

Figure 17. Space-filling model of benzene and two water molecules primarily belonging to the  $\pi$  cloud.

Partial molar internal energy of transfer for benzene calculated from simulation results comes out to be  $-70.15$  kcal/mol with error bounds estimated to be  $\pm 30.0$  kcal/mol. This calculation used a value of  $-8.65$  kcal/mol for the energy of water as calculated in a previous study.<sup>18</sup> A recent, 3000K long run using the force-biased sampling scheme predicted a value of  $-8.75$  kcal/mol for the energy of water.<sup>10</sup> By use of this value, the partial molar internal energy of transfer of benzene is calculated to be  $-48.6$  kcal/mol, with the estimated error bound still about  $\pm 30.0$  kcal/mol. The calculated transfer energy also has a large error associated with it because it is a small quantity derived from the difference of two large numbers known only with a considerable

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degree of statistical uncertainty. This number can also be expected to be quite sensitive to the well depth of the benzene-water interaction energy in the in-plane region. The energy difference of 1 kcal/mol between the function used herein and that of Karlstrom et al. propagated over 20 in-plane interactions could change the calculated transfer energy by 30%. Experience with similar problems in liquid water system<sup>15</sup> indicates that the calculated structural characteristics of the system are not highly sensitive to small changes in energetics, and thus the description of the essential nature of the benzene hydration complex set forth herein is expected to remain valid.

Finally, we pursued the question of sensitivity of results to choice of potential function, with an additional simulation, identical with that previously described, except that the attractive part of the benzene-water potential was everywhere set to 0. The complete simulation also involved 1700K configurations with ensemble averages formed over the last 1000K. The computed energetics are given in column B of Table I. Here the transfer energy is reduced to  $-1.86$  kcal/mol, still with large error bounds. Thus, the attractive part of the benzene-water potential influences the transfer energy significantly, with the experimental value bracketed by the two simulation results reported herein. The structural indices turned out to be essentially insensitive to this change in benzene-water potential, which indicates the steric contribution to the structure of the  $\pi$  cloud to be quite significant. Although a water hydrogen is proximal to the  $\pi$  cloud in this model, the nature of the interactions is not exclusively hydrophilic.

Further studies are underway to improve the quality of energetics in the potential function and in the simulation results, and determination of a potential of mean force for the benzene-benzene interaction is in progress.

Registry No. Benzene, 71-43-2; water, 7732-18-5.

## Reactive Scattering of $O(^3P)$ with Toluene

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**Abstract:** In a crossed molecular beam study, the reaction of  $O(^3P)$  + toluene, at 9.7 kcal/mol collision energy, is shown to give primarily radical products,  $CH_3$  + phenoxy and  $H$  + cresoxy, under single-collision conditions. There is no evidence of intersystem crossing to a stable singlet species, cresol, as was previously observed in the  $O$  + benzene reaction. The isotropic angular distributions of the product suggest that the mechanism involves formation of a long-lived triplet biradical intermediate.

The chemical reactions of oxygen atoms with aromatic hydrocarbons remain only poorly understood in spite of efforts directed at elucidating the reaction mechanisms by many workers in the field. Knowledge of the mechanism of the initial reactions of these systems is important for understanding many combustion processes, but the bulk reactions are sufficiently complex, with highly reactive primary radical products producing secondary products, that identification of the primary mechanism is difficult in multicollision environments. For the prototypical reaction,  $O$  + benzene, the primary reaction channels were identified in a previous crossed molecular beam study<sup>1</sup> in which two competing reactions were observed. One channel, with products  $H$  atom and

phenoxy radical, is a simple substitution reaction which is similar to a major reaction occurring in many  $O(^3P)$  + unsaturated hydrocarbon reactions. The second channel, which becomes more important at higher collision energies, is the production of a long-lived adduct, that is, the  $O$ -benzene triplet adduct appears to undergo collisionless intersystem crossing and rearrangement to singlet phenol which is sufficiently stable to live more than a millisecond in the absence of collisions and reaches the detector as an adduct. These results raise the question of when intersystem crossing will compete effectively with decomposition of the triplet adduct. The reaction of oxygen atoms with acetylene appears to involve similar processes.<sup>2</sup> If  $H$  atom migration on the triplet

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(1) Sibener, S. J.; Buss, R. J.; Casavecchia, P.; Hirooka, T.; Lee, Y. T. *J. Chem. Phys.* 1980, 72, 4341.

(2) Buss, R. J.; Baseman, R. J.; Casavecchia, P.; Hirooka, T.; Lee, Y. T. 8th International Symposium on Molecular Beams, Cannes, France, 1981. Baseman, R. J.; Buss, R. J.; Lee, Y. T. in preparation.

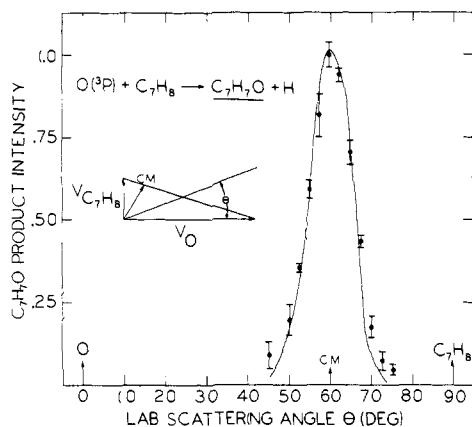


Figure 1. Laboratory angular distribution of mass 107 signal. Solid line is calculated best-fit distribution.

surface has a much higher potential energy barrier than the energy required to produce  $C_2HO + H$ , as implied in recent theoretical calculations,<sup>3</sup> then the experimental observation of the production of  $CH_2 + CO$  in competition with the  $C_2HO + H$  channel implies that hydrogen atom elimination competes with intersystem crossing to the singlet state which precedes the H migration to form singlet ketene which then dissociates to  $CO + CH_2$  products.

In order to better understand the initial chemical reactions of oxygen atoms with aromatic hydrocarbons, one of the simpler substituted aromatics, toluene ( $C_6H_5CH_3$ ), has been investigated. We report here identification of several primary products under single-collision conditions.

### Experimental Section

Molecular beams of the two reactants were crossed at a  $90^\circ$  angle, and the products were detected with an electron bombardment quadrupole mass spectrometer which rotates in the plane of the two beams.<sup>4</sup> The oxygen atoms were produced in a discharge<sup>5</sup> of 200-W rf in 200 torr of a 5%  $O_2$  in helium mixture, followed by expansion through a 0.19-mm-diameter orifice. A slotted disk mounted on the shaft of a synchronous electric motor was installed before the detector to measure velocity distributions of the beams and product with the time-of-flight (TOF) method. The oxygen atoms were found to have a peak velocity of 2350 m/s with a speed ratio of 6.6.

Pure toluene vapor, in approximate equilibrium with the liquid at  $75^\circ C$ , was expanded through a 0.1-mm-diameter orifice, heated to  $140^\circ C$  to prevent condensation and dimer formation during the supersonic expansion. The velocity of toluene was measured to be 672 m/s with a speed ratio of 3.7. Both beams were skimmed and collimated to 2-mm width at the collision region. The most probable collision energy was 9.7 kcal/mol.

Angular distributions of product were obtained by repeated scans of 100-s count at each angle taken every  $2.5^\circ$ . The oxygen beam was chopped with a 150-Hz tuning fork, and the signal was taken to be the difference between chopper-closed and chopper-open count.

TOF of the product was obtained near the canonical center-of-mass (CM) angle,  $60^\circ$  from the O atom beam, using the cross-correlation method employing a slotted disk with a pseudorandom sequence of 255 elements and 12- $\mu s$  time resolution. Typical counting time was 1.7 h at each mass.

### Results and Analysis

Signal was observed at masses 78, 79, 106, 107, and 108, and angular distributions were obtained for each. In addition, signal at masses 65 and 91 was observed in TOF measurements. The mass 107 signal, shown in Figure 1, was the most intense, 200 counts/s at the peak angle, which coincides with the most probable CM angle. The angular distribution is very narrowly peaked about the CM angle, characteristic of a product formed by the elimination of a very light particle from the relatively massive O-toluene adduct. All other angular and TOF distributions (mass 78, 79,

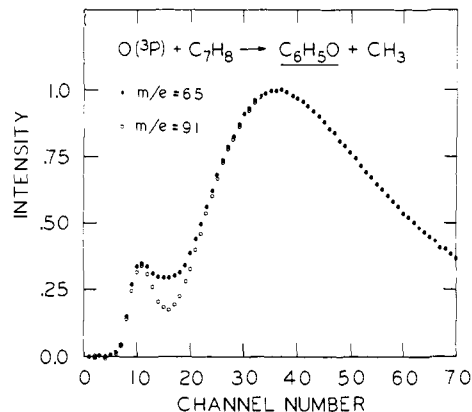


Figure 2. Time-of-flight distributions of mass 65 and mass 91 taken at the center-of-mass angle,  $59^\circ$ . The channel width is 12  $\mu s$ .

106, and 108) are superimposable on the mass 107 angular and TOF distributions, indicating that they arise from a common neutral parent through cracking in the electron bombardment ionizer. If C-H bond cleavage, leading to H atom and methylphenoxy radical, is the primary reaction, we expect to see parent mass 107 ions ( $C_7H_7O^+$ ), daughter ions of various masses including 106, 79, and 78, and a small amount of mass 108 ions from the  $^{13}C$  and  $^2H$  isotopic impurities in the 107 product. From the natural abundance of these isotopes, the 108/107 ratio should be 0.077. Experimentally the 108/107 intensity ratio is  $0.075 \pm 0.003$ , which strongly suggests that H atom elimination is a primary product and that the mass 108 does not arise from the formation of an O-toluene adduct which lives milliseconds to reach the detector. More conclusively, the width of the mass 107 (and 108) angular distribution is found to be wider than the centroid distribution, which is only possible if a particle has been emitted from the O-toluene complex. Were the 108 signal to arise from a long-lived O-toluene adduct which reaches the ionizer, the angular distribution would be exactly superimposable on the centroid distribution.

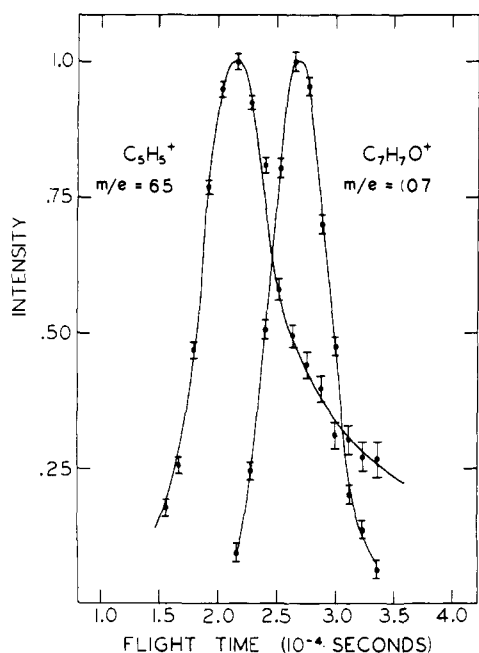
Observation of the  $CH_3$  elimination proved to be more troublesome. The products,  $CH_3$  and phenoxy radicals, are very difficult to observe directly because the parent ion of phenoxy, mass 93, is obscured by elastic scattering of toluene ( $^{13}C$  contaminant) while detection of the light  $CH_3$  is kinematically unfavorable. In the O + benzene study,<sup>1</sup> the phenoxy radical product fragmented in the ionizer to give mass 65 as the major daughter ion, greatly exceeding the parent in intensity. Although mass 65 is also a minor daughter ion of toluene, we found that the reactive contribution to the mass 65 signal could be separated in the TOF spectra. In Figure 2 are shown the TOF spectra of mass 91 (essentially pure toluene) and mass 65. The 91 spectrum contains two major features, a fast and narrow elastic toluene peak and a broad slow peak of background toluene effusing into the detector chamber with a Maxwell-Boltzmann distribution. It is obvious that the mass 65 spectrum contains an extra component falling between the main peaks. The shape of the reactive component was obtained by subtracting the two spectra (after correcting for the difference in ion flight times) and is shown in Figure 3 together with the TOF spectrum of mass 107, obtained at the same angle. The displacement in time and increased width of the mass 65 data unambiguously confirm the existence of a second primary reaction channel which we identify as the methyl elimination to give phenoxy radical.

From the relative intensities of the reactive signal at mass 65 and the signal at mass 107, we can obtain a rough estimate of the branching ratio. The integrated TOF signal for the  $CH_3$  elimination is 4.8 times that for the H atom elimination. To obtain the relative cross section, the raw signal must be corrected for total detection efficiency, which includes ionization cross section, ionizer fragmentation, and kinematic differences for the two species. For these purposes, the kinematic factor is the most significant because the difference between elimination of the H atom, mass 1, compared to the  $CH_3$ , mass 15, results in a much

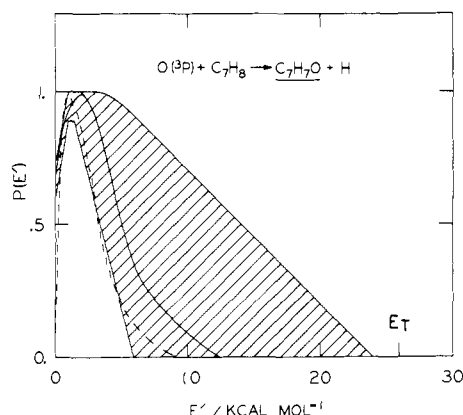
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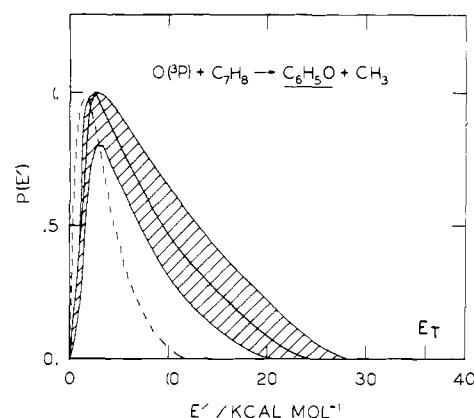
**Figure 3.** TOF spectra of mass 107 and mass 65 at the center of mass angle. The mass 65 has been corrected for elastic contributions.



**Figure 4.** Product translational energy distribution for the H atom elimination channel. Solid line with shaded area showing uncertainty is the experimental. Dashed line is phase space calculation.

higher efficiency for detecting the mass 107 product which is not scattered into as large a volume. The procedure for obtaining the kinematic factor is, first, to fit the data with a CM angular and velocity distribution and, then, to use these to calculate the integrated laboratory intensity at the CM angle for each reaction channel. It is found that the ratio of kinematic factors  $k(\text{CH}_3)/k(\text{H}) = 0.05$  at the peak of the mass 107 product angular distribution, which means that for equal reaction cross sections, we would observe H-atom elimination signal 20 times that of the methyl elimination. With the assumption that the total ionization cross section and fragmentation effects are equal for the two products, we find that the H-atom elimination is only 1% (less than 5% and greater than 0.5%) of the overall reaction.

In order to obtain the product translational energy,  $P(E)$ , and the CM angular distribution,  $T(\theta)$ , flexible functional forms were assumed, and a trial-and-error method was employed to produce a best fit to the laboratory angular and TOF data. The mass 107 data were consistent with an isotropic  $T(\theta)$ , suggesting that the mechanism involves initial formation of a complex which lives many rotational periods before H atom loss. The best-fit  $P(E)$ , shown in Figure 4, has large uncertainty because the detected particle is so heavy relative to the leaving group that its final velocity is insensitive to the translational energy. The product is found to average relatively low energy, 3.6 kcal/mol in translation, slightly higher than the statistical phase space calculation.



**Figure 5.** Product translational energy distribution for the methyl elimination channel. Solid line with shaded area, is experimental determination; dashed line, phase space calculation.

The  $\text{CH}_3$  elimination channel was fit rather well by the  $P(E)$  shown in Figure 5 and an isotropic  $T(\theta)$ . The average translational energy is higher than for the H atom channel, 8.0 kcal/mol, and it is also seen to be somewhat higher than the statistical calculation predicts.

## Discussion

The oxygen atom approaches a toluene molecule on a triplet potential energy surface and, being electrophilic in nature, probably attacks the aromatic ring as opposed to the aliphatic side group. There are several stable molecules with the formula  $\text{C}_7\text{H}_8\text{O}$ , including the cresols and methoxybenzene, but all have singlet ground states and are accessible only with atomic rearrangements. The O-toluene adduct is probably one of several triplet diradical species analogous to those formed in the reactions of  $\text{O}(^3\text{P})$  with other unsaturated hydrocarbons.<sup>6</sup>

In the absence of collisions, the fate of the O-toluene adduct should depend on the relative ease of three general processes: (1) simple bond cleavage, with loss of a H atom or  $\text{CH}_3$  group yielding radical products, (2) molecular elimination, such as loss of  $\text{H}_2$ , leaving benzaldehyde, and (3) intersystem crossing with atomic rearrangement leading to a stable singlet species. In a completely collision-free environment, process 3 would also lead to decomposition products, but the lifetime would be exceedingly long, greater than milliseconds. A number of studies of this reaction in the gas phase have contributed to our present knowledge of the mechanism. An early study by Jones and Cvetanovic<sup>7</sup> found the major reaction product to be a material of low volatility, a tar, which suggests that radical primary products may be important. In that study as well as subsequent bulk-phase experiments,<sup>8</sup> cresols and usually phenol were observed, and the distribution of cresols strongly favored ortho and para, suggesting the electrophilic nature of the oxygen attack. Deducing the primary reaction mechanism from these works is complicated by the uncertainty concerning the secondary reaction of the radical products and the importance of collision-induced intersystem crossing. In the reaction  $\text{O} + \text{benzene}$ , two primary reactions were observed under single collision conditions. The H-atom elimination was found to compete with intersystem crossing to give singlet phenol. The H-atom channel was major, about 85% of the total at collision energy, 6.5 kcal/mol. In contrast, the reaction with toluene is found here to result exclusively in radical products, principally  $\text{CH}_3 + \text{phenoxy}$  with a small amount of H + cresoxy radical. There is no evidence for stabilized singlet species such as cresol. The experiment is very sensitive to the occurrence of such stabilization, and we can

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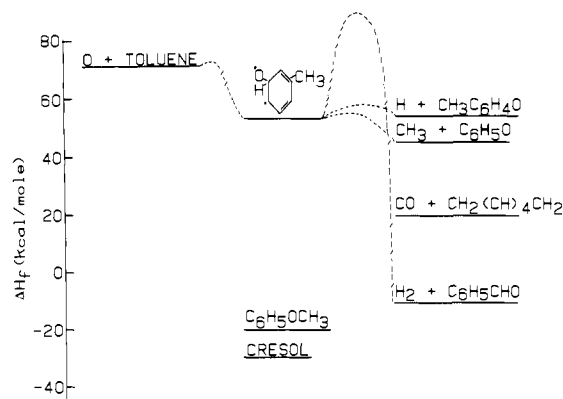


Figure 6.  $O(^3P)$  + toluene energy level diagram. Heats of formation at 300 °C in kcal/mol.

conclude that this process is less than 10% of the H-atom elimination, that is, less than 0.1% of the overall.

The energetics of the reaction are shown in Figure 6 with published heats of formation used where possible and others estimated by using group contributions.<sup>9</sup> The exothermicity of the  $CH_3$  loss ( $\Delta H = -25$  kcal/mol) is significantly greater than that for H-atom elimination ( $\Delta H = -16$  kcal/mol), and even with the inclusion of the probable exit channel barriers, the  $CH_3$  channel is energetically favored. The barriers are present because the reverse reaction is not a typical radical-radical recombination but is the addition of a radical to an unsaturated site yielding a diradical. The energy of the triplet diradical intermediate can be estimated from Benson's group additivity rules or by using 83 kcal/mol<sup>10</sup> as a typical  $S_0-T_1$  excitation for a phenol. Both methods give 53 kcal/mol for the heat of formation, and this makes the diradical almost unbound with respect to  $CH_3$  loss. Whether this process is truly accessible depends, however, on the preferred site for oxygen attack on the ring and the subsequent mobility of atoms or groups in the adduct. If the O atom either makes facile 1,2 shifts or remains associated with the  $\pi$  system as a whole, then the C-H and C- $CH_3$  cleavages will be competing processes for unimolecular decay. RRKM calculations for the two processes, using the energetics shown in Figure 6, results in the ratio  $\sigma_H/\sigma_{CH_3} = 0.05$ , in reasonably good agreement with the experimental results.

Typical electrophilic substitution is generally regarded as resulting from a localized attack of the electrophile. If this is true of  $O +$  toluene, then attack on the ring carbons with H atoms attached should lead preferentially to H-atom loss, and the ratio of H to  $CH_3$  loss would be determined more by entrance channel preference for the different addition sites. The methyl-containing ring carbon is the most electron-rich site but also has the greatest steric hindrance, and it is unclear why addition to this carbon would be so overwhelmingly favored. The experimental branching ratio is more easily explained by assuming either a delocalized addition of O to the ring or facile oxygen migration in the adduct.

It would appear that collisionless intersystem crossing in  $O +$  toluene does not play a significant role in contrast to  $O +$  benzene. The factors which influence the ease of intersystem crossing in these triplet diradicals are not well-known, but the availability of a facile decomposition route like the methyl elimination may shorten the lifetime of the complex sufficiently to prevent significant surface crossing from occurring.

Our tentative identification of the two products as phenoxy and cresoxy radicals is not definitive due to the limitations of the mass spectral data. It is impossible to rule out other processes such as ring opening and complex fissions, but the barriers to these would probably be prohibitive. A previous study of  $O +$  toluene by Sloane<sup>11</sup> used effusive beams of reactants in a near single collision environment. Products were detected by electron bombardment ionization with variable electron energy to measure appearance potentials of the ions. Products were observed at mass 108, 106, and 80 and were identified as an addition complex (mass 108), benzaldehyde (mass 106), and an open-chain olefin ( $C-H_2(CH)_4CH_2$ ). No mass 107 product was reported. Those results are in poor agreement with our conclusion from this study, and the reasons for the discrepancies are not readily apparent, although the stabilized adduct in Sloane's study may have been from secondary collisions.

The product translational energy distributions obtained in this experiment are not as well determined as in other reactions with more favorable kinematics; however, several features are useful for understanding the reaction dynamics. The highest product translational energy observed in both channels is less than 20 kcal/mol, in agreement with the exothermicities of the reactions. The elimination of a molecular species is typically far more exothermic and would lead to more translational energy.

Both experimental  $P(E)$  average slightly more energy in translation than the phase space calculations (dashed line) predict. This deviation is a common feature in reactions for which there is an exit channel barrier; the parting molecules tend to pick up some of this energy in translation as they descend the barrier. As explained earlier, both reaction channels should have exit channel barriers, similar in size to those for the addition of H or  $CH_3$  to a double bond, 3 or 8 kcal/mol, respectively.

### Conclusion

The reaction of oxygen atoms with toluene leads to a long-lived complex, probably the triplet diradical, which dissociates preferentially to radical products, 1% H + cresoxy radical and 99%  $CH_3 +$  phenoxy. Unlike the  $O +$  benzene reaction, intersystem crossing to a stable singlet species does not occur to a detectable extent. The products are isotropically distributed with translational energy somewhat greater than statistical, presumably because an exit channel barrier increases the partitioning of energy to relative motion.

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**Registry No.** O atom, 17778-80-2;  $O_2$ , 7782-44-7; toluene, 108-88-3.

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