Kinetics and Mechanisms of Some Atomic Oxygen Reactions

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Abstract

Mechanisms and kinetics of some reactions of the ground electronic state of oxygen atoms, \( O(3P) \), are briefly summarized. The summary refers to reactions of oxygen atoms with several different types of organic and inorganic compounds such as alkanes, alkenes, alkynes, aromatics, and some oxygen, nitrogen, halogen and sulfur derivatives of these compounds. References to some recent compilations and critical evaluations of reaction rate constants are given.

Introduction

The low lying electronic states of free oxygen atoms are (with their relative energy levels in Kcal/mol given in parentheses):
\[ \begin{align*}
3P_2 & \text{ (0.0)},
3P_1 & \text{ (0.45)},
3P_0 & \text{ (0.65)},
1D_2 & \text{ (45.36)},
1S_0 & \text{ (96.59)}. \\
\end{align*} \]
The energy differences between the three triplets \( 3P \) states are quite small and they are usually jointly referred to as the ground electronic state of oxygen atoms. The excitation energy of the first singlet state \( 1D_2 \) is 45 Kcal/mol and that of the second singlet state \( 1S_0 \) is 96 Kcal/mol. All these states may play a role in atmospheric chemistry. The present summary of the chemical properties of free oxygen atoms is confined to \( O(3P) \), the ground electronic state, although some differences in the respective chemical behaviors are briefly mentioned.

Several different methods have been used to generate free \( O \) atoms for laboratory studies of their chemical behavior, as for example

\[
\begin{align*}
O_2 + e & \rightarrow 20 + e \\
NO_2 + hv & \rightarrow O + NO \\
N_2O + Hg^* & \rightarrow O + N_2 + Hg \\
O_3 + hv & \rightarrow O + O_2 \\
N + NO & \rightarrow 0 + N_2
\end{align*}
\]
Over the past three decades, we have made use in our laboratory at the National Research Council in Ottawa, Canada, of all of these methods. After allowance for the specific features of the individual techniques used and the accompanying reaction environments generated, the results obtained were mutually consistent. We have found the mercury photosensitized decomposition of \( \text{N}_2\text{O} \) (Rn. 3) to be particularly convenient and have used it most extensively. \( \text{N}_2 \) formed in this reaction provides a direct count of the number of the ground state oxygen atoms generated and \( \text{N}_2\text{O} \) itself is likely to react at an appreciable rate with free radicals and atoms only at elevated temperatures.

In the following it will be possible only to present a concise summary of the main features of 0 atom reactions with different types of chemical compounds and to list several references to more detailed accounts and bibliography. The summary consists of two parts, dealing respectively with 1) the main features of the reaction mechanisms and 2) the trends in the reaction rates under different reaction conditions.

**Reaction Mechanisms**

**Types of primary mechanisms of oxygen atom reactions**

Interaction of free oxygen atoms with a molecule of particular type may in principle result in one of the following types of chemical change: 1) "Abstraction" by the 0 atom of an atom from the compound, 2) "Addition" (attachment) of the 0 atom to the compound, 3) "Replacement" by the 0 atom of an atom or atomic group (radical) from the compound. Replacement includes also the isotope exchange reactions of oxygen atoms. The term "Displacement" generally implies that in a "Replacement" process the attachment of the \( \text{O}(3\text{P}) \) atom and departure of the displaced atom or radical take place simultaneously. A particular type of addition is 4) "Insertion" of the 0 atom between two bound atoms in the compound (i.e. insertion of the 0 atom into a chemical bond in the compound). In as much as one of these types of chemical change can be identified and shown to result directly from the chemical interactions in the primary reaction step, it represents the primary reaction mechanism.

Mechanisms of oxygen atom reactions are determined by identifying the primary reaction products. However, a primary reaction product may sometimes be unstable and very short-lived and therefore difficult to observe experimentally. Thus, for example, if an addition is followed rapidly by fragmentation of the adduct, it may simulate an abstraction or a displacement and be classified as such. An example\(^1\) of a mechanistic ambiguity of this kind is provided by the reaction of \( \text{O}(3\text{P}) \) with \( \text{H}_2\text{S} \)

\[
\text{O}(3\text{P}) + \text{H}_2\text{S} \rightarrow [\text{H}_2\text{SO}]^* \rightarrow \text{products}
\]
which appears to proceed entirely or predominantly by H atom abstraction. In fact, many "Replacement" or "Displacement" reactions may actually be additions followed by rapid fragmentation. Regardless of such ambiguities, discussion of reaction mechanisms in terms of basic types of chemical change is generally useful and informative.

Abstraction reactions of O atoms

In the reactions of O(3P) atoms with alkanes (RH) the reaction products observed (under appropriate conditions to minimize secondary reactions) are H₂O and alkyl radicals (R) formed by abstraction of H atoms by O atoms. The primary reaction mechanism is

\[ O(3P) + RH \rightarrow OH + R \]  

(7)

The spin-forbidden insertion to produce an alcohol (ROH) does not occur. In contrast to this, the allowed insertion of the electronically excited singlet O(1D₂) atoms into the CH bonds of alkanes to form "hot" (vibrationally excited) alcohols occurs readily.²

Attack of O(3P) atoms on aldehydes (RCHO) (and some other alkane derivatives, such as alcohols, thiols, haloalkanes etc) also involves H atom abstraction, e.g.

\[ O(3P) + RCHO \rightarrow OH + RCO \]  

(8)

The suggested different reaction path, such as addition of O(3P) to acetaldehyde to form acetic acid

\[ O(3P) + CH₃CHO \rightarrow CH₃COOH \]  

(9)

apparently does not occur.³,⁴

In the case of simple alkenes, at least at not too elevated temperatures and with O(3P) atoms not kinetically excited ("hot"), abstraction cannot compete effectively with the very rapid O(3P) addition to the double bond. However, at sufficiently high temperature, or with sufficiently "hot" O(3P) atoms, abstraction of H atoms should be expected to become more important.

Addition reactions of O atoms

One of the most important kinetic properties of O(3P) atoms is their ability to add rapidly to unsaturated CC bonds or to S atoms in some sulfur containing organic compounds.

In the gas phase O(3P) reaction with alkenes two general types of products due to the initial addition of O(3P) are observed under normal laboratory conditions: 1) stabilized adducts and 2) the products formed by fragmentation of the initial adducts (including products from secondary reactions of the free radical fragments
formed. The stabilized adducts are of two types: 1) those formed by attachment of 0 atoms to the double bond (the epoxides) and 2) those formed by molecular rearrangement of the initial adducts, which are almost exclusively carbonyl compounds (aldehydes and ketones). The rearrangement products are formed by 1,2 C to C shift of a H atom (or less frequently radical group) from the C atom to which O(3P) adds to the other C atom of the original double bond. Formation of epoxides is nonstereospecific: with either cis- or trans-2-butene, for example, both cis- and trans-2-butene oxide are produced and their ratio is different in the two reactions and is also temperature dependent.

The products observed in O-alkene reactions are generalized in a set of "predictive" rules, which define the expected compounds from particular reactions and also define the basic reaction mechanism. It is not possible in a brief summary to present in a satisfactory way all the aspects of the versatile behavior of O(3P) atom alkene reactions and a detailed reaction mechanism. The subject has been recently discussed in some depth by Cvetanovic and Singleton. The overall sequence of events can be described in a simplified manner using the O(3P) reaction with cis-2-butene as an example:

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \\
\text{O} + \quad \text{C} = \text{C} \quad \rightarrow \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H}
\end{array}
\]

(triplet biradical)

\[
\rightarrow \text{cis-1,2-epoxybutane}^* + \text{trans-1,2-epoxybutane}^*
\]

\[
\rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_3^* + (\text{CH}_3)_2\text{CHCHO}^*
\]

Pressure independent fragmentation (into CH3, etc)

To explain the observed products, it is necessary to postulate that the initial adduct is a triplet biradical. This intermediate subsequently rapidly rearranges into highly vibrationally excited ("hot") epoxides and carbonyl compounds or undergoes a rapid "pressure independent" fragmentation (which may also include displacements, as defined in an earlier section). The "hot" epoxides and carbonyl compounds undergo at lower pressures a "pressure dependent fragmentation" and tend to be collisionally stabilized at higher pressures. In condensed media the pressure dependent fragmentation is suppressed, as expected.
The $O(^3P)$ reaction with cyclopentene illustrates some interesting rearrangement and fragmentation reactions dictated by a particular structure of a structurally constrained system. The initial triplet biradical in this system undergoes partly the usual rearrangement into the "hot" cyclopentene oxide and cyclopentanone but it also undergoes the equivalent of the pressure independent fragmentation (or "displacement") which in this case, because the "displaced" group is part of the original cyclopentene ring, leads to the formation of a ring-opened biradical. The latter undergoes substantial molecular cleavage (into ethylene and acrolein) and a ring closure (mainly into the C4-ring cyclobutyl aldehyde and to a minor extent into the C6-ring dyhydropyrane by incorporating the oxygen atom into the closed ring).

The general mechanism of $O$ atom addition to alkynes resembles that for the addition to alkenes. Fewer mechanistic studies have been done so far for $O$ atom additions to aromatic hydrocarbons. In the $O(^3P)$ reaction with benzene the main product is a non-volatile material difficult to characterize. However, the direct adduct, phenol, is also formed in smaller amounts (about 13% of the benzene consumed). In the reaction with toluene, 15-20% of the $O$ atoms reacted are recovered as the direct adduct, cresol. An interesting directional effect is observed: only o-cresol and p-cresol (in a ratio of about 3:1) with very little or no m-cresol are formed. The directional effect is consistent with the electrophilic character of $O(^3P)$ atoms.

$O(^3P)$ atoms rapidly add to S atoms functionally bound in organic sulfides and disulfides, as for example in dimethyl sulfide and dimethyl disulfide. Some of the kinetic features of these addition reactions are similar to those in the analogous alkene reactions.

**Reaction Rates**

Determination of the rate constants of $O(^3P)$ reactions is experimentally demanding and some early measurements were subject to large uncertainties. Determination of relative rates instead of the absolute values proved very useful for probing into the trends in rates as the structure of compounds reacting with oxygen atoms is varied. Reliable techniques are now also available for determination of absolute values of the rate constants. One of these, the phase shift technique for absolute measurements of the rate of $O(^3P)$ atom reactions, was developed and extensively used in our laboratory. Another excellent and much used technique is the resonance fluorescence method. Gratifyingly, comparison of results obtained by these absolute techniques and with the earlier relative rate determinations shows remarkably good agreement.
Several examples of $O(3P)$ rate constants ($\text{in } 10^{12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$) obtained by these three techniques at 298K are listed below.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Phase-shift technique</th>
<th>Resonance-fluorescence technique</th>
<th>Relative*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.42</td>
<td>0.49</td>
<td>0.45</td>
</tr>
<tr>
<td>Propylene</td>
<td>2.28</td>
<td>2.21</td>
<td>2.6</td>
</tr>
<tr>
<td>1-Butene</td>
<td>2.42</td>
<td>2.46</td>
<td>2.6</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>10.6</td>
<td>10.3</td>
<td>10.6</td>
</tr>
<tr>
<td>Isobutene</td>
<td>10.4</td>
<td></td>
<td>11.2</td>
</tr>
<tr>
<td>Trimethylethylene</td>
<td>31.1</td>
<td></td>
<td>35.4</td>
</tr>
<tr>
<td>Tetramethylethylene</td>
<td>45.8</td>
<td>47.7</td>
<td>45.4</td>
</tr>
<tr>
<td>Dimethylsulfide</td>
<td>31.1</td>
<td></td>
<td>33.3</td>
</tr>
<tr>
<td>Dimethyldisulfide</td>
<td>60.2</td>
<td></td>
<td>59.9</td>
</tr>
</tbody>
</table>

* Relative rates normalized to absolute values

Trends in the values of rate constants of $O(3P)$ reactions are reviewed and discussed in a number of publications.\textsuperscript{5,6,14-16} The electrophilic trend in the rate constants of $O(3P)$ reactions with alkenes is demonstrated by the monotonous increase in the rates as the number of alkyl group substituents at the double bond is increased. A number of numerical correlations, such as correlation with the ionization potentials of the olefins or with the rates observed with the same olefins reacting with another electrophilic reagent, provide additional support for the electrophilic character of these atom-molecule reactions.

**Data Bases for $O(3P)$ Reactions**

Compilations and critical evaluation of chemical kinetic data for the elementary reactions of $O(3P)$ atoms with unsaturated hydrocarbons are currently conducted by the Chemical Kinetics Data Center of the National Bureau of Standards. This activity is a part of a larger effort directed towards the development of a comprehensive general evaluated chemical kinetic data base. More specifically, it is a part of an extensive data base, currently developed by the Chemical Kinetics Data Center, which deals with chemical oxidation processes, in particular those involved in thermal combustion and in the atmospheric chemistry. The data bases are intended to provide easily accessible sources of critically evaluated rate data for use in computer modeling and in general research.
The following compilations and critical evaluations have been completed or are currently in progress:


(2) "Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol", W. Tsang. (Submitted for publication)


(4) "Chemical Kinetic Data Base for Combustion Chemistry. Part 4. t-Butyl, i-Butyl, and i-Butane", W. Tsang. (In preparation).

(5) "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen O(3P) with Unsaturated Hydrocarbons". R. J. Cvetanovic. (Submitted for publication).


References
