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ARTICLES

Reactions Involving Hot O(^{3}P) Atoms and Isomeric 2-Butene

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The low-pressure gas-phase investigation is reported on the reactions involving high-energy O(^{3}P) atoms with *cis*- and *trans*-2-butene. Gas chromatographic analysis of stable hydrocarbon end products revealed a complex spectrum of compounds containing carbonyl, epoxide, and alcohol groups. The large distribution of alcohol products was a distinct feature in these hot atom systems, indicating that OH radical formation was important. These analyses revealed differences in the internal energy levels of the reaction intermediates formed through the greater pressure dependence exhibited by the degree of stereospecific addition of oxygen atoms to *trans*-butene then reaction with *cis*-butene and through the greater degree of internal rearrangement and carbon–carbon bond scission exhibited by the trans intermediate. Direct measurements using on-line mass spectrometry also revealed that CO product signals were 14.6 times higher from reactions with *cis*-butene than with *trans*-butene, indicating greater reactivity of the cis π-bond toward oxygen atom attack. Similarly, these direct analyses revealed that OH product signals were 1.7 times higher from reactions with *cis*-butene, suggesting that in addition to direct H abstraction an indirect pathway involving mutual interaction with the substrate's π-bond may have contributed, in part, to those OH products observed in these studies. Kinetic energy moderator studies supported this hypothesis through the different moderator dependencies exhibited by the OH product signals seen to arise from high-energy oxygen atom reactions with the two stereoisomers.

Introduction

In recent years, studies in hot oxygen atom chemistry have been recognized for their fundamental importance to understanding the complex chemical and physical processes occurring as a consequence of energy transfer in reactive atom–molecule collisions for numerous photochemical,[1] combustion,[2] and atmospheric processes.[3] Practical concerns have also been expressed within the aerospace industry over oxygen atom initiated surface damage sustained by space vehicles traveling at high velocity (8 km/s) in low earth orbits (100–200 km) where ground-state oxygen atoms are prevalent.[4a,b]

Unfortunately, hot oxygen atom chemistry is a poorly understood field because fundamental studies using conventional nucleogenic sources are difficult to carry out because of the extremely short half-life of the atom's principal radioactive isotope, ^{15}O.[5] Nonnucleogenic methods for generating these species either are not well characterized or are energy limited. The latter is true for supersonic expansion of seeded atomic beams[6] and for laser photodissociation.[7] Both techniques are limited to translational energies of less than 1 eV.

Recently, we described a novel technique for generating ^{3}P ground-state oxygen atoms with translational energies that exceeded 1 eV.[8] The technique relies on ion beam sputtering of metal oxide targets for its source of oxygen atoms. Sputtering on Ta_2O_5 with 40-keV argon ions was shown to proceed predominantly by a collision cascade mechanism, where the neutral atoms possessed a nominal energy of 6 eV from a distribution that extended to about 20 eV. The present paper reports on the first application of the above source to a study on the consequences of excess translational energy in reactive $O(^3P)$ collisions with isomeric butenes.

In general, the reactions of thermal $O(^3P)$ atoms with alkenes have been thoroughly investigated from the standpoint of both the kinetics and the nature of the reaction. Largely through the pioneering work of Cvetanovic,[9] we have come to realize that there is a predictable nature to the $O(^3P)$ + alkene system at room temperature and at normal laboratory pressures. Under such conditions, the atom will undergo dominant, if not exclusive, addition to the carbon–carbon double bond. This addition is nonstereospecific and presumably yields an excited triplet biradical intermediate that either decomposes depending on the pressure or else stabilizes after certain internal rearrangements have occurred. The following reactions have been observed in bulk experiments on the addition of $O(^3P)$ to 2-butene.

$$\begin{array}{llr}
C_4H_8 + O(^3P) & \longrightarrow C_3H_7 + HCO & (1)\\
& \longrightarrow C_2H_5 + CH_3CO & (2)\\
& \longrightarrow CH_3 + C_2H_5CO & (3)\\
& \longrightarrow CH_3CHO + C_2H_4^{*} & (4)\\
& \qquad\quad \hookrightarrow C_2H_2 + H_2 & \\
& \longrightarrow C_4H_6O + H_2 & (5)\\
& \longrightarrow C_4H_8O & (6)
\end{array}$$

Several dissociative pathways (reactions 1–5) can yield a variety of alkanoyl and alkyl radical products. However, complete dissociation to CO tends to become prevalent in this system, as well as with other alkenes, when the pressure under which the studies are carried out is lowered. Even so, pressure-independent fragmentation is apparent in a number of these bulk systems[9b] and has been linked to a direct displacement mechanism postulated by Lee and co-workers to be an important reaction for the single-collision conditions of their crossed molecular beam experiments.[10]

One of several internal rearrangements may become available to the biradical which would ultimately lead to a variety of stabilized products shown in reaction 6. On the one hand, ring closure may occur to produce an excited epoxide. Of course, the ring-closing process would require numerous molecular collisions involving the intermediate in order to facilitate its conversion to the singlet state. Likewise, intramolecular 1,2-hydrogen atom migration may occur to yield an excited carbonyl product. It has long been recognized that such migrations are, at least in principle, viable pathways for rearrangement of free alkyl radicals.[11] There is, in fact, considerable evidence supporting the occurrence of such migrations in singlet biradicals, particularly in those rearrangements that are exothermic.[12] The evidence is less convincing, however, for the triplet biradical. This is due in part to the difficulty in generating such intermediates and to the rapidity with which they convert to the singlet state under multiple-collision conditions. This is also due to the fact that such migrations tend to have much higher energies of activation in the triplet biradical than in the singlet. Finally, 1,2-migration of a methyl group may also occur in the biradical. This would, of course, alter the carbon skeleton in the final carbonyl product.

Although hydrogen atom abstraction yielding a hydroxyl radical product is the exclusive reaction in $O(^3P)$–alkane systems, it is only very minor in the alkene systems (less than 2% of the total reaction).[9b] It has long been presumed that this abstraction channel should become more important at higher temperatures. In fact, the work of Kleinermanns and Luntz[13] showed a trend of increasing relative cross sections for hydroxyl radical formation from propylene and 1-butene as a function of kinetic energy in a range extending up to about 0.7 eV. Unfortunately, little could be said of the magnitude of the abstraction channel relative to π-bond addition.

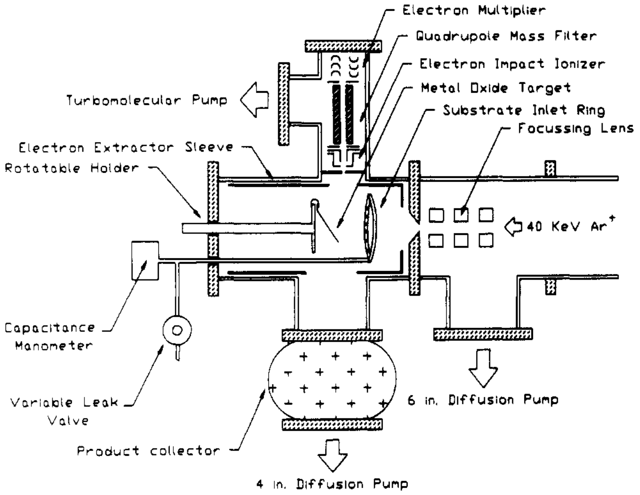

Figure 1. Schematic of vacuum chamber where oxygen atoms were generated and reacted.

Key reasons for undertaking the present investigation were to assess the effects of kinetic energy on the pathways yielding OH radicals and to determine whether the stereoconfiguration of the substrate plays a significant role in the overall chemistry.

Experimental Section

Apparatus. The chamber used for oxygen atom generation and reaction is shown schematically in Figure 1. An in-depth description of the system and its operating characteristics can be found elsewhere.[8] A 150-cm isotope separator (High Voltage Corp.) was utilized for generating and mass resolving a beam of 40-keV argon ions. This beam was focused through a 4.8-mm entrance aperture to the sputtering chamber with an electrostatic lens. A Ta_2O_5 target was rotated on axis to the beam at an angle of 30° measured from the surface normal.

The oxide target was prepared from a 0.05-mm-thick tantalum foil (Atomergic Chemetals Corp.) that was cleaned in a hot mixture of alconox and 1,1,1-trichloroethane for 1 h and then rinsed twice with boiling distilled water and once with methanol. The oxide was generated on the cleaned surface by anodizing an electrolyte solution of 0.01 N KI.[14] Although oxide thicknesses were not measured, the process yielded what appeared to be a uniform gray coating that surpassed thicknesses that could be matched to specific interference colors.

In previous studies,[8] it was found that oxygen atoms sputtered from Ta_2O_5 were dominantly neutral and resided exclusively in their ^3P ground electronic spin state. Energy distributions of the sputtered atoms were measured at specific scatter angles using a retarding potential grid method.[8] Results were shown to coincide with a modified Thompson model describing linear collision cascades.[15] Figure 2 shows the angle-integrated energy distribution measured from this system. A peak energy of 6 eV is expected with a distribution that extends throughout the 1–20-eV range.

Under typical running conditions, 15 μA of ion beam current was focused onto the oxide target and yielded oxygen atom fluxes of better than 10^{15} atoms cm^{-2} s^{-1}. *cis*-Butene and *trans*-butene gases (Phillips Petroleum gold label purity, 99.997%) were introduced into the sputtering chamber at pressures ranging between 8×10^{-5} and 2.8×10^{-2} Torr. Absolute pressures were monitored using a capacitance manometer (MKS Baratron gauge) and controlled using a sapphire-seated variable leak valve (Varian). Studies were also carried out using neon gas as an kinetic energy moderator by premixing the butene and neon gases in a 4-L Pyrex storage bulb at the desired composition and then by introducing the mixture as one through the same leak valve.

Product Analysis. Stable products were continuously collected during the course of a run on a 92-cm × 7.6-cm-diameter liquid nitrogen cooled collector mounted perpendicular to the gas flow.

TABLE I: Relative Distributions of Oxygenated Hydrocarbon Products Observed from Hot O(^{3}P) Atom Reactions with *cis*-2-Butene[a]

	substrate pressure, Torr					
product observed	8.0×10^{-5}	5.6×10^{-4}	5.6×10^{-3}	1.0×10^{-2}	1.6×10^{-2}	2.8×10^{-2}
propanal	5.3 ± 1.1	2.7 ± 0.5	4.2 ± 1.2	1.8 ± 0.5	1.3 ± 0.5	0.5 ± 0.2
acetone	30.8 ± 1.0	24.7 ± 4.1	1.2 ± 0.9	5.6 ± 0.2	3.8 ± 0.2	1.4 ± 0.6
2-propyn-1-ol	1.0 ± 0.5	0.8 ± 0.3	0.8 ± 0.2	1.4 ± 0.9	1.3 ± 0.7	0.6 ± 0.2
dimethyl epoxide[c]	18.2 ± 0.7	18.8 ± 1.7	24.4 ± 2.4	25.8 ± 1.0	26.9 ± 2.6	26.5 ± 2.1
butanone	3.8 ± 0.7	9.6 ± 2.4	13.3 ± 0.9	7.3 ± 1.9	5.3 ± 0.9	1.6 ± 0.3
3-buten-2-one	18.9 ± 2.0	27.4 ± 1.2	34.1 ± 1.5	33.2 ± 3.9	35.0 ± 6.7	39.6 ± 2.9
2-methyl-2-propenal	nd	nd	0.2 ± 0.1	1.4 ± 0.5	2.1 ± 0.9	3.0 ± 1.5
3-buten-2-ol	15.9 ± 1.8	13.7 ± 2.4	9.6 ± 1.2	20.2 ± 3.8	21.1 ± 1.5	24.4 ± 2.2
2-buten-1-ol[c]	6.1 ± 2.1	2.3 ± 0.9	1.3 ± 0.6	5.1 ± 1.2	3.2 ± 1.1	2.4 ± 1.5

[a] Distributions were based only on those oxygenated hydrocarbons that were observed in the gas chromatographic analysis. Errors represent standard deviations on three separate runs. [b] Analysis and compound identification were performed by gas chromatography–mass spectrometry. [c] Cis and trans isomers.

TABLE II: Relative Distributions of Oxygenated Hydrocarbon Products Observed from Hot O(^{3}P) Atom Reactions with *trans*-2-Butene[a]

	substrate pressure, Torr					
product observed[b]	8.0×10^{-5}	5.6×10^{-4}	5.6×10^{-3}	1.0×10^{-2}	1.6×10^{-2}	2.8×10^{-2}
propanal	17.1 ± 5.6	11.7 ± 0.7	6.2 ± 2.4	6.9 ± 1.1	6.3 ± 1.6	0.9 ± 0.3
acetone	56.6 ± 5.1	53.3 ± 8.5	29.6 ± 10.1	21.4 ± 2.7	16.1 ± 1.6	4.7 ± 0.4
2-propyn-1-ol	2.0 ± 0.6	1.2 ± 0.5	0.8 ± 0.2	0.7 ± 0.2	0.6 ± 0.1	0.2 ± 0.1
dimethyl epoxide[c]	nd	4.7 ± 0.9	14.1 ± 4.1	16.6 ± 4.7	13.9 ± 4.1	21.3 ± 5.6
butanone	10.5 ± 1.4	16.1 ± 1.9	21.5 ± 3.2	16.9 ± 3.5	15.4 ± 1.6	2.5 ± 0.5
3-buten-2-one	13.8 ± 6.4	9.8 ± 4.7	10.3 ± 5.9	15.9 ± 4.2	18.8 ± 1.2	25.2 ± 4.4
2-methyl-2-propenal	nd	nd	nd	2.7 ± 0.9	5.9 ± 1.1	12.9 ± 1.8
3-buten-2-ol	nd	2.5 ± 0.3	13.9 ± 5.9	13.7 ± 4.2	14.9 ± 5.1	26.3 ± 5.4
2-buten-1-ol[c]	nd	0.6 ± 0.2	3.6 ± 1.7	5.2 ± 1.0	8.1 ± 1.3	6.0 ± 0.7

[a] Distributions were based only on those oxygenated hydrocarbons that were observed in the gas chromatographic analysis. Errors represent standard deviation on three separate runs. [b] Analysis and compound identification were performed by gas chromatography–mass spectrometry. [c] Cis and trans isomers.

Depending on the conditions of an experiment (i.e., the substrate pressure used in an experiment), run times generally ranged between 1 and 8 h of collection to ensure adequate product for analysis. At the completion of a run, the collector was isolated from the sputtering chamber and the pumping station, and the contents were transferred in vacuo to a processing manifold that concentrated the products relative to the bulk amount of substrate gas that also condensed on the collector.

This manifold consisted of a solid adsorbent trap (Porapak N, Analabs Inc.) that was used to selectively strip out all oxygenated and higher boiling hydrocarbon products from the substrate gas. The technique described here is very similar to what is used for bulk gas processing in atmospheric analysis.[16] Once concentrated, the products were desorbed and condensed into 2-mL volume gas injection loops for analysis by gas chromatography–mass spectrometry (GC–MS).

Analyses of products by GC–MS were performed on a Finnegan 5100 instrument. A 30-m × 0.25-mm-i.d. fused silica capillary colume containing a film thickness of 0.25-μm DB-Wax (J&W Scientific, Inc.) was used for product separation. Products were identified by their mass spectrum using electron impact ionization and quadrupole mass filtering and compared against calibrated standards to convert integrated ion counts to relative yields.

In addition to the routine analyses performed on collected products, an on-line quadrupole mass analyzer (Dycor 200 mass range head with electron multiplier detector) provided direct product signal measurements for OH (*m*/*e* 17) and CO (*m*/*e* 28). The analyzer was coupled to the sputtering chamber via a differentially pumped aperture that allowed only a small fraction of the chamber gas to be sampled. The detector region was maintained below 10^{-6} Torr by a turbomolecular pump (Balzer Inc.). Signals were acquired while manually chopping the argon ion beam through the action of a slide valve in order to modulate the oxygen atom source on and off. Products signals were then corrected for system background at each mass, which was acquired when the source was off.

Results and Discussion

General Mechanistic Considerations. Relative distributions of oxygenated hydrocarbon products observed from high-energy O(^{3}P) atoms reactions with *cis*- and *trans*-2-butene were listed in Tables I and II, respectively, for substrate pressures ranging from 8×10^{-5} to 2.8×10^{-2} Torr. As these distributions only reflected time-averaged measurements based on those products detected during gas chromatographic analysis, they were not meant to reflect absolute product yields. Even so, certain qualitative aspects of the overall chemistry were worth noting.

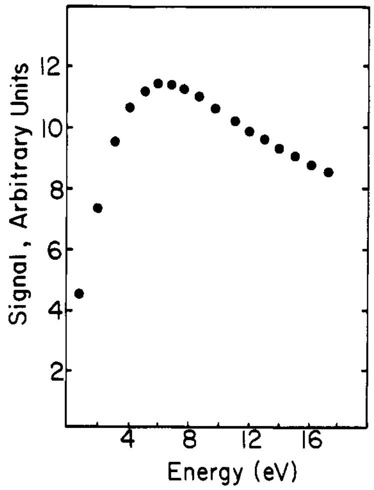

Figure 2. Angle-integrated energy distribution of sputtered oxygen atoms.

Similar to earlier bulk experiments, various carbonyl and epoxide products were observed in the stabilized C_4O product fraction. Unlike these earlier studies, however, alcohol products occupied a large fraction of this spectrum, indicating that OH radical formation was an important feature in the present hot atom experiments. Previous work carried out by Cventanovic at very high reaction temperatures showed evidence for alcohol formation in O(^{3}P) + alkene systems, presumably through OH radical addition to the substrate's π-bond.[9] A similar mechanism of alcohol formation could account for the present observations.

Interestingly, alcohol distributions were noticeably higher with *cis*-butene than with the trans isomer, indicating greater reactivity

TABLE III: Mass Spectrometer Detector Signals for OH and CO Products Arising from Hot $O(^3P)$ Atom Reactions with *cis*- and *trans*-2-Butene

component pressure, Torr			detector signal,[a] A			
			OH product		CO product	
2-butene	neon	% neon	*trans*-butene	*cis*-butene	*trans*-butene	*cis*-butene
5.6×10^{-3}		0	8.8×10^{-8}	1.7×10^{-7}	2.5×10^{-8}	3.6×10^{-7}
1.1×10^{-3}		0	2.2×10^{-8}	3.2×10^{-8}	6.0×10^{-9}	7.3×10^{-8}
1.0×10^{-4}		0	1.4×10^{-9}	2.5×10^{-9}	4.0×10^{-10}	6.9×10^{-9}
1.1×10^{-3}	4.5×10^{-3}	80	2.6×10^{-9}	6.7×10^{-9}	2.4×10^{-9}	3.0×10^{-8}
1.0×10^{-4}	5.5×10^{-3}	98	6.0×10^{-12}	6.4×10^{-11}	1.0×10^{-10}	1.3×10^{-9}

[a] The OH product was measured by the detector ion signal intensity at *m/e* 17, while the CO product was measured at *m/e* 28. Signals were corrected for system background by modulating the oxygen atom source on and off.

of this cis π-bond toward addition of the radical. This is not unreasonable since the trans π-bond should be less reactive due to substituent shielding of that bond.

Oxygen Atom Reaction through π-Bond Addition. Three products within the C_4O product spectrum, butanone and *cis*- and *trans*-dimethyl epoxides, were linked with oxygen atom reaction with the butene substrate through π-bond addition. Butanone exhibited a very different pressure dependence from that of the epoxide products or any of the other C_4O products. Its relative distribution was observed to rise and then fall off with increased substrate pressure. The initial rise was attributed to collision-induced stabilization of the addition intermediate, as was probably the case for all the C_4O products. However, the subsequent falloff in butanone may have reflected the increased efficiency for epoxide formation through ring closure, due to collision-induced electron spin conversion of the addition intermediate. This reaction intermediate presumably existed as a triplet biradical on initial formation, which meant that electronic spin conversion must have preceded any ring-closing process.

Oxygen Atom Reaction through Direct Displacement. Unlike butanone, products such as 3-buten-2-one and 2-methyl-2-propenal exhibited a continual rise in distribution with increasing substrate pressure, suggesting that they originated from different reaction intermediates than the addition biradical. A primary reaction mechanism involving direct H displacement could account for such a distinction, although there is no direct evidence to support this. Likewise, products such as propanal and acetone could be accounted for through direct CH_3 displacement, although the pressure dependence exhibited by both products strongly suggested that a major part of their contribution arose from secondary decomposition. Even so, one cannot rule out the consideration that aside from π-bond addition and H abstraction, mechanisms such as H displacement, as well as CH_3 displacement, are probably important features of the primary atom–molecule reaction scheme in these complex systems.

Comparison between Isomeric Butenes of the Intermediate's Rearrangement and Decomposition Pathways. A comparison between isomeric butene substrates of the relative distribution of the product 2-methyl-2-propenal revealed significantly higher values from reactions with *trans*-butene than with the cis isomer, indicating a greater ability of the trans reaction intermediate to undergo CH_3 migration. Likewise, a higher distribution of butanone indicated a greater ability of the trans intermediate to undergo H migration.

Decomposition of the intermediates via carbon–carbon bond scission also appeared more prevalent from reactions with *trans*-butene, based on relative product distributions of acetone and propanal. As described earlier, the pressure dependences of both products showed trends reflecting major contributions from secondary decomposition rather than direct CH_3 displacement.

These qualitative observations appeared to reflect a general phenomenon that oxygen atom reactions with *trans*-butene lead to intermediates of higher internal energies than did reactions with *cis*-butene, thus better enabling them to undergo internal rearrangements as well as decomposition.

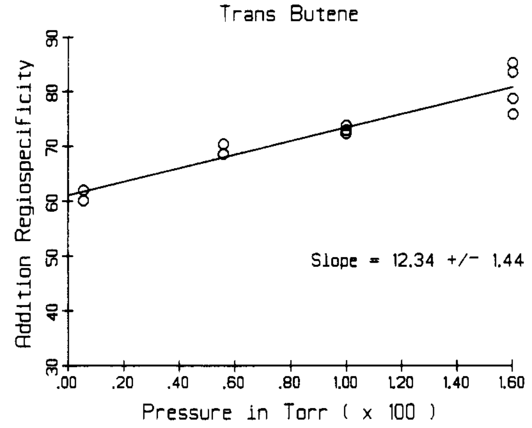

Figure 3. Percentage of stereospecific $O(^3P)$ addition to *trans*-butene plotted as a function of pressure.

Pressure Dependences of the Stereospecific Addition Pathways. The stereospecific behavior arising from oxygen atom addition to the isomeric butene substrates was investigated as another means to support the above argument relating substrate stereoconfiguration with intermediate internal energy differences. The degree of stereospecific addition was measured from the distribution of isomeric dimethyl epoxide products formed as a result of ring closure. For reactions with *trans*-butene, the trans epoxide product signified the stereospecific pathway. Likewise, for reactions with *cis*-butene, the cis epoxide product signified the stereospecific pathway.

While it is true that in single pressure bulk experiments greater nonstereospecificity was observed from oxygen atom addition to *cis*-butene than to *trans*-butene,[9,17] little could be inferred about the internal energy levels of the intermediates formed under these circumstances. This was because thermodynamic arguments predicted such behavior on the grounds that *trans*-dimethyl epoxide was more stable than the cis isomer. However, it was possible to eliminate such factors from consideration in the present work by comparing the amount of change that occurred in the stereospecific behavior over a broad range of substrate pressures. The rationale for this was that differences in the pressure dependences of these pathways should reflect differences in the internal energy levels of the reaction intermediates.

The percentage of stereospecific oxygen atom addition to *trans*-butene was plotted in Figure 3 as a function of the substrate's pressure. Results from 11 consecutive runs conducted at pressures ranging between 5.6×10^{-4} and 1.6×10^{-2} Torr showed that the stereospecificity increased linearly by 19%. A least-squares fit of the data yielded a slope of 12.34 with a standard deviation of 1.44.

Likewise, the percentage of stereospecific oxygen atom addition to *cis*-butene was plotted in Figure 4. Unlike the trans system, results from 11 consecutive runs conducted at pressures ranging between 8.0×10^{-5} and 1.6×10^{-2} Torr showed that the stereospecificity increased by less than 2%. A least-squares fit of the data yielded a slope of only 1.12 with a standard deviation of 0.49.

The greater pressure dependence exhibited by the stereospecific addition of oxygen atoms to *trans*-butene than by reaction with the cis isomer lent additional support to the hypothesis that reactions with *trans*-butene lead to intermediates of higher internal energy.

Mechanistic Considerations Regarding OH Radical Formation. Detector signals reflecting absolute levels of OH and CO products

TABLE IV: OH and CO Product Signal Ratios from Hot O(^{3}P) Atom Reactions with *cis*- and *trans*-2-Butene

component pressure, Torr			cis-to-trans product signal ratio		OH-to-CO product signal ratio	
2-butene	neon	% neon	OH ratio	CO ratio	*trans*-butene	*cis*-butene
5.6×10^{-3}		0	1.9	14.4	3.5	0.5
1.1×10^{-3}		0	1.5	12.2	3.7	0.4
1.0×10^{-4}		0	1.8	17.3	3.5	0.4
1.1×10^{-3}	4.5×10^{-3}	80	2.6	12.5	1.1	0.2
1.0×10^{-4}	5.5×10^{-3}	98	10.7	13.5	<0.1	<0.1

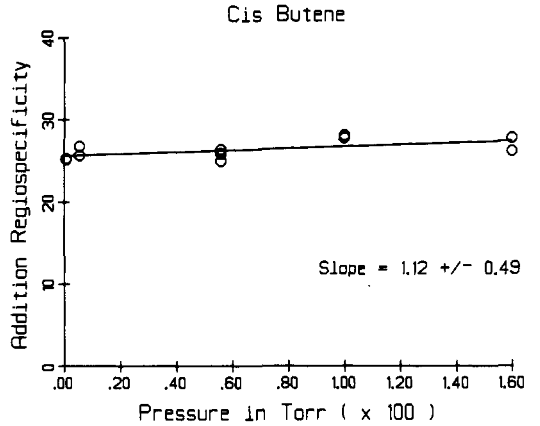

Figure 4. Percentage of stereospecific O(^{3}P) addition to *cis*-butene plotted as a function of pressure.

formed from oxygen atom reactions with the 2-butene stereoisomers were acquired through on-line mass spectrometric measurements and were listed in Table III as a function of substrate pressure. Product signal ratios calculated from these data were listed in Table IV in order to compare the absolute differences existing in both the OH and CO signals between the two stereoisomer systems. Similarly, OH-to-CO signal ratios were calculated and listed in the same table in order to compare differences in the reaction pathways yielding OH and CO products within each system.

Results showed that CO product signals were, on the average, 14.6 times higher from oxygen atom reactions with *cis*-butene than from reactions with *trans*-butene, indicating greater reactivity of the cis π-bond toward oxygen atom attack. Surprisingly, OH product signals were, on the average, 1.7 times higher from reactions with *cis*-butene than from reactions with *trans*-butene. The shielding effect imposed by the trans substituents on the π-bond should render that bond not only less reactive toward oxygen atom attack but also less reactive toward OH radical addition. Also, the H atoms on these trans substituents should have greater availability for abstraction by the oxygen atoms. Combined, these features should have resulted in higher absolute OH product signals arising from reactions with *trans*-butene than with the cis isomer. The opposite behavior observed suggested that OH radicals were not formed entirely through direct H abstraction but that at least part of their contribution in these hot atom studies may have reflected the actions of an indirect pathway involving mutual interaction with the substrate's π-bond.

An indirect pathway was proposed where oxygen atom addition to the π-bond was followed by H migration across the newly carbon–oxygen bond. Final cleavage of that bond would then release a OH radical that was indistinguishable from that formed through direct abstraction.

Energy Considerations Regarding an Indirect Pathway for OH Radical Formation. The viability of the proposed indirect pathway for OH formation depended on whether or not sufficient internal energy existed within the reaction intermediate to satisfy the energy requirements for hydrogen atom migration. Theoretical calculations suggested that hydrogen atom migrations of this nature tended to have exceptionally high activation energies for triplet biradicals. Values of the order of 50 kcal/mol were predicted in some instances.[18] Even so, such constraints could easily have been satisfied in the present hot atom studies. Preliminary studies conducted in this laboratory have shown evidence for similar migrations occurring within the triplet ($^3B_2$) dioxymethylene biradical (H_2COO) formed through hot O(^{3}P) addition to formaldehyde at similar pressures.[19] The energy of activation for this migration was predicted to fall in excess of 30 kcal/mol.[20]

Of course, an additional consideration is that the pressures at which the present studies were carried out were probably high enough to promote collision-induced electronic spin conversion of the biradical. Our observation of epoxide products proved this point. The energy constraints for hydrogen atom migration on the singlet intermediate are substantially less,[18] therefore implying that such migrations might be more facile under these circumstances.

Such an indirect pathway for OH formation should have reflected not only differences in the π-bond reactivity but also differences in the internal energy levels of the primary reaction intermediates. As described earlier, the pressure dependence exhibited by trans reaction intermediates reflecting a greater degree of stereospecific addition, coupled with a greater tendency of these intermediates toward rearrangement and carbon–carbon bond scission, supported the argument that oxygen atom addition to *trans*-butene leads to intermediates of high internal energy than did reaction with *cis*-butene. Intuitively, one might expect a larger portion of those intermediates formed in the reactions with *trans*-butene to yield OH through this indirect pathway. In fact, a comparison of the OH-to-CO product signal ratios that were listed in Table IV, revealed values that were 8 times higher from reactions with *trans*-butene than with *cis*-butene. However, it may be wise not to read too much significance into this ratio as it may have reflected other unrelated aspects of reaction as well. For instance, differences in the π-bond reactivities between the two stereoisomer substrates could have accounted for such differences observed in the OH-to-CO product signal ratios simply by the effects they would have on the absolute CO product signal.

OH and CO Product Signal Dependences on Kinetic Energy. The effect of oxygen atom kinetic energy on the reaction pathways yielding both OH and CO products was investigated using neon gas as a moderator to lower the average energy of the atom at reaction. Product signals for OH and CO, acquired through on-line mass spectrometric measurements, were listed in Table III as a function of substrate and moderator partial pressures. Signal ratios were also calculated from these data and listed in Table IV to reflect, on the one hand, differences between the two stereoisomer systems in the absolute moderator dependences of each of the two products and, on the other hand, to reflect differences within each stereoisomer system between the OH and CO moderate dependences.

An additional manipulation in the raw signal data from Table III corrected for the fact that as the moderator concentration increased, the substrate partial pressure decreased, causing a reduction in the number of reactive collisions and, therefore, a reduction in the product signals detected. Data were normalized by dividing the appropriate product signal, measured at a specific moderator concentration, by the product signal measured at the same substrate pressure without moderator. These normalized data were listed in Table V. Results showed that OH, as well as CO product signals, exhibited moderator dependences in both stereoisomer systems. The CO product signals exhibited similar dependences between the *cis*- and *trans*-butene systems, decreasing 4–5-fold with up to 98% neon concentration. On the other hand, OH product signals exhibited different dependences between stereoisomer substrates, decreasing 250-fold in *trans*-butene as

TABLE V: Energy Dependencies of the OH and CO Forming Pathways Arising from Hot O(^{3}P) Atom Reactions with *cis*- and *trans*-2-Butene

	normalized product signal[a]			
	OH product		CO product	
% neon	*trans*-butene	*cis*-butene	*trans*-butene	*cis*-butene
0	1	1	1	1
80	0.12	0.21	0.40	0.40
98	0.004	0.026	0.25	0.19

[a] Raw ion signals from Table III were normalized in the neon moderator studies by dividing the appropriate product signal measured at a specific moderator concentration by the product signal measured at the same substrate pressure, but without moderator. This action corrects for the natural decrease in raw product signal due to the decrease in substrate pressure when moderator is added.

compared with decreasing only 38-fold in *cis*-butene. This observation lent support to the hypothesis that more than one reaction pathway to OH may have been operative in these hot atom experiments.

Interestingly, the ratio of OH product signals arising from *cis*- and *trans*-butene increased from an average of 1.7 without moderator to 10.7 with 98% neon. This value closely approached what was presumed to be the difference in stereoisomeric π-bond reactivities, as measured by the CO product signal ratio, and suggested that OH formation in heavily moderated reactions may have reflected this difference in bond reactivities. In other words, the presence of moderator may have suppressed all contributions to the OH signal arising from the direct H abstraction pathway, leaving only those contributions from the indirect pathway.

Conclusions

Our investigation of the low-pressure gas-phase reactions involving high-energy O(^{3}P) atoms with *cis*- and *trans*-2-butene revealed a complex spectrum of products comprised, in part, of carbonyl and epoxide compounds that were similar in nature to those that were observed in previous bulk studies. The one distinguishing feature of the present hot atom studies, however, was the large distribution of alcohol products observed in the above spectrum, indicating the importance of OH formation at high kinetic energies.

Direct measurements using on-line mass spectrometry revealed not only that CO product signals were substantially higher from hot oxygen atom reactions with *cis*-butene than with *trans*-butene, reflecting the greater reactivity of this cis π-bond, but also that OH product signals were also higher from these same reactions, suggesting that an indirect pathway involving interaction with the substrate's π-bond may have contributed, in part, to OH formation. Kinetic energy moderator studies supported this hypothesis by demonstrating that different moderator dependences existed in the OH product signals seen to arise from oxygen atom reactions with the two stereoisomer substrates.

An indirect pathway yielding OH radicals was proposed that involved π-bond addition, 1,2-hydrogen atom migration, and final carbon–oxygen bond scission. Such an indirect pathway would not only reflect differences in the reactivity of the π-bonds toward oxygen atom attack but also reflect differences in the internal energy levels of the reaction intermediates. Analysis of stable end products revealed that addition of oxygen atoms to *trans*-butene led to reaction intermediates of higher internal energy than did reactions with the cis stereoisomer. Therefore, one might expect a larger portion of those intermediates formed with the trans substrate to yield OH by this indirect pathway. However, the validity of this agrument still remains to be seen.

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Registry No. O, 17778-80-2; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; propanal, 123-38-6; acetone, 67-64-1; 2-propynal, 624-67-9; *cis*-2,3-epoxybutane, 1758-33-4; 2-butanone, 78-93-3; 3-buten-2-one, 78-94-4; 2-methyl-2-propenal, 78-85-3; 3-buten-2-ol, 598-32-3; *cis*-2-buten-1-ol, 4088-60-2; *trans*-2,3-epoxybutane, 21490-63-1; *trans*-2-buten-1-ol, 504-61-0.

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