20.2%, 9.8 g; methyl acrylate, 49 g, 24 h, 26.0%, 1.0 g; ethyl acrylate, 30 g, 20 h, 70 °C, 22.8%, 2.0 g; acrylonitrile, 54 g, 12 h, 21.0%, 1.7 g; methyl vinyl ketone, 30 g, 12 h, 42 °C, 15.5%, 0.7 g; cyclopentadiene, 41 g, 48 h, 30 °C, 32.3%, 11.2 g; 1,3-cyclohexadiene, 4 g in 5 mL of C_6H_5Cl, 7 days, 31.5%, 3.5 g; 1,3-cycloheptatriene, 0.9 g in 2 mL of C_6H_5Cl, 7 days, 25.4%, 1.2 g; bicyclo[4.2.1]nona-2,4,7-trien-9-one, 1.3 g in 2 mL of C_6H_5Cl, 7 days, 17.9%, 2.0 g; bicyclo[4.2.2]deca-2,4,7,9-tetraene, 0.2 g in 2 mL of C_6H_5Cl, 7 days, 0.2 g; cycloheptatriene, 2.6 g, 7 days, 33.7%, 1.1 g.

Synthesis of Hydroperoxides. Indan was autoxidized without initiator for 12 h at 110 °C. Iodometry showed a hydroperoxide content of 13.4% by weight. The solution was used without concentration. Tetralin was autoxidized without initiator for 12 h at 80 °C. Iodometry showed a hydroperoxide content of 14.5% by weight. The solution was used without concentration. Cycloheptatriene (9.2 g) and 0.2 g of hematoporphyrin were stirred in an oxygen atmosphere for 5 h at 0 °C in Pyrex while illuminated with a 370-W sunlamp. The product had a broad absorption band at 1650–1700 cm^{-1} (tropone). This crude oxidate was used directly in the ESR experiments.

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Competition between Reactive Sites in the Reactions of Oxygen Atoms and Hydroxyl Radicals with Phenylacetylene and Styrene

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Abstract: The products of the reactions of oxygen atoms and hydroxyl radicals with phenylacetylene and styrene were identified under single-collision conditions to determine whether these electrophiles prefer to react with either the ring or the unsaturated side chain. Previous work in another laboratory found that at 0.4 kPa oxygen atoms react exclusively with the C_2H group of phenylacetylene. The results obtained here under single-collision conditions show that the reactions of OH with phenylacetylene and of O and OH with styrene yield products which are typical of attack on both the ring and the side chain. The results for O + phenylacetylene are consistent with this trend. Qualitative arguments based on frontier electron theory support these findings.

Introduction

A recent publication by Blumenberg et al.[1] indicated that, given a choice between an alkynyl group and an aryl group in the same molecule, an oxygen atom reacts exclusively with the alkynyl group. At 0.4 kPa in a flow reactor, they found that the reaction of an oxygen atom with phenylacetylene gave only products characteristic of attack on the terminal alkynyl carbon atom. Since it is well-known that O(^{3}P) and OH react rapidly with alkenes,[2-5] alkynes,[4,6] and arenes,[7-10] the present investigation was undertaken to verify the O(^{3}P) + phenylacetylene results under single-collision conditions. The reactions of O(^{3}P) with styrene and OH with phenylacetylene and styrene were also studied to find out if a similar degree of selectivity was exhibited in these reactions.

One possible reason for the apparent selectivity observed by Blumenberg et al. is that C_2H may deactivate the ring for electrophilic radical addition. Another possibility is that the reaction of O(^{3}P) with the triple bond of phenylacetylene, a spin-allowed reaction, may be favored over reaction with the ring because of the spin-forbidden nature of the O(^{3}P) + arene reaction.[11] In the work reported here, deactivation of the aryl ring by unsaturated substituents might affect the selectivity of both the O(^{3}P) and OH reactions, whereas competition between spin-forbidden and spin-allowed paths would occur only for the oxygen atom reactions. It should be possible to distinguish between the two possibilities by identifying the products of these reactions. We expect that other information concerning the detailed mechanism of these reactions might also be obtained from this investigation.

Experimental Section

The apparatus used in this work has been described previously.[11] The two reactants collide in one chamber of a two-chamber vacuum system, and products are collimated before they enter the second
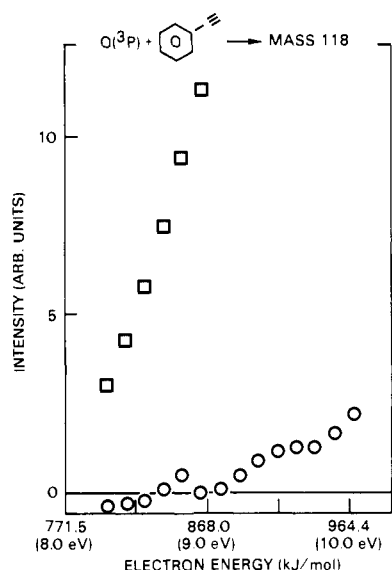
Figure 1. Ionization efficiency measurement for the product at m/e 118 from $O(^3P)$ + phenylacetylene. The squares show the uncorrected measurements and the circles show the measurement after correction for the finite energy spread in the energy of the ionizing electrons.

Figure 2. Ionization efficiency measurement for the product at m/e 90 from $O(^3P)$ + phenylacetylene: □, uncorrected measurements; O, corrected measurements.

chamber where they are detected with a quadrupole mass spectrometer. The mass spectrometer is fixed at an angle of 0° with respect to the oxygen atom beam. Experiments were performed with beam intersection angles of 60 and 90°. Oxygen atoms were produced as before[11] by flowing a mixture of oxygen and helium through a microwave discharge. Hydroxyl radicals were produced by the reaction of H atoms with NO_2 in the flow tube source.[12]

Before entering the ionizer, the products were modulated by a mechanical chopper located in the mass spectrometer chamber. Synchronous ion counting was used in conjunction with a signal averager to rectify the signal from the reaction products.[13]

Possible products were first identified by obtaining a product mass spectrum at a fixed electron energy and without modulation. That a reactive collision product originated in the collision volume was verified by synchronous ion counting and by alternately uncrossing and crossing the two reactant beams. The ionization efficiencies of products which yielded sufficient signal were then measured. These and other tests[11] eliminated spurious signals due to impurities in either reactant beam and reactions on the walls of the chamber and in the ionizer.

To check the accuracy of product ionization potential measurements, the ionization efficiencies of helium, argon, benzene, styrene, and phenylacetylene were measured. The raw ionization efficiency data were first smoothed before the correction for the ionizing electron energy spread was made.[11,14] This method yielded ionization potentials within 10 kJ (0.1 eV) of the accepted values[15] for all the above atoms and molecules.

The average relative kinetic energy of collision for all these reactions, assuming effusive flow at 300 K, was 3.2 kJ/mol. Although the reactant flows were not strictly effusive ($\lambda/d \simeq 3$), the deviation from effusive flow and hence from Maxwell–Boltzmann velocity distributions has a small and unimportant effect on the calculated relative kinetic energy.

The diffuse, uncollimated nature of the reactant gases ensures that collisions with a wide variety of intersection angles and velocities take place. Collision complexes have been detected with this apparatus[11,12] which are constrained to appear at the center of mass velocity vector (for example, 70° for OH + trimethylbenzene intersecting at 90°). The detectability of predominantly backward scattered products has been discussed previously.[11]

Results

$O(^3P)$ + Phenylacetylene. Two products were observed for the reaction of oxygen atoms with phenylacetylene. The oxygen atom–phenylacetylene adduct was observed at m/e 118, and the hydrocarbon fragment due to CO emission was observed at m/e 90. The reaction path to produce HCO and C_7H_5, which
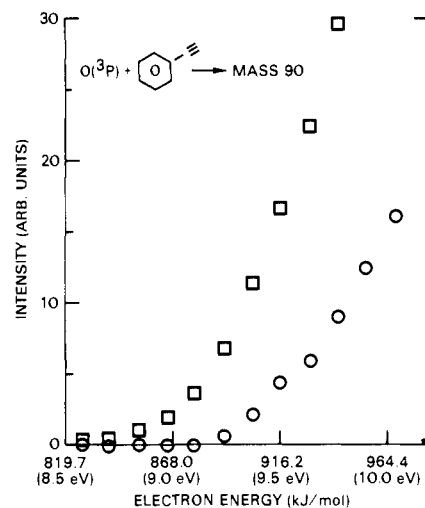
Blumenberg et al. found to make up 25% of the product,[1] was not observed. A signal at m/e 89 was detected, but the tests previously described showed that this signal was due to a process other than reaction in the collision region. A careful search was made for the HCO product at m/e 29 and for DCO from O + phenylacetylene-*d* at m/e 30. No signal was detected at either of these masses.

The ionization efficiency measurement for the product at m/e 118 is shown in Figure 1. This figure shows the measured intensity as a function of electron energy and the intensity which has been corrected for the spread in energy of the ionizing electrons. The ionization potential obtained is in the range 870–910 kJ (9–9.4 eV), somewhat higher than that expected for a phenol. The ionization potentials of ethynylphenol and other C_8H_6O isomers have not been measured, so it is not possible to verify the structure of the adduct.

The oxygen atom beam attenuation was about 10% during this measurement, so it is likely that at least some of the adducts are stable in the absence of potentially stabilizing collisions for the ~0.5-ms flight time from the collision volume to the mass spectrometer.

One ionization efficiency measurement for the m/e 90 product is shown in Figure 2. The measured ionization potential for this product (an average of several determinations) is approximately 880 kJ (9.1 eV), which is in reasonable agreement with the ionization potential of an open-chain C_7H_6 molecule having the structure $HC\equiv C-CH=CH-C\equiv CCH_3$. A similar compound with a hydrogen atom replacing the methyl group has an ionization potential of 878 kJ (9.10 eV) as determined by photoionization.[16] The extra methyl group may lower slightly the ionization potential, but nevertheless the agreement is reasonable. The ionization potential of the corresponding cyclic olefin is not known. The open-chain product is expected, however, if the reaction path yielding this product involves attack on the aromatic ring.[11] The ionization potential of phenylmethylene, which may be formed from attack on the triple bond, has not been measured. It could, of course, be within experimental error of the measured value obtained here. If it were larger than that, it would be hidden under the signal of the product with the lower ionization potential. As a result, the identity of the m/e 90 product cannot be unambiguously identified from these measurements.

The m/e 90 product could not be positively identified by its fragmentation pattern owing to the low signal level and interference from fragmentation of the adduct. An experiment

Table I. Observed Reaction Paths for O(^{3}P) + Phenylacetylene and Styrene[a]

O(^{3}P) + C$_6$H$_5$C≡CH	→	C_8H_6O
	→	CO + C_7H_6
O(^{3}P) + C$_6$H$_5$CH=CH$_2$	→	C_8H_8O
	→	CO + C_7H_8
	→	HCO + $C_6H_5CH_2$

[a] Italicized products were those actually observed

Figure 3. Corrected ionization efficiency measurement for the m/e 120 product from O(^{3}P) + styrene.

with carbon-13 labeled phenylacetylene may provide the best means to determine whether the carbon atom contained in the CO which accompanies the formation of this product was originally a member of the ring or a ring substituent.

O + Styrene. Products were observed at m/e 120, 92, and 91 for O(^{3}P) + styrene. The ionization efficiency measurement for the m/e 120 product is shown in Figure 3. The ionization potential of ~935 kJ/mol (9.7 eV) obtained from this measurement seems rather high for a phenol, but again the effect on the ionization potential of the vinyl group attached to the ring is unknown. This product might be phenylacetaldehyde, a product which could result from O addition to the terminal vinyl carbon atom. Although the ionization potential of phenylacetaldehyde is not known, aldehydes have ionization potentials in the range 915-970 kJ (9.5-10 eV).[15]

The product at m/e 92 is probably the result of CO leaving the adduct. Its ionization efficiency measurement is shown in Figure 4.[25] The ionization potential obtained from this measurement is ~790 kJ (8.2 eV). If the carbon atom is removed from the ring in a manner typical to the O atom reaction with benzene, the expected product would be H$_3$C—CH=CHC≡CCH=CH$_2$ or a similar open-chain isomer. The ionization potential of H$_2$C=CHC≡CCH=CH$_2$ is 820 kJ,[16] and, since addition of the methyl group might change the ionization potential by 10 or 20 kJ, the measured value is in reasonable agreement. Another C$_7$H$_8$ compound, methylfulvene, has an ionization potential of 801.8 kJ.[17] As a result, no firm conclusion can be made about the precise structure of this product. At least some of the product results from ring attack, because CO emission from the vinyl group would probably yield toluene, whose ionization potential is 849 kJ.[15]
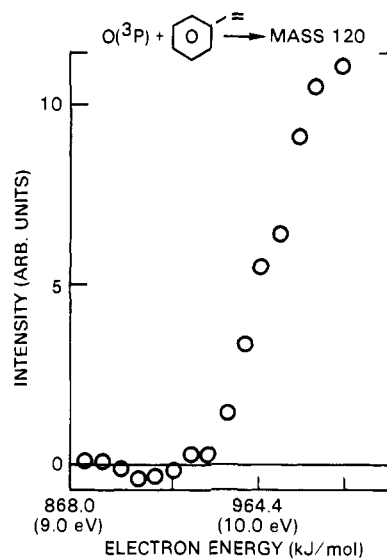
A summary of the observed reaction paths for O + phenylacetylene and styrene is given in Table I.

OH + Phenylacetylene. Products were observed for the OH + phenylacetylene reaction at m/e 119 and 119, Mass 119 is the OH–phenylacetylene adduct which is sufficiently long lived to reach the detector. Its measured ionization potential (see Figure 6[25]) is about 780 kJ. This value agrees well with the ionization potentials of OH–aromatic adducts previously observed in this laboratory.[12]

The product at m/e 118 is due to a hydrogen atom displacement reaction. Experiments carried out with OD showed that, as in the case of OH + aromatic hydrocarbons,[12] the hydroxyl group remains intact in the reaction product. Product analysis for OH + phenylacetylene-d_1 showed that both the deuterium atom and the ring hydrogen atoms were displaced. The ratio of signals at m/e 119 and 118 for OH + phenylacetylene-d_1 ranged from 2.5 at an ionizing energy of 820 kJ to 3.0 at 945 kJ. These results are only qualitative because absolute detection efficiencies cannot be measured in these experiments.

OH + Styrene. Products were observed for this reaction at m/e 121, 120, 94, 93, and 91. The measured ionization potential of the m/e 121 product is ~770 kJ (see Figure 7[25]). This value is also in agreement with previously measured OH–aromatic adducts.[12]

The H atom displacement product signal at m/e 120 was very small, too small to obtain an ionization efficiency measurement.

Table II. Observed Reaction Paths for OH + Phenylacetylene and Styrene

OH(^{2}Π) + C$_6$H$_5$C$_2$H	→	C_8H_7O
	→	H + $C_6H_5C_2OH$
	→	H + $C_6H_4(OH)C_2H$
OH(^{2}Π) + C$_6$H$_5$C$_2$H$_3$	→	C_8H_9O
	→	C$_2$H$_3$ + C_6H_5OH
	→	C$_2$H$_4$ + C_6H_5O
	→	H_2CO + $C_6H_5CH_2$

The product at m/e 94 is probably phenol, which results from displacement of the ethenyl radical from the ring. In contrast to phenylacetylene, this side-chain displacement is exothermic by ~10.5 kJ/mol. The measured ionization potential of 790 kJ (Figure 8[25]) agrees well with values for phenol previously measured elsewhere and in this laboratory.[11,12]

The product at m/e 93 is somewhat of a mystery. Its ionization potential (~840 kJ/mol, Figure 9[25]) is very close to that of the phenoxy radical (853 kJ[15]). The product with OD has a mass of 94, so the deuterium seems to be transferred exclusively to the more massive fragment. This may mean that the corresponding m/e 28 product is CO, but then the m/e 93 product must be an unsaturated hydrocarbon radical. These radicals typically have ionization potentials which are less than 770 kJ if they have an open-chain structure. Other possibilities are vinyl cyclopentenyl and cycloheptadienyl radicals; neither ionization potential has been measured.

The m/e 91 product has an ionization potential of 752 kJ (see Figure 10[25]), and is most likely the benzyl radical. This reaction is characteristic of OH attack on the vinyl group rather than attack on the ring.

Table II gives a summary of the observed reaction paths for OH + phenylacetylene and styrene. The results show that paths characteristic of reaction with both the ring and the side chain have been observed.
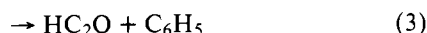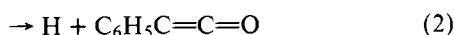
Discussion

The factors which affect reactivity at different positions of the same molecule can be determined most reliably by calculating the potential energy surface of the reactions in question. Accurate calculations for large reacting systems such as these would be prohibitively expensive, so a simpler approximate index of reactivity would be useful. One such index, developed by Fukui and co-workers, is based on frontier electron densi-

Table III. Frontier Electron Densities for Electrophilic Free Radical Attack on Phenylacetylene and Styrene

$C_6H_5C\equiv CH$ 2 1 position	$C^2_{m,r} +$ $C^2_{m+1,r}$(phenylacetylene)	$C_6H_5CH=CH_2$ 2 1 $C^2_{m,r} +$ $C^2_{m+1,r}$(styrene)
1	0.34	0.50
2	0.14	0.23
substituent ring carbon	0.51	0.41
ortho	0.20	0.18
meta	0.10	0.09
para	0.53	0.44

ty.[22,23] According to this index, the relative reactivity of different positions to free-radical electrophilic attack is determined by $C^2_{m,r} + C^2_{m+1,r}$, where $C_{m,r}$ is the coefficient for the highest occupied π molecular orbital at position r and $C_{m+1,r}$ is the coefficient for the lowest unoccupied π orbital at position r. The value of $C^2_{m,r} + C^2_{m+1,r}$, the frontier electron density, has been calculated for phenylacetylene and styrene using the ab initio SCF–MO calculation program GAUSSIAN 70.[24] The results are shown in Table III. Both molecular orbitals consist exclusively of out of plane 2p orbitals on the carbon atoms. The most reactive positions of phenylacetylene are the terminal alkynyl carbon, the ring carbon atom attached to the acetylene chain, and the ring carbon atom in the para position. These same carbon atoms are also predicted to be the most reactive positions for styrene. How the results correlate with these calculations will now be discussed.

O + Phenylacetylene. The products to be expected for this reaction based on other studies of the reaction of oxygen atoms with hydrocarbons containing carbon–carbon triple bonds[1,19] are the following:
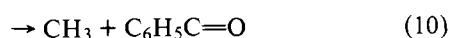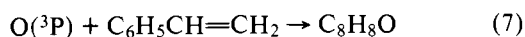
$$O + C_6H_5C\equiv CH \rightarrow CO + C_6H_5CH \quad (1)$$

$$\rightarrow H + C_6H_5C=C=O \quad (2)$$

$$\rightarrow HC_2O + C_6H_5 \quad (3)$$

$$\rightarrow HCO + C_7H_5 \quad (4)$$

Addition to the aromatic ring and addition followed by decomposition should give the following products:

$$\rightarrow C_8H_6O \quad (5)$$

$$\rightarrow CO + HC\equiv CCH=CHC\equiv CCH_3 \quad (6)$$
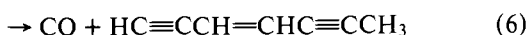
Only reactions 5 and either 1 or 6 (or both) were observed. The frontier electron density of phenylacetylene indicates that reactions 1, 2, and 4–6 are likely. Why reactions 2 and 4 are not observed is not understood at this time. Since the $C_6H_5C=C=O$ product of reaction 2 should appear near the center of mass velocity vector, it should have been detected if it were an important reaction path. Reaction 4 may be endothermic.
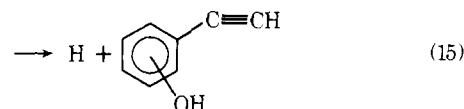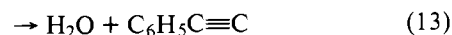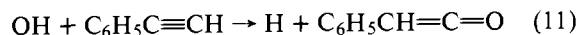
O + Styrene. The reactions expected for O + styrene, based on previous single-collision work with alkenes[1,18] and aromatics,[11] are the following:

$$O(^3P) + C_6H_5CH=CH_2 \rightarrow C_8H_8O \quad (7)$$

$$\rightarrow CO + H_2C=CHC\equiv CCH=CHCH_3 \quad (8)$$

$$\rightarrow C_6H_5CH_2 + HCO \quad (9)$$

$$\rightarrow CH_3 + C_6H_5C=O \quad (10)$$

The absence of reaction 10 indicates that the terminal vinyl carbon atom is the favored position of attack, assuming that the oxygen atom does not migrate once it attaches to a carbon atom.

Since reactions 7 and 8 are likely to be spin forbidden and reaction 9 is spin allowed, it appears that there is no large discrimination between spin-forbidden and spin-allowed paths for the reaction of $O(^3P)$ with styrene. Since branching ratios cannot be determined from these measurements, it is not possible to obtain a quantitative comparison between the two types of reaction paths.

OH + Phenylacetylene. The reaction paths expected for this reaction are the following:
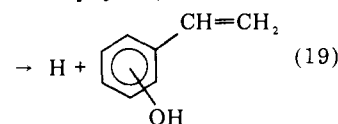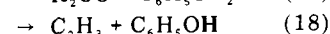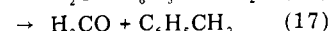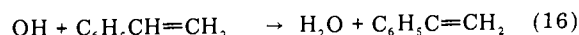
$$OH + C_6H_5C\equiv CH \rightarrow H + C_6H_5CH=C=O \quad (11)$$

$$\rightarrow H_2C=C=O + C_6H_5 \quad (12)$$

$$\rightarrow H_2O + C_6H_5C\equiv C \quad (13)$$

$$\rightarrow C_8H_7O \quad (14)$$

$$\longrightarrow H + \text{(ring with } C\equiv CH \text{ and OH substituents)} \quad (15)$$

Reactions 11–13 are expected based on reactions of OH with substituted acetylenes.[20] Reactions 14 and 15 are expected based on reaction with the aromatic ring.

The absence of reaction 12 probably means that the OH attacks the terminal acetylene carbon much more readily than the carbon atom attached to the ring. This is consistent with the frontier electron density of phenylacetylene (see Table III).

The results obtained here for OH + phenylacetylene show that OH attacks the terminal alkynyl carbon atom, and also attacks the ring in an undetermined location. Attack at the C_2H-substituted ring carbon atom cannot be verified because the exact structure of the OH–phenylacetylene adduct is unknown.

**OH + Styrene.** The reaction paths expected for OH + styrene are the following:

$$OH + C_6H_5CH=CH_2 \quad \rightarrow H_2O + C_6H_5C=CH_2 \quad (16)$$

$$\rightarrow H_2CO + C_6H_5CH_2 \quad (17)$$

$$\rightarrow C_2H_3 + C_6H_5OH \quad (18)$$

$$\rightarrow H + \text{(ring with } CH=CH_2 \text{ and OH substituents)} \quad (19)$$

$$\rightarrow C_8H_9O \quad (20)$$

Reaction 17 is expected based on the reaction of OH with propylene, and reactions 18–20 are expected based on reaction with the aryl ring. As Table II shows, (17)–(20) are observed.

Reaction 18 could conceivably proceed in two ways. The hydroxyl radical could attach to the vinyl-substituted ring carbon atom and displace C_2H_3. The OH could also attach to another ring position (the para position is probably favored), and this complex may decompose by C_2H_3 leaving. A hydrogen-atom migration would then yield phenol.

An unexpected path observed for this reaction is

$$OH + C_6H_5CH=CH_2 \rightarrow C_6H_5O + C_2H_4 \text{ (or } CO + C_7H_9) \quad (21)$$
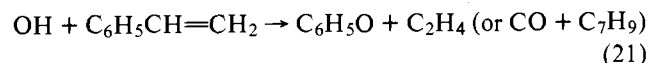
Previous arguments demonstrate that CO and C_7H_9 are probably not the products. It is difficult, however, to explain the observation that the hydroxyl hydrogen atom remains exclusively with the heavier product.

The reactivities, based on the frontier electron density for styrene, are consistent with the observed products of the reactions of OH with styrene. The hydroxyl radical attacks the terminal vinyl carbon (reaction 17), the vinyl-substituted ring

carbon atom (reactions 21 and perhaps 18), and an undetermined H-substituted ring location (reactions 19, 20, and perhaps also 18).

Conclusions

The reactions of $O(^3P)$ with styrene and of OH with phenylacetylene and styrene show no strong preference for reaction either with the aryl ring or with the unsaturated side chain under the conditions reported here. Qualitative arguments based on frontier electron theory support this lack of preference. We are unable to say conclusively whether the same lack of preference is exhibited in the reaction of $O(^3P)$ with phenylacetylene. Our results for this reaction, however, are consistent with the trends observed in the other three reactions.

Supplementary Material Available: Figures 4-10: ionization efficiency measurements of m/e 91 and 92 from $O(^3P)$ + styrene, m/e 119 from OH + phenylacetylene, and m/e 121, 94, 93, and 91 from OH + styrene (7 pages). Ordering information is given on any current masthead page.

References and Notes

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Consideration of the Mechanism of the Transition Metal Catalyzed Olefin Metathesis Reaction. Metathesis of *cis,cis*-2,8-Decadiene

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Abstract: The analysis of the scrambling pattern of the acyclic olefins resulting from the metathesis of 1,7-diene systems allows a distinction to be made between two general classes of mechanisms of this reaction. This analysis requires no scrambling of the labels in the starting materials or products. These experimental restrictions are firmly established by examining the metathesis of a mixture of *cis,cis*-2,8-decadiene and *cis,cis*-2,8-decadiene-*1,1,1,10,10,10-d₆*. The 2-butene produced in this reaction has a cis/trans ratio of 5 at low conversion. The cis/trans ratio approaches an equilibrium value as the conversion of the diene approaches completion. Extrapolation of a plot of *cis-/trans-*2-butene vs. label ratio to zero stereoisomeric scrambling (trans/cis = 0) gives values of the isotopic label ratio resulting from zero scrambling. The extrapolated value is that expected for a one-carbon chain (carbene) mechanism. These studies allow distinctions between the mechanisms to be made at high (20–30%) conversions.

Introduction

The mechanism of the olefin metathesis reaction has provided one of the most challenging problems in organometallic chemistry.[1] Only within the past 2 years have systems been designed which begin to reveal the important mechanistic features of this reaction.[2-4] Several of these studies have been carried out to determine if the reaction proceeds by a "pairwise" interchange of carbons between two olefins or through

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a one-carbon chain reaction described as a carbene mechanism. The critical steps of these mechanisms are outlined below.

Of the various studies, only those using terminally labeled 1,7-dienes serve to distinguish between the two mechanisms.[1a,2,4] Owing to the simplicity of the system, all of the various scrambling schemes can be analyzed in an exact fashion. For example, it was shown that metathesis of an equal mixture of 1,7-octadiene-*1,1,8,8-d₄* and 1,7-octadiene-*d₀* should produce the completely randomized ethylene-*d₄:-d₂:-d₀* equilibrium mixture of a 1:2:1 ratio if the one-carbon interchange is operative. Alternatively, if the reaction proceeds by a "pairwise" interchange an ethylene-*d₄:-d₂:-d₀* ratio of 1: ≤