

methyl-*tert*-butylbenzenes by  $\text{CH}_5^+$  represents a gas-phase counterpart of the fast dealkylation of similar substrates promoted by strong acids and acidic catalysts.<sup>30,31</sup>

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## Reaction of O(<sup>3</sup>P) Atoms with Toluene and 1-Methylcyclohexene

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**Abstract:** The products and mechanisms of the reaction of O(<sup>3</sup>P) atoms with toluene and 1-methylcyclohexene have been investigated at 50–400 Torr total pressure over the temperature range 296–423 K. With toluene the volatile addition products observed were phenol, *o*-, *m*-, and *p*-cresol, along with CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and a large amount of nonvolatile polymeric tar. The reaction of O(<sup>3</sup>P) atoms with 1-methylcyclohexene produced CO and the C<sub>7</sub>H<sub>12</sub>O addition product isomers 1-methyl-1,2-epoxycyclohexane, 2-methylcyclohexanone, 1-methylcyclopentencarboxaldehyde, methyl cyclopentyl ketone, 2-methyl-5-hexenal, 1-hepten-6-one, and 2-methyl-2-hexenal. These products are discussed in terms of a general mechanism for the gas-phase addition of O(<sup>3</sup>P) atoms to aromatic and cyclic unsaturated hydrocarbons.

## Introduction

While much work has been carried out on the products and mechanisms of the gas-phase reactions of O(<sup>3</sup>P) atoms with simple olefins,<sup>1–13</sup> mainly by Cvetanovic and coworkers,<sup>1–7</sup> there are less data available for the reaction of O(<sup>3</sup>P) atoms with aromatic hydrocarbons<sup>5,14–18</sup> and with cyclic olefins.<sup>2,5,7,13</sup>

The product studies on the reaction of O(<sup>3</sup>P) atoms with aromatic hydrocarbons<sup>14–18</sup> have shown that tar or polymer formation is extensive with the major volatile addition products being phenolic. In the case of the cyclic olefins, Cvetanovic and coworkers<sup>2,5,7</sup> have reported the products obtained from the reaction of O(<sup>3</sup>P) atoms with cyclohexene and cyclopentene, the latter system being studied in detail.<sup>7</sup> The major products for these compounds are the cyclic epoxide and ketone, together with ring-contracted and ring-opened isomers.

In this work, as part of an investigation into the rates and products of the reactions of O(<sup>3</sup>P) atoms with a variety of unsaturated organic compounds,<sup>19,20</sup> we have studied the products obtained from the reaction of O(<sup>3</sup>P) atoms with toluene and 1-methylcyclohexene to determine the effect of aromaticity on the reaction mechanism. These compounds are not only of interest from the fundamental grounds of structure and reactivity, but also because of their possible significance in polluted atmospheres.

## Experimental Section

The experimental system has been described in detail previously,<sup>19,20</sup> and only the essential details will be given here. Ground-state oxygen atoms were produced by the mercury photosensitization of N<sub>2</sub>O in a closed circulating reaction system. The volumes of the reaction and circulating systems were 4000 and 1043 cm<sup>3</sup> for the studies on toluene and 1-methylcyclohexene, respectively. The reaction system was enclosed by a furnace whose temperature

could be held constant to better than  $\pm 1$  K over the temperature range 295–425 K.

Samples ( $5 \text{ cm}^3$ ) were periodically removed for analysis using a Carle gas-sampling valve. In all cases, the  $\text{N}_2$  yield from the  $\text{N}_2\text{O}$  photosensitization was used in an internal actinometer to monitor the number of  $\text{O}(^3\text{P})$  atoms produced during the irradiations.

The experimental details for the two reaction systems studied are as follows.

**$\text{O}(^3\text{P}) + \text{Toluene}$ .** Reactions were carried out at  $373 \pm 2$  K in order to avoid problems associated with adsorption of reaction products on the glass and/or stainless steel components of the gas-sampling system. The product samples were split into two fractions:  $\text{CO}$  and  $\text{N}_2$  were analyzed by gas chromatography on a  $5 \text{ ft} \times \frac{1}{4}$  in. Linde Molecular Sieve 13X column at  $296 \pm 2$  K using a thermal-conductivity detector, while the organic products were detected by gas chromatography using a flame-ionization detector. Thus,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were analyzed on a  $6 \text{ ft} \times \frac{1}{8}$  in. Poropak Q column at  $296 \pm 2$  K, while the volatile phenolic products were analyzed on a  $10 \text{ ft} \times \frac{1}{8}$  in. 3% polyphenyl ether on DCMS Chromosorb W column at  $388 \pm 2$  K. In all cases, gas chromatographic peaks were identified by comparison of their retention times with those of authentic samples and were quantified by calibration using known pressures of the reagents in the reaction system.

A few subsidiary experiments were carried out at  $296 \pm 2$  K in a 9.4-cm path length cylindrical quartz cell fitted with  $\text{NaCl}$  end windows. The reactions were monitored by in situ infrared absorption spectroscopy using a Perkin-Elmer 221 spectrophotometer.

All chemicals used were of  $\geq 98\%$  purity.

**$\text{O}(^3\text{P}) + 1\text{-Methylcyclohexene}$ .**  $\text{CO}$  and  $\text{N}_2$  were analyzed as described above, while the volatile organic products were analyzed by gas chromatography on a  $10 \text{ ft} \times \frac{1}{8}$  in.  $\beta,\beta$ -oxydipropionitrile on 80–100 mesh Firebrick column at  $363 \pm 2$  K using a flame-ionization detector.

Identification of the gas chromatographic peaks were made by comparison of their retention times with those of authentic samples, wherever possible, and for the organic products by elucidation of their structures from nuclear magnetic resonance, infrared, and mass spectrometric data.

In order to have sufficient reaction product to obtain pure samples for spectral identification, a flow system similar to that described by Grovenstein and Mosher<sup>17</sup> was used, and samples of the reaction products were separated and collected by preparative gas chromatography. A flow of  $3.5 \text{ cm}^3 \text{ s}^{-1}$  of  $\text{N}_2\text{O}$  was bubbled through mercury, then through 1-methylcyclohexene, and the resulting flow stream was irradiated in a quartz photolysis tube by a spiral low-pressure mercury resonance lamp. Condensable products and unreacted 1-methylcyclohexene were trapped out at  $196 \pm 2$  K, with a typical reactant conversion of  $\sim 11\%$ . This flow system was operated at  $296 \pm 2$  K and  $735 \pm 10$  Torr total pressure (mainly  $\text{N}_2\text{O}$ ). Identical gas chromatographic peaks were observed with this system as with experiments carried out at lower conversions and at lower total pressures in the closed circulating system. With the  $\beta,\beta$ -oxydipropionitrile column operated at  $363 \pm 2$  K, six of the seven product peaks were collected in quantities sufficient to obtain nuclear magnetic resonance (NMR) (Varian A60 and A60D instruments), infrared (Perkin-Elmer 221 spectrophotometer), and mass spectra (Finnigan 3100D and 3200E quadrupole mass spectrometers).

1-Methyl-1,2-epoxycyclohexane was synthesized by an adaption of Hibbert and Burt's procedure.<sup>21</sup> 1-Methylcyclohexene ( $3.0 \text{ cm}^3$ ,  $0.025 \text{ mol}$ ) was added to a solution of  $5.2 \text{ g}$  of *m*-chloroperbenzoic acid (85% purity,  $0.025 \text{ mol}$ ) in  $100 \text{ cm}^3$  of methylene chloride. The solution was stirred for 3–4 h at 273 K. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the resulting solution was washed with (a) excess 10% sodium sulfite solution to remove any remaining peracid, (b) 10% sodium carbonate to remove any remaining benzoic acid, and (c) water to remove carbonate and any traces of benzoic acid. The solution was then dried over anhydrous sodium sulfate and filtered, and the methylene chloride was removed under vacuum. Gas chromatographic analysis of the product showed the 1-methyl-1,2-epoxycyclohexane to be  $\geq 98\%$  purity, with the remainder being mainly unreacted 1-methylcyclohexene. Commercially available 1-methylcyclohexene and 2-methylcyclohexanone had purity levels  $\geq 98\%$  as confirmed by combined gas chromatography–mass spectrometric analyses.

Calibration of the gas chromatograph for  $\text{CO}$  and  $\text{N}_2$  was car-

ried out by gas sampling known pressures of these compounds.

Calibration using liquid samples of 1-methyl-1,2-epoxycyclohexane and 2-methylcyclohexanone showed them to produce equal responses, in terms of peak areas, and it was assumed that this response was valid for liquid injection of all the other  $\text{C}_7\text{H}_{12}\text{O}$  isomers observed in this work.<sup>22</sup> Gas-phase sampling via the Carle valve from the reaction system of identical pressures of 1-methyl-1,2-epoxyhexane and 2-methylcyclohexanone yielded a relative response for these two compounds of 2.43:1 at  $296 \pm 2$  K and 1.17:1 at  $423 \pm 1$  K. This deviation from unity of the relative responses for gas sampling probably results from adsorption of the more polar compounds on the stainless steel components of the gas-sampling system. When the relative amounts of 1-methyl-1,2-epoxycyclohexane and 2-methylcyclohexanone produced at 400 Torr total pressure and  $296 \pm 2$  K were corrected for the relative response factor of the gas-sampling system, they were within 2% of that obtained by direct liquid injection of the product mixture collected from the flow system at  $735 \pm 10$  Torr total pressure and  $296 \pm 2$  K. Responses for gas sampling of the other products at 296 K were then derived by comparison of the direct liquid injection of the flow study products with the gas-phase sampling of the reaction carried out at 400 Torr total pressure, assuming the product distribution to be identical.

Gas chromatographic calibration factors for samples from the gas-phase system at  $423 \pm 1$  K were based on the fact that only a 17% difference in response between 1-methyl-1,2-epoxycyclohexane and 2-methylcyclohexanone was observed. Responses for the other products were derived by interpolation based on their relative retention times. A maximum error of  $\pm 10\%$  in the product yields was expected in this case.

## Results and Discussion

**$\text{O}(^3\text{P}) + \text{Toluene}$ .** This reaction was studied extensively at  $373 \pm 2$  K over the pressure range of 80–400 Torr of  $\text{N}_2\text{O}$ , with toluene pressures ranging from 2–10 Torr. The reaction products observed were  $\text{CO}$ , *o*-cresol, *m*-cresol, *p*-cresol, phenol, an unknown, and a reddish-yellow tar. The product yields, relative to the  $\text{N}_2$  yield, are given in Table I, along with the yields of the volatile addition products expressed as a percentage of the total volatile addition products. No benzaldehyde, benzyl alcohol, or biphenyl were detected. In addition, small amounts of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were observed in experiments carried out at  $296 \pm 2$  K and  $423 \pm 1$  K, with the  $\text{CH}_4/\text{N}_2$  ratio being determined as 0.01 at  $296 \pm 2$  K.

Room-temperature experiments, monitoring the reaction by infrared absorption spectroscopy, showed the production of  $\text{CO}$  and  $\text{CH}_4$  and small amounts of a very broad carbonyl band at  $\sim 1725 \text{ cm}^{-1}$ . The latter band remained after evacuation of the cell, suggesting that it was associated with the tar. An NMR spectrum of the reddish-yellow tar material in acetone-*d*<sub>6</sub>- $\text{CDCl}_3$  showed no evidence of aromatic protons. Instead, a very broad signal from methine protons and from protons in methyl groups was observed, suggesting a mixture of materials.

Table I also gives the product data obtained at room temperature by Jones and Cvetanovic<sup>15</sup> and by Grovenstein and Mosher.<sup>17</sup> It can be seen that there is general agreement on the products obtained from this reaction and that the volatile addition products account for only a small fraction (15–25%) of the  $\text{O}(^3\text{P})$  atoms consumed. However, there are differences in the relative amounts of the individual phenolic compounds observed, with Grovenstein and Mosher<sup>17</sup> finding more *m*-cresol than either Jones and Cvetanovic<sup>15</sup> or the present work. Also, the present observation of phenol is in agreement with Grovenstein and Mosher,<sup>17</sup> while Jones and Cvetanovic<sup>15</sup> did not detect this product. In all cases, extensive tar formation was observed, and the present finding of the lack of aromaticity in the tar is in agreement with the work of Boocock and Cvetanovic<sup>14</sup> on the reaction of  $\text{O}(^3\text{P})$  atoms with benzene. The detection of

**Table I.** Product Yields Observed from the Reaction of O(<sup>3</sup>P) Atoms with Toluene

Product A	This work <sup>a</sup>		Ref 15 <sup>b</sup>		Ref 17 <sup>c</sup>
	A/N <sub>2</sub>	% yield <sup>d</sup>	A/N <sub>2</sub>	% yield <sup>d</sup>	% yield <sup>d</sup>
Phenol	0.02	8.7 ± 1.9			8.0
<i>o</i> -Cresol	0.20	80.5 ± 1.7	0.12	78	58.8
<i>m</i> -Cresol	0.01 <sup>e</sup>	4.7 ± 0.7 <sup>e</sup>	0.034 <sup>f</sup>	22 <sup>f</sup>	15.3
<i>p</i> -Cresol					17.9
CO	0.140 ± 0.018		0.093 (100 Torr) 0.059 (680 Torr)		
H <sub>2</sub> O			0.07		
CH <sub>4</sub>	0.01 <sup>g</sup>				
C <sub>2</sub> H <sub>6</sub>	0.005 <sup>g</sup>				

<sup>a</sup>  $P_{\text{total}} = 80\text{--}400$  Torr N<sub>2</sub>O;  $T = 373 \pm 2$  K. Includes 6.1% of an unknown. <sup>b</sup>  $P_{\text{total}} = 385 \pm 5$  Torr N<sub>2</sub>O;  $T = 298$  K. No pressure dependence of the cresol yields noted on pressure from 100 to 680 Torr N<sub>2</sub>O. <sup>c</sup>  $P_{\text{total}} = 740 \pm 4$  Torr N<sub>2</sub>O;  $T = 303 \pm 1$  K. Volatile addition products analyzed only. <sup>d</sup> Yield of the observed volatile addition products = 100%. <sup>e</sup> *m*-, *p*-cresol not separated; mass spectra show *m*-cresol ≤ 10% of the *p*-cresol. <sup>f</sup> *m*-, *p*-cresol not separated; infrared spectra show *m*-cresol ≤ 4–5% of total cresol yield. <sup>g</sup> At 296 ± 2 K.

**Table II.** Product Yields from the Reaction of O(<sup>3</sup>P) Atoms with 1-Methylcyclohexene (N<sub>2</sub> = 1)

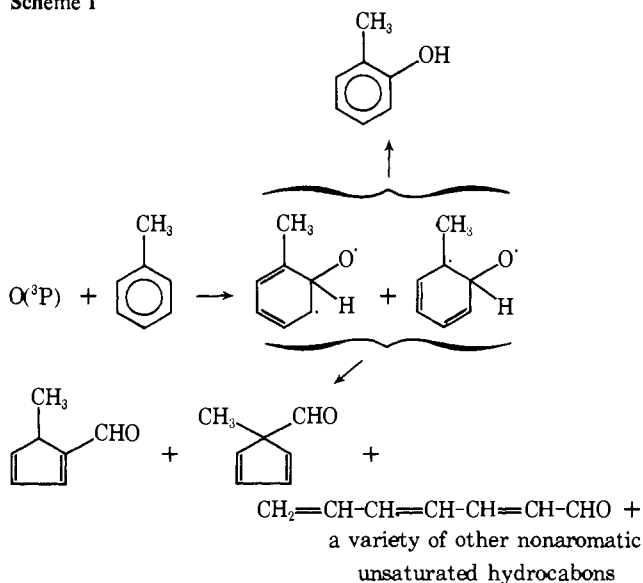
<i>T</i> , K	<i>P</i> <sub>total</sub> , Torr	MCXO <sup>a</sup>	MCXN <sup>b</sup>	MCPA <sup>c</sup>	MCPN <sup>d</sup>	MHA <sup>e</sup>	X <sub>1</sub> <sup>f</sup>	X <sub>2</sub> <sup>g</sup>	CO	ΣO( <sup>3</sup> P)
296 ± 2	55	0.315	0.070	0.050	0.030	0.036	0.040	0.004	0.020	0.565
		±	±	±	±	±	±	±	±	±
296 ± 2	115	0.063	0.021	0.010	0.009	0.006	0.010	0.0005	0.005	0.125
		±	±	±	±	±	±	±	±	±
296 ± 2	210	0.306	0.066	0.036	0.029	0.037	0.042	0.003	0.014	0.533
		±	±	±	±	±	±	±	±	±
296 ± 2	210	0.017	0.002	0.002	0.004	0.002	0.004	0.0002	0.004	0.035
		±	±	±	±	±	±	±	±	±
296 ± 2	400	0.355	0.090	0.044	0.036	0.051	0.056	0.006	0.010	0.648
		±	±	±	±	±	±	±	±	±
296 ± 2	400	0.028	0.005	0.005	0.001	0.007	0.003	0.0007	0.002	0.052
		±	±	±	±	±	±	±	±	±
296 ± 2	400	0.369	0.122	0.062	0.042	0.053	0.070	0.007	0.007	0.732
		±	±	±	±	±	±	±	±	±
423 ± 1	170	0.015	0.009	0.003	0.004	0.004	0.004	0.0003	0.002	0.014
		±	±	±	±	±	±	±	±	±
423 ± 1	170	0.340	0.070	0.038	0.032	0.042	0.053	0.005		0.580
		±	±	±	±	±	±	±		±
423 ± 1	170	0.015	0.004	0.003	0.001	0.004	0.003	0.0003		0.030
		±	±	±	±	±	±	±		±

<sup>a</sup> MCXO, 1-methyl-1,2-epoxycyclohexane. <sup>b</sup> MCXN, 2-methylcyclohexanone. <sup>c</sup> MCPA, 1-methylcyclopentene-carboxaldehyde. <sup>d</sup> MCPN, methyl cyclopentyl ketone. <sup>e</sup> MHA, 2-methyl-5-hexenal. <sup>f</sup> X<sub>1</sub>, ~60% 1-hepten-6-one + ~40% 2-methyl-2-hexenal. <sup>g</sup> X<sub>2</sub>, unknown, tentatively identified as 3-methyl-2-oxepene (see text).

CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> in the present work suggests the presence of CH<sub>3</sub> radicals which can abstract an H atom to form CH<sub>4</sub> or recombine to form C<sub>2</sub>H<sub>6</sub>.

The available evidence suggests that the initial reaction step is that of addition of an oxygen atom to the aromatic ring, predominantly in the ortho position, followed by isomerization of phenolic compounds or ring cleavage or contraction to form a variety of highly reactive olefinic species which will consume O(<sup>3</sup>P) atoms in secondary reactions, ultimately producing a tar or polymer containing few or no aromatic protons. Thus at 373 K, the rate constant for the reaction of O(<sup>3</sup>P) atoms with toluene is  $1.3 \times 10^8$  l. mol<sup>-1</sup> s<sup>-1</sup>,<sup>23</sup> while it is expected that the rate constants for the reaction of O(<sup>3</sup>P) atoms with the olefinic product species will be  $\sim 1 \times 10^{10}$  l. mol<sup>-1</sup> s<sup>-1</sup>.<sup>15,19,20,24</sup> Also, it is likely that the reaction will undergo fewer secondary reactions at higher temperatures where the rate constant for O(<sup>3</sup>P) atoms with toluene will approach those for O(<sup>3</sup>P) atoms with the olefinic products, as may be indicated by the data in Table I. A possible reaction sequence is shown in Scheme I for attack at the ortho position. The formation of phenol presumably proceeds by addition of an O(<sup>3</sup>P) atom at the 1 position, followed by an intermolecular methyl migration and subsequent H-atom abstraction by the phenoxy radical to form phenol and by the methyl radical to form CH<sub>4</sub>.

**O(<sup>3</sup>P) + Methylcyclohexene.** The products from this reaction were studied at 296 ± 2 K over the range 55–400 Torr total pressure of N<sub>2</sub>O and at 423 ± 1 K at 170 Torr total pressure of N<sub>2</sub>O with typically 1–3 Torr of 1-methyl-

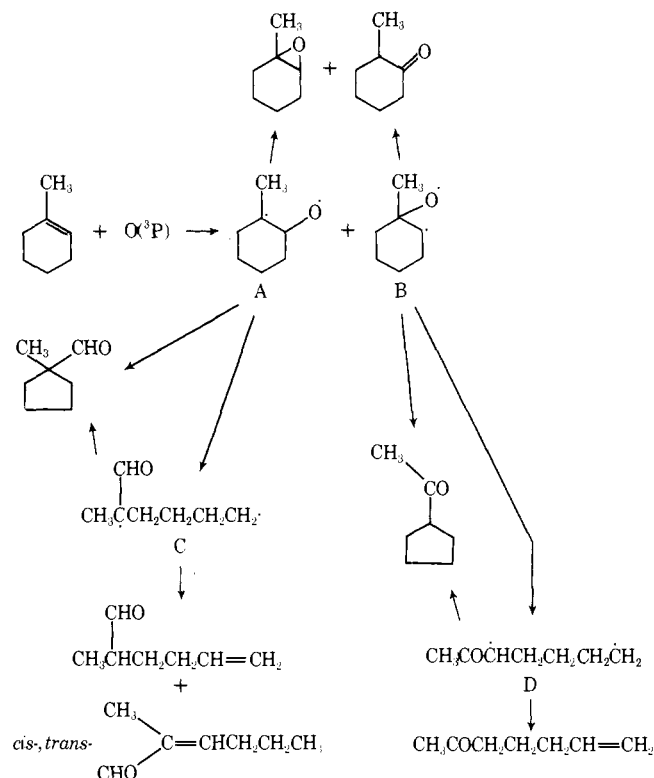
**Scheme I**

cyclohexene. As noted above, the product peaks observed on the β,β-oxydipropionitrile column under these conditions were identical with those obtained from the flow system at 296 ± 2 K and 735 ± 10 Torr total pressure of N<sub>2</sub>O. The six products collected by preparatory gas chromatography from the flow-system study were all shown by combined gas chromatography–mass spectrometry to be isomers of mo-

molecular formula  $C_7H_{12}O$ . NMR and infrared spectra were obtained<sup>25</sup> for all of these products, and two of the major ones were found to have NMR, infrared, and mass spectra and gas chromatographic retention times identical with those of 2-methylcyclohexanone and 1-methyl-1,2-epoxycyclohexane. The NMR, infrared, and mass spectra of the other collected unknowns allowed them to be identified<sup>25</sup> as 1-methylcyclopentenecarboxaldehyde, methyl cyclopentyl ketone, 2-methyl-5-hexenal, and a product peak which was identified as a mixture of 1-hepten-6-one and 2-methyl-2-hexenal, the latter probably a mixture of *cis* and *trans*, all of which are in accord with the mechanism shown below. The mass spectrum of the seventh product peak was obtained using combined gas chromatographic-mass spectrometric analysis,<sup>25</sup> and its possible identity is discussed below. CO was also detected as a reaction product.

Table II shows the product/ $N_2$  ratios obtained at  $296 \pm 2$  and  $423 \pm 1$  K, while Figure 1 shows some of the product/ $N_2$  ratios at  $296 \pm 2$  K plotted against the  $N_2O$  pressure. It can be seen that all of the addition products show a slight increase in yield with increasing total pressure as expected if they arise from a highly energetic intermediate which can be quenched to yield stable addition products. On the other hand, the CO yield decreases with increasing pressure, as expected for a fragmentation product formed from an energetic intermediate. The data at  $423 \pm 1$  K are very similar to those obtained at  $296 \pm 2$  K showing the effect of temperature on the system to be very slight.

By analogy with the very extensive work of Cvetanovic and coworkers<sup>1-7</sup> on the reaction mechanism for the reactions of  $O(^3P)$  atoms with a variety of olefinic systems, the simplified reaction scheme shown in Scheme II can account Scheme 11



for all the addition products observed. 1-Methyl-1,2-epoxycyclohexane may be formed from either of the initially formed biradicals A or B by ring closure, while 2-methylcyclohexanone may be formed from A by a 1,2 H atom shift or from B by 1,2 methyl migration. 1,2 ring contraction leads to 1-methylcyclopentenecarboxaldehyde and methyl cyclopentyl ketone from A and B, respectively, probably via

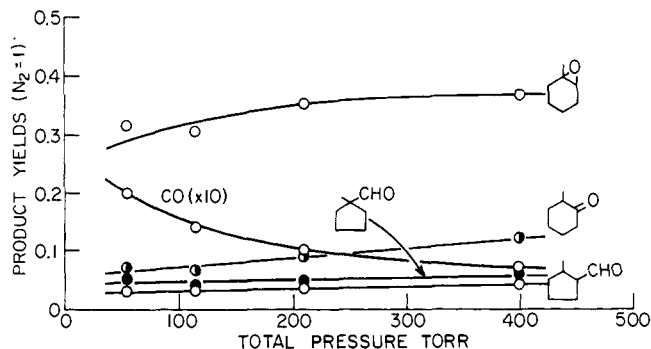
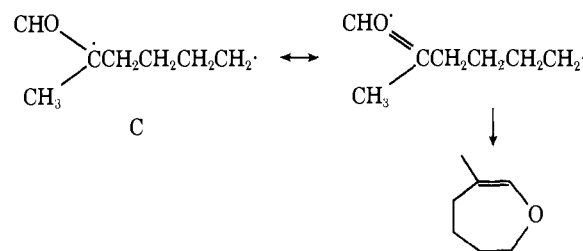


Figure 1. Plot of selected product yields ( $N_2 = 1$ ) against total  $N_2O$  pressure for the reaction of  $O(^3P)$  atoms with 1-methylcyclohexene at  $296 \pm 2$  K. (Data for 2-methyl-5-hexenal and products  $X_1$  and  $X_2$  are omitted for clarity.)

either a concerted reaction, previously shown to occur for the reaction of  $O(^3P)$  atoms with cyclopentene at 77 K,<sup>6,26</sup> or via ring opening  $\alpha$  to the oxygen atom position to give the biradicals C and D, which can then either recycle to 1-methylcyclopentenecarboxaldehyde and to methyl cyclopentyl ketone, respectively, or can isomerize to form the open-chain unsaturated aldehydes and ketones observed. Fragmentation, such as to CO, of the vibrationally or electronically excited products formed will be more important at low pressures in the absence of stabilizing collisions, and hence the addition product yields will increase with pressure while the fragmentation product yields will decrease, as observed.

In this system, an estimate of the relative amounts of the biradicals A and B formed can be obtained from the yields of 1-methylcyclopentenecarboxaldehyde and methyl cyclopentyl ketone and also from the yields of the open chain unsaturated ketones and aldehydes. It can be seen from Table II that biradical A is formed  $\sim 60$ – $65\%$  of the time, in agreement with the work of Cvetanovic and coworkers,<sup>5-7</sup> which shows that the  $O(^3P)$  atom adds predominantly to the less substituted of the two doubly bonded carbon atoms. Analogous to the observation of dihydropyran from the reaction of  $O(^3P)$  atoms with cyclopentene,<sup>7</sup> it is possible that the unknown product,  $X_2$ , observed in the present work is the unsaturated ether, 3-methyl-2-oxepin, formed from the cyclization of an isomeric form of the biradical C. This is



not inconsistent with the mass spectrum observed for this product, which shows predominant mass peaks at  $m/e$  112, 97, 71, and 69. In addition, the short retention time observed on the  $\beta,\beta$ -oxydipropionitrile column is consistent with the low polarity expected for this compound.

The present reaction system shows great similarity with the reactions of  $O(^3P)$  atoms with cyclohexene (major products 1,2-epoxycyclohexane, cyclohexanone, and cyclopentenecarboxaldehyde) and cyclopentene, the latter being extensively studied by Cvetanovic, Ring, and Doyle.<sup>7</sup> There the major products observed were the analogous 1,2-epoxycyclopentane, cyclopentanone, and cyclobutenecarboxaldehyde, together with equal amounts of ethylene and acrolein. Smaller amounts of ring-opened products identified as

4-pentenal, dihydropyran, and possibly 2-pentenal were also observed.<sup>7</sup>

### Conclusions

From this and previous work,<sup>1-18</sup> the reactions of O(<sup>3</sup>P) atoms with simple cyclic olefins and with the aromatic hydrocarbons can be satisfactorily explained in terms of a general mechanism, such as shown above. The difference in products between the cyclic olefins and aromatic hydrocarbons arises because of the difference in the rate constants for reaction of O(<sup>3</sup>P) atoms with the reactant and with the reaction products. Thus, the reaction of O(<sup>3</sup>P) atoms with the aromatic hydrocarbons is slow<sup>23</sup> and produces largely highly reactive unsaturated products (the rate constants for reaction of O(<sup>3</sup>P) atoms with *o*-cresol have, however, been shown to be only approximately eight times faster than with toluene at room temperature).<sup>27</sup> However, for the simple olefins, the initial reaction is very fast and forms largely saturated, and hence unreactive, products. Thus, the extent of secondary reactions is much smaller in these cases, as observed.

**Note Added in Proof.** J. J. Havel and K. M. Chan, *J. Am. Chem. Soc.*, **97**, 5800 (1975), have recently investigated the products and mechanisms of the reactions of O(<sup>3</sup>P) atoms with cyclic and bicyclic hydrocarbons, including cyclohexene. The products observed for cyclohexene are analogous to those observed in the present work for 1-methylcyclohexene.

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## Chiral Nuclear Magnetic Resonance Solvating Agents. Resolution, Determination of Enantiomeric Purity, and Assignment of Absolute Configuration of Cyclic and Acyclic Sulfinates Esters

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**Abstract:** Incomplete but stereoselective reaction of (*S*)-2-methyl-1-butylmagnesium chloride or (*S*)-2-phenyl-1-butylmagnesium chloride with racemic alkyl *p*-tolylsulfonates or sultines, namely 3*H*-2,1-benzoxathiole 1-oxide (**11**) and 3*H*-2,1-benzoxathiane 1-oxide (**12**), affords, upon recovery of unreacted material, sulfonates or sultines enriched (8–64% ee) in the *S* enantiomers. In the presence of resolved 1-phenyl-2,2,2-trifluoroethanol, 1-(1-naphthyl)-2,2,2-trifluoroethanol, or 1-phenyl-2,2,3,3,4,4,4-heptafluoro-1-butanol, the enantiomers of a variety of alkyl alkyl- or arylsulfonates have nonidentical <sup>1</sup>H NMR spectra, allowing for direct determination of enantiomeric purity and, on the basis of the relative field positions of the enantiomeric resonances, correlation of absolute configuration. Specific solvation models are proposed to account for the origin and sense of the spectral nonequivalence. Similar <sup>1</sup>H NMR studies of **11** and **12** in the presence of chiral 1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol provide for determination of enantiomeric purity. The solvation model for sulfonates is employed to assign absolute configurations to sultines **11** and **12**, based on the relative field positions of the enantiomeric resonances. The validity of the configurational assignment for **11** is established rigorously by stereospecific chemical correlation to (–)-menthyl (–)-(*S*)-*p*-tolylsulfinate, while supporting evidence is given for that of **12**. CD spectra of **11** and **12** are reported.

The recently reported<sup>2</sup> <sup>1</sup>H NMR method for assignment of absolute configuration to sulfoxides using chiral 1-aryl-2,2,2-trifluoroethanols (**1**) is based on a postulated two-point interaction stabilizing short-lived diastereomeric sol-

vates **2** and **3**. The primary interaction is a hydrogen bond from the acidic hydroxyl of **1** to the basic sulfinyl oxygen, while the secondary stabilizing force consists of the dipolar attraction of the electron-poor carbonyl proton to the elec-