

Direct rate measurements showing negative temperature dependence for reaction of atomic oxygen with *cis*-2-butene and tetramethylethylene

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Reported in this paper are the first direct rate measurements showing a negative temperature dependence for the reaction of ground state atomic oxygen with *cis*-2-butene and tetramethylethylene. Wide variations made in the experimental conditions (e.g., total pressure, O atom concentration, and olefin concentration) of these two systems have shown that the measured rate constants were uninfluenced by secondary reactions. The absence of any dependence of the measured rate constants on total pressure at several temperatures indicate that the reactions investigated were bimolecular processes. When expressed in the form of an Arrhenius equation, the observed negative temperature dependence results in an apparent negative activation energy, i.e., $k_{cis-2-B} = (9.69 \pm 0.96) \times 10^{-12} \exp(319 \pm 63 \text{ cal mol}^{-1}/RT)$ and $k_{TME} = (5.58 \pm 1.07) \times 10^{-12} \exp(1570 \pm 120 \text{ cal mol}^{-1}/RT)$. Units are in cubic centimeters per molecule seconds. If a threshold energy of 0.0 cal mole⁻¹ is assigned to the reaction of O(³P) with TME, the temperature dependence of the pre-exponential term for a rate expression of the form $k = A(T) \exp(-E_0/RT), E_0 \geq 0$ is calculated to be T^{-2} . These new results are discussed in terms of both collision and transition state theories.

INTRODUCTION

In previous papers from this laboratory^{1,2} we reported the results of rate measurements on the reactions of atomic oxygen in its ground electronic state O(³P) with two terminal olefins, ethylene and 1-butene. This work has now been extended to the measurement of the rate parameters for two internal olefins, *cis*-2-butene and 2,3-dimethyl-2-butene (tetramethylethylene, TME). This study has been prompted by the apparent inconsistencies between the absolute rate data of Elias³ for the reactions of atomic oxygen with olefins, and the relative rate data of Cvetanovic.⁴ The relative rate constants determined by Cvetanovic⁴ predict that the pre-exponential factors [using the Arrhenius equation $k = A \exp(-E/RT)$] for the oxygen atom-olefin reactions are about the same and that the differences in reactivity for various olefins are due primarily to differences in activation energies. The results of Elias,³ however, indicate that both the pre-exponential factors and the activation energies are important in determining differences in reactivity. An added impetus was given to this work by the prediction of negative temperature dependencies for the higher olefin reactions when the relative rate data of Cvetanovic⁴ are put on an absolute basis using the rate constant for O + C₂H₄ previously measured in this laboratory.² Since

previous studies¹⁻⁴ of the reactions of atomic oxygen with olefins have all indicated that these reactions are not termolecular processes, the direct measurement of a negative temperature dependency for reactions of atomic oxygen with *cis*-2-butene and TME would be of fundamental importance to the further refinement of existing reaction rate theories. Reported in this study, therefore, are direct measurements of the rate constants for both of the above reactants at several different temperatures and pressures. The technique employed in this investigation was again that of flash photolysis-resonance fluorescence.

EXPERIMENTAL

The flash photolysis-resonance fluorescence technique used in this study has been discussed in detail previously.² In these experiments, a mixture of a few mtorr of the olefin, about one torr of molecular oxygen, and several torr of a diluent gas was flash photolyzed, producing on the order of 0.05 to 0.005 mtorr of atomic oxygen. A small portion of the atomic oxygen was continuously excited by an atomic oxygen resonance lamp, and the decay of oxygen atoms in the mixture was monitored by following the fluorescence of the atomic oxygen resonance radiation. The fluorescence signal was recorded on a multichannel analyzer, and multiple flashes (>100) were used to generate one

kinetic decay curve. In these experiments, the time base (dwell time per channel) was either 107 or 50 μ sec. In the latter case, the time base was controlled by an external oscillator using a recently developed signal averager for the Northern multichannel analyzer.^{5,6} Kinetic runs were performed with the concentration of olefin in great excess over that of atomic oxygen, so that the first-order loss of atomic oxygen prevailed.

In the course of the experiments with TME, it was found that reactant consumption due to reaction with atomic oxygen could be an important experimental factor when the olefin concentration was low. This is illustrated by the results given in Table I. The same stock reaction mixture was flash photolyzed in each of the listed runs under identical experimental conditions, with only the number of flashes between fillings being varied. A drastic decrease in the apparent rate constant was observed with an increasing number of flashes per filling, indicating significant olefin consumption. Care was therefore taken to conduct experiments under conditions where the total olefin consumption was small (<5%).

Matheson Gold Label helium and argon (all better than 99.999% stated purity) were used throughout this work. The oxygen was also Matheson Gold label, but had a stated purity of 99.99%. The *cis*-2-butene was Phillips research grade (>99.9% purity) and the TME was supplied by Aldrich Chemical Company. The organic reagents were purified by repeated degassing at 77 °K. In the preparation of gas mixtures, low pressures (<5 torr) were measured using a Granville-Phillips capacitance manometer and higher pressures (to 760 torr) were measured using a two-turn Wallace and Tiernan gauge. Gas mixtures could be prepared with a precision of about 3%. A discussion on other sources of systematic and random error in the flash photolysis-resonance fluorescence technique can be found in Ref. 2.

RESULTS

Rate measurements were made on the reaction of atomic oxygen with *cis*-2-butene over the tem-

TABLE I. Dependence of the apparent first-order rate constant for O + TME on the number of flashes per filling.^a

| Flashes per filling | First-order k (sec ⁻¹) |
|---------------------|--------------------------------------|
| 5 | 890 |
| 10 | 840 |
| 20 | 770 |
| 50 | 336 |

^aTotal pressure, 40 torr, He; oxygen pressure, 1 torr; TME pressure, 0.316 mtorr; flash energy, 45 J.

perature range 268–443 °K. These results are presented in Table II. It will be noted that over this temperature range the *cis*-2-butene partial pressure was varied from 0.95 to 2.63 mtorr and the total pressure was varied from 20 to 100 torr. By changing the flash intensity, the radical concentration was also varied by a factor of 8. Finally, SO₂ was used as the oxygen atom source in one measurement to further test for kinetic complications. Both helium and argon were used as diluent gases in all the experiments mentioned above. As can be seen from Table II, none of the above variations (except temperature) produced any change in the measured rate constant outside of the experimental error. At several temperatures, rate measurements were also made using a sapphire window on the flash lamp, which restricted the photolysis radiation to wavelengths greater than about 1420 Å (10% transmission).⁷ The results obtained using sapphire agreed within experimental error with those obtained with LiF as the flash lamp window (see Table II). As discussed previously,² the invariance of the rate constant under these widely different experimental conditions would strongly indicate that the reaction under investigation was not being influenced by secondary processes.

The results on *cis*-2-butene are plotted in Arrhenius form in Fig. 1. A linear least squares fit of all of the data to the Arrhenius equation gave

$$k(\textit{cis}\text{-}2\text{-C}_4\text{H}_8) = (9.69 \pm 0.96) \times 10^{-12} \exp[(319 \pm 63 \text{ cal mol}^{-1})/RT] \times \text{cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1},$$

where the error limits are the standard errors of the least squares fit. It should be noted, however, that the error limits from the least squares fit do not reflect completely the random errors (3%–5%) associated with each point. These errors arise primarily from the preparation of the gas mixtures and the first-order fit of the data from the multichannel analyzer. For this reason, error limits also were derived from a consideration of those lines with maximum and minimum slopes which could be drawn through the error bars associated with the rate constants at each of the individual temperatures. For the *cis*-2-butene reaction, the error limits derived in this manner were ± 213 cal mol⁻¹ in the activation energy and $\pm 1.09 \times 10^{-12}$ cm³ molecule⁻¹ · sec⁻¹ in the pre-exponential factor.

Rate measurements were made on the reaction of atomic oxygen with 2,3-dimethyl-2-butene (TME) at 298 °K and approximately 352 °K. The rate constant for this reaction was extremely fast, making rate measurements very difficult and limiting the range of experimental conditions over which experiments could be performed. Rate constants were measured at total pressures of 20 and 40 torr, and

TABLE II. Rate measurements on the reaction of atomic oxygen with *cis*-2-butene.

| Temperature (°K) | <i>cis</i> -2-C ₄ H ₈ (mtorr) | O ₂ (torr) | Total pressure (torr) | Flash energy ^b (J) | First-order rate constant (sec ⁻¹) | Bimolecular rate constant $k \times 10^{11}$ (cm ³ molecule ⁻¹ · sec ⁻¹) |
|------------------|---|------------------------------------|-----------------------|-------------------------------|--|--|
| 268 | ... | 1.0 | 20Ar | 80 | 41 | ... |
| 268 | 2.11 | 1.0 | 20Ar | 80 | 1460 | 1.87 |
| 270 | ... | 1.0 | 20Ar | 80 ^c | 43 | ... |
| 270 | 0.95 | 1.0 | 20Ar | 80 ^c | 645 | 1.78 |
| 273 | ... | 1.0 | 40He | 45 | 90 | ... |
| 273 | 1.34 | 1.0 | 40He | 45 | 883 | 1.71 |
| 298 | ... | 0.75 | 20Ar | 45 | 47 | ... |
| 298 | ... | 1.0 | 40He | 45 | 70 | ... |
| 298 | 0.98 | 0.2 | 40He | 15 | 626 | 1.82 |
| 298 | 1.05 | 0.75 | 20Ar | 31 ^c | 619 | 1.62 |
| 298 | 1.38 | 1.0 | 40He | 15 | 873 | 1.80 |
| 298 | 1.58 | 0.5(SO ₂) ^a | 20Ar | 42 | 954 | 1.72 |
| 298 | 2.36 | 1.0 | 40He | 11 | 1294 | 1.63 |
| 298 | 2.42 | 1.0 | 40He | 58 | 1428 | 1.73 |
| 298 | 2.42 | 1.0 | 40He | 20 | 1387 | 1.68 |
| 298 | 2.42 | 1.0 | 40He | 20 | 1367 | 1.65 |
| 298 | 2.42 | 1.0 | 40He | 80 | 1428 | 1.73 |
| 298 | 2.42 | 1.0 | 40He | 92 | 1428 | 1.73 |
| 361 | ... | 1.0 | 20Ar | 45 ^c | 58 | ... |
| 361 | 1.32 | 1.0 | 20Ar | 36 ^c | 588 | 1.50 |
| 361 | 2.63 | 1.0 | 20Ar | 36 ^c | 1126 | 1.52 |
| 402 | ... | 1.0 | 40Ar | 80 | 42 | ... |
| 402 | 2.63 | 1.0 | 40He | 80 | 954 | 1.47 |
| 402 | 2.63 | 1.0 | 40Ar | 80 | 963 | 1.46 |
| 421 | ... | 1.0 | 60Ar | 80 ^c | 35 | ... |
| 421 | 2.63 | 1.0 | 100Ar | 80 ^c | 898 | 1.47 |
| 443 | ... | 1.0 | 20Ar | 80 | 89 | ... |
| 443 | 1.58 | 1.0 | 20Ar | 39 ^c | 769 | 1.43 |
| 443 | 3.16 | 1.0 | 20Ar | 54 ^c | 1074 | 1.43 |

^aFlash photolysis of SO₂ used as O atom source.^bA flash energy of 80 J corresponds to $\sim 1.8 \times 10^{13}$ photons at $\lambda < 1800 \text{ \AA}$ at the cell.^cSapphire window on flash lamp.

at TME pressures of 0.3–1.5 mtorr. Both LiF and sapphire windows were used on the flash lamp at alternate times during the course of these experiments. The results of the experiments on TME are presented in Table III. The first-order rate constants in Table III was derived from the intercept at zero flashes per filling of the data from Table I.

The rate data on O + TME are plotted in Arrhenius form in Fig. 2. (The high temperature results in this figure have been averaged at 352 °K.) A linear least squares fit to all of the data gave

$$k(\text{TME}) = (5.58 \pm 1.07) \times 10^{-12} \exp[(1570 \pm 120 \text{ cal mol}^{-1})/RT] \times \text{cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1},$$

where the error limits are the standard errors from the least squares fit. Error limits based on lines having maximum and minimum slopes when drawn through the attached error bars were $\pm 350 \text{ cal mol}^{-1}$ in the activation energy and $\pm 3.3 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \cdot \text{sec}^{-1}$ in the pre-exponential factor.

DISCUSSION

As indicated in the Introduction, if the relative rate data of Cvetanovic⁴ are put on an absolute ba-

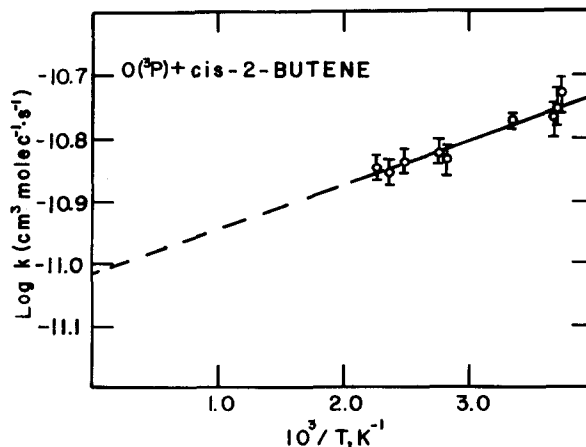


FIG. 1. Arrhenius plot for the reaction of ground-state atomic oxygen with *cis*-2-butene.

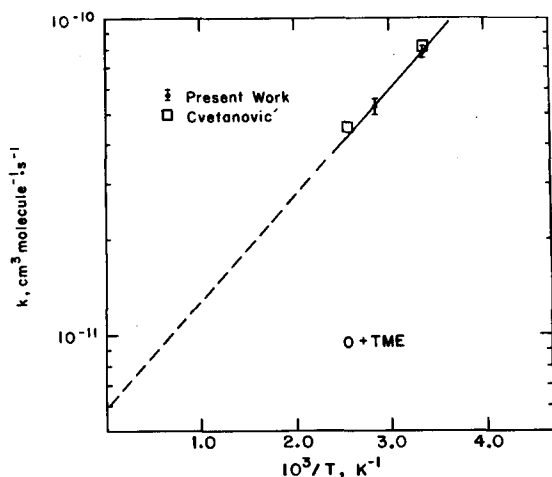


FIG. 2. Arrhenius plot for the reaction of ground-state atomic oxygen with tetramethylethylene.

sis using the value for $O + C_2H_4$ obtained earlier in this laboratory, negative temperature dependencies are predicted for several of the atomic oxygen-olefin reactions. In the present work, the existence of these negative temperature dependencies has been confirmed for two olefins: *cis*-2-butene and TME.

Although the reactions of atomic oxygen with *cis*-2-butene and TME are very fast, using the flash photolysis-resonance fluorescence technique, it was possible to operate under experimental conditions such that secondary reactions removing atomic oxygen were not important. This was demonstrated by carrying out wide variations in the experimental conditions without observing any change in the measured rate constant. If other bimolecular mechanisms had been important in the consumption of O atoms (e.g., reactions involving secondary radical species) it is expected that these processes would become more important at higher tempera-

tures, leading to a positive temperature dependency. Only in the event that the bimolecular secondary reaction resulted in the production of O atoms could an increase in the temperature result in an apparent slower decay in the O atom concentration. This type of secondary reaction, however, would depend on the square power of the flash intensity. As can be seen from the data in Table II, no variation in the rate constant was observed upon changing the flash intensity by as much as a factor of 8 (*cis*-2-butene experiments).

Another possible explanation for the observed negative temperature dependence would be that the reactions under investigation are not, in fact, simple second-order bimolecular processes, but instead, termolecular reactions. The argument against the latter possibility is that in both olefins studied in this work, as well as those olefins studied previously,^{1,2} the measured second-order rate constants showed no dependence on total pressure. Even so, it could be argued that for the lowest pressures employed in this study (20 torr) the reaction was termolecular, but with the measured rate constant at the high pressure limiting value. Hence, experimentally it would appear as a second-order rate constant. At higher temperatures, then, where the high pressure limit for the reaction would occur at higher pressures, the reaction might be in the falloff pressure region. Under these conditions, the temperature dependence for these reactions would be negative. If this were actually the case, however, the rate constants measured at high temperatures would be expected to show a pressure dependence. Although the pressure data at high and low temperatures are limited in this study, in those experiments where a pressure variation was made no dependence was found in the calculated second-order rate constant. It must be concluded, therefore, that what has been measured in this study is a negative temperature

TABLE III. Rate measurements on the reaction of atomic oxygen with 2, 3-dimethyl-2-butene.

| Temperature (°K) | TME (mtorr) | O ₂ (torr) | Total pressure (torr) | Flash energy (J) | First-order rate constant (sec ⁻¹) | Bimolecular rate constant $k \times 10^{11}$ (cm ³ molecule ⁻¹ · sec ⁻¹) |
|------------------|-------------|-----------------------|-----------------------|------------------|--|--|
| 298 | 0.316 | 1 | 40He | 45 | 905 ^a | 8.16 |
| 298 | 1.58 | 1 | 20Ar | 20 | 4120 | 7.91 |
| 298 | 1.58 | 1 | 20Ar | 45 ^b | 4210 | 8.09 |
| 298 | 1.58 | 1 | 20Ar | 45 ^b | 3910 | 7.50 |
| 348 | 0.516 | 1 | 40He | 39 | 810 | 5.08 |
| 348 | 1.66 | 1.5 | 20Ar | 34 | 2482 | 5.32 |
| 352 | 2.2 | 2 | 20Ar | 22 | 3100 | 5.06 |
| 355 | ... | 1 | 20Ar | 40 | 31 | ... |
| 355 | 1.32 | 1.5 | 20Ar | 24 | 2000 | 5.32 |
| 355 | 2.11 | 1 | 20Ar | 29 | 3200 | 5.54 |

^aExtrapolated; see Table I.

^bSapphire flash lamp window.

dependence for a second-order process. As further evidence supporting the above conclusion, a recent study has been completed in which absolute rate parameters were measured for the reaction of ground state atomic sulfur $S(^3P)$ with *cis*-2-butene and TME.¹⁵ In both systems the rate constants measured again exhibited negative temperature dependences. In the latter study, however, extensive changes in pressure (factors of 5–10) at both high and low temperatures were made. In all cases, the calculated second-order rate constants were found to be independent of pressure.

Although the characteristic reaction path for atomic oxygen–olefin reactions is addition to the double bond, recent kinetic evidence^{1b} has indicated that H atom abstraction can become competitive if the C–H bond is sufficiently weak. For the TME reaction, the contribution from this path is probably very small. For the *cis*-2-butene reaction, however, the abstraction reaction could be of some importance at the higher temperatures. If this is correct, then the true temperature dependence corresponding to the addition reaction is even more negative than that reported.

From the present results, it is apparent that a negative value for the activation energy arises if the simple form of the Arrhenius expression

$$k = A \exp(-E/RT) \quad (I)$$

is used. If the activation energy for a simple bimolecular reaction is equated to the threshold energy for that reaction, however, a negative value for the activation energy is not meaningful. A second possibility is that the observed negative temperature dependence is due to a T^{-n} term in the pre-exponential factor, i. e.,

$$k = A(T) \exp(-E_0/RT), \quad E_0 \geq 0. \quad (II)$$

For the reaction of atomic oxygen with TME, if a threshold energy of zero is chosen, the present data require $A(T)$ to be proportional to T^{-2} .

From collision theory, the rate constant for a reaction can be interpreted in terms of an energy dependent cross section for the reaction.^{8–10} The temperature dependence of the reaction, then, is a function not only of the temperature dependence of the collision frequency and the activation energy for the reaction, but also of the energy dependence of the reaction cross section:

$$k = (\pi\mu)^{-1/2} (2/KT)^{3/2} \int_0^\infty \sigma(E) E \exp(-E/kT) dE, \quad (III)$$

where $\sigma(E)$ is the energy dependent reaction cross section. The above expression assumes that the internal states of the species do not affect the probability of reaction. Using this rate expression, a negative temperature dependence for the pre-exponential factor requires a cross section which in-

creases rapidly at the threshold energy, reaches a maximum, and then decreases as energy is increased. Therefore, the colliding pairs with greater energy (relative velocity) have a smaller probability of reaction. As the temperature is increased, and the average energy of the colliding pairs increases, the number of collisions resulting in reaction will decrease. The most extreme use of an energy dependent cross section would be if the reaction could occur at only one energy. In this case, the energy dependence of the cross section can be represented by a delta function,

$$\sigma(E) = \sigma \delta(E - E_0). \quad (IV)$$

Using this form of the cross section, the rate expression becomes

$$k = (\pi\mu)^{-1/2} (2/kT)^{3/2} \sigma E_0 \exp(-E_0/kT). \quad (V)$$

Therefore, the strongest negative temperature dependence of the pre-exponential factor predicted by Eq. (III) is $T^{-3/2}$. This is to be compared with the observed T^{-2} dependence found in this work for the O + TME reaction.

Using transition state theory, the temperature dependence of an atom–molecule reaction may be expressed as¹¹

$$k \propto T^{-1/2} (Q^*/Q) \exp(-E_0/kT), \quad (VI)$$

where Q^* is the partition function of the transition state and Q is the partition function of the reactant molecule. In this expression, the relative translational partition function and the internal partition function for the atom have been factored out. Similar expressions were used by Westenberg and deHaas¹² and by Atkinson and Cvetanovic¹³ for atomic oxygen addition reactions.

Using Eq. (VI) to define k , a strong negative temperature dependence would result if the transition state were very tight, with vibrational modes of higher frequency than in the molecule. This, however, requires that the bonds in the transition state be stronger than in the reactant molecule, an unlikely situation. In addition, if rotational modes are tied up by the addition of the oxygen atom to the olefin, the temperature dependence will be more negative. An alternative explanation for the observed negative temperature dependence would be that the cross section, in the case of collision theory, or the transmission coefficient, in the case of transition state theory, was dependent on the reactant quantum state. This, in fact, would be the case if the reaction were more probable for olefins in their lower vibrational states.

It is seen from both Eqs. (III) and (VI) that a negative temperature dependence of the pre-exponential factor will be apparent only if the threshold energy for the reaction is small. If E_0 is large, any effect of the shape of the cross section will be

lost in the large dependence of the rate constant on the activation energy term, $\exp(-E/RT)$. The activation energy from the Arrhenius equation would then approximately equal the threshold energy for the reaction.

In a related study, Connor, Van Roodselaar, Fair, and Strauz¹⁴ measured a negative temperature dependence for the reaction of atomic tellurium with TME. These authors suggested that the temperature dependence of this reaction and those involving other Group VI atoms could be rationalized by assuming that the activation energy is dependent upon the location of the crossing point of a triplet (reactant) surface and a singlet (product) surface. In this simplified model, the triplet surface has a slight "well," with little or no energy barrier. The crossing point of the singlet surface could then be on the repulsive portion of the triplet surface above the zero of energy as defined by the reactant surface, or below the zero of energy in the well; the former case corresponds to a positive temperature dependence, and the latter to a negative temperature dependence.

The only other absolute rate data for either reaction reported in this work is that of Elias³ for *cis*-2-butene. At room temperature, the rate constant measured by Elias agrees with the value measured in this work within the experimental error of both techniques. The higher temperature point of Elias, however, not only differs significantly from the present value, but also indicates a positive temperature dependence for the reaction. The reason for this discrepancy is not immediately apparent. It is possible, however, that higher activation energy secondary reactions were important in olefin consumption in the higher temperature rate determinations of Elias.

The relative rate data of Cvetanovic,⁴ put on an absolute basis using the value for the ethylene reaction obtained in this laboratory, are in reasonable agreement with the present data at room temperature for both the *cis*-2-butene and tetramethylethylene reactions. Especially important is the agreement between the present data on the TME reaction and the results of Cvetanovic⁴ (see Fig. 2). Both studies show a negative temperature dependence for this reaction. It also should be noted that if the complete set of rate constants now measured in this laboratory for O(³P)-olefin reactions are expressed in terms of Arrhenius equations, the results support the earlier conclusion of Cvetanovic.⁴ That is, in general, the variations observed in the rate constant for different olefins are due primarily to changes in the Arrhenius activation energy. (The above statement should not be interpreted to mean that the authors believe the resulting negative Arrhenius activation energies for the compounds *cis*-2-butene and TME are in any way directly re-

lated to the more fundamental quantity, the threshold energy.)

In the present work, the first direct measurements of negative temperature dependence for reactions of atomic oxygen with olefins have been reported. More recent direct rate measurements in this laboratory¹⁵ also have shown that the reactions of S(³P) with *cis*-2-butene and TME exhibit negative temperature dependences. This phenomenon is probably not limited to the reactions of atomic oxygen and sulfur with olefins, but should be observed at least for the reactions of the other Group VIa atoms with olefins. A possible explanation for the observed second-order kinetics for atomic oxygen and sulfur-olefin reactions is that the formation of the observed addition products⁴ involves a spin-forbidden step. Hence, the probability for the reverse step, regenerating atomic oxygen or sulfur, is greatly reduced.

The observation of a negative temperature dependence for these addition reactions is expected to be of importance in several applications of elementary rate data to macroscopic systems, particularly in the area of high temperature phenomena. For example, if the addition rate constant decreases with temperature, other reaction paths might become more probable at high temperatures. In the atomic oxygen-TME reaction, for example, the abstraction of atomic hydrogen probably becomes more important at lower temperatures than would be the case if the addition reaction had a zero temperature dependence. Also, if the rate constant is measured at room temperature and found to be very rapid (>10% of collision frequency), it is frequently assumed that the activation energy for the reaction is near zero and it therefore has little temperature dependence. While the assumption that the threshold energy for the reaction is small is probably reasonable, the conclusion that there is little temperature dependence might not be true. For the O+TME reaction, the room temperature rate constant is greater than one-half of the collision frequency (assuming a 4 Å collision diameter), implying a very low threshold energy. However, this reaction is obviously not independent of temperature having a negative temperature dependence of T^{-2} . Since a negative temperature dependence must now be considered a possibility for any rapid reaction, the extrapolation of these rate constants from room temperature to flame temperatures should be made with caution.

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