for the second argument, we feel that lack of significant pressure effects on the reaction rates within a particular pressure range does not necessarily provide evidence for or against intermediate complex formation.

Conclusions

In conclusion, the calculated curves in Figure 6 match very well the curvatures in the experimental Arrhenius plots and explain in a simple manner the apparent negative activation energies for some of the olefins. While this cannot be accepted as conclusive evidence, it provides strong support for the intermediate complex postulate, which has to be regarded as a serious possibility. The values of E and ω in this discussion were chosen to illustrate the curvatures in Figures 5–8 and are not intended to be taken literally. However, the figures show that the curvatures in the Arrhenius plots of some of the $O(^3P)$ + olefin reactions can be accounted for in transition state theory by the nonexponential temperature dependence of the entropies of activation. It should be pointed out that any temperature