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Photochemical Reactions of Oxygen Atoms with Toluene, *m*-Xylene, *p*-Xylene, and Mesitylene: An Infrared Matrix Isolation Investigation

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The photolysis of toluene/ozone, *m*-xylene/ozone, *p*-xylene/ozone, and mesitylene/ozone mixtures in argon matrices at 12 K with UV light of $\lambda \geq 280$ nm leads to products with ketene functionalities. The identification of the molecular structures of these products is based on deuterium isotopic shifts and agreement with density functional calculations. Other products from the toluene/O atom reaction include methylphenol and benzyl alcohol; phenols are also formed from the reaction of xylenes with O atoms and from the reaction of mesitylene with O atoms.

Introduction

The gas-phase reactions of methyl-substituted benzenes with oxygen atoms have been the subject of several studies.[1−7] As a result, many data are available for these reactions including specific rate constants, activation energies, product identifications and distributions, as well as mechanistic information. Cvetanovic[1] studied the reactions of toluene with oxygen atoms, prepared from mercury-photosensitized decomposition of nitrous oxide, at room temperature and found *o*-cresol, *p*-cresol, carbon monoxide, water, and a polymeric material (major product) of unknown composition as products. Sloane[3] studied the reactions of toluene and mesitylene with oxygen atoms under single collision conditions in crossed molecular beams where the average collision energy was 2.6 kJ/mol; benzaldehyde and 3,5-dimethylbenzaldehyde were found as products. Mulder and coworkers[7] studied the reactions of toluene with oxygen atoms, using microwave discharge of nitrous oxide as the source of oxygen atoms, in a flow reactor at ambient temperature in a helium atmosphere. They found hydroxytoluenes, phenol, and benzaldehyde as products. There has been one report of the photochemical reactions of benzene and methylbenzenes in solid oxygen matrices.[8] Products of these reactions include 2,4-hexadiendials and methylated 2,4-hexadiendials. In view of the contrasting gas-phase results, we have undertaken a matrix isolation study of the reaction of oxygen atoms with methylbenzenes in order to better understand the mechanism of electrophilic oxygen atom additions with aromatic systems and the directing effects which methyl groups have on these reactions.

We have recently reported a novel photochemical reaction[9] between benzene and O(^{3}P) atoms in a solid argon matrix at 12 K. It was shown that oxygen atom addition to benzene leads to the formation of 2,4-cyclohexadienone which subsequently photolyzes at $\lambda \geq 360$ or 280 nm to yield butadienylketene (1,3,5-hexatrien-1-one). In the present study, we report the results of photochemical reactions of oxygen atoms with the following methylated benzenes: toluene, *m*-xylene, *p*-xylene, and mesitylene. In each case, ketenes are products of reaction. Each reaction was studied using ^{16}O and ^{18}O isotopes of oxygen, as well as standard and deuterated isotopomers of each hydrocarbon. The shifts in the infrared spectra, due to isotopic substitution, allow the assignment of molecular structure and assessment of directing effects that the methyl group has on the oxygen atom reaction with methylbenzenes in the formation of the ketene products. We have performed density functional calculations on ketene products at the B3LYP/6-311G(d,p) level of theory in order to aid in the assignment of the infrared bands. The focus of this paper will be on the ketene products; products containing the O−H functional group will also be discussed.

Experimental

Normal toluene (99.5+%, Aldrich) was distilled over sodium prior to use. Toluene, toluene-α,α,α-d_3 (99.8 atom % D, C/D/N isotopes), toluene-2,3,4,5,6-d_5 (99.7 atom % D, C/D/N isotopes), toluene-d_8 (99.7 atom % D, C/D/N isotopes), *m*-xylene-H_{10} (99+%, Aldrich), *m*-xylene-d_{10} (98.5 atom % D, C/D/N isotopes), *p*-xylene-H_{10} (99+%, Aldrich), *p*-xylene-d_{10} (99+ atom % D, Aldrich), mesitylene-H_{12} (98%, Aldrich), and mesitylene-d_{12} (98 atom % D, Aldrich) were freed of relatively volatile impurities by three consecutive freeze−pump−thaw cycles at liquid nitrogen temperature. The substrate vapors were warmed to room temperature and expanded into an evacuated sample chamber and diluted with argon (99.995%, Air Products) to an Ar:substrate mole ratio of 100:1. Standard ozone ^{16}O−^{16}O−^{16}O, and the ^{18}O−^{18}O−^{18}O isotopomer of ozone, were made by passing an electric discharge, from a Tesla coil, through a sample of oxygen gas (99.996%, Air Products; ^{18}O isotope from Euriso-top, 98.01% enrichment) contained in a glass U tube which was submerged in liquid nitrogen. In this way the ozone condensed to the solid phase on the walls of the glass tube as it formed. The solid ozone was freed of residual oxygen molecules by pumping at 77 K. The purified ozone was then warmed to room temperature, expanded into a separate evacuated sample chamber, and diluted with argon to an Ar:O_3 mole ratio of 100:1.

The IR spectrometer and accompanying vacuum chamber have been described in detail elsewhere.[10] The samples were codeposited on a gold-mirrored matrix support at a combined rate of 8.4 mmol/h for a total of 24.2 mmol. The matrix support was held at 12 K with a closed-cycle, single-stage helium refrigerator (APD Cryogenics, model DE-202). The temperature was measured at the cold plate with a gold/chromel thermo-

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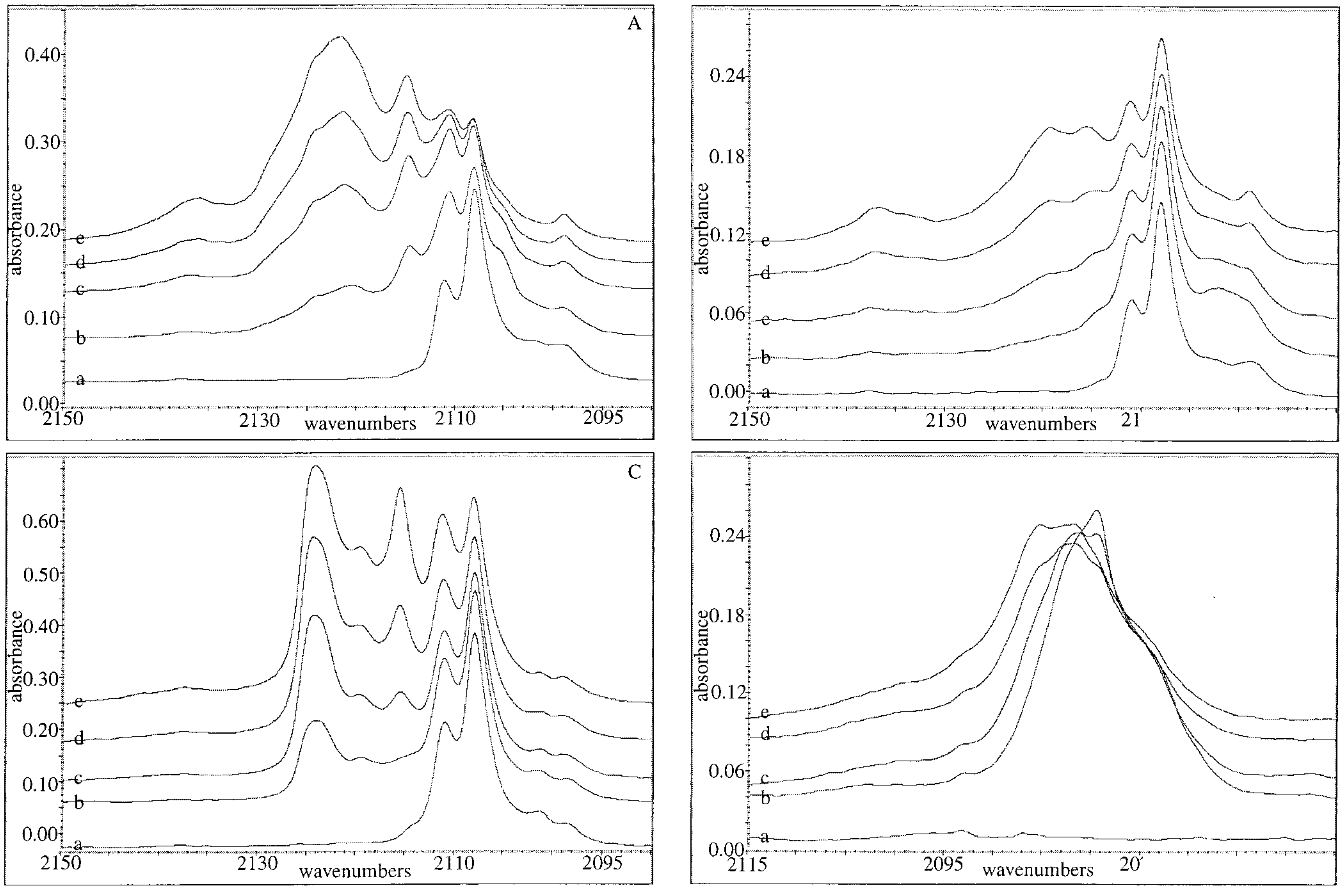


Figure 1. Photolysis-time dependence of infrared, ketene-product absorption bands. (A) toluene-H_8, ^{16}O; (B) *m*-xylene-H_{10}, ^{16}O; (C) *p*-xylene-H_{10}, ^{16}O; (D) mesitylene-H_{12}, ^{18}O. (a) Spectra before photolysis, (b) 10 min photolysis, (c) 30 min, (d) 60 min, (e) 120 min. ^{18}O isotopomer is shown in D as this product band is obscured by ozone absorption when the ^{16}O isotope is used.

couple. All infrared spectra were recorded using a Nicolet 740 FTIR spectrometer at 1 cm^{-1} resolution; data spacing was set to 0.12 cm^{-1} intervals. After recording the initial spectra, the samples were subjected to the photolyzing radiation of a 200 W Hg−Xe arc lamp (lamp model UXL 200H Hg Xe by Ushio and model A 1010 lamp housing by Photon Technology International). The radiation was filtered through a 51 mm water cell and a 280 nm Hoya cut-off filter before coming in contact with the matrix sample. The temperature of the matrix sample did not rise above 14 K during any photolysis interval. All matrix spectra were successively photolyzed at precise time intervals.

The ab initio calculations were performed using the Gaussian 94 suite of programs[11] running on either a Cray C98/8512 or a Silicon Graphic Power Challenge computer. The density functional[12,13] of Becke, Lee, Yang, and Parr, known as B3LYP was used to treat electron correlation using the 6-311G(d,p) basis set.[14−17] Analytic gradients were used in the geometry optimizations with all electrons correlated. All stationary points were verified to be true minima by calculation of normal vibrational modes using the analytic second derivative method in the harmonic approximation. Calculated vibrational modes were scaled[18,19] by the factor 0.96325. Zero-point energies were added to the electronic potential energies of each species in order to obtain relative energies at 0 K.

Results

The photostability of all methylbenzenes used in this study was tested by irradiation of 100/1 Ar:substrate matrices using a 280 nm cutoff filter; no new bands were detected in any case.

Upon irradiation of 200/1/1 Ar:O_3:methylbenzene matrices with photons of $\lambda \leq 280$ nm, strong product absorption bands appeared near 2100 cm^{-1}, indicating the formation of products with the ketene functional group. Figure 1, parts A−D, shows the photolysis-time dependence of these infrared absorption bands from the reaction of $O(^3P)$ atoms with toluene, *m*-xylene, *p*-xylene, and mesitylene. Product band intensities increase with increasing photolysis time, with the exception of the ketene product resulting from the mesitylene/O atom reaction. The ketene-product band from mesitylene is shown in Figure 1D with the ^{18}O isotope of oxygen, as this band was obscured by ozone absorption near 2110 cm^{-1}. This band is also different from the others in that there is a noticeable shift to higher frequency on going from 10 min photolysis to 120 min photolysis. This observation suggests that the product is formed in two types of matrix sites with the one at higher frequency dominating at longer photolysis times.

Tables 1, 3, and 5 summarize the observed frequencies of ketene product band absorptions from the reactions of isotopomers of methylbenzenes with oxygen atoms. Table 7 summarizes the observed frequencies of O−H and O−D product band absorptions. Tables 2, 4, and 6 summarize the B3LYP/6-311G(d,p) calculated asymmetric stretching frequencies of all possible ketene products from these reactions. Where conformational isomerism is possible, calculations were performed only on those species which would be expected to be most stable; i.e., trans isomers were favored over cis isomers. The rationale for excluding 116 of 128 possible conformational isomers is twofold: (1) the benefits of having all computational data seem small in comparison with the computational cost, and

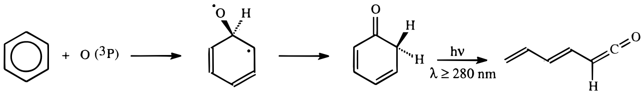
TABLE 1: Observed Ketene Product Absorptions from Reaction of O Atoms with Isotopomers of Toluene

reaction	ketene bands (cm^{-1})	$\Delta\nu_{16}$ (cm^{-1})	reaction	ketene bands (cm^{-1})
^{16}O + toluene-H_8				2095.9
	2121.9	NA	^{18}O + toluene-H_8	2093.7
	2115.1	NA		2087.7
				2085.6
				2083.3
^{16}O + toluene-α,α,α-d_3				2092.9
	2121.5	−0.4	^{18}O + toluene-α,α,α-d_3	2088.3
	2115.6	+0.5		2086.0
d_3			d_3	2083.3
^{16}O + toluene-2,3,4,5,6-d_5				2095.2
	2118.4	−3.5	^{18}O + toluene-2,3,4,5,6-d_5	2091.1
	2116.1	+1.0		2089.1
				2083.8
				2079.8
^{16}O + toluene-d_8				2091.1
	2119.4	−2.5	^{18}O + toluene-d_8	2089.2
	2117.0	+1.9		2083.5
				2079.8

more importantly, (2) conjugated pi systems with multiple possible stable conformations photoisomerize when subjected to ultraviolet radiation. Therefore, while the most stable conformation of a molecule may not be formed as an initial product, the initial ketene products are expected to photoisomerize under the experimental conditions. The computational data is used as an aid in assigning the molecular structure of the ketene products. The directing effect that methyl groups have on the electrophilic aromatic substitution reactions of oxygen atoms with the methyl-substituted benzenes toluene, *m*-xylene, *p*-xylene, and mesitylene is determined from a knowledge of the structure of the resulting ketene products.

Discussion

In our previous report[9] of the oxygen atom−benzene reaction, it was shown that the following mechanism accounts for the observation of the product butadienylketene.

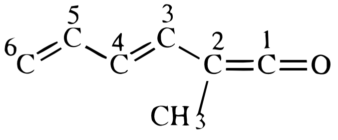


The initial step of the reaction is electrophilic aromatic addition of the oxygen atom to the benzene ring, followed by a 1,2 hydrogen shift resulting in 2,4-cyclohexadienone, the keto tautomer of phenol. This keto product is photolyzed to butadienylketene by near-ultraviolet light. Since the reaction is electrophilic in nature, it will be influenced by directing effects of substituents on the ring.

We have found that the reaction of toluene with oxygen atoms in solid argon matrices leads to the formation of ketene products, as documented in Figure 1 and Table 1. For a given infrared mode, the square of the frequency ratio gives the reduced mass ratio in the diatomic approximation for isotopic substitution. The product band at 2121.9 cm^{-1} shifts to 2093.7 cm^{-1} upon substitution with ^{18}O, yielding a reduced mass ratio of 1.027. The product band at 2115.1 cm^{-1} shifts to 2087.7 cm^{-1} upon substitution with ^{18}O, yielding a reduced mass ratio of 1.026. The asymmetric stretch of a ketene group can be modeled as a vibration of the central carbon atom against stationary oxygen and carbon atoms on either side; therefore $\mu_{18}/\mu_{16} = 1.020$. Since there is reasonable agreement of the experimental reduced mass ratios with that calculated using the diatomic approximation, it is concluded that the measured shifts, and therefore the products, are consistent with the ketene group.

Assuming that the photomechanism for the formation of a ketene from reaction of toluene with O atoms is analogous to benzene, then there is the possibility of forming five distinct molecular products. If the oxygen atom adds ortho to the methyl group then the possible ketene products, which are consistent with the above mechanism, are 2-methyl-1,3,5-hexatrien-1-one (2-MHO) and 6-methyl-1,3,5-hexatrien-1-one (6-MHO), depending on whether the migrating hydrogen atom moves to the methyl site or to the adjacent, non-methylated site. (6-MHO is actually 1,3,5-heptatrien-1-one, but we will refer to it as 6-MHO in the interest of maintaining consistency in nomenclature.) Addition of the oxygen atom to the meta site of toluene can yield 5-methyl-1,3,5-hexatrien-1-one (5-MHO) and 3-methyl-1,3,5-hexatrien-1-one (3-MHO); addition to the para site can result in only 4-methyl-1,3,5-hexatrien-1-one (4-MHO).

In order to determine which products are formed, it is necessary to make an initial examination of Table 2. First, a brief explanation of nomenclature. Shown below is the structure and numbering scheme of *s-trans*, *s-trans*-(*E*)-2-methyl-1,3,5-hexatrien-1-one. The hydrogens along the backbone have been omitted for clarity. The symbol (*E*) refers to the conformation of the doubly substituted carbon−carbon double bond between carbons 3 and 4. If the molecule were the 6-methyl isomer, then there would be need for two letters of *E*/*Z* designation. The first would correspond to the same double bond and the second to the bond between carbons 5 and 6. The *s-trans*, *s-trans* designation indicates that the orientation of the two single bonds in the molecule are each trans. The first trans is meant to refer to the single bond closest to the ketene functionality, or the C2−C3 bond; the remainder refers to the C4−C5 single bond.



2-MHO

Now an examination of Table 2 to determine what trends are evident in the calculated properties of methylhexatrienones. As the methyl group is moved from the 2 position to the 5 position of 1,3,5-hexatrien-1-one, the general trend is for the ketene frequency to increase. This increase is most apparent on going from 2- to 3-MHO, and from 3- to 4-MHO. Also, when hydrogen is substituted by deuterium, there is a tendency for the asymmetric ketene mode to couple with a C−D stretching

TABLE 2: B3LYP/6-311G(d,p) C_7H_8O Ketene Asym. Frequencies

C_7H_8O ketene	^{16}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})	^{18}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})
s-trans, *s-trans*-(*E*)-2-methyl-1,3,5-hexatrien-1-one, H_8 isotopomer	2115.1	N/A	2086.8	NA
d_3 isotopomer	2117.0 [89.2]	+1.9	2080.4 [66.6]	−6.4
	2088.5 [10.8]	−26.6	2096.8 [33.4]	+10.0
d_5 isotopomer	2114.9	−0.2	2086.6	−0.2
d_8 isotopomer	2116.8 [89.1]	+1.7	2080.3 [67.0]	−6.5
	2088.5 [10.9]	−26.6	2096.7 [33.0]	+9.9
s-trans, *s-trans*-(*E*)-3-methyl-1,3,5-hexatrien-1-one, H_8 isotopomer	2122.4	N/A	2094.0	NA
			2095.1 [75.9]	+1.1
d_3 isotopomer	2122.5	+0.1	2091.4 [24.1]	−2.6
d_5 isotopomer	2117.4	−5.0	2089.2	−4.8
d_8 isotopomer	2117.4	−5.0	2088.6 [81.8]	−5.4
			2093.0 [18.2]	−1.0
s-trans, *s-trans*-(*E*)-4-methyl-1,3,5-hexatrien-1-one, H_8 isotopomer	2126.9	N/A	2098.2	NA
d_3 isotopomer	2127.0 [98.2]	+0.1	2098.8 [83.8]	+0.6
	2093.5 [1.8]	−33.4	2093.0 [16.2]	−5.2
d_5 isotopomer	2122.6	−4.3	2094.1	−4.1
d_8 isotopomer	2122.7 [98.0]	−4.2	2095.6 [49.4]	−2.6
	2093.5 [2.0]	−33.4	2092.1 [50.6]	−6.1
s-trans, *s-trans*-(*E*)-5-methyl-1,3,5-hexatrien-1-one, H_8 isotopomer	2127.7	N/A	2099.1	NA
d_3 isotopomer	2127.7	0.0	2099.3 [98.3]	+0.2
			2091.5 [1.7]	−7.6
d_5 isotopomer	2122.1	−5.6	2094.0	−5.1
d_8 isotopomer	2122.2	−5.5	2094.4 [88.7]	−4.7
			2091.2 [88.7]	−7.9
s-trans, *s-trans*-(*E*,*E*)-6-methyl-1,3,5-hexatrien-1-one, H_8 isotopomer	2126.3	N/A	2097.9	NA
d_3 isotopomer	2126.4 [97.3]	+0.1	2098.0 [95.1]	+0.1
	2080.3 [2.7]	−46.0	2080.2 [4.9]	−17.7
d_5 isotopomer	2120.8	−5.6	2092.7	−5.2
d_8 isotopomer	2120.9 [97.1]	−5.4	2093.0 [93.4]	−4.9
	2080.2 [2.9]	−46.1	2080.1 [6.6]	−17.8

vibration from the methyl group, so that the resulting asymmetric ketene mode appears higher in frequency, rather than lower, as one might expect. The extent of this mixing is reported in Table 2 by listing the intensity of all bands which are mixed with the ketene asymmetric stretch as a percentage of the total intensity of these bands.

Also reported in Tables 2, 4, and 6 are the frequency shifts on going from the perhydrogen isotopomer of a 1,3,5-hexatrien-1-one molecule to isotopomers which contain deuterium. These shifts are labeled $\Delta\nu$, and are defined as the difference in frequency of a deuterium-containing isotopomer with respect to the perhydrogen isotopomer. When the ^{18}O isotopomer of oxygen is used the ketene bands shift to lower wavenumber and yield an exceedingly complex spectrum. No spectral assignments have been made on the basis of the calculated shifts when the ^{18}O isotope is used as these are generally more complex than the shifts due to the ^{16}O isotope. The ^{18}O spectra may be more complex than the ^{16}O spectra due to more efficient coupling of methyl C−D and ketene modes.

An examination of the data in Table 1 for the ^{16}O isotopomers reveals two noticeable trends: the observed ketene band at 2121.9 cm^{-1} moves toward lower frequency as deuterium is incorporated into the molecule, while the band at 2115.1 cm^{-1} moves toward higher frequency as the molecule becomes deuterated. This observation is supportive of the conclusion that these two bands are due to two unique molecular species, not to the same molecular species trapped in different lattice sites. Moreover, the molecule with the 2115.1 cm^{-1} absorption must have the methyl group closer to the ketene functional group than the molecule with the 2121.9 cm^{-1} absorption, for reasons discussed above. The 2115.1 cm^{-1} band has experimentally observed $\Delta\nu$ values of +0.5, +1.0, and +1.9 cm^{-1} for products containing the d_3, d_5, and d_8 isotopomers, respectively. The only ketene molecule of Table 2 with positive calculated values of $\Delta\nu$ (greater than +0.1 cm^{-1}) is *s-trans*, *s-trans*-(*E*)-2-methyl-1,3,5-hexatrien-1-one. Therefore, the 2115.1 cm^{-1} absorption is assigned to 2-MHO.

The remaining mode at 2121.9 cm^{-1} must be due to either the 3-, 4-, 5-, or 6-MHO molecule. The 3-, 5-, and 6-MHO molecules all have calculated $\Delta\nu$ values for the d_5 and d_8 isotopes greater than or equal in magnitude to 5.0 cm^{-1}. 4-MHO has $\Delta\nu$ near −4 cm^{-1}. Since, in the experiment, there is at most a $\Delta\nu$ of −3.5. cm^{-1}, this absorption most likely arises from *s-trans*, *s-trans*-(*E*)-4-methyl-1,3,5-hexatrien-1-one. In our previous report,[39] we found that the B3LYP/6-311G(d,p) level of theory is able to accurately distinguish between butadienylketene and 4-cyclo-penteneketene molecules from the $\Delta\nu$ values of their ketene asymmetric stretching modes, therefore we use this parameter when assigning structures to the various ketene product molecules.

Since 2-MHO and 4-MHO are products of this reaction, the methyl group is acting as an ortho/para director. The question then remains: if 2-MHO and 4-MHO are observed, why is not 6-MHO observed also? The answer to this question is that 6-MHO most likely is formed. In Figure 1A, there is a shoulder band at 2124.5 cm^{-1} on the main 2121.9 cm^{-1} absorption which we assign as 6-MHO since it has the highest observed frequency in this region.

There are four possible products from the reaction of O atoms with *m*-xylene (1,3-dimethylbenzene). If the oxygen atom adds at the 2 position, the resulting ketene product would be 2,6-dimethyl-1,3,5-hexatrien-1-one (2,6-DMHO). Addition at the 4 position will result in either 2,4-dimethyl-1,3,5-hexatrien-1-one (4,6-DMHO) or 4,6-dimethyl-1,3,5-hexatrien-1-one (2,4-DMHO). Addition at the 5 position will result in only 3,5-dimethyl-1,3,5-hexatrien-1-one (3,5-DMHO).

According to the data in Table 3, there are two main ketene absorptions at 2119.4 and 2116.0 cm^{-1} for products containing only standard isotopes. These bands shift to 2092.0 and 2086.9 cm^{-1}, respectively, upon substitution with ^{18}O. The correspond-

TABLE 3: Observed Ketene Product Absorptions from Reaction of O Atoms with Isotopomers of *m*- and *p*-Xylene

reaction	ketene bands (cm^{-1})	$\Delta\nu_{16}$ (cm^{-1})	reaction	ketene bands (cm^{-1})
^{16}O + *m*-xylene-H$_{10}$	2119.4	NA	^{18}O + *m*-xylene-H$_{10}$	2092.0
	2116.0	NA		2086.9
				2081.9
^{16}O + *m*-xylene-d$_{10}$	2120.9	+1.5	^{18}O + *m*-xylene-d$_{10}$	2086.6
	2113.4	−2.6		2081.7
	2104.9			
^{16}O + *p*-xylene-H$_{10}$	2124.5	NA		2096.7
	2119.7	NA	^{18}O + *p*-xylene-H$_{10}$	2092.1
	2115.8	NA		2087.6
				2084.5
				2082.3
^{16}O + *p*-xylene-d$_{10}$			^{18}O + *p*-xylene-d$_{10}$	2092.7
	2126.1	+1.6		2087.2
	2120.8	+5.0		2084.8
				2078.9

TABLE 4: B3LYP/6-311G(d,p) C$_8$H$_{10}$O Ketene Asym. Frequencies

C$_9$H$_{10}$O ketene	^{16}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})	^{18}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})
s-cis, *s-trans*-(*E*)-2,4-dimethyl-1,3,5-hexatrien-1-one, H$_{10}$ isotopomer	2106.4	N/A	2078.7	NA
d$_{10}$ isotopomer	2109.2 [79.9]	+2.8	2096.1 [61.7]	+17.4
	2093.0 [4.1]	−13.4	2090.7 [4.3]	+12.0
	2085.5 [16.0]	−20.9	2073.2 [34.0]	−5.5
s-trans, *s-trans*-(*E*)-2,5-dimethyl-1,3,5-hexatrien-1-one, H$_{10}$ isotopomer	2114.3	N/A	2086.2	NA
d$_{10}$ isotopomer	2116.8 [89.5]	+2.5	2095.8 [36.2]	+9.6
	2087.0 [10.5]	−27.3	2079.3 [63.8]	−6.9
s-trans, *s-trans*-(*E*,*E*)-2,6-dimethyl-1,3,5-hexatrien-1-one, H$_{10}$ isotopomer	2113.3	N/A	2085.3	NA
d$_{10}$ isotopomer	2115.2 [86.3]	+1.9	2095.2 [33.6]	+9.9
	2086.5 [10.2]	−26.8	2080.5 [8.5]	−4.8
	2079.7 [3.5]	−33.6	2077.7 [57.9]	−7.6
s-trans, *s-cis*-(*E*)-3,5-dimethyl-1,3,5-hexatrien-l-one, H$_{10}$ isotopomer	2122.2	N/A	2093.9	NA
d$_{10}$ isotopomer	2117.1	−5.1	2092.3 [27.0]	−1.6
			2088.7 [32.4]	−5.2
			2087.3 [40.6]	−6.6
s-trans, *s-trans*-(*E*,*E*)-3,6-dimethyl-1,3,5-hexatrien-1-one, H$_{10}$ isotopomer	2120.1	N/A	2091.9	NA
d$_{10}$ isotopomer	2115.2 [96.5]	−4.9	2091.7 [16.6]	−0.2
	2079.6 [3.5]	−40.5	2086.8 [72.2]	−5.1
			2079.3 [11.2]	−12.6
s-trans, *s-trans*-(*E*,*E*)-4,6-dimethyl-1,3,5-hexatrien-1-one, H$_{10}$ isotopomer	2124.7	N/A	2096.3	NA
d$_{10}$ isotopomer	2120.6 [95.1]	−4.1	2094.8 [28.3]	−1.5
	2093.3 [2.1]	−31.4	2091.0 [65.3]	−5.3
	2080.3 [2.8]	−44.4	2080.1 [6.4]	−16.2

ing reduced mass ratios are 1.026 for the 2119.4 cm^{-1}/2092.0 cm^{-1} pair and 1.028 for the 2116.0 cm^{-1}/2086.9 cm^{-1} pair. These reduced mass ratios are in good agreement with that for a ketene group calculated in the diatomic approximation; therefore, we conclude that these bands result from absorption of a ketene functional group.

These two distinct ketene bands have experimental $\Delta\nu$ values of +1.5 and −2.6 cm^{-1}, when the ^{16}O isotopomer is deuterated (Table 3). Also, there is a third band at 2104.9 cm^{-1} which appears on deuteration. This band was probably overlapping either the 2119.4 or 2116.0 cm^{-1} band when standard isotopes were used. Therefore, there are three ketene products formed in this reaction. Upon comparing the $\Delta\nu$ values with those computed for possible product structures in Table 4, we find that there is best agreement when the observed product bands are assigned as follows: the 2119.4 cm^{-1} band is due to 2,6-DMHO, and the 2116.0 cm^{-1} band is due to 4,6-DMHO. The band at 2104.9 cm^{-1} in Table 3 for the deuterated products is assigned to 2,4-DMHO based on its low frequency: the closer the methyl groups are to the ketene group, the lower the ketene asymmetric stretching frequency. The oxygen atom has added only at the 2 and 4 positions, and not the 5 position, of *m*-xylene: the methyl groups direct the oxygen atom to ortho and para positions.

In *p*-xylene (1,4-dimethylbenzene), because of symmetry, there is only one unique position available for substitution by the oxygen atom which leads to two possible products: 2,5-dimethyl-1,3,5-hexatrien-1-one (2,5-DMHO) and 3,6-dimethyl-1,3,5-hexatrien-1-one (3,6-DMHO). There are three observed ketene product bands in the ketene region at 2124.5, 2119.7, and 2115.8 cm^{-1} (Table 3). These bands are shown in Figure 1C. These bands shift to 2096.7, 2092.1, and 2087.6 cm^{-1}, yielding reduced mass ratios of 1.027, 1.027, and 1.027, respectively. Because these reduced mass ratios are in good agreement with that calculated for a ketene group in the diatomic approximation, we conclude that these bands result from absorption of a ketene group. It is likely that one of these bands is either a site splitting or it results from absorption of a conformational isomer, since there can be only two products of this reaction which are consistent with the reaction mechanism. The band at 2119.7 cm^{-1} is the weakest, and we will assume that this band is the one due to packing effects or conformational isomerism. Upon substitution with deuterium, the experimental $\Delta\nu$ values are then +1.6 and +5.0 cm^{-1}. The band at 2115.8 cm^{-1} is assigned to 2,5-dimethyl-1,3,5-hexatrien-1-one, and the band at 2124.5 cm^{-1} is assigned to 3,6-dimethyl-1,3,5-hexatrien-1-one for the following reasons: the 2115.8 cm^{-1} mode has a more positive $\Delta\nu$ than the 2124.5 cm^{-1},

TABLE 5: Observed Ketene Product Absorptions from Reaction of O Atoms with Isotopomers of Mesitylene

reaction	ketene bands (cm^{-1})	$\Delta\nu$ (cm^{-1})	reaction	ketene bands (cm^{-1})
^{16}O + mesitylene-H_{12}	2104.0	N/A	^{18}O + mesitylene-H_8	2085.6 2081.9
^{16}O + mesitylene-d_{12}	2112.9 2094.4	+8.9 −9.6	^{18}O + mesitylene-d_8	2085.6 (second band obscured)

TABLE 6: B3LYP/6-311G(d,p) $C_9H_{12}O$ Ketene Asym. Frequencies

$C_9H_{12}O$ ketene	^{16}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})	^{18}O isotopomers frequency (cm^{-1}) [% intensity]	$\Delta\nu$ (cm^{-1})
s-cis, *s-trans*-(*E*,*E*)-2,4,6- trimethyl-1,3,5-hexatrien-1-one, H_{12} isotopomer	2105.6	N/A	2078.3	NA
d_{12} isotopomer	2108.6 [80.4] 2092.6 [4.5] 2084.4 [15.1]	+3.0	2095.6 [13.3] 2089.9 [10.7] 2072.4 [76.0]	−5.9

indicating a stronger coupling of the methyl C−D stretching mode with the ketene asymmetric stretch; and this mode has the lower frequency of the two, which implies that a methyl group is closer to the ketene group.

Now, we consider the case of the O atom−mesitylene reaction. Mesitylene (1,3,5-trimethylbenzene) has only one unique site for substitution, and because of symmetry, there is only one predicted ketene product which is consistent with the stated mechanism: 2,4,6-trimethyl-1,3,5-hexatrien-l-one (2,4,6-TMHO). We observe one product band with maximum absorption at 2104.0 cm^{-1} for the reaction of standard isotopes (Table 5). This band shifts to 2085.6 and 2081.9 cm^{-1} upon ^{18}O substitution, yielding reduced mass ratios of 1.018 and 1.021, respectively. Because these reduced mass ratios are in agreement with that calculated for a ketene group in the diatomic approximation, we conclude that these absorptions are due to molecules containing the ketene functional group. The observation of two ketene absorptions in the ^{18}O products implies that there are either two conformers of 2,4,6-TMO present in the matrix, or the molecule is present in two types of packing sites.

Upon reaction of C_9D_{12} mesitylene with ^{16}O the ketene mode shifts to 2112.9 and 2094.4 cm^{-1}, yielding experimental $\Delta\nu$ values of +8.9 and −9.6 cm^{-1}. The B3LYP/6-311G(d,p) level of theory predicts $\Delta\nu$ values of +3.0 and −21.2 cm^{-1} for the two strongest modes of *s-cis*, *s-trans*-(*E*,*E*)-2,4,6-TMHO which have ketene asymmetric stretching character (Table 6). From the experiment, the estimated relative intensity of the 2094.4 and 2112.9 cm^{-1} modes is I (2094.4 cm^{-1})/I (2112.9 cm^{-1}) = 4.8. Because the 2094.4 cm^{-1} mode is the most intense we assign this as the main ketene mode, while the 2112.9 cm^{-1} mode is assigned as a C−D stretch which is mixed with the ketene asymmetric stretch. Even though the density functional method predicts that the C−D stretch lies slightly lower in frequency than the ketene mode, experimental evidence supports the opposite, as explained above. The 9.6 cm^{-1} redshift in the $C=C=O$ asymmetric stretch in the deuterated molecule (Table 5) can be explained by resonance between this band and the 2112.9 cm^{-1} band, effectively shifting the bands to lower and higher frequencies, respectively.

Shown in Figure 1D is the photolysis-time dependence of the ketene product band intensity for this reaction. The ketene band has maximum intensity at 10 min photolysis and gradually decreases during the remaining photolysis time. Similar behavior is observed when the reaction is carried out with the ^{18}O isotope. This ketene product is highly susceptible to photolysis at these wavelengths. This behavior is quite different from the other ketene products.

TABLE 7: Alcohol Product Band Absorptions from Reaction of O atoms with Methylbenzenes

reaction	band center (cm^{-1})	integrated A (cm^{-1})	assignment
^{16}O + toluene-H_8	3635.6	0.645	methylphenol
^{16}O + toluene-d_3	3635.3	0.645	methylphenol
	2686.5	0.053	benzyl alcohol
^{16}O + toluene-d_5	3638.4	0.113	benzyl alcohol
	2684.5	0.339	methylphenol
^{16}O + toluene-d_8	2684.5	0.419	methylphenol
^{16}O + *m*-xylene-H_{10}	3640.9		
	3638.9	0.394	*m*-dimethylphenol
	3637.2		
^{16}O + *m*-xylene-d_{10}	2685.3	0.248	*m*-dimethylphenol
	3641.0		
^{16}O + *p*-xylene-H_{10}	3635.7	0.287	*p*-dimethylphenol
	3633.0		
^{16}O + *p*-xylene-d_{10}	2683.9	0.110	*p*-dimethylphenol
^{16}O + mesitylene-H_{12}	3639.8		
	3635.1	0.536	trimethylphenol
	3631.8		
^{16}O + mesitylene-d_{12}	2686.6	0.441	trimethylphenol

Ketenes are not the only products from the reaction of oxygen atoms with methylbenzenes. Products which contain the hydroxy functional group are also observed. Table 7 lists all observed O−H and O−D stretching frequencies and integrated absorbances of product bands which result from these reactions. In the reaction of normal toluene with ^{16}O, one band is observed at 3635.6 cm^{-1}. When ^{16}O reacts with toluene-α,α,α-d_3, bands are observed at 3635.3 and 2686.5 cm^{-1}. These bands are assigned to methylphenol and benzyl alcohol, respectively.

In the reactions of *m*-xylene-H_{10}, *p*-xylene-H_{10}, and mesitylene-H_{12} with ^{16}O, three sharp peaks are observed in the 3641−3632 cm^{-1} region for each product. Only one peak is observed for each product in the 2683−2687 cm^{-1} region, when *m*-xylene-d_{10}, *p*-xylene-d_{10}, and mesitylene-d_{12} react with ^{16}O atoms. Since there is only one set of O−H/O−D product bands in these reactions, they are assigned as originating from the corresponding phenols. This assignment is based on the observation that the intensity of the benzyl alcohol band from the toluene reaction is always smaller than the intensity of the phenol band, suggesting that the phenol is the kinetically favored product (assuming equal infrared absorption intensities). We expect this relationship to hold for the di- and trimethylbenzenes as well.

As we have concluded in our previous report on the benzene/oxygen atom reaction, phenol is most likely formed by addition of the oxygen atom to the benzene ring followed by migration of the hydrogen atom from the resulting tetragonal carbon atom to the radical center on O. Benzyl alcohol is most likely formed via a mechanism where the O atom abstracts a H atom from the methyl group of toluene forming a benzyl radical/OH radical pair which recombine to form benzyl alcohol.[20] The electrophilic addition mechanism is kinetically favored since the first step is a bond-forming step and the second step involves only the migration of a H atom. In the mechanism leading to formation of benzyl alcohol the first step involves homolytic cleavage of a C−H bond. Consequently, this mechanism should require higher energetics and thus be kinetically slower.

Conclusions

Ketene products are observed from the photochemical reaction of O(^{3}P) atoms with toluene, *m*-xylene, *p*-xylene, and mesitylene in solid argon matrices at 12 K. The toluene/O atom reaction results in 2-methyl-1,3,5-hexatrien-1-one, 4-methyl-1,3,5-hexatrien-1-one, and 6-methyl-1,3,5-hexatrien-1-one. Methylphenol and benzyl alcohol are also observed. 2,6-Dimethyl-1,3,5-hexatrien-1-one, 2,4-dimethyl-1,3,5-hexatrien-1-one, and 4,6-dimethyl-1,3,5-hexatrien-1-one are products of the O atom reaction with *m*-xylene. *m*-Dimethylphenol is also a product of this reaction. When O atoms react with *p*-xylene the following products are observed: 2,5-dimethyl-1,3,5-hexatrien-1-one, 3,6-dimethyl-1,3,5-hexatrien-1-one, and p-dimethylphenol. The O atom/mesitylene reaction results in 2,4,6-trimethyl-1,3,5-hexatrien-1-one and trimethylphenol. From the molecular structure of the ketene products, it is concluded that the methyl groups are acting as ortho/para directors in these electrophilic aromatic addition reactions.

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