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A KINETIC STUDY OF RADICAL-AROMATIC HYDROCARBON REACTIONS

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Molecular Sciences Group
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Co-Principal Investigators:

Dr. A.R. Ravishankara   Dr. F.P. Tully

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PROGRESS REPORT

During the first 21 months of our DOE program, we have constructed a "slow flow" high temperature flash photolysis-resonance fluorescence apparatus which utilizes an all quartz reactor. This apparatus has been used to measure absolute rate constants as a function of temperature and pressure for the reactions of OH radicals with the following prototype aromatic hydrocarbons:

$$\mathrm{OH} + \mathrm{C_6H_6} \xrightarrow{k_1} \text{Products} \qquad 250\text{-}981\ \mathrm{K} \tag{1}$$

$$\mathrm{OH} + \mathrm{C_6D_6} \xrightarrow{k_2} \text{Products} \qquad 250\text{-}981\ \mathrm{K} \tag{2}$$

$$\mathrm{OH} + \mathrm{C_6H_5CH_3} \xrightarrow{k_3} \text{Products} \qquad 213\text{-}1046\ \mathrm{K} \tag{3}$$

$$\mathrm{OH} + \mathrm{C_6H_5CD_3} \xrightarrow{k_4} \text{Products} \qquad 250\text{-}966\ \mathrm{K} \tag{4}$$

$$\mathrm{IG} + \mathrm{C_6D_5CD_3} \xrightarrow{k_5} \text{Products} \qquad 250\text{-}961\ \mathrm{K}\ . \tag{5}$$

In the following sections details of the kinetic investigations are described. We are, at present, analyzing the non-exponential OH decays that were obtained in the temperature range of 325-425 K to extract both thermodynamic and kinetic information on the OH-Aromatic adduct. Concurrently attempts are being made to assign branching ratios for various reactive channels as a function of temperature using the measured kinetic isotope effects.

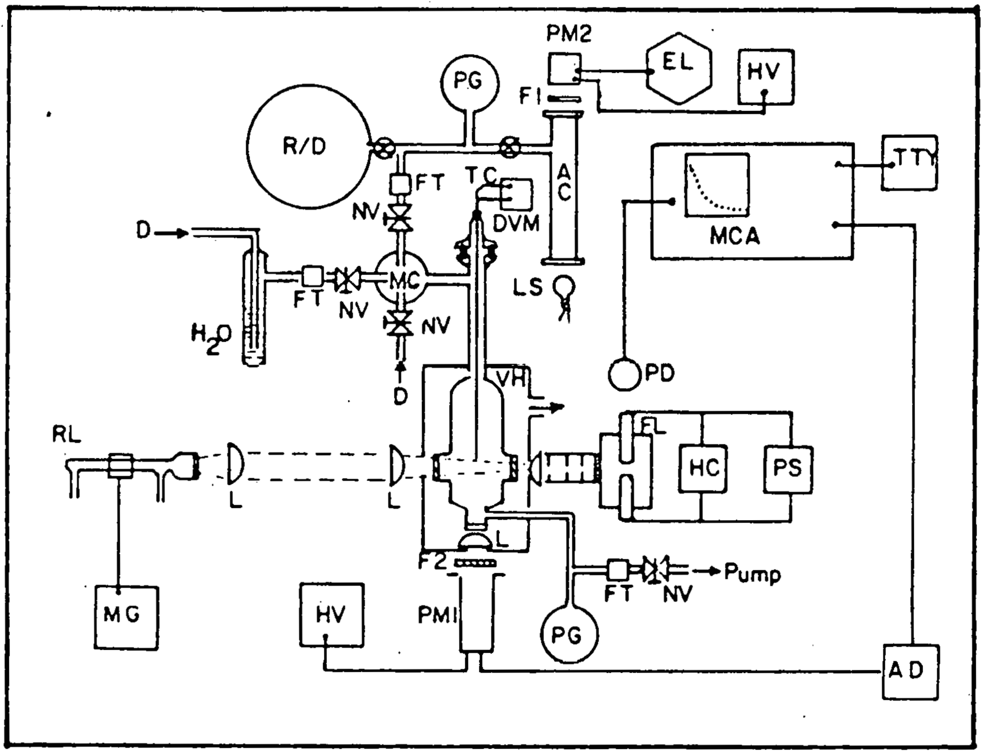
A flash photolysis-resonance fluorescence system designed for $O(^3P)$ and $H(^2S)$ reaction studies is now under construction, and is expected to be in operation in the next few weeks. It is anticipated that the optimization of the system followed by data acquisition on $O(^3P)$ atom reactions will be well underway during the current year.

Experimental

The utilization of the flash photolysis-resonance fluorescence technique to study the reactions $OH(^2\pi)$ radicals is well established and is amply described in the literature.[1,2,3] Recently, we have modified this technique to permit rate constant measurements up to ∿ 1000K; a discussion of apparatus modifications necessary to carry out high temperature measurements, is given elsewhere.[4] Hence, we will limit the following discussion to a brief review with elaboration only on those features that are necessary to understand this work.

A schematic diagram of the experimental apparatus is shown in Figure 1. The principal components are (1) a thermostated reaction cell, (2) a spark discharge flashlamp perpendicular to one face of the cell, (3) a CW OH resonance lamp perpendicular to the photolysis beam, (4) a photomultiplier/bandpass filter combination for monitoring OH resonance fluorescence perpendicular to both the photolysis and the resonance radiation beams, and (5) a signal averager and fast photon counting electronics.

During the course of this investigation two separate reactors were utilized. For low temperature studies, i.e., 213-350 K, an all pyrex-jacketed reactor with an internal volume of ∿ 150 cm^3 was used. The cell was maintained at a known constant temperature by cicrulating either methanol (213-298 K) or ethylene glycol (298-350 K) from a thermostated bath through the outer jacket. For high temperature studies, i.e., 298-1050 K, an all quartz reactor with an internal volume of ∿ 300 cm^3 was used. The reaction cell was resistively heated using electrically insulated tantalum wire windings mounted to its graphite-coated outer surface. The



AC - Absorption Cell
AD - Amplifier-Discriminator
D - Diluent Gas
DVM - Digital Voltmeter
EL - Electrometer
F1 - 253.7 nm Bandpass Filter
F2 - 309.5 nm Bandpass Filter
FL - Flashlamp
FT - Flow Transducer
HC - High Voltage Capacitor
HV - High Voltage
L - Lens
LS - Light Source (Hg Pen-ray Lamp)

MC - Mixing Chamber
MCA - Multichannel Analyzer
MG - Microwave Generator
NV - Needle Valve
PD - Photo Diode
PG - Pressure Guage
PMI - Photomultiplier 1P28
PM2 - Photomultiplier RCA 8850
PS - High Voltage Power Supply
R/D - Reactant/Diluent Gas
RL - Resonance Lamp
TC - Thermocouple
TTY - Teletype
VH - Vacuum Housing

Figure 1. Schematic Diagram of a High Temperature Flash Photolysis-Resonance Fluorescence Apparatus.

temperature of the gaseous mixtures inside reactor was directly measured with a retractable chromel-alumel thermocouple (encased in a quartz tube) which was introduced into the reactor through a cajon ultra-torr fitting. It was found that temperature gradient in the vicinity of the reaction zone was very small (i.e., $\Delta T \simeq 5K$ at ∿ 1000K).

OH radicals were produced by flash photolysis of H_2O at wavelengths between the onset of absorption at ∿ 185 nm and the suprasil cutoff at ∿ 165 nm (flash duration ∿ 50 μsec). Following the flash, weakly focused OH resonance lamp radiation continuously excited resonance fluorescence in the 0-0 band of the $A^2\Sigma^+ - X^2\pi$ system; the resulting fluorescence emanating in the direction perpendicular to both the resonance excitation beam and the photolysis beam was collected by a lens and focused onto a photolmultiplier fitted with an interference filter (309.5 nm peak transmission, 10 nm FWHM). Signals were obtained by photon counting and then fed into a signal averager operating in the multichannel scaling mode. For each decay rate measured, sufficient flashes were averaged to obtain a well defined temporal profile over at least a factor of ten variation in [OH].

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under "slow-flow" conditions. The flow rate through the cell was such that each photolysis flash encountered a fresh mixture (photolysis repetition rate ∿ 0.3 Hz). The aromatic hydrocarbon (RH) was flowed from a 12ℓ bulb containing an RH/diluent mixture, while the water mixture was generated by bubbling diluent gas through distilled water at room temperature and a pressure of 800 Torr. The RH/diluent mixture, the water mixture, and additional diluent gas were premixed before entering the reaction cell. Concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates (measured using calibrated mass flow meters) and the total pressure. The fraction of aromatic hydrocarbon in the RH/diluent mixture was checked frequently by simultaneous measurements of the total pressure (of the mixture) and the aromatic hydrocarbon absorption at 253.7 nm. The measurements were carried out using a mercury pen-ray lamp as the light source, a 70 cm long absorption cell, and a bandpass filter-photomultiplier tube combination. The absorption cross section (at 253.7 nm) used to determine the concentration of each aromatic hydrocarbon was measured during the course of the experiments; they were: C_6H_6, 3.67×10^{-19} cm^2; $C_6H_5CH_3$, 4.78×10^{-19} cm^2; C_6D_6, 2.39×10^{-19} cm^2; $C_6H_5CD_3$, 5.26×10^{-19} cm^2; $C_6D_5CD_3$, 4.51×10^{-19} cm^2.

The diluent gases used in this study had the following stated purities: Ar > 99.9995%, He > 99.9999%, SV_6 > 99.99%. They were used without further purification. Benzene (C_6H_6) and toluene (C_7H_8) were obtained from J.T. Baker, Co., and each had an analyzed purity of > 99.99%. The deuterated aromatics were obtained from Merck, Sharpe and Dohme, Canada, Ltd. Their chemical purity was greater than 99.99% and their isotopic purity was as follows: C_6D_6 (> 9.96% D), $C_6H_5CD_3$ (99.0% D), and $C_6D_5CD_3$ (> 99.5% D). All these hydrocarbons were degassed before use.

Results

All experiments were carried out under pseudo-first order conditions with [RH] >> [OH]. Under such experimental conditions, unless there are secondary reaction complications, the rate of disappearance of OH radicals follows a simple exponential rate law:

$$[OH]_t = [OH]_o \, e^{-(k[RH] + k_d)t} \equiv [OH]_o \, e^{-k't} \qquad \text{I}$$

$$\text{i.e., } k' \equiv k[RH] + k_d \qquad \text{II}$$

where k_d is the first order OH disappearance rate in the absence of RH; this loss is due to diffusion of OH from the viewing zone of the reactor as well as reaction with background impurities. k is the bimolecular rate constant for the reaction,

$$OH + RH \xrightarrow{k} \text{products} \quad .$$

In the temperature intervals 400 to 1000 K and 213 to 320 K, we did indeed observe exponential OH decays such as those shown in Figure 2. The slope of the line gives k'. k' was then measured as a function of [RH]. As seen from Equation II, k' varies linearly with [RH]. Figure 3 shows a plot of k' vs. [RH] the slope of which gives the bimolecular rate constant k. The solid lines drawn through the points are the least squares fit of these points to a straight line.

In the temperature range 325-425 K, two unusual phenomena were observed. (a) The OH decay curves were non-exponential, with the leading part of the decay faster than the tail. In addition, at very long times, the decay became exponential with a rate equal to k_d, the rate constant measured in the absence of aromatic hydrocarbon (Figure 4 shows one such

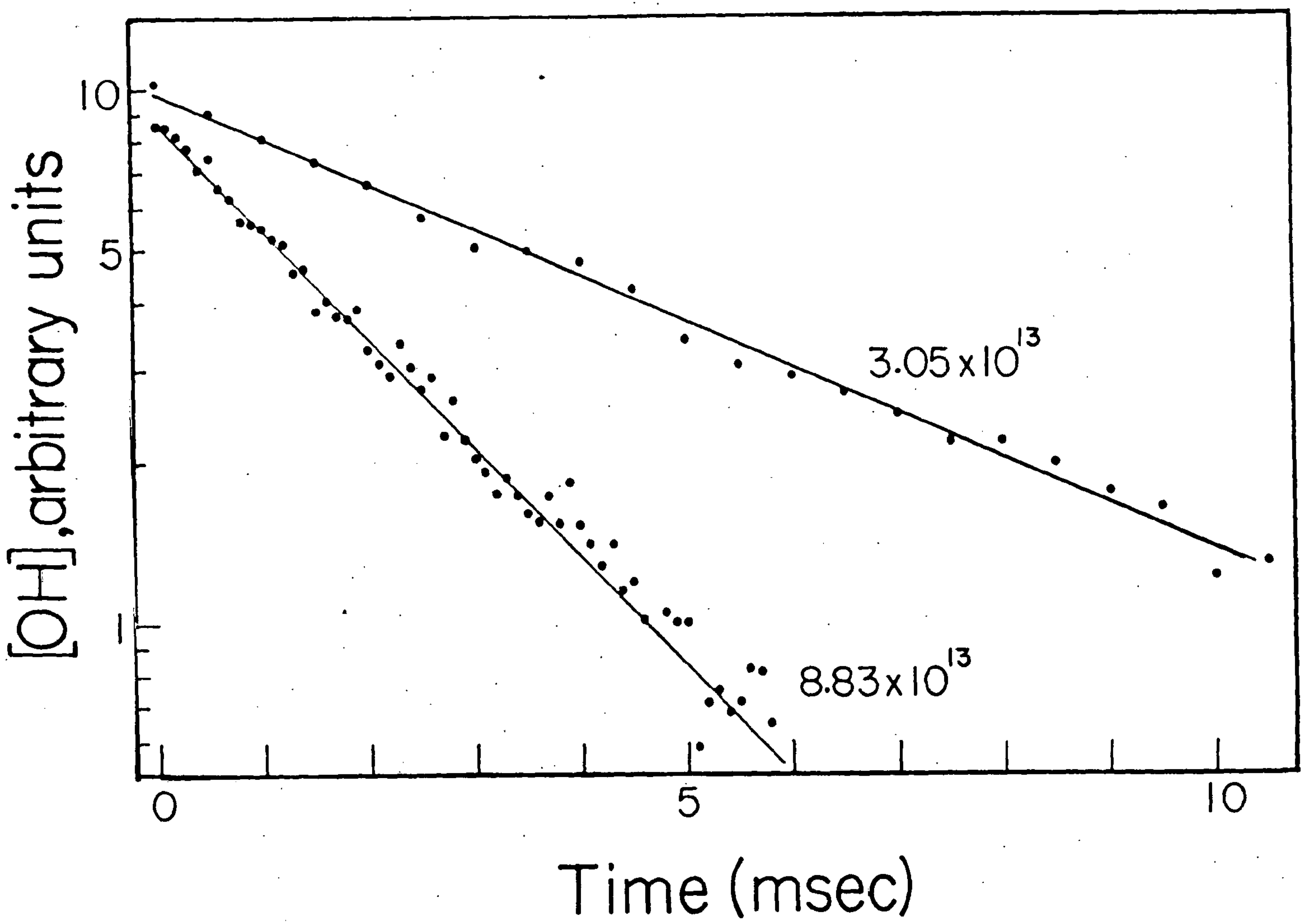


Figure 2. Typical OH Temporal Profiles Following Flash Photolysis of H_2O/Toluene/Diluent Mixture. Experimental Conditions: T = 793K, P = 100 Torr (Ar), Flash Energy = 88 J, $[H_2O]$ = 180 mTorr. Concentrations of Toluene are given next to the decay curves.

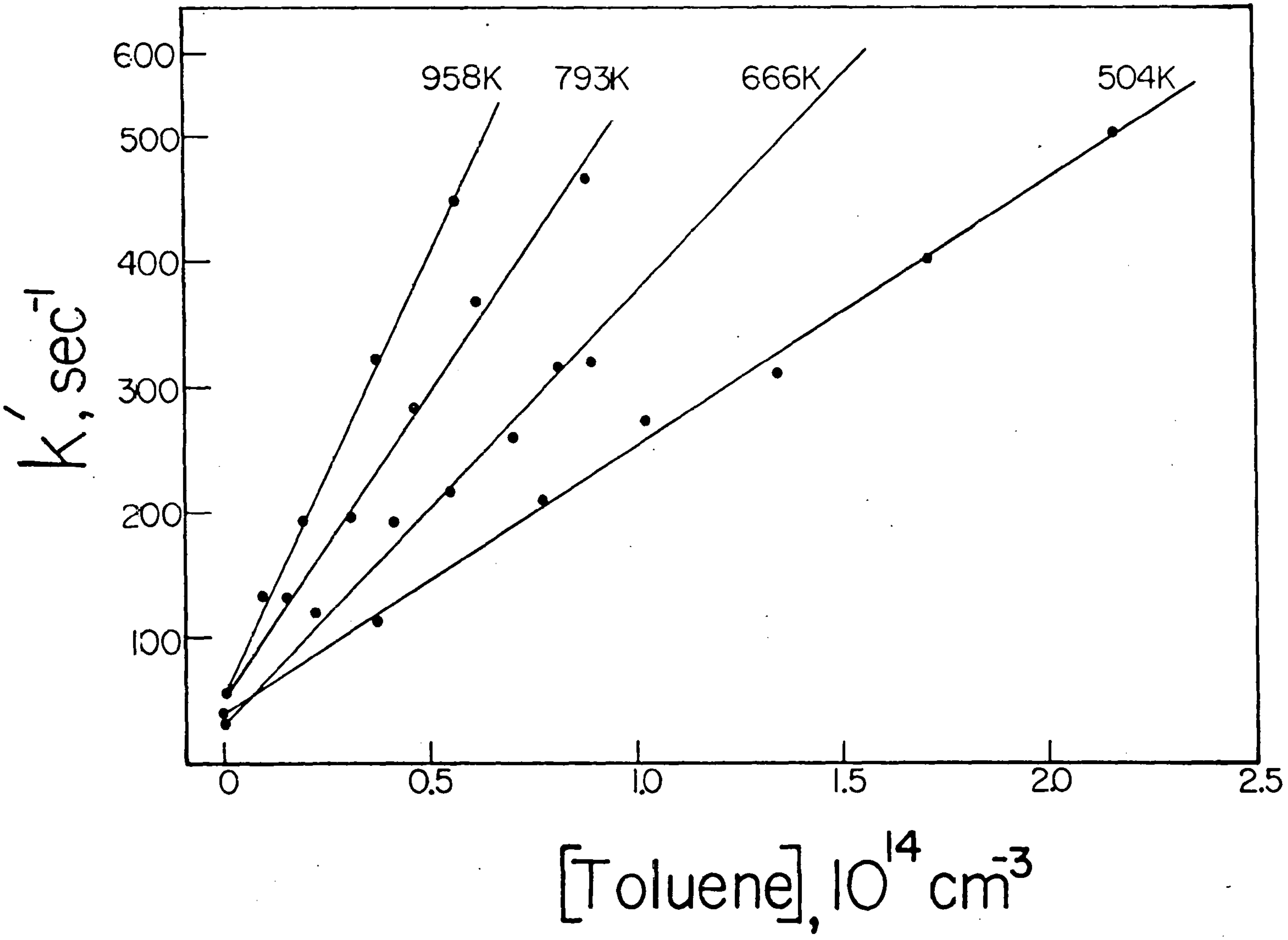


Figure 3. Typical Plots of the Pseudo-First Order Rate Constant vs [toluene] at Four Temperatures. Solid lines are obtained from linear least-squares analyses.

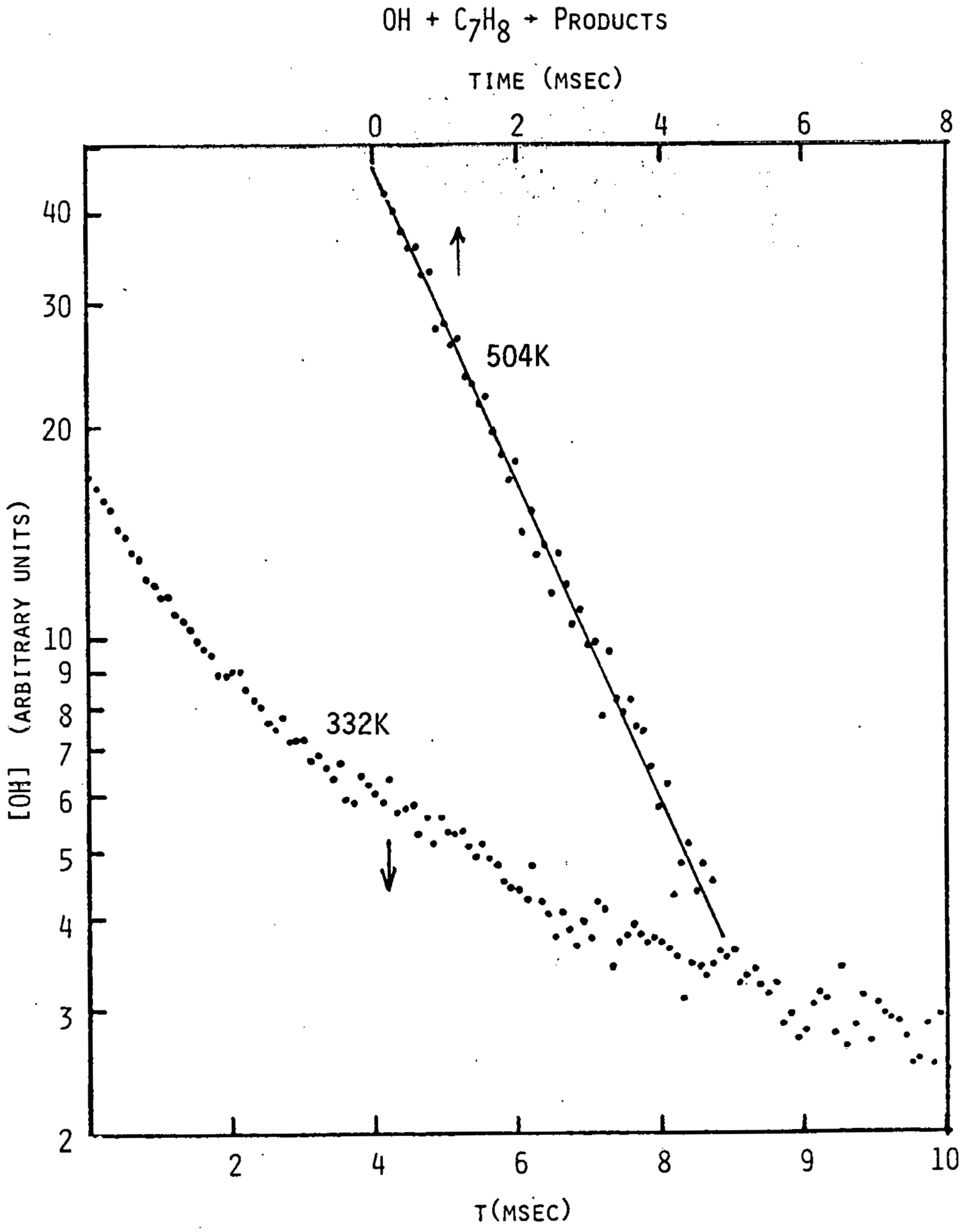


Figure 4. Typical Non-Exponential OH Temporal Profile Obtained Between 325-425 K for Reaction (3). For comparison an exponential OH decay obtained at 504K is also shown.

decay curve). (b) The bimolecular reaction rate coefficient (derived from the dependence of the initial slope of [RH]) decreased dramatically with increasing temperature.

Individual values of k' along with all pertinent experimental conditions are listed in Tables I-V. The bimolecular rate coefficients at various temperatures are given in Table VI, and pictorially represented in Figures 5 and 6 as plots of $\ell n k$ vs. 1/T (the conventional Arrhenius approach).

As seen in Figures 5 and 6, at low temperatures i.e., 213-325 K, the bimolecular rate constants are quite insensitive to changes in temperature with the exception of Reaction (3); k_3 seems to increase slowly with decreasing temperatures. It is also apparent that the bimolecular rate coefficients for all three toluenes are, within say 25%, the same. Similar behavior is observed for C_6H_6 and C_6D_6. At temperatures greather than 420K, k_1-k_5 all increase monotonically with increasing temperatures.

Table I. Rate Constant Data for the Reaction of OH with Benzene (C_6H_6).

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
250	50 (He)	70	60	0	80	
				4.80	135	
				11.23	182	
				11.90	221	
				15.73	273	
				19.92	300	
				26.11	377	
				31.09	402	
				38.31	467	1.11 ± 0.15
250	50 (Ar)	70	60	0	30	
				3.9	87	
				6.76	123	
				10.96	123	
				14.92	172	
				19.47	255	
				24.13	313	
				29.73	365	1.11 ± 0.06
250	100 (He)			0	40	
		130	70	7.26	150	
		130	70	12.46	169	
				12.5	180	
				13.87	195	
				14.14	220	
		130	30	14.43	196	
			70	20.96	332	
				25.64	330	
				25.97	274	
			30	27.79	360	
			70	27.91	340	
				29.16	381	

Temperature K	Diluent Gas Pressure Torr	[H_2O], mTorr	Flash Energy J	[C_6H_6] 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
				34.66	481	
				38.79	451	
			30	40.32	552	
			70	40.84	540	
				43.68	442	
				50.14	511	
				51.44	550	
				58.61	575	
				70.23	705	
				77.87	775	0.93 ± 0.09
250	100 (Ar)	70	70	0	46	
				3.00	87	
				6.43	122	
				7.08	136	
				14.35	234	
				18.51	260	
				19.50	261	
				22.07	317	
				24.50	299	
				26.58	346	
				37.52	462	
				47.96	535	1.04 ± 0.08
250	200 (He)	70	70	0	51	
				7.98	114	
				18.59	296	
				28.87	344	
				34.41	448	
				52.27	626	1.11 ± 0.13
270	50 (Ar)	100	70	0	28	
				6.45	109	
				11.18	172	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
				14.73	215	
				20.48	281	
				25.75	339	
				29.13	374	
				33.43	414	1.16 ± 0.05
270	100 (Ar)	120	70	0	41	
				1.53	56	
				4.18	94	
				7.85	141	
				10.08	179	
				12.80	206	
				18.11	258	
		120	120	18.32	246	
				19.21	258	
				23.25	339	1.20 ± 0.09
298	25 (He)	150	70	0	69	
				6.64	136	
				14.68	248	
				28.46	394	
				41.80	522	
				51.78	643	1.10 ± 0.05
	50 (He)	150	70	0	75	
				5.25	142	
				7.36	185	
				9.00	208	
				13.21	246	
				15.42	248	
				16.88	277	
				19.63	308	
				21.49	300	
				25.35	384	1.11 ± 0.24

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
298	50 (Ar)	120	60	0	27	
				1.51	52	
				5.74	98	
				7.29	120	
				9.76	144	
				13.13	199	
				16.55	228	
				19.57	261	1.20 ± 0.06
298	100 (He)	150	70	0	50	
				3.27	101	
				5.15	128	
				6.74	134	
				7.16	128	
				9.66	202	
				9.85	188	
				12.35	208	
				12.51	217	
				13.36	235	
298	100 (He)	150	70	15.67	244	
				17.56	278	
			70	18.67	240	
			70	18.83	290	
		300	120	22.13	345	
		75	38	22.31	332	
		150	70	26.91	425	
		150	120	27.20	424	
		150	60	27.46	385	
		150	70	37.01	9530	1.25 ± 0.06
298	100 (Ar)	120	60	0	25	
				4.07	65	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
				7.02	100	
				9.60	158	
				10.97	163	
				14.80	196	
				18.32	250	
				20.17	258	
				26.45	338	
				32.81	444	
				47.68	608	1.24 ± 0.09
298	200 (Ar)	130	70	0	52	
				7.25	165	
				14.44	244	
		130	120	14.45	258	
		260	70	14.76	253	
		130	70	23.46	344	
				31.47	452	
				39.74	523	
				44.36	607	1.19 ± 0.12
298	100 (SF_6)	130	70	0	94	
				6.13	159	
				9.10	200	
				17.45	291	
				22.01	351	
				26.67	393	
				32.26	445	1.11 ± 0.05
545	100 (Ar)	150	90	0	39	
				7.56	84	
				15.13	122	
				22.93	159	
				32.37	224	
				42.32	274	
				54.20	330	0.543 ± 0.023

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
620	100 (Ar)	150	90	0	40	
				4.38	70	
				9.35	106	
				13.56	141	
		300	130	13.59	139	
		150	90	16.59	152	
				20.03	168	
				25.08	202	
				33.73	255	
				42.73	321	0.639 ± 0.029
719	100 (Ar)	190	90	0	48	
				2.98	85	
				3.01	89	
				6.86	133	
				11.05	165	
				17.67	241	
				23.29	305	
				23.48	284	
				29.11	363	
				39.58	449	1.02 ± 0.04
816	101 (Ar)	140	90	0	50	
				3.69	105	
				6.23	142	
				7.60	176	
				11.47	218	
		140		11.75	235	
		70		14.24	253	
		140		18.01	309	
		234		21.65	341	
		140		27.10	441	1.59 ± 0.09

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{13} cm^{-3}	k', s^{-1}	k_1, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
917	102 (Ar)	190	80	0	47	
				2.37	109	
				4.25	156	
				5.58	167	
				6.03	189	
				10.27	266	
				13.12	292	
				16.20	376	
				18.65	440	
				22.45	504	2.26 ± 0.10
981	101 (Ar)	182	80	0	52	
				2.75	116	
				6.40	206	
		157		7.68	252	
		182		7.87	260	
				10.94	294	
				13.37	350	
				16.33	408	
				19.33	451	2.35 ± 0.23

Table II. Rate Constant Data for the Reaction of OH with Benzene-d_6 (C_6D_6).

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{14} cm^{-3}	k_2', s^{-1}	k_2, 10^{-13} $cm^{-3}molecule^{-1}s^{-1}$
250	100 (Ar)	75	62	0	31	
				0.81	126	
				1.39	186	
				2.33	302	
				3.41	414	
				4.83	551	10.8 ± 0.5
298	100 (Ar)	150	62	0	27	
				0.63	116	
				1.43	209	
				2.18	302	
				2.99	379	
				3.48	450	11.9 ± 0.5
	20 (Ar)	150	62	0	64	
				0.69	128	
				0.86	153	
				1.74	239	
				2.21	312	
				3.38	425	10.9 ± 0.7
298	20 (He)	150	62	0	109	
				0.94	172	
				1.19	217	
				1.79	267	
				1.80	285	
				2.45	342	
				3.32	406	
				3.50	424	
				3.99	472	9.20 ± 0.81
561	100 (Ar)	190	80	0	34	
				1.70	74	

Temperature K	Diluent Gas Pressure Torr	[H_2O], mTorr	Flash Energy J	[C_6H_6] 10^{14} cm^{-3}	k_2', s^{-1}	k_2, 10^{-13} cm^{-3}molecule^{-1}s^{-1}
				1.71	92	
				3.11	124	
		370		4.49	179	
		190	8	4.54	179	
				4.59	143	
			80	5.92	191	
			120	5.92	197	
			80	9.67	283	
				9.85	253	
				9.89	260	2.27 ± 0.30
649	100 (Ar)	190	80	0	46	
				0.81	81	
				1.78	111	
				3.62	175	
				4.58	209	
				5.55	237	
				6.62	252	
				8.12	285	3.00 ± 0.32
734	101 (Ar)	186	80	0	53	
				0.96	111	
				1.84	150	
				3.13	216	
				3.25	211	
				4.68	281	
				6.21	354	4.81 ± 0.19
830	100 (Ar)	190	80	0	58	
				0.60	108	
				1.25	150	
				2.07	225	
				2.82	259	
				4.13	360	7.20 ± 0.46

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_6]$ 10^{14} cm^{-3}	k_2', s^{-1}	k_2, 10^{-13} $cm^{-3}molecule^{-1}s^{-1}$
917	100 (Ar)	190	80	0	66	
				0.50	123	
				0.88	159	
				1.57	231	
				2.35	306	
				3.01	386	10.4 ± 0.3
981	101 (Ar)	197	80	0	72	
				0.31	113	
				0.67	144	
				1.20	214	
				1.87	272	10.8 ± 1.0
250	100 (Ar)	75	62	0	31	
				0.81	126	
				1.39	186	
				2.33	302	
				3.41	414	
				4.83	551	10.8 ± 0.5
298	100 (Ar)	150	62	0	27	
				0.63	116	
				1.43	209	
				2.18	302	
				2.99	379	
				3.48	450	11.9 ± 0.5
	20 (Ar)	150	62	0	64	
				0.69	128	
				0.86	153	
				1.74	239	
				2.21	312	
				3.38	425	10.9 ± 0.7

Table III. Rate Constant Data for the Reaction of OH with Toluene ($C_6H_5CH_3$).

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
213	100 (Ar)	40	62	0	20	
				1.69	154	
				3.47	236	
				3.98	337	
				5.11	458	
				6.93	574	8.20 ± 0.54
231	100 (Ar)	50	62	0	35	
				1.51	164	
				2.75	262	
				4.01	396	
				6.98	638	8.73 ± 0.39
248	100 (Ar)	75	62	0	39	
				3.15	315	
				4.68	401	
				7.76	685	
				9.63	798	7.97 ± 0.56
260	100 (Ar)	100	62	0	29	
				1.49	131	
				2.80	236	
				4.14	348	
				5.80	488	
				8.47	722	
				11.26	971	8.35 ± 0.37
271	100 (Ar)	150	62	0	41	
				2.46	231	
				4.78	394	
				6.88	523	
				8.92	719	7.44 ± 0.55

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} cm^{-3} $molecule^{-1}$ s^{-1}
298	25 (Ar)	150	106	1.60	193	
				6.15	400	
				8.28	559	
				11.81	714	
	25 (Ar)	150	34	2.17	185	
				4.50	315	
				6.25	432	
				9.20	602	
	25 (Ar)	150	62	0	37	
				1.01	142	
				2.47	251	
				5.27	425	
				6.79	503	
				8.46	639	5.78 ± 0.62
	100 (Ar)	150	62	1.71	283	
				3.31	357	
				4.79	478	
				7.49	641	
				11.50	868	
	100 (Ar)	150	34	0	22	
				3.22	224	
				4.59	267	
				6.89	457	
				8.98	586	
298	100 (Ar)	150	106	2.53	207	
				6.02	404	
				8.27	560	
				12.80	894	6.36 ± 0.69

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
	100 (SF_6)	150	62	0	91	
				3.83	356	
				8.01	593	
				11.22	840	6.55 ± 0.49
	20 (He)	150	62	3.38	281	
				6.36	468	
				9.52	617	
				12.98	748	
				15.79	880	4.72 ± 0.46
	40 (He)	150	62	1.58	222	
				3.55	334	
				7.12	522	
				11.29	757	
				15.64	987	5.44 ± 0.07
	100 (He)	150	62	1.82	193	
				4.96	383	
				7.27	559	
				12.07	788	
				15.56	1033	6.00 ± 0.43
320	100 (Ar)	150	62	0	25	
				2.29	156	
				4.33	273	
				6.55	457	
				9.04	575	6.25 ± 0.57[a]
332	100 (Ar)	150	62	0	35	
				2.06	96	
				6.34	317	
				8.44	452	
				10.61	579	
				13.67	734	5.4 ± 1.1[a]

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
352	100 (Ar)	172	97	0	30	
				0.39	166	
				0.79	326	3.61[ab]
397	100 (Ar)	170	97	0	32	
				1.91	54	
				4.21	82	
				5.72	102	1.36[ab]
442	100 (Ar)	170	97	0	30	
				3.42	92	
				5.94	135	
				8.88	172	1.72[ab]
504	98 (Ar)	172	88	0	32	
				3.67	112	
				7.71	186	
				10.25	257	
				13.45	309	
				17.13	400	
				21.66	502	2.16 ± 0.08
565	100 (Ar)	181	88	0	36	
				4.48	138	
				8.37	237	
				11.94	322	
				17.81	471	2.45 ± 0.05
567	101 (Ar)	169	80	0	30	
				2.91	105	
				5.25	159	
				8.21	227	
				8.68	246	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
				10.77	280	
				14.09	389	2.49 ± 0.12
666	102	164	80	0	40	
				2.21	118	
				4.11	191	
				5.48	216	
				7.03	258	
				8.14	315	
				8.91	317	
				11.02	416	3.26 ± 0.29
694	98 (Ar)	175	88	0	52	
				2.25	125	
				3.76	182	
				5.80	272	
				9.00	370	
				12.16	485	3.58 ± 0.16
793	100 (Ar)	179	88	0	54	
				1.48	131	
				3.05	196	
				4.62	282	
				6.09	349	
				8.83	465	4.67 ± 0.19
868	103 (Ar)	189	88	0	60	
				1.42	141	
				2.42	185	
				3.64	271	
				4.92	335	
				6.67	426	5.54 ± 0.27

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CH_3]$ 10^{13} cm^{-3}	k_3', s^{-1}	k_3, 10^{-12} cm^{-3} $molecule^{-1}$ s^{-1}
958	101 (Ar)	182	88	0	56	
				0.93	132	
				1.91	193	
				3.73	320	
				5.63	447	6.87 ± 0.23
1046	100 (Ar)	183	88	0	64	
				0.56	118	
				1.04	147	
				1.90	253	
				2.52	299	9.5 ± 1.0

a) Non-exponential OH Temporal Profile; $k_3' \equiv$ initial slope.

b) Non-Linear Dependence of k_3' on [RH]; k_3 = initial slope of k_3' vs. [RH] Plot.

Table IV. Rate Constant Data for the Reaction of OH with Toluene-d_8 ($C_6D_5CD_3$).

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6D_5CD_3]$ 10^{13} cm^{-3}	k_5', s^{-1}	k_5, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
250	20 (Ar)	110	60	6.65	511	
				10.08	738	
				13.34	922	
				16.18	1048	
				19.82	1273	5.67 ± 0.40
250	100 (Ar)	110	60	3.20	283	
				6.10	466	
				8.87	671	
				11.62	819	
				14.61	1006	6.04 ± 0.48
270	100 (Ar)			2.93	255	
				5.75	457	
				8.52	655	
				11.31	799	
				13.91	950	6.36 ± 0.52
298	20 (He)	120	60	0	117	
				2.32	226	
				3.88	314	
				8.93	509	
				10.32	655	
				14.93	812	4.91 ± 0.34
				19.32	1060	
298	20 (Ar)	170	70	0	70	
			36	1.77	192	
			76	1.84	187	
		350	115	2.38	223	
		170	120	2.81	224	
		170	36	3.13	240	
		170	76	3.39	272	
		170	70	3.43	254	
		170	70	4.55	333	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6D_5CD_3]$ 10^{13} cm^{-3}	k_5', s^{-1}	k_5, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
		350	115	4.96	338	
		170	36	4.98	325	
		170	115	5.47	387	
		170	70	6.59	412	
		170	70	6.71	434	
			76	6.93	470	
			36	6.99	478	
		350	115	7.67	502	
		170	70	7.87	523	
		170	115	8.13	556	
		170	70	8.75	550	
		350	115	9.06	615	
		170	36	9.22	571	
		170	36	9.77	562	
		170	70	10.06	641	
			36	10.46	648	
			36	11.73	698	
			76	12.77	769	
		170	115	13.24	821	5.46 ± 0.22
298	20 (Ar)	170	70	13.40	820	
		170	70	16.51	909	
		170	70	19.82	1167	5.38 ± 0.18
298	35 (Ar)	150	60	0	49	
				1.83	175	
				4.63	345	
				5.62	401	
		75	35	6.25	407	
		285	35	6.35	447	
		150	115	6.52	421	
		150	35	6.78	445	
		150	60	7.98	526	5.81 ± 0.43

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6D_5CD_3]$ 10^{13} cm^{-3}	k_5', s^{-1}	k_5, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
298	100 (Ar)	150	60	0	30	
				1.29	136	
				2.19	180	
				3.37	262	
				4.93	363	
				5.98	423	
				6.76	468	6.40 ± 0.20
466	100 (Ar)	197	90	0	30	
				8.98	110	
				17.52	149	
				27.19	236	
				35.78	294	0.73 ± 0.07
566	103	180	90	0	38	
				4.98	97	
				10.48	149	
				12.07	196	
				20.74	268	
				26.12	308	
				32.22	373	1.15 ± 0.05
712	103	198	90	0	45	
				2.21	100	
				4.65	149	
				7.28	217	
				9.90	259	
				14.18	358	2.18 ± 0.10
841	102	218	90	0	63	
				1.13	86	
				3.06	139	
				4.88	193	
				7.62	270	2.76 ± 0.14

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6D_5CD_3]$ 10^{13} cm^{-3}	k_5', s^{-1}	k_5, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
961	102	220	90	0	76	
				0.74	100	
				1.66	143	
				2.58	195	
				3.93	255	
				5.28	308	4.52 ± 0.25

Table V. Rate Constant Data for the Reaction OH with Toluene-d_3 ($C_6H_5CD_3$).

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CD_3]$ 10^{13} cm^{-3}	k_4', s^{-1}	k_4, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
250	100 (Ar)	120	60	0	70	
				2.59	204	
				3.03	234	
				4.92	369	
				5.61	358	
				7.24	525	
				7.40	476	
				9.03	625	
				9.70	589	
				12.57	765	
				13.91	849	5.62 ± 0.52
269	100 (Ar)	120	60	0	33	
				2.40	179	
				4.39	303	
				6.86	466	
				8.92	579	
				11.00	691	
				13.14	817	5.97 ± 0.17
298	100 (Ar)	150	60	0	25	
			120	1.32	134	
			60	1.39	124	
			60	2.52	156	
				2.70	192	
				2.86	196	
			120	3.97	264	
			60	4.11	307	
				5.05	274	
				5.34	359	
				5.38	347	
				6.68	424	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CD_3]$ 10^{13} cm^{-3}	k_4', s^{-1}	k_4, 10^{-12} cm^{-3}molecule^{-1}s^{-1}
				7.26	413	
				8.09	518	
				9.25	563	
				11.38	685	
				14.11	827	5.63 ± 0.30
517	101	150	80	0	39	
				3.53	90	
		200		6.61	137	
		100		6.71	128	
		150		10.71	188	
				13.63	226	
		200		20.44	321	
		150		24.12	330	
				29.95	411	1.23 ± 0.09
560	101 (Ar)	180	80	0	38	
				4.66	117	
				9.08	182	
				13.86	237	
				17.33	306	
				23.70	387	1.46 ± 0.08
563	100 (Ar)	185	80	0	37	
				4.96	111	
				10.31	169	
				14.61	245	
				19.89	325	
				25.70	392	1.40 ± 0.08
565	102 (Ar)	185	80	0	41	
				4.89	109	
				8.96	164	

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CD_3]$ 10^{13} cm^{-3}	k_4', s^{-1}	k_4, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
				13.47	232	
				18.30	282	
				23.83	381	
				30.10	464	1.41 ± 0.06
566	101 (Ar)	185	80	0	44	
				4.68	105	
				8.95	167	
				13.96	247	
				19.68	306	
				25.47	377	1.32 ± 0.08
652	100 (Ar)	193	90	0	50	
				2.93	117	
				5.31	161	
				8.36	239	
				12.09	320	
				16.80	416	2.10 ± 0.07
742	103 (Ar)	200	90	0	56	
				2.93	113	
				4.21	176	
				6.29	251	
				9.59	357	
				13.57	472	3.01 ± 0.10
818	104 (Ar)	212	90	0	66	
				2.16	141	
				4.01	217	
				5.90	292	
				7.52	346	
				9.13	399	3.59 ± 0.13

Temperature K	Diluent Gas Pressure Torr	$[H_2O]$, mTorr	Flash Energy J	$[C_6H_5CD_3]$ 10^{13} cm^{-3}	k_4', s^{-1}	k_4, 10^{-12} $cm^{-3}molecule^{-1}s^{-1}$
891	102 (Ar)	220	90	0	61	
				1.88	138	
				3.06	214	
				4.15	270	
				6.32	352	
				8.64	451	4.55 ± 0.34
966	103 (Ar)	220	90	0	67	
				0.86	120	
				1.54	146	
				1.84	182	
				1.69	234	
				3.87	306	
				5.11	362	5.92 ± 0.42

Table VI. Rate Constants for the Reactions of OH with Aromatic Hydrocarbons as a Function of Temperature.

Temperature K	k, 10^{-12} $cm^3 molecule^{-1} s^{-1}$				
	C_6H_6	C_6D_6	$C_6H_5CH_3$	$C_6H_5CD_3$	$C_6D_5CD_3$
213			8.20 ± 0.54		
231			8.73 ± 0.39		
248			7.97 ± 0.56		
250	1.04 ± 0.08	1.08 ± 0.05		5.62 ± 0.52	6.04 ± 0.48
260			8.35 ± 0.37		
269				5.97 ± 0.17	
270	1.20 ± 0.09				6.36 ± 0.52
271			7.44 ± 0.55		
298	1.24 ± 0.09	1.19 ± 0.05	6.36 ± 0.69	5.63 ± 0.30	6.40 ± 0.20
320			6.25 ± 0.57[a]		
332					
352					
466					0.73 ± 0.07
504			2.16 ± 0.08		
517				1.23 ± 0.09	
545	0.543 ± 0.023				
560				1.46 ± 0.08	
563		0.227 ± 0.030			
565			2.45 ± 0.05	1.41 ± 0.06	
566				1.32 ± 0.08	1.15 ± 0.05
567			2.49 ± 0.12		

Temperature K	k, 10^{-12} $cm^3 molecule^{-1} s^{-1}$				
	C_6H_6	C_6D_6	$C_6H_5CH_3$	$C_6H_5CD_3$	$C_6D_5CD_3$
620	0.639 ± 0.029				
649		0.300 ± 0.032			
652				2.10 ± 0.07	
666			3.26 ± 0.29		
694			3.58 ± 0.16		
712					2.18 ± 0.10
719	1.02 ± 0.04				
734		0.481 ± 0.019			
742				3.01 ± 0.10	
693			4.67 ± 0.19		
816	1.59 ± 0.09				
818				3.59 ± 0.13	
830		0.720 ± 0.046			
841					2.76 ± 0.14
868			5.54 ± 0.027		
891				4.55 ± 0.34	
917	2.26 ± 0.13	1.04 ± 0.03			
958			6.87 ± 0.23		
961					4.52 ± 0.25
966				5.92 ± 0.42	
981	2.35 ± 0.23	1.08 ± 0.10			
1046			9.5 1.0		

NOTE: a) Below 350K, the numbers quoted are for 100 Torr Ar, i.e., at the high pressure limit of the reactions

b) All errors are ± 2σ

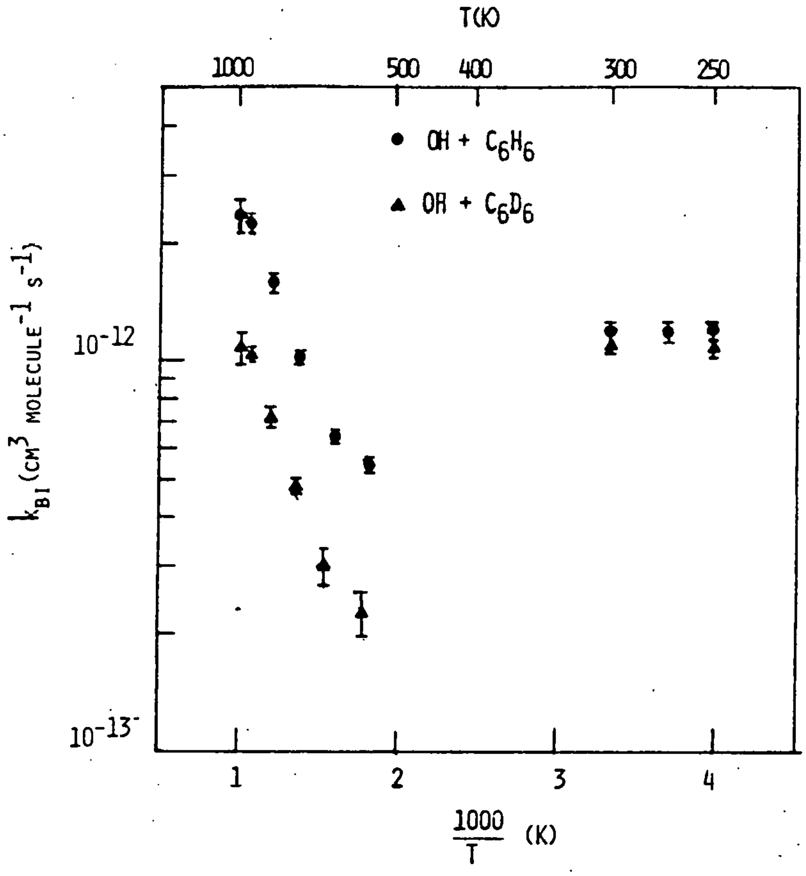


Figure 5. Arrhenius Plots of ℓnk vs. 1000/T (K) for Reaction of OH with C_6H_6 and C_6D_6. Data obtained between 320-450 K (where pseudo-first order bahavior was not observed) are not shown.

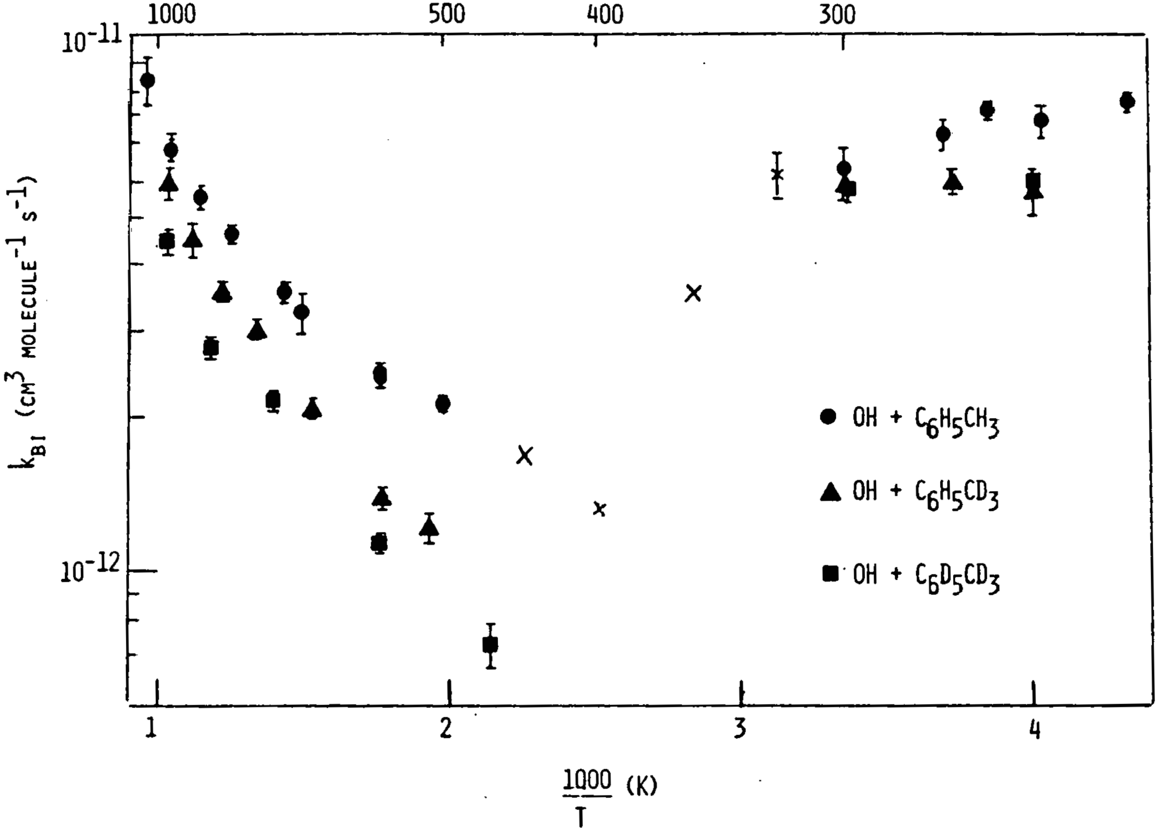


Figure 6a. Arrhenius Plot of ℓnk vs. 1000/T for Reaction of OH with Three Substituted Toluenes. X represents data obtained under non first-order conditions.

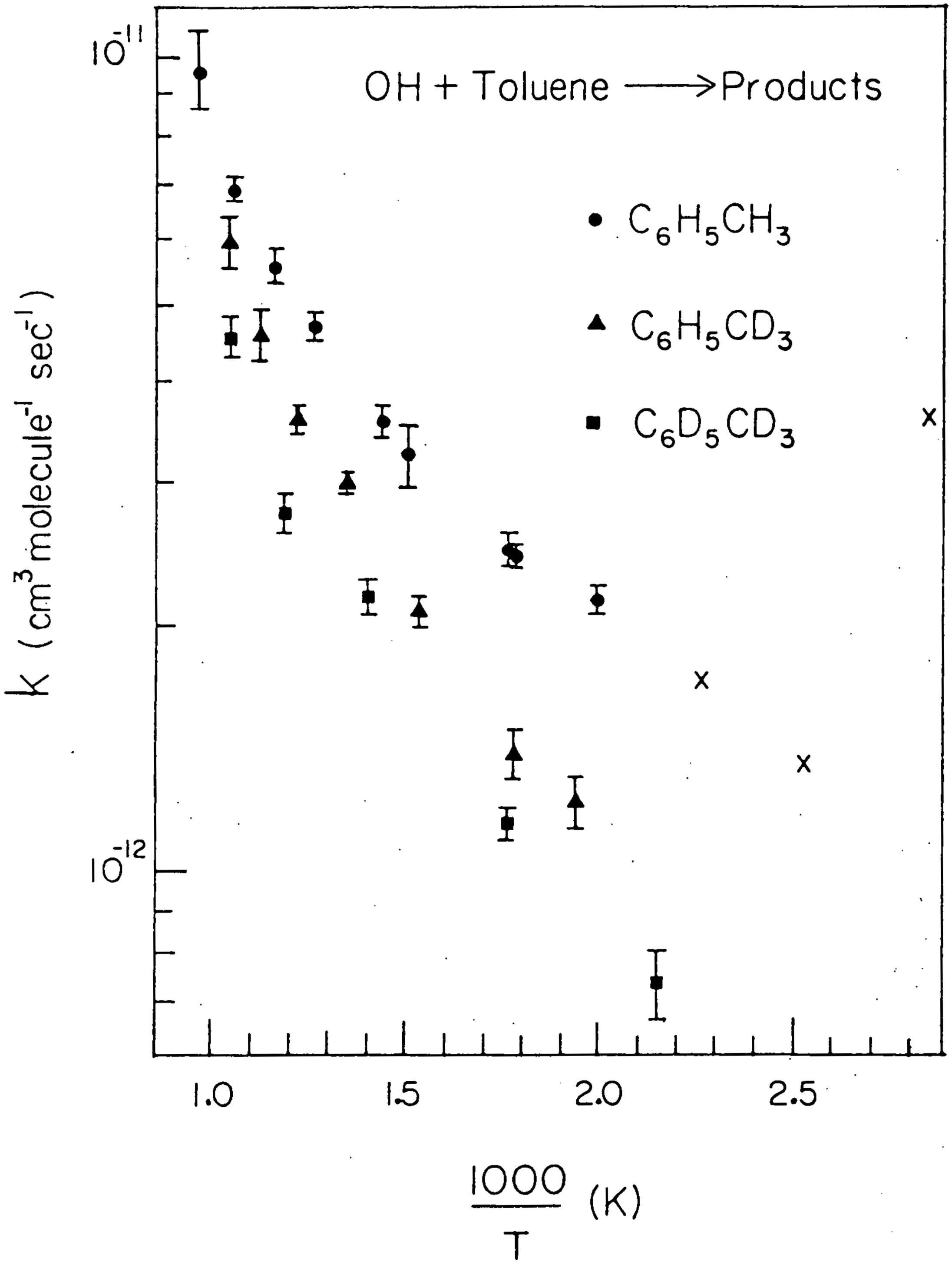


Figure 6b. High Temperature Data for the Reaction of OH with Toluenes.

Discussion

All experiments were carried out under pseudo-first order conditions with [RH]/[OH] > 100. The concentration of the reactant RH was varied by at least a factor of five. At most temperatures the [OH] decays were exponential and k' vs. [RH] plots linear, thereby confirming the existence of pseudo-first order conditions. (The exceptions are discussed later).

In previous OH reaction kinetic investigations in our laboratory,[5] under conditions similar to the present measurements, it was demonstrated that radical-radical reactions of the type H + OH and OH + OH were of negligible importance. Moreover, both calculations, as well as experimental variations of the OH concentration in this study, confirm the negligible contribution of the above processes, as well as others such as OH + R·, to the measured rate constants (see Table I-V).

Aromatic hydrocarbons absorb quite strongly in the wavelength range 165 nm (suprasil cutoff) - 280 nm.[6] Therefore it is possible to flash photolyze RH leading to the formation of some reactive photofragments which could then react with OH. Both modeling calculations and the independence of the measure rate constant to variations in photolysis flux showed that the reactions of aromatic hydrocarbon photofragments were negligible. Absorption of light in the wavelength region ∿ 230 to 280 nm by benzene and toluene induce fluorescence. We checked to see if this fluorescence was being detected through the 310 nm bandpass filter; the fluorescence signal was absent.

Comparison with Previous Studies

Tables VII and VIII list the 298K values of k_1 and k_3 which have now been reported. Our results, as seen in the table, are in remarkably good agreement with results of Perry et.al.[7] and Hanson et.al.[8] We found little evidence for a pressure dependence of k_1. This pressure independence indicates that Reaction (1) is at its high pressure limiting value even at 25 Torr He, in contrast to the findings of Davis et.al.[9] Davis et.al.'s 100 Torr He value of k_1 is significantly higher than that measured in the present study. There is no apparent reason for this discrepancy, since k_2 values of Davis et.al. agree quite well with our measurements (vide infra). We believe that now it can be safely concluded, based on the independence of the measured value of k_1 on pressure (20-200 Torr) and identity (He, Ar, SF_6) of the diluent gas, that Reaction (1) is at its high pressure limit above 25 Torr.

The value of k_3 measured by us is in excellent agreement with all previous measurements, as seen in Table VIII. We confirm the slight pressure dependence for Reaction (3) over the pressure range 20-100 Torr. These results indicate that Reaction (2) is at its high pressure limit at pressures above 100 Torr.

There is only one previous investigation where k_1 and k_3 were measured as a function of temperature. Perry et al measured k_1 and k_3 over a limited temperature range of 296-473 K. Our observations are qualitatively, very similar to those of Perry et.al.[7] However, since their data did not extend to temperatures less that 298K or greater than 475K, their Arrhenius parameters had large errors. Therefore, it is not worthwhile to quantitatively compare data except to mention that the agreement is quite good within the stated errors.

Table VII. Comparison of Our Results for OH + Benzene Reaction with Previous Measurements at 298K.

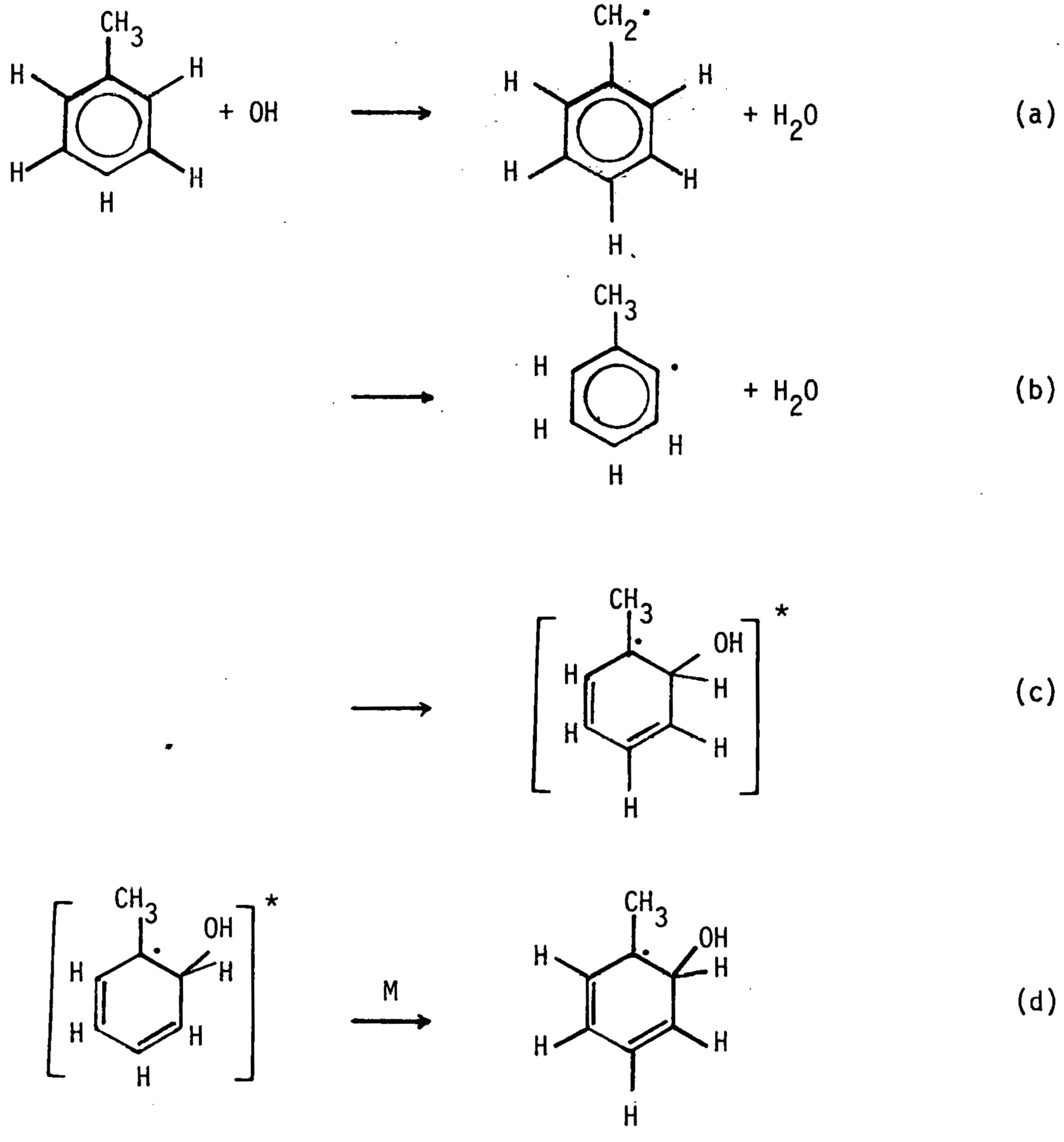
Diluent	Pressure Torr	k, 10^{-12} $cm^3 molecule^{-1} s^{-1}$			
		This Work	Davis et al. Ref.(9)	Perry et al. Ref.(7)	Hansen et al. Ref.(8)
He	3		0.85 ± 0.08		
He	20		1.36 ± 0.09		
He	25	1.10 ± 0.05			
He	50	1.11 ± 0.24			
He	100	1.25 ± 0.06	1.59 ± 0.12		
Ar	50	1.20 ± 0.06			
Ar	100	1.21 ± 0.09		1.20 ± 0.15	1.24 ± 0.12
Ar	200	1.19 ± 0.12			
SF_6	100	1.11 ± 0.05			

Table VIII. Comparison of Our Results for OH + Toluene Reaction with Previous Data at 298K.

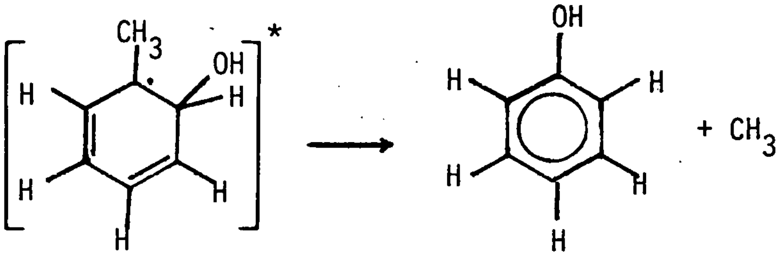
Diluent	Pressure Torr	k, 10^{-12} cm^{3}molecule^{-1}s^{-1}			
		This Work	Davis et al. Ref.(9)	Perry et al. Ref.(7)	Hansen et al. Ref.(8)
He	3		3.60 ± 0.26		
He	20	4.72 ± 0.46	5.00 ± 0.18		
He	40	5.44 ± 0.07			
He	100	6.00 ± 0.43	6.11 ± 0.40		
Ar	25	5.78 ± 0.62			
Ar	100	6.36 ± 0.69		6.40 ± 0.54	5.78 ± 0.58
SF_6	100	6.55 ± 0.49			

Reaction Mechanisms

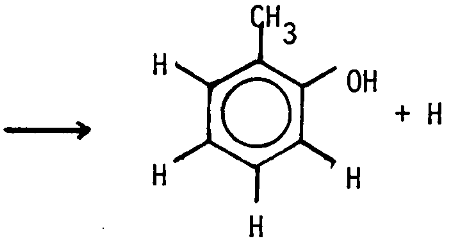
OH radicals can react with aromatic hydrocarbons via either addition to the aromatic ring or via abstraction of an hydrogen atom. Using toluene as an example, the reaction pathways could be represented as follows:



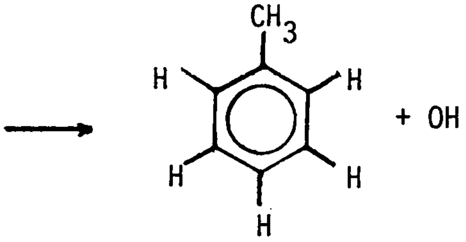
For convenience, the addition and ring hydrogen abstraction are shown to occur in the ortho position; in reality they could occur at meta or para positions also. The unstabilized complex can undergo rearrangement or eliminate a fragment:



(e)

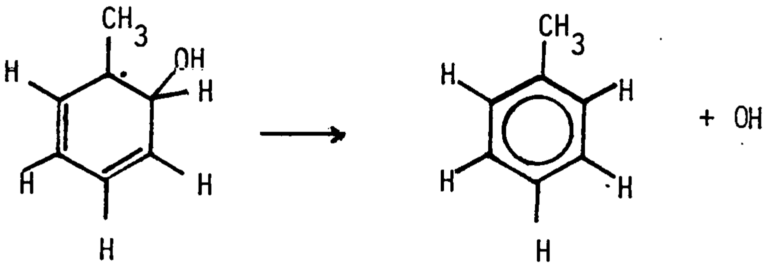


(f)



(g)

Reaction (g), in our experiment, would merely lead to a slower OH reaction rate constant. The stabilized addition complex could also undergo thermal bimolecular decomposition,



(h)

The thermal decomposition occurs on the same time scale as the decay of OH reactant when the temperature is between 325K and 425K, as evidenced by the non-exponential OH temporal profile. The extent of deviation of the temporal profile from exponential decay indicates that the lifetime of the stabilized addition complex is in the range of a few msec at these tempueraures. At higher temperatures, the unimolecular decomposition becomes so fast that it is instantaneous on the time scale of the experiment and hence merely decreases the rate of OH reaction with aromatic hydrocarbon through the addition channel. At lower temperatures, i.e., < 298K, the complex has lifetimes in the range of seconds and therefore decomposition is not observed.

OH can react with benzene via either ring hydrogen abstraction or addition to the ring. If the ring hydrogen abstraction occurs to a significant extent, a primary kinetic isotope effect would be expected when all hydrogen atoms are replaced by deuterium atoms. Since k_1, is, within experimental error, the same as k_2 at temperature below 298K, it can be concluded that the addition reaction is the dominant pathway at low temperature. Again, the temperature independence of k_1 and k_2 (below 298K) confirms this conclusion.

At temperatures greater than 400K, k_1 is at least a factor of 2 faster than k_2, as to be expected when hydrogen atom transfer (i.e., abstraction) is involved in the reaction. The temperature dependence of k_1 and k_2 are very similar to that observed for reactions involving a primary hydrogen atom abstraction by OH.

Over the temperature interval 298 to 400 K, k_1 and k_2 decrease by almost an order of magnitude giving a clear break in the Arrhenius plots.

This break signifies a transition in reaction mechanism from addition channel domination at $T < 298$ to abstraction channel domination at $T < 400K$.

In the case of toluene the conclusions noted for the case of benzene are valid; $k_3 \sim k_4 \simeq k_5$ at $T < 298K$ where addition is dominant and $k_3 > k_4 \sim k_5$ in the temperature range of 400-700 K where abstraction is dominant. These relationships identify abstraction of a hydrogen atom from the side chain to be significant in the 400-700 K regime. Above 800K, $k_3 \simeq k_4 > k_5$, indicating the growing importanct of the ring hydrogen abstraction.

It should be noted that ober the temperature range of 298-213 K, k_3 is slightly ($\sim$ 15%), but consistantly, larger than k_4 and k_5. We interpret this result to mean that side chain hydrogen abstraction from toluene contributes $\sim$ 20% to the measured value of k_3 at T less than 298K.

The above reaction mechanisms are completely consistent with previous investigations of OH-Aromatic hydrocarbon reactions which involved rate coefficient measurements[7-9] as well as reaction product identifications.[10] We are currently quantifying the branching ratios for all pathways as a function of temperature. We are also analyzing the non-exponential decays obtained at $300 < T < 420K$ to obtain thermodynamic and kinetic data on the addition complex.

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