

The excited singlet state of monochlorobenzene couples with the decomposing levels to give phenyl radicals and chlorine atoms and with the triplet manifold.<sup>11</sup> The probability of the transition from the excited singlet state to the decomposing levels should be dependent on the vibrational energy since the photodecomposition quantum yield increases with increasing the excitation energy. The vibrational relaxation in the solid matrix, being faster than radiationless decay processes from the excited singlet state, can transfer the molecule to the lowest excited singlet state which results in the increased fluorescence quantum yield in the solid matrix. Experiments in the vapor phase, such as wavelength and pressure effects on  $\Phi_F$ , must clarify complicated mechanisms mentioned above and are now undertaken.<sup>9</sup>

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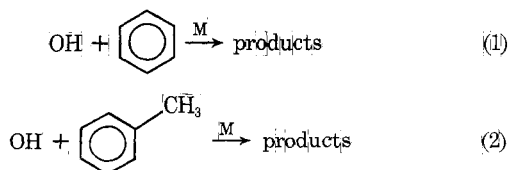
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### A Kinetics Study of the Reaction of the OH Free Radical with Aromatic Compounds. I. Absolute Rate Constants for Reaction with Benzene and Toluene at 300°K

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Sir: Whereas considerable work has been reported on the reaction of OH with paraffinic and olefinic hydrocarbons,<sup>1-8</sup> virtually no systematic study has been carried out on aromatics. We wish to report, therefore, a recent study completed in our laboratory involving the reaction of OH with two aromatic compounds, benzene and toluene.



To the best of our knowledge, the absolute rate constants given represent the first absolute rate constants reported for these organic species. The importance of these new measurements (in addition to their obvious fundamental

TABLE I: Rate Constant Measurements for Reaction of OH with Benzene at 298°K<sup>a</sup>

Helium, Torr	H <sub>2</sub> O, mTorr	Ben- zene, mTorr	Flash ener- gy, J	k <sub>1</sub> , sec <sup>-1</sup>	10 <sup>12</sup> k <sub>bimolec</sub> , cc mole- cule <sup>-1</sup> sec <sup>-1</sup>
3	100	0	88	210	
3	100	2	88	267	
3	100	4	88	322	
3	100	8	88	430	0.849 ± 0.08
20	100	0	88	68	
20	100	0.5	88	87	
20	100	3	88	205	
20	100	5	88	295	
20	100	5	88 <sup>b</sup>	330	
20	100	5	45	290	
20	100	5	180	330	
20	100	8	88	420	1.36 ± 0.09
100	100	0	88	36	
100	100	3	88	190	
100	200	6	88	350	
100	100	9	88	500	1.59 ± 0.12

<sup>a</sup> CaF<sub>2</sub> window used in all experiments. <sup>b</sup> 150 flashes/gas filling (for all other experiments only 30 flashes/filling was used).

TABLE II: Rate Constant Measurements for Reaction of OH with Toluene at 298°K<sup>a</sup>

Helium, Torr	H <sub>2</sub> O, mTorr	Tol- uene, mTorr	Flash energy, J	k <sub>2</sub> , sec <sup>-1</sup>	10 <sup>12</sup> k <sub>bimolec</sub> , cc molecule <sup>-1</sup> sec <sup>-1</sup>
3	100	0	88	210	
3	100	1	88	325	
3	100	1.5	88	390	
3	100	2	88	450	
3	100	3	88	565	3.60 ± 0.26
20	100	0	88	68	
20	100	0.5	88	170	
20	100	1	88	240	
20	100	1.5	88	330	
20	100	1.5	88 <sup>b</sup>	310	
20	100	1.5	45	290	
20	100	1.5	180	350	
20	100	2	88	390	
20	100	3	88	555	
20	100	4.5	88	790	5.00 ± 0.18
100	100	0	88	36	
100	100	1	88	250	
100	100	2	88	425	
100	100	3	88	630	6.11 ± 0.40

<sup>a,b</sup> See corresponding footnotes to Table I.

significance to kinetics) lies in the fact that OH-aromatic reactions are of major concern in the combustion of non-leaded gasoline and in the formation of photochemical smog. For example, recent examinations of the emissions from cars running on regular nonleaded gasoline have shown that over 20% of the hydrocarbons emitted were aromatics.<sup>9</sup>

In this study the reaction of OH with benzene and toluene was followed by monitoring the concentration of OH as a function of time. The detection technique for OH was

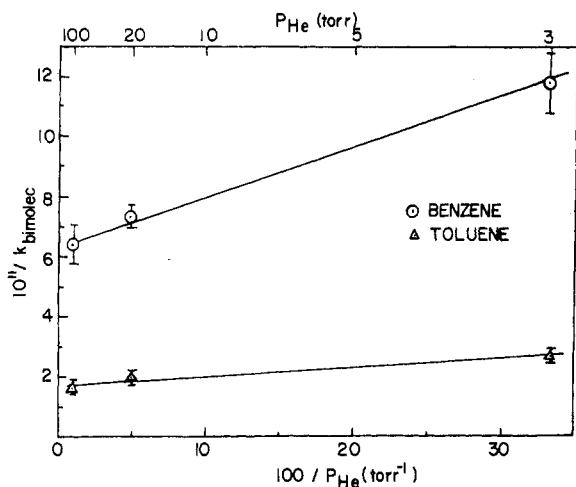


Figure 1. A  $1/k$  vs.  $1/p$  Lindemann plot showing the pressure dependence of the reaction of OH with benzene and toluene.

that of resonance fluorescence which has been discussed in detail in previous publications.<sup>10,11</sup> The photolysis of  $H_2O$  (in the region above the  $CaF_2$  cut off at 1250 Å) as a source of OH has also been described in earlier work.<sup>11</sup>

In all experiments reported here, gas mixtures were made up using an all-glass gas handling system. The toluene and benzene used in this study were from Fischer Scientific Co. and had a purity level of 99.96% or better. All low-pressure measurements of toluene, benzene, and  $H_2O$  were made using a MKS Baratron. High-pressure measurements (10–800 Torr) were made with a two-turn Bourdon gauge (Wallace and Tiernan Type FA145). The precision to which gas mixtures could be prepared, with the exception of  $H_2O$ , was estimated to be ~3% or better.

The results from experiments performed at various total helium pressures are shown in Tables I and II. Of considerable interest here is the observed pressure dependence for the reaction of OH with both benzene and toluene; also there is the fact that for both compounds rather large  $k$  values were measured at 100 Torr He pressure,  $k_1 = 1.59 \pm 0.12 \times 10^{-12}$  and  $k_2 = 6.11 \pm 0.40 \times 10^{-12}$   $cm^3$  molecule<sup>-1</sup> sec<sup>-1</sup>. In each case, the bimolecular rate constants reported were obtained from the slope of a plot of the pseudo-first-order rate constant  $k$  vs. the aromatic concentration. The nonzero value for  $k$  at zero reactant pressure represents the loss rate of OH due to diffusion out of the sampling region.<sup>10,11</sup> A close examination of the pressure dependence shown in Tables I and II for benzene and toluene indicates that over the pressure range studied in this work the reported rate constants are in the pressure fall off region for each reaction (e.g., the rate constant is not a true third-order rate constant nor is it a true bimolecular rate). The rate constant reported, therefore, is calculated in the form of a bimolecular rate constant at each total gas pressure employed. To better estimate the high-pressure limiting  $k$  value for these processes, a Lindemann plot ( $1/k$  vs.  $1/p$ ) is given for both aromatics in Figure 1. This figure clearly shows that benzene has a greater pressure dependency than toluene as might be expected; but, somewhat surprisingly, it also indicates that a very significant fraction of the total reaction of toluene with OH proceeds by the addition of OH to the aromatic ring. The evidence here is the fact that the change in the effective bimolecular rate constant from 3 Torr to 100 Torr is nearly a factor of 2. Since only the addition reaction would show a pressure dependence, it is

concluded that at least half of the total reaction is additions. Because of the weak benzyl carbon–hydrogen bond in toluene it is to be expected that some abstraction is also occurring although our data only indicate that the importance of this process is probably less than 50% of the total reaction. The dependence of the bimolecular rate constant on the total pressure for both reactions 1 and 2 can be explained on the basis of OH adding directly to the aromatic ring. A possible explanation for the observed difference in the pressure dependency for the two reactions is the larger number of degrees of freedom available in the case of toluene for stabilization of the transition complex. Figure 1 also indicates that toluene is more reactive than benzene by at least a factor of 4. This can be explained by the higher efficiency of the addition process for reaction 2, but also important, as indicated above, is the fact that reaction 2 can proceed by abstraction as well as by addition. The second process would involve abstracting a hydrogen atom from the methyl group on toluene.

There has been much speculation as to whether OH only abstracts the  $\alpha$  hydrogens of branched aromatics or whether addition to the ring is possible. This study indicates that the addition process is very important for toluene and will therefore have a very significant effect on the product distribution resulting from reaction 2.

Concerning the possible role of aromatics in smog formation, an examination of Figure 1 would indicate that at near atmospheric pressure (for the case of  $M = He$ ) the respective rate constants for processes 1 and 2 would probably be very close to their 100-Torr values,  $1.59 \times 10^{-12}$  and  $6.11 \times 10^{-12}$   $cm^3$  molecule<sup>-1</sup> sec<sup>-1</sup>. Using an estimated OH steady-state concentration for the atmosphere of  $5 \times 10^6$  molecules/cc would therefore give a  $1/e$  lifetime for benzene and toluene of ~36 and 10 hr under daylight conditions. (This would probably be even shorter if rate constants for  $M = N_2$  were to be used.) From these simple calculations, along with available concentration data, aromatic compounds would now appear to contribute to the formation of photochemical smog in areas involving heavy automobile traffic.

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