A kinetic study of the reaction of atomic hydrogen with iodobenzene

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Abstract

The rate constant for the reaction of H atoms with phenyl iodide has been measured using the laser flash-photolysis technique with detection of H by resonance fluorescence. The data over 295–907 K are summarized by the expression $k = 1.45 \times 10^{-18} T^{2.50} \exp(74/T)$ cm³ molecule⁻¹ s⁻¹ with a 95% confidence limit for k of $\pm 8\%$. *Ab initio* analysis suggests the dominant products are phenyl and hydrogen iodide.

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1. Introduction

Reactions of hydrogen atoms with alkyl iodides have been the subject of several kinetic studies [1–7], motivated in part by the potential contributions of iodine to combustion chemistry [8]. Interesting kinetics have been observed in some cases, such as Cl-atom addition [9] and O-atom addition followed by elimination of HOI [10]. Rather less attention has been paid to aryl iodides, which are of fundamental interest because they exhibit a range of mechanisms in radical reactions. For example, the reaction $\text{CH}_3 + \text{C}_6\text{H}_5\text{I}$ appears to proceed via I-atom abstraction [11], as does $\text{I} + \text{C}_6\text{H}_5\text{I}$ [12]. The $\text{Cl} + \text{C}_6\text{H}_5\text{I}$ reaction was proposed to take place by an addition/I-atom elimination path [13], while $\text{OH} + \text{C}_6\text{H}_5\text{I}$ appears to take place by addition below room temperature, and by H-atom abstraction at higher temperatures [14].

We use $\text{C}_6\text{H}_5\text{I}$ as a photolytic source of C_6H_5 to study the chemistry of phenyl radicals, and in the course of this work have characterized the process

In this Letter, we report the first kinetic information concerning reaction (1), obtained with the time-resolved resonance fluorescence technique over 295–907 K.

2. Experimental section

The experiments were performed with the laser flash-photolysis technique using resonance fluorescence detection of H. Details of the apparatus and its operation have been previously described [15–18]. Therefore, only a brief description of the experiment will be presented here. The atomic hydrogen was generated by excimer laser (Lambda Physik Compex 102) photolysis of the precursor NH_3 at 193 nm. The relative concentration of H atoms was monitored by time-resolved resonance fluorescence at the Lyman- α wavelength, 121.6 nm. This probe radiation was produced by a microwave discharge lamp with a flow of 0.2% H_2 in 0.14 mbar of Ar. Fluorescence was detected using a solar-blind photomultiplier tube with pulse counting. Typically 200–2500 fluorescence vs time profiles were summed at each set of conditions, with a repetition rate of 2 Hz. The temperature T in the reaction zone was measured as in previous work [19]. The experiments were conducted in a large excess of Ar bath gas to thermalize the system and to slow diffusion of H to the reactor walls. The $\text{C}_6\text{H}_5\text{I}$ and NH_3 concentrations were derived from

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the mole fractions of these species in manometrically prepared mixtures with Ar, the total pressure P , T , and the gas flows which were measured with calibrated mass-flow controllers. The average residence time of gas mixtures in the heated reactor before photolysis, τ_{res} , was varied to check for possible pyrolysis of the iodobenzene and for mixing effects. Low photolysis energies F were employed, to minimize secondary chemistry involving photolysis or reaction products.

All experiments were carried out under pseudo-first-order conditions with $\text{C}_6\text{H}_5\text{I}$ in large excess over H , and with fixed precursor concentration $[\text{NH}_3]$. Thus, the H atom temporal profile is dominated by reaction (1), with other loss processes described by an effective first-order decay constant k_2

A typical time-resolved fluorescence signal decay of atomic H is shown as the inset in Fig. 1. After the photolysis pulse, the variation of $[\text{H}]$ is described by

$$d[\text{H}]/dt = -(k_1[\text{C}_6\text{H}_5\text{I}] + k_2)[\text{H}] = -k_{\text{ps1}}[\text{H}] \quad (3)$$

which implies an exponential decay of $[\text{H}]$ with time t

$$[\text{H}] = [\text{H}]_0 \exp(-k_{\text{ps1}} t) \quad (4)$$

k_2 increased as the pressure was lowered, and increased as the temperature was raised, which is consistent with the idea that k_2 reflects mainly diffusion of H atoms out of the observation zone. This loss was seen to be sensibly exponential. The $\text{H} + \text{NH}_3$ reaction also makes a minor contribution to k_2 at the highest temperatures [20]. k_{ps1} and its statistical error were obtained by non-linear fitting of the observed fluorescence, with an allowance for a constant background arising from scattered probe radiation and/or fluorescent species, to the form of Eq. (4) [21,22].

Fig. 1. Plot of k_{ps1} vs $[\text{C}_6\text{H}_5\text{I}]$ at 295 K and 68 mbar Ar pressure. The inset shows the exponential decay of $[\text{H}]$ with $[\text{C}_6\text{H}_5\text{I}] = 2.0 \times 10^{14} \text{ molecule cm}^{-3}$. Error bars represent $\pm 1\sigma$ statistical uncertainty.

We note that a long-lived reaction product fluoresced sufficiently to raise the background after photolysis by typically 3% of the H -atom signal, but because this emission decayed very slowly, changes in $[\text{H}]$ were isolated by the short time scale. The second-order $\text{H} + \text{C}_6\text{H}_5\text{I}$ rate constant k_1 was found from the slope of linear plots of k_{ps1} vs typically six values of $[\text{C}_6\text{H}_5\text{I}]$, from 0 to $[\text{C}_6\text{H}_5\text{I}]_{\text{max}}$ (see Fig. 1). k_2 is the intercept. The absolute concentration $[\text{H}]$ was not measured (and is not required for the determination of k_{ps1}), but we can estimate the initial concentration $[\text{H}]_0$ from $[\text{NH}_3]$ and its absorption cross-section at 193 nm [23]. Because $\text{C}_6\text{H}_5\text{I}$ might absorb on the reactor surface, the $\text{C}_6\text{H}_5\text{I}$ mixtures were flowed through the apparatus for at least 3 h before experiments were begun, to passivate the surfaces.

Reagent grade $\text{C}_6\text{H}_5\text{I}$ (98%, Aldrich) was distilled from room temperature to 77 K before use, and NH_3 (MG Industries, 99.99%) was purified by freeze-pump-thaw cycles at 77 K. Ar (Air Products, 99.9997%) was used directly from the cylinder.

3. Results

The experimental conditions and 39 results for the second-order rate constant for the reaction of $\text{C}_6\text{H}_5\text{I} + \text{H}$ are summarized in Table 1 along with the statistical error in plots of k_{ps1} vs $[\text{C}_6\text{H}_5\text{I}]$. The results demonstrate the invariance of k_1 with both the total pressure and the $[\text{C}_6\text{H}_5\text{I}]/[\text{H}]_0$ ratio. The independence of the k_1 results from F shows that secondary chemistry involving photolysis or reaction products was negligible, and confirms that pseudo-first-order conditions were attained.

Kumaran et al. have studied the unimolecular dissociation of $\text{C}_6\text{H}_5\text{I}$ to $\text{C}_6\text{H}_5 + \text{I}$ over 1082–1416 K [24]. Their theoretical ‘model (b)’ for the high-pressure limit, extrapolated down to our highest temperature, implies that, at the longest residence time in the reactor, ca. 40% of the $\text{C}_6\text{H}_5\text{I}$ might be expected to dissociate. The invariance of our k_1 data with τ_{res} suggests that little dissociation in fact occurred, in part because the initially cold gas flow does not spend all of τ_{res} at the temperature of the reaction zone. Any C_6H_5 produced will be rapidly consumed by reaction with $\text{C}_6\text{H}_5\text{I}$, with a rate constant of about $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [25]. At 900 K and with a typical $[\text{C}_6\text{H}_5\text{I}] = 4 \times 10^{13} \text{ molecule cm}^{-3}$, a steady state concentration of around $1.5 \times 10^{10} \text{ molecule cm}^{-3}$ would be attained, which is too small to perturb the $[\text{H}]$ profiles.

In Fig. 2 the data are presented in Arrhenius form. Curvature can clearly be seen. An empirical fit to the data, weighted by the uncertainties in k_1 and T , gives

$$k_1 = (1.45 \pm 2.01) \times 10^{-18} T^{2.50 \pm 0.19} \times \exp((74 \pm 89)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

95% statistical errors for k_1 from this expression are up to 6%. Combining this in quadrature with an estimated propagated 5% error arising from potential uncertainties in the

Table 1
Summary of measurements of the rate constant k_1 for $\text{H} + \text{C}_6\text{H}_5\text{I}$

T (K)	τ_{res} (s)	F (mJ)	P (mbar)	$[\text{NH}_3]$ (10^{14} molecule cm^{-3})	$[\text{C}_6\text{H}_5\text{I}]_{\text{max}}$ (10^{13} molecule cm^{-3})	$[\text{H}]_0$ (10^{11} molecule cm^{-3})	k_2 (s^{-1})	$k_1 \pm \sigma_{k_1}$ (10^{-12} cm^3 molecule $^{-1}$ s^{-1})
295	3.0	0.06	69	7.72	31.0	5.3	68	2.72 ± 0.15
295	3.0	0.04	69	7.72	31.0	3.5	77	2.60 ± 0.15
295	3.0	0.02	69	7.72	31.0	1.6	77	2.52 ± 0.10
295	5.2	0.08	68	8.77	25.4	7.5	50	3.65 ± 0.14
295	5.2	0.05	68	8.77	25.4	4.8	45	3.31 ± 0.09
295	5.2	0.03	68	8.77	25.4	2.6	49	2.95 ± 0.11
295	2.2	0.09	29	6.55	25.3	6.3	149	2.38 ± 0.16
295	2.2	0.06	29	6.55	25.3	4.3	136	2.49 ± 0.15
295	2.2	0.03	29	6.55	25.3	2.0	140	2.30 ± 0.09
295	3.2	0.10	72	1.49	23.4	1.6	51	2.41 ± 0.21
295	3.2	0.06	72	1.49	23.4	1.0	54	2.33 ± 0.17
296	3.1	0.06	69	1.66	35.0	1.1	71	2.70 ± 0.23
297	4.6	0.01	83	2.42	51.2	0.3	70	3.11 ± 0.19
407	3.9	0.14	71	6.87	17.2	10.6	107	6.81 ± 0.23
407	3.9	0.06	71	6.87	17.2	4.6	119	6.25 ± 0.22
407	3.9	0.04	71	6.87	17.2	3.0	113	6.16 ± 0.18
407	3.9	0.02	71	6.87	17.2	1.7	94	6.62 ± 0.21
515	2.9	0.11	68	6.59	17.9	8.0	234	9.63 ± 0.72
515	2.9	0.07	68	6.59	17.9	5.0	218	10.4 ± 0.84
515	2.9	0.03	68	6.59	17.9	2.5	252	9.82 ± 0.63
515	5.8	0.08	135	6.25	12.3	5.3	125	12.3 ± 0.91
515	5.8	0.05	135	6.25	12.3	3.7	160	12.3 ± 0.95
517	1.4	0.14	68	4.71	16.3	7.3	358	8.89 ± 0.74
517	1.4	0.08	68	4.71	16.3	4.2	359	9.01 ± 0.56
615	1.9	0.06	71	2.50	8.76	1.6	325	18.3 ± 1.37
619	2.5	0.11	71	3.36	13.9	4.0	228	12.9 ± 0.15
620	2.8	0.11	137	3.15	13.0	3.7	200	12.7 ± 0.93
622	1.1	0.07	31	1.52	6.27	1.2	521	12.7 ± 1.15
622	1.1	0.04	31	1.52	6.27	0.6	523	13.3 ± 1.01
770	2.9	0.15	136	4.49	13.6	7.4	352	26.1 ± 0.75
770	2.9	0.09	136	4.49	13.6	4.5	342	28.8 ± 0.99
771	1.5	0.21	69	6.22	12.3	14.4	488	23.1 ± 1.81
771	1.5	0.14	69	6.22	12.3	9.6	506	22.9 ± 1.57
901	1.7	0.22	68	3.80	7.86	9.2	661	41.3 ± 2.72
901	1.7	0.14	68	3.80	7.86	5.9	737	43.1 ± 2.01
907	1.8	0.23	148	4.03	9.71	10.2	674	40.9 ± 1.75
907	1.8	0.14	148	4.03	9.71	6.2	607	37.6 ± 1.92
907	0.6	0.20	33	1.77	4.82	3.9	1010	39.9 ± 2.43
907	0.6	0.13	33	1.77	4.82	2.5	1035	38.1 ± 2.17

P , T and flow measurements leads to 95% confidence limits of $\pm 8\%$.

4. Discussion

The curvature in Fig. 2 might reflect the influence of low frequency modes in the transition state for a single channel, or the combined effect of multiple channels. Several reaction paths for reaction (1) are thermodynamically feasible

The reaction enthalpies for (1b) and (1c) are derived from the literature values of $\Delta_r H_{298}$ for C_6H_5 [25], $\text{C}_6\text{H}_5\text{I}$ [26], H , HI , and I [27] and have uncertainties of at least 6 kJ mol^{-1} . $\Delta_r H_{298}^0$ for (1a) was estimated from the DFT calculations of Tsao et al., who derived a binding enthalpy for 6-iodocyclohexadienyl, where H adds *ipso* to the I atom, of about 11 kJ mol^{-1} relative to $\text{C}_6\text{H}_6 + \text{I}$ [28]. This small value means this $\text{C}_6\text{H}_6\text{I}$ isomer is not stable enough to be a final product, but it could be an intermediate. Pathway (1d), where H adds to one of the C atoms not bonded to I, was assumed to have the same thermochemistry as the addition of H to benzene [29].

Path (1b) presumably could take place via I-atom elimination from a $\text{C}_6\text{H}_6\text{I}$ intermediate, or by a concerted mechanism. Similarly, channel (1c) could take place via

Fig. 2. Arrhenius plot for $\text{H} + \text{C}_6\text{H}_5\text{I}$. Error bars represent 2σ . The solid line is an empirical fit to the form $k_1 = AT^B \exp(-C/T)$ (see text).

direct abstraction or elimination of HI from a $\text{C}_6\text{H}_5\text{I}$ intermediate. Assuming a similar reaction endothermicity as in the case of $\text{H} + \text{C}_6\text{H}_6$, abstraction of H to form H_2 plus an iodo-phenyl radical will be negligibly slow [29]. A comparison of the rate constant for $\text{H} + \text{C}_6\text{H}_5\text{I}$ with that for $\text{H} + \text{C}_6\text{H}_6$ addition to make cyclohexadienyl [29] is shown in Fig. 3, which indicates that addition to the benzene ring *ortho*, *meta* or *para* to the I atom (pathway (1d)) would be too slow to account for our observations, although a small branching ratio is not excluded. $\text{H} + \text{CH}_3\text{I}$ and $\text{H} + \text{C}_2\text{H}_5\text{I}$ are also shown in Fig. 3, and it may be seen that reaction (1) is slightly slower than the $\text{H} + \text{alkyl iodide}$ reactions, which is consistent with the stronger C–I bond in the aromatic system: DH_{298} for $\text{C}_6\text{H}_5\text{I}$, CH_3I and $\text{C}_2\text{H}_5\text{I}$ is 279 $\pm$ 6, 237.2 ± 1.3 and 236.8 ± 1.7 kJ mol^{-1} , respectively.

Fig. 3. Comparison of rate constants for $\text{H} + \text{C}_6\text{H}_5\text{I}$ (solid line) with those for $\text{H} + \text{C}_2\text{H}_5\text{I}$ (dotted line), $\text{H} + \text{CH}_3\text{I}$ (dashed line), and $\text{H} + \text{C}_6\text{H}_6$ (dash-dot).

Ab initio calculations have been carried out to gain further insight into the reaction mechanism. Geometries and frequencies (unscaled) were obtained with the B3LYP density functional [30], the cc-pVTZ basis set for carbon and hydrogen [31], and the cc-pVTZ-PP basis set of Peterson et al. [32] for iodine. This triple zeta basis set includes an effective core potential to account for scalar relativistic effects. Vector relativistic effects (spin-orbit splitting) are important for I atoms, whose energy at 0 K was corrected downwards by 30.3 kJ mol^{-1} [33]. Refined single-point energies were derived with QCISD theory [34] and the same basis set. Calculations were carried out with the GAUSSIAN 03 program suite [35] and the results are summarized in Table 2. QCISD is variational and largely unaffected by spin-contamination. This property is important because several of the species considered had Hartree–Fock spin expectation values $\langle S^2 \rangle$ significantly greater than the ideal value of 0.75 for a doublet radical (see Table 2). Spin-contamination was much less significant in the density functional calculations.

Two reaction paths were characterized, and are shown in Fig. 4. The theoretical 0 K reaction enthalpies, combined with $H_{298} - H_0$ values either from the literature [25,27] or computed here (17.9 kJ mol^{-1} for $\text{C}_6\text{H}_5\text{I}$), yield $\Delta_r H_{298} = -204$ and -15 kJ mol^{-1} for channels (1b) and (1c), respectively. These values are in reasonable agreement with the experimental data given above. Channel (1b), addition of H to the C atom bound to I, yields the 6-iodocyclohexadienyl radical which dissociates very easily to benzene + atomic iodine. The short lifetime for 6-iodocyclohexadienyl makes it unlikely that it more rapidly eliminates HI to leave phenyl, or that it could be collisionally stabilized. A significant barrier was found at the entrance of this addition path, which would make it too slow to contribute significantly to the kinetics. This $\text{C}_6\text{H}_5\text{I}$ species has extremely weak C–I bonding, with a computed DH_0 of about 3 kJ mol^{-1} (based on the assumption that the spin-orbit splitting of atomic I is not quenched in $\text{C}_6\text{H}_5\text{I}$) which is typical for a van der Waals interaction. Our binding energy is smaller than that computed by Tsao et al. [28]. Presumably our larger basis set is less vulnerable to basis set superposition error, and we would expect QCISD theory to be more reliable than the BH&HLYP functional employed previously [28].

Relaxed scans at the B3LYP/cc-pVTZ-PP level for channel (1c), direct abstraction of I by H, were performed with a series of fixed I–H separations, and at each separation the rest of the structure was optimized to an energy minimum. The results indicate there is no classical energy barrier. This channel then appears to be dominant, and proceeds via a weakly bound exit complex between phenyl and hydrogen iodide. The empirical rate constant expression (5) can be considered in the context of transition state theory, where an expression of the form $D(T)\exp(-E/RT)$ is expected. E is the energy barrier and $D(T)$ is a temperature dependent term reflecting the ratios of the partition functions for the transition state and the reactants, which

Table 2
Ab initio energies and frequencies of reactants, products, and transition states for the $C_6H_5I + H$ reaction

Species	Frequencies ^a (cm ⁻¹)	$\langle S^2 \rangle$	Energy ^b (au)
H		0.750	-0.49981
I		0.760 (0.753) ^c	-296.87521
HI	2317	0.000	-297.49934
C_6H_5	402 429 602 621 678 725 818 899 972 995 1002 1020 1053 1075 1178 1178 1307 1328 1469 1477 1576 1631 3158 3164 3177 3179 3190	1.335 (0.757) ^c	-231.06357
C_6H_6	414 415 624 624 691 727 866 869 988 989 1015 1022 1031 1062 1062 1177 1200 1200 1335 1390 1518 1519 1637 1637 3158 3168 3168 3183 3184 3194	0.000	-231.75526
C_6H_5I	152 219 267 413 464 628 670 708 753 852 931 987 1010 1017 1037 1081 1098 1186 1207 1311 1351 1475 1509 1615 1619 3167 3175 3188 3196 3199	0.000	-528.05548
C_6H_5IH	11 24 28 122 143 403 429 601 624 674 726 814 900 970 994 10011019 1054 1076 1179 1179 1306 1328 1469 1477 1573 1631 2280 3160 3166 3179 3182 3191	1.337 (0.757) ^c	-528.56576
C_6H_6I	18 47 93 408 411 618 620 697 718 863 880 993 996 1008 1025 1030 1054 1062 1180 1195 1202 1340 1391 1511 1517 1612 1629 3168 3179 3180 3192 3194 3202	1.201 (0.753) ^c	-528.63185
C_6H_6I TS	-950 147 206 257 392 442 451 501 623 658 698 757 840 923 985 1005 1012 1024 1056 1100 1183 1205 1297 1349 1470 1493 1592 1602 3170 3178 3193 3203 3205	1.370 (0.770) ^c	-528.53969

^a B3LYP/cc-pVTZ-PP.

^b QCISD/cc-pVTZ-PP including ZPE; 1 au $\approx$ 2625.5 kJ mol⁻¹.

^c B3LYP value.

Fig. 4. Potential energy diagram for $H + C_6H_5I$ reaction paths, based on QCISD/cc-pVTZ-PP/B3LYP/cc-pVTZ-PP calculations.

can be approximately expressed in the form AT^n [36]. Cohen has noted that n could be as high as 2.2, or even larger if the transition state is very loose [36]. Such values of n with $E \approx 0$ are approximately consistent with the parameters in Eq. (5). A more detailed rationalization would require a variational transition state theory analysis.

5. Conclusions

The laser flash-photolysis resonance fluorescence technique has been used to measure the rate constant for the reaction of H atoms with iodobenzene. The temperature dependence of the rate constant shows non-Arrhenius behavior, and *ab initio* analysis of the possible reaction pathways suggests the dominant products are $HI + C_6H_5$,

rather than the more thermodynamically stable products $C_6H_6 + I$.

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