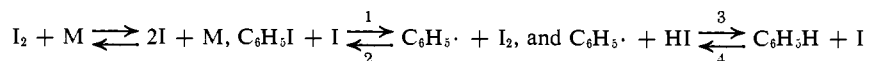# Kinetics of the Reaction of Iodobenzene and Hydrogen Iodide. The Heat of Formation of the Phenyl Radical and Its Implications on the Reactivity of Benzene[1]

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Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025. Received January 25, 1967
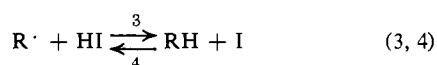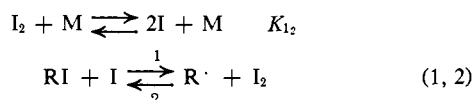
Abstract: The kinetics of the reaction of iodobenzene and hydrogen iodide were studied in the gas phase from 375 to 500°. The rate data were consistent with the free-radical mechanism

$$I_2 + M \underset{2}{\overset{1}{\rightleftarrows}} 2I + M, \; C_6H_5I + I \underset{2}{\overset{1}{\rightleftarrows}} C_6H_5\cdot + I_2, \text{ and } C_6H_5\cdot + HI \underset{4}{\overset{3}{\rightleftarrows}} C_6H_5H + I$$

and resulted in $\log(k_1, \text{l. mole}^{-1} \sec^{-1}) = (11.36 \pm 0.06) - (28.4 \pm 0.2)/\theta$. The assumption that $E_2 = 0 \pm 1$ kcal/mole yields $\Delta H_f{}^\circ{}_{298}(C_6H_5\cdot,g) = +80.0 \pm 1$ and $DH{}^\circ{}_{298}(C_6H_5-H) = 112.3 \pm 1$ kcal/mole. This is 5 to 10 kcal/mole higher than previous literature values, but nevertheless is found to be consistent with kinetic data on the pyrolysis of iodo- and bromobenzene. The discrepancy between this present work and data from radical "abstraction" reactions from benzene cannot be reconciled, indicating that these reactions proceed by a complex mechanism. A mechanism for "abstraction" from benzene is proposed and illustrated for the thermal chlorination and bromination of substituted benzenes. It is shown to be in quantitative, as well as qualitative, agreement with the available data.

The reactions of organic iodides with hydrogen iodide proceed by the free-radical mechanism[2]

$$I_2 + M \underset{}{\rightleftarrows} 2I + M \qquad K_{I_2}$$

$$RI + I \underset{2}{\overset{1}{\rightleftarrows}} R\cdot + I_2 \qquad (1, 2)$$

$$R\cdot + HI \underset{4}{\overset{3}{\rightleftarrows}} RH + I \qquad (3, 4)$$

This mechanism has been independently verified for $RH = CH_4$ by kinetic measurements on $CH_3I + HI$[3] and $CH_4 + I_2$,[4] and equilibrium measurements for $CH_3I + HI \rightleftharpoons CH_4 + I_2$.[5] A study of the kinetics of the conversion of RI results in Arrhenius parameters for k_1 (*i.e.*, A_1 and E_1). These combined with the assumption that $E_2 \cong 0$[6] yields a value for $\Delta H_{1,2}{}^\circ$ and, therefore, $\Delta H_f{}^\circ(R\cdot)$ provided $\Delta H_f{}^\circ(RI)$ is known. The values of $\Delta H_f{}^\circ(R\cdot)$, so obtained, define by eq 5 the bond dissociation energies in organic molecules.

$$DH{}^\circ(R-X) = \Delta H_f{}^\circ(X) + \Delta H_f{}^\circ(R\cdot) - \Delta H_f{}^\circ(R-X) \quad (5)$$

In this paper we consider the kinetics of the reaction of iodobenzene with hydrogen iodide and the heat of formation of the phenyl radical.

Experimental Section

The reaction of phenyl iodide with HI was followed by measuring the iodine partial pressure spectrophotometrically (λ 500 mμ) as a function of time. The temperature range covered was 375 to 500°. The apparatus has been described in detail previously.[5]

(1) (a) This investigation was supported in part by a research grant (AP 00353-03) from the Air Pollution Division, Public Health Service, U. S. Department of Health, Education, and Welfare. (b) Presented in part at the 2nd Western Regional Meeting of the American Chemical Society, San Francisco, Calif., Oct 1966 and at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

(2) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, 34, 514 (1961).

(3) M. C. Flowers and S. W. Benson, *ibid.*, 38, 882 (1963).

(4) C. A. Goy and H. O. Pritchard, *J. Phys. Chem.*, 69, 3040 (1965).

(5) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, 87, 4053 (1965).

(6) M. Christie, *Proc. Roy. Soc.* (London), A224, 411 (1958), has measured for $CH_3 + I_2 \longrightarrow CH_3I + I$ a value of $E_2 < 1$ kcal/mole, and this has been supported by ref 4 and 5.

a. Materials. Iodobenzene was obtained from Eastman Organic Chemical Co. and purified by gas–liquid chromatography on an F and M Prepmaster, using an SE-30 silicone oil column. Glc analysis showed it to be >99% pure. The benzene was Baker Reagent Grade and was used without further purification. Iodine was obtained from the Mallinckrodt Chemical Co. and was vacuum sublimed prior to use. Anhydrous HI was obtained from the Matheson Co. and purified by vacuum distillation.

b. Procedure. At each experimental temperature, the absorbance coefficient, α^λ, of C_6H_5I, HI, I_2, and C_6H_6 (equivalent to the absorption coefficient times the path length) was determined at 270, 280, and 500 mμ. Beer's law was found to hold to an OD of 2.0 to within ±2%; 380 mμ was used as an optical window ($\alpha^{380}_{C_6H_5I} \sim 5 \times 10^{-4}$ torr^{-1}). [At the higher temperatures, 460 to 500°, it was observed that phenyl iodide decomposed slightly as indicated by an increase in absorbance at 270, 280, and 500 mμ. This was, however, severely inhibited by I_2, so that all experiments (including calibration of C_6H_5I at 500°) at these temperatures were performed with from 1 to 5 torr of I_2 added initially.]

The absorbance of the evacuated cell ($\sim 10^{-5}$ torr) was determined at 270, 280, 380, and 500 mμ. Then the desired pressure of I_2 (when used) was admitted and its absorbance measured at these wavelengths, whereupon C_6H_5I was admitted and the absorbance and pressure again recorded. The agreement between the measured pressure and that calculated from the absorbance at 270 and 280 mμ was better than 2%. The desired pressure of HI was then expanded into the vessel and the absorbance at 500 mμ was recorded as a function of time with a synchronous motor chart drive. Kinetic measurements were made exclusively at 500 mμ, as this was the most sensitive wavelength for following the reaction (0.005 torr of I_2 could be detected) and gave a direct determination of the I_2 partial pressure (no other species absorbs at 500 mμ). The rate of the reaction was determined by the approximation $d(I_2)/dt = \Delta(I_2)/\Delta t$. The interval $\Delta(I_2)$ was adjusted to yield an estimated error in $d(I_2)/dt$ of 2 to 5%.

Results

Preliminary experiments were made at 400 and 460° to verify the stoichiometry of the reaction. These results are summarized in Table I and indicated that no important side reactions occurred.

A steady-state treatment of the mechanism, neglecting reaction 4, results in the rate expression

$$\frac{d(I_2)}{dt} = \frac{K_{I_2}{}^{1/2} k_1 (C_6H_5I)(I_2)^{1/2}}{1 + \left(\dfrac{k_2}{k_3}\right)\dfrac{(I_2)}{(HI)}} \quad (6)$$

Table I. Comparison of the Observed Increase in Iodine and Decrease in Iodobenzene Partial Pressures for the Reaction $C_6H_5I + HI \rightarrow C_6H_6 + I_2$

Temp, °C	$(I_2) - (I_2)_0$, torr; λ 500 mμ	$(C_6H_5I)_0 - (C_6H_5I)$, torr λ 280 mμ	λ 270 mμ
397.5[a]	1.47	1.58	1.49
	2.88	2.96	2.89
	3.93	3.98	3.91
	4.70	4.69	4.59
463.5[b]	2.76	2.77	2.74
	4.22	4.35	4.24
	5.09	5.24	5.16
	5.65	5.81	5.75

[a] $(C_6H_5I)_0 = 9.08$, $(HI)_0 = 11.1$, $(I_2)_0 = 0.07$ torr. [b] $(C_6H_5I)_0 = 7.1$, $(HI)_0 = 18.1$, $(I_2)_0 = 4.4$ torr.

This equation may be rearranged to yield

$$\frac{(I_2)}{(HI)} = \frac{K_{I_2}^{1/2}k_1k_3}{k_2}\frac{(C_6H_5I)(I_2)^{1/2}}{d(I_2)/dt} - \frac{k_3}{k_2} \quad (7)$$

When the ratio I_2/HI fell in the range 0.1 to 2.0, as in the experiments at 435 to 500°, the data were treated according to eq 7, and the values of k_3/k_2 and k_1[7] were obtained directly. A plot of the data at 500° is given in Figure 1. The value of k_3/k_2 obtained in this manner was estimated to be accurate to 8% and k_1 to 5%, due to the compensating changes in slope and intercept.

For the experiments at 375 to 400°, ratios of I_2/HI were in the range 0.01 to 0.1 so that the denominator of the right-hand side of eq 6 was ~ 1. Under such conditions the data were appropriately treated according to eq 6 with a value of k_2/k_3 extrapolated from the data in the range 435 to 500°. The value so obtained was 5 ± 0.5 and was used at 400 and 375°. Note that a 10% error in k_2/k_3 will yield less than a 2% error in k_1. All the data obtained at 404° are given in Figure 2. The three runs included span a threefold variation in HI concentration and provide direct evidence that the rate is independent of the HI concentration and dependent on the square root of the I_2 concentration at low I_2/HI ratios, as predicted by the mechanism. The slope of this curve gave $K_{I_2}^{1/2}k_1$ from which k_1 may be derived;[7] the estimated uncertainty was 5%. This value of k_1 may then be used in an inhibited run (i.e., high value of $(I_2)/(HI)$, see Table II) to experimentally determine $k_3/k_2 = 0.215$ at 402°. [The data represented by open circles in Figure 2 show that the initial rate of formation of iodine is greater than that predicted. This was generally observed in all runs at less than 1% conversion, as well as in the pyrolysis of 100 torr of HI at 400°. We suspect that this enhanced rate of formation of iodine resulted from the oxidation of HI by trace amounts (10^{-3} to 10^{-2} torr) of oxygen. The stoichiometry may be $4HI + O_2 \rightarrow 2I_2 + 2H_2O$.]

The experimental values for k_1 and k_3/k_2 are summarized in Table II and yield

$$\log (k_1, \text{l./mole sec}) = 11.36 \pm 0.06 - \frac{28.4 \pm 0.2}{\theta} \quad (8)$$

$$\log (k_3/k_2) = -0.14 \pm 0.3 - \frac{1.6 \pm 1}{\theta} \quad (9)$$

The errors are one standard deviation; $\theta = 2.303RT$ kcal/mole.

(7) Thermodynamic data for $K_{I_2}^{1/2}$ were obtained in "JANAF Interim Thermochemical Tables," D. P. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963.
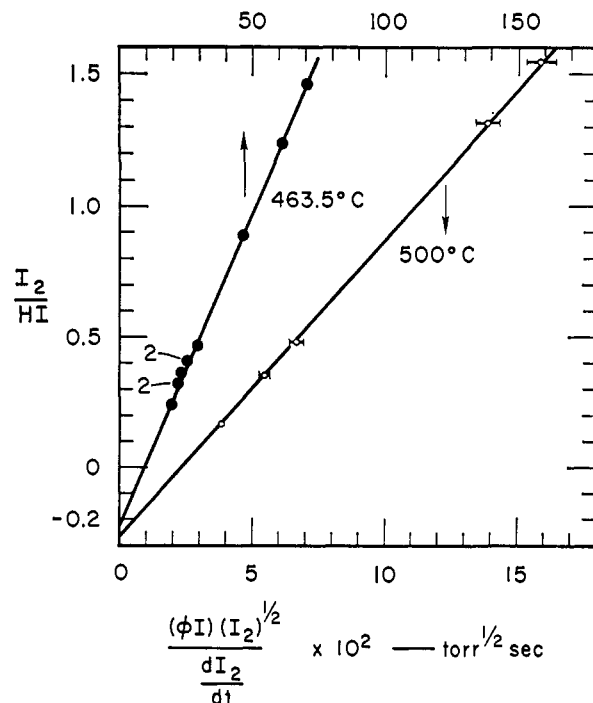

Figure 1. Plot of $(I_2)/(HI)$ vs. $(C_6H_5I)(I_2)^{1/2}/\text{rate}$ at 460 and 500° Numerals denote overlapping data.
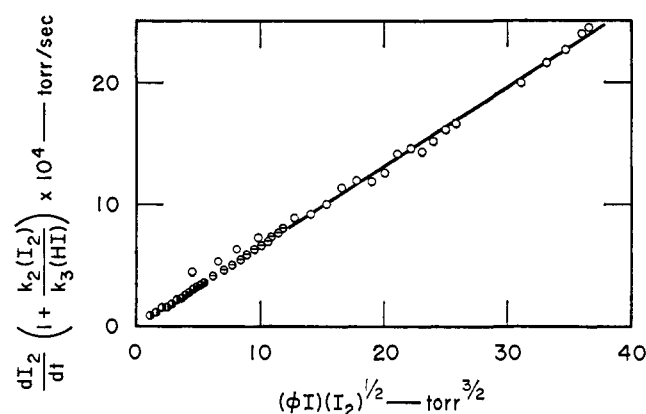

Figure 2. Plot of rate$(1 + k_2(I_2)/k_3(HI))$ vs. $(C_6H_5I)(I_2)^{1/2}$ at 404°. Initial conditions in torr and per cent reaction of last point are: O, $C_6H_5I = 21.1$, $HI = 59.4$, 44%; $\ominus$, $C_6H_5I = 11.7$, $HI = 24.5$, 11%; $\bullet$, $C_6H_5I = 5.75$, $HI = 44.7$, 30%.

These experimental data may be combined with the thermodynamic data of Table III and the assumption that $E_2 = 0 \pm 1$ kcal/mole to yield the following rate constants at the mean temperature 700°K (units of l./mole sec): $k_2 = 10^{9.74}$, $k_3 = 10^{9.60 - 1.6/\theta}$, and $k_4 = 10^{12.18 - 43.0/\theta}$. The logarithm of Arrhenius preexponential factor (log A) in k_1 is 11.36 (l. mole^{-1} sec^{-1} units) and falls in the range of values previously reported, namely 11.4 for CH_3I,[3] 11.0 for C_2H_5I,[8a] and 10.9 for CH_3COI.[8b] The A factor may be expressed in terms of collision theory as

$$A = pZe^{1/2}$$

where p is a steric factor, generally less than unity, and Z is the collision frequency. The $e^{1/2}$ arises as a result

(8) (a) D. B. Harley and S. W. Benson, J. Chem. Phys., **39**, 132 (1963); (b) H. E. O'Neal and S. W. Benson, ibid., **37**, 540 (1962); (c) R. Walsh and S. W. Benson, J. Am. Chem. Soc., **88**, 4570 (1966).

Table II. Kinetic Data for the Reaction $C_6H_5I + HI \rightleftharpoons C_6H_6 + I_2$

Temp, °C	Pressure, torr C_6H_5I	HI	I_2	$d(I_2)/dt$ $\times 10^3$ torr sec^{-1}	$k_1 \times 10^3$, torr^{-1} sec^{-1}	k_3/k_2	Expt no.	$K_{I_2}^{1/2}$, torr$^{1/2}$
500	7.58	42.28	7.73	54.6				
	4.60	44.30	10.71	31.6				
	4.67	14.87	5.26	19.6				
					44.0	0.26	3	9.82×10^{-2}
	3.38	13.59	6.54	13.1				
	8.03	4.03	5.27	13.2				
	7.66	3.66	5.64	11.4				
463.5	6.38	7.08	6.29	3.45				
	5.26	5.96	7.41	2.34				
	4.73	5.43	7.94	1.89				
	6.13	17.13	5.37	6.32				
					19.9	0.22	3	5.435×10^{-2}
	4.34	15.34	7.16	4.01				
	16.14	13.84	3.32	15.0				
	15.28	12.98	4.18	13.6				
	14.51	12.21	4.95	12.5				
436.5	2.24	8.94	2.86	0.490				
	3.18	9.88	1.92	0.729				
	7.42	10.32	1.98	1.76				
					8.82	0.25	3	3.374×10^{-2}
	4.83	7.73	4.57	0.925				
	20.0	4.84	1.75	3.32				
	18.91	3.71	2.89	2.40				
435.5	10.32	9.62	5.95	2.00				
	9.59	8.89	6.69	1.74				
					9.15	0.22	1	3.313×10^{-2}
	7.58	6.88	8.70	1.02				
	6.95	6.25	9.33	0.831				
404[a]	20.63	58.93	0.47	0.887				
	19.85	58.15	1.25	1.32				
	19.31	57.61	1.79	1.45				
	11.32	24.12	0.38	0.423				
	11.14	23.94	0.56	0.484	3.62	0.20[b]	3	1.81×10^{-2}
	10.83	23.63	0.87	0.533				
	5.54	44.54	0.21	0.181				
	5.20	44.20	0.55	0.245				
	4.43	43.43	1.32	0.292				
402[a]	7.95	20.05	0.25	0.215				
	7.80	19.90	0.40	0.260				
	7.54	19.64	0.66	0.289				
					3.42	0.20[b]	2	1.735×10^{-2}
	3.98	11.38	0.25	0.105				
	3.75	11.15	0.50	0.125				
	3.36	10.76	0.89	0.132				
402[c]	20.73	3.43	8.77	0.282	3.42	0.22		
	20.25	2.95	9.25	0.232	3.42	0.21		
375[a]	5.74	9.04	0.061	0.0187				
	5.71	9.01	0.093	0.0234				
	5.67	8.97	0.131	0.0280				
					1.48	0.20[b]	2	0.971×10^{-2}
	9.63	11.43	0.0715	0.0364				
	9.57	11.37	0.136	0.0467				
	9.49	11.29	0.213	0.0575				

[a] Representative data. [b] Extrapolated value. [c] Experimental determination of k_3/k_2.

of the $T^{1/2}$ dependence in Z. By taking the mean collision diameter as 5 A at 725°K, log $Ze^{1/2}$ = 11.52, so that $p \cong 1$. A value of p near unity implies little need for orientation in the collision pair and corresponds to a loose transition state in the language of transition-state theory.[9]

The value obtained for log (A_3/A_2) = -0.14 ± 0.3 compares favorably with previous determinations which have yielded[8a-c] -0.5 ± 0.3. From this comparison, one might prefer the lower end of the error range, i.e., log A_3/A_2 = -0.5, and consideration of log A_4 reenforces this preference. For reaction 4, at 725°K

(9) S. W. Benson, "Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 271-781.

and a mean collision diameter of 5 A, log $Ze^{1/2}$ = 11.75 (l. mole^{-1} sec^{-1} units). This is about 0.4 log unit lower than given above and would require $p \cong$ 3 or, on the other hand, a mean diameter of about 8 A. Neither of these alternatives is readily justified, and therefore, they indicate a more negative value for log A_3/A_2. Consequently, the preferred values for k_3 and k_4, based upon log (k_3/k_2) = $-0.5 - (0.4/\theta)$, become (l. mole^{-1} sec^{-1} units) log k_3 = $9.24 - (0.4/\theta)$ and log k_4 = $11.82 - (41.8/\theta)$. From the assumption that $E_2 = 0$, we have $\Delta H_{1,2}°(700°K)$ = 28.4 ± 1 kcal/mole, this value corrected to 298° yields $\Delta H_{1,2}°$ (298°K) = 28.9 ± 1 kcal/mole, and therefore, $\Delta H_f°_{298}$ ($C_6H_5\cdot$,g) = $+80.0 \pm 1$ kcal/mole. This may be used

Table III. Summary of Thermodynamic Data
for Ideal Gas at 1 Atm[a]

Compd	S°_{298}, eu	$\Delta H_f^{\circ}_{298}$, kcal/mole	C_p, cal deg^{-1} mol^{-2} 298°	500°	700°	S°_{700}, eu	$\Delta H_f^{\circ}_{700}$, kcal/ mole
I_2	62.3	14.9	8.8	8.9	9.0	69.9	0.0
I	43.2	25.5	5.0	5.0	5.0	47.4	18.3
HI	49.4	6.3	7.0	7.1	7.4	55.4	−1.5
C_6H_6[b]	64.3	19.8	19.5	32.8	41.8	90.3	16.0
C_6H_5·[c]	69.2	...	19.2	31.5	39.5	94.1	...
C_6H_5I[d]	84.8	40.5 ± 0.2	24.3	36.9	44.7	109.2	30.5

[a] Data from ref 7, unless indicated. [b] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa, 1953. [c] Estimated from benzene, assuming 3000-, 1400-, and 1200-cm^{-1} vibrational frequencies have been lost. [d] S° and C_p from D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956); $\Delta H_f^{\circ}(1)$ from A. S. Carson, E. M. Carson, and B. Wilmshurst, *Nature*, **170**, 320 (1952); and L. Smith, *Acta Chem. Scand.*, **10**, 884 (1956); ΔH_v from D. R. Stull, *Ind Eng. Chem.*, **39**, 517 (1947).

with eq 5 to yield $DH^{\circ}_{298}(C_6H_5-I) = 65.0 \pm 1$ kcal/ mole and $DH^{\circ}_{298}(C_6H_5-H) = 112.3 \pm 1$ kcal/mole.

Discussion

Several values for $DH^{\circ}_{298}(C_6H_5-H)$, ranging from 102 to 107 kcal/mole, have been previously reported and these will be considered separately.

Butler and Polanyi[10] have studied the pyrolysis of C_6H_5I at 510° in a flow system with H_2 carrier gas. The partial pressure of C_6H_5I was 30 μ, and the reaction was carried to $\sim$3% completion (Figure 3). Under these conditions, the primary mode of decomposition is[11]

$$C_6H_5I \longrightarrow C_6H_5 \cdot + I \qquad (10)$$
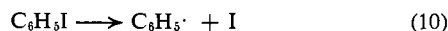
The Arrhenius parameters for k_{10} are given by transition state theory as

$$k_{10} = \frac{ekT}{h}\exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{E_a}{\theta}\right) = 10^{14.3 - (E/\theta)} \text{ sec}^{-1} \qquad (11)$$

in which a value of $\Delta S^{\ddagger} = 3 \pm 2$ eu has been assumed.[12] The measured value for k_{10} at 783°K is $10^{-2.1}$ sec^{-1} and yields $E_{10} = 59$ kcal/mole; assuming $E_{-10} \cong 0$, then $\Delta H_{10}^{\circ}(800°K) = \Delta E_{10}^{\circ}(800°K) + RT_{mean} = 60.6$ kcal/mole. Correcting to 298°K yields $DH^{\circ}_{298}(C_6H_5-H) = 108$ kcal/mole.

Ladacki and Szwarc[13] have measured the rate of pyrolysis of bromobenzene from 1050 to 1150°K, using the toluene carrier technique. They found that the rate-limiting step was

$$C_6H_5Br \longrightarrow C_6H_5 \cdot + Br \qquad (12)$$
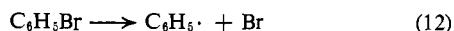
and a least-squares analysis of their results gave

$$\log k_{12} = 13.3 - (70.9/\theta) \text{ sec}^{-1}$$

With the assumption that $E_{-12} = 0$, then

$$\Delta H_{12}^{\circ}(1100°K) = 70.9 + RT_{mean} = 73 \text{ kcal/mole}$$

$\langle \Delta C_p \rangle$ from 1100 to 300°K is essentially zero, so that

(10) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).
(11) The I partial pressure is too low for reaction 1 to compete, *i.e.*, $k_1(I)/k_{10} \leq 0.1$.
(12) For this bond-breaking reaction, one would expect a slightly positive entropy of activation. The value assumed corresponds to $A_{-10} = 10^{9.5}$ l./mole sec and appears reasonable in view of th∍ fact that A_2 is $10^{9.7}$ l./mole sec.
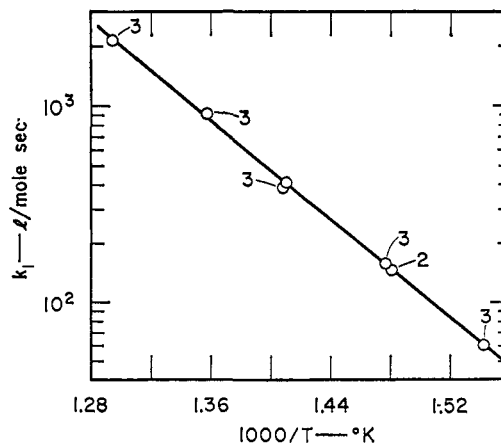(13) M. Ladacki and M. Szwarc, *Proc. Roy. Soc.* (London), **A219**, 341 (1953).

Figure 3. Arrhenius plot for the reaction $C_6H_5I + I \rightarrow C_6H_5 \cdot + I_2$. Numerals indicate number of combined experiments.

$\Delta H_{12}^{\circ}(298°) = 73$ kcal/mole, and from the heat of formation[14,15] of bromobenzene, $DH^{\circ}_{298}(C_6H_5-H) = 105.5$ kcal/mole. However, as in the case of iodobenzene, the entropy of activation should be positive rather than negative, a value of $\Delta S^{\ddagger} = 3 \pm 2$ eu being preferred. This results in $\log k_{12} = 14.3 - (75.9/\theta)$ from the observed rate constant of 0.13 sec^{-1} at 1080°K, and yields $DH^{\circ}_{298}(C_6H_5-H) = 110.5$ kcal/mole. It should also be noted that these parameters yield an Arrhenius curve barely distinguishable from that given by Ladacki and Szwarc.

Within the different experimental scatter then, the pyrolysis data are found to yield bond dissociation energies consistent with the present work. Duncan and Trotman-Dickenson[16] have studied the kinetics of reaction 13 and combined their results with those of Trotman-Dickenson and Steacie[17] on reaction −13 to obtain $DH^{\circ}_{298}(C_6H_5-H) = 102$ kcal/mole.

Fielding and Pritchard[18] have obtained Arrhenius parameters for reactions 13 and 14. Combining these values with those for the reverse reactions,[17,19,20a] they obtained $DH^{\circ}(C_6H_5-H) = 105$ and 107 kcal/mole.

$$C_6H_5 \cdot + CH_4 \rightleftarrows C_6H_6 + CH_3 \qquad (13)$$

$$C_6H_5 \cdot + CF_3H \rightleftarrows C_6H_6 + CF_3 \qquad (14)$$

These values are based upon the assumption that the reverse reactions (−13 and −14) take place as direct abstraction reactions.[16] However, Whittle and co-workers[20] have presented convincing evidence that "abstraction" of hydrogen from the aromatic ring by trifluoromethyl radicals occurs *via* addition to form a cyclohexadienyl radical and subsequent disproportionation. Szwarc and Levy[21] have shown that methyl radicals add to benzene at a rate competitive with the abstraction of hydrogen from isooctane, as do trifluoro-

(14) A. S. Carson, E. M. Carson, and B. Wilmshurst, *Nature*, **170**, 320 (1952).
(15) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).
(16) F. J. Duncan and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4672 (1962).
(17) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).
(18) W. Fielding and H. O. Pritchard, *J. Phys. Chem.*, **66**, 821 (1962).
(19) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).
(20) (a) S. W. Charles and E. Whittle, *ibid.*, **56**, 794 (1960); (b) S. W. Charles, J. T. Pearson, and E. Whittle, *ibid.*, **57**, 1356 (1961); (c) R. D. Giles and E. Whittle, *ibid.*, **62**, 128 (1966).
(21) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955).

methyl radicals.[22] It therefore appears quite reasonable to expect the gas-phase reactions of methyl and trifluoromethyl radicals with benzene to be similar, so that the reported kinetic parameters[17,19] are not applicable to reactions -13 and -14. Indeed, the discrepancy between the values reported by Trotman-Dickenson[16] and Pritchard[18] for $DH°_{298}(C_6H_5-H)$ and the present work may be taken as evidence for a more complex mechanism for "abstraction" in benzene.[23] The high value for $DH°_{298}(C_6H_5-H)$ tends to make this a general conclusion which may be illustrated by a detailed consideration of the thermal chlorination and bromination of substituted benzenes.

These reactions, which result in nuclear substitution, have been studied by Kooyman and co-workers.[24] They have treated their data qualitatively and suggested a one-step bimolecular mechanism. We, however, feel that a free-radical mechanism, involving cyclohexadienyl radicals and cyclohexadiene as intermediates, is not only in qualitative accord with the experimental data, but is also in quantitative agreement with the kinetic observations for chlorination and semiquantitative agreement for bromination.[25]

The proposed mechanism, illustrated for *para* addition and *meta* substitution, is
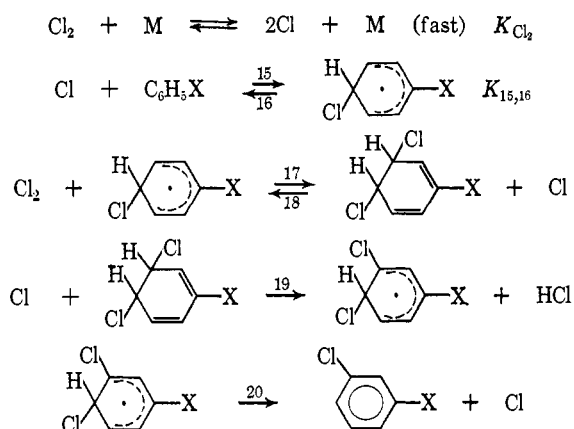
This yields, with the usual steady-state assumption

$$\frac{d(\text{product})}{dt} = \frac{k_{17}k_{19}}{k_{18} + k_{19}} K_{15,16}K_{Cl_2}^{1/2}(C_6H_5X)(Cl_2)^{1/2}$$

(21)

Applying this equation to the data (Table IV) on chlorination,[24] we find for $X = CF_3$

$$\frac{k_{17}k_{19}}{k_{18} + k_{19}} K_{15,16} = 10^{6.5 + 9/\theta}$$

(22)

From the Arrhenius parameters assignable to k_{17}, k_{18}, and k_{19} (see Appendix), we obtain

$$\frac{k_{17}k_{19}}{k_{18} + k_{19}} \cong 10^{10 - 3/\theta} \text{ l. mole}^{-1} \text{ sec}^{-1}$$

(23)

(22) A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961); A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).
(23) The average of ref 16 and 18 gives $E_{13} = 9.3 \pm 2$ kcal/mole. This combined with $\Delta H_{13}° = -8.3 \pm 1.4$ kcal/mole from the present work results in $E_{-13} = 17.6 \pm 2.5$ kcal/mole for direct abstraction.
(24) E. C. Kooyman, "Advances in Free Radical Chemistry," Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 137.
(25) (a) R. J. Albers and E. C. Kooyman, *Rec. Trav. Chem.*, **83**, 930 (1964); (b) J. de Graaf and H. Kwart, *J. Phys. Chem.*, **67**, 1458 (1963).

and from eq 23

$$K_{15,16}(700°K) = 10^{-3.5 + 12/\theta} \text{ l. mole}^{-1} \text{ sec}^{-1}$$

(24)

Under typical reaction conditions, this gives a negligible steady-state concentration of diene of about 0.3 mole % $C_6H_5CF_3$. At lower temperatures cyclohexadiene and other addition products will represent an appreciable part of the over-all yield, as is observed in the photochlorination of benzene and its derivatives.[26]

The uncertainties in (24) should be less than a power of ten in the preexponential factor and 3 kcal/mole in the activation energy so that similar limits hold for (24). Therefore

$$\Delta H_{15,16}° = \Delta E_{15,16}° - RT_{\text{mean}} = -13.4 \pm 3 \text{ kcal/mole}$$

(25)

This leads to a value (see Appendix) of 25.5 ± 3 kcal/mole for the stabilization energy of the substituted cyclohexadienyl radical, which is in good agreement with the value of 24.5 ± 3 kcal/mole derived from the data of Suart[27] and Benson and Shaw[28] for cyclohexadienyl radical. The data for bromination (Table IV)

Table IV. Rate Data for the Chlorination and Bromination of Benzotrifluoride in the Gas Phase

Temp, °C	Cl_2, mmoles/l.[a]	% conversion[b]	Contact time, sec	Log $(k_{17}k_{19}K_{15,16}/k_{18} + k_{19})$[c]	% conversion (calcd)
350	2.4	40	177	9.65	40[d]
400	1.2	39	146	9.42	39
450	1.08	50	140	9.07$_3$	58
	Br_2				
400	4.8	28	142	6.50	28[e]
450	4.17	37	107	6.41	42

[a] Steady state. [b] Based on $C_6H_5CF_3$. [c] Log $K_{Cl_2}^{1/2} = 1.86 - 28.6/\theta$; log $K_{Br_2}^{1/2} = 1.75 - 22.6/\theta$ from ref 7; $\theta = 2.303RT$ kcal/mole. [d] Calculated by eq 22 and 23. [e] Calculated by eq 22 and 30.

lead to the following relationship for the relevant rate constants

$$\log\left(\frac{k_{17}k_{19}}{k_{18} + k_{19}}K_{15,16}\right) = (6.5 \pm 1) - (0 \pm 3)/\theta$$

(26)

and are also consistent with the observed value of the cyclohexadienyl stabilization energy.

The rapid exchange reactions observed by Kooyman and co-workers[24] can readily be accounted for by reactions 15 and 16 and would be expected to be fast when $DH°(C-X) < DH°(C-Y)$.

Thus, the reaction of chlorine with nitrobenzene (Y = Cl and X = NO_2) has been reported to occur quantitatively at 275°. The rate of exchange will be given by

$$\text{rate} = k_{15'}K_{Cl_2}^{1/2}(C_6H_5NO_2)(Cl_2)^{1/2}$$

(26) H. P. Smith, W. A. Noyes, Jr., and E. J. Hart, *J. Am. Chem. Soc.*, **55**, 4444 (1933); E. J. Hart and W. A. Noyes, Jr., *ibid.*, **56**, 1305 (1934).
(27) R. D. Suart, Thesis, University of British Columbia, Vancouver, B. C.
(28) S. W. Benson and R. Shaw, to be submitted.

$k_{15'}$ may be estimated at $10^{9.2 - 4/\theta}$ (the A factor for addition should be $\sim 10^{10}$ so that addition at a particular site is $\sim 10^{10}/6 = 10^{9.2}$), with $(Cl_2) = 10^{-2.2}$ moles/l. Then

$$\text{rate}/(C_6H_5NO_2) \simeq 10^{-2.9} \text{ sec}^{-1}$$

In this case, NO_2 acts as a catalyst for establishing the Cl_2–Cl equilibrium.

Levine and Noyes[29] have studied the exchange of radioactive iodine with iodobenzene and p-nitroiodobenzene in solution ($Y = I^*$ and $X = I$). They found that exchange occurred by two paths, one of which was first order in aromatic and half-order in iodine. For this path they proposed a free-radical mechanism formally equivalent to that suggested here, so that

$$(\text{rate})_{ex} = 0.5k_{15'}K_{I_2}^{1/2}(C_6H_5I)(I_2)^{1/2}$$

The rate constant for exchange in the temperature range of 170–200° was

$$\log (k_{ex}, 1.^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1}) = 10.5 - 35/\theta$$

so that

$$\log (k_{15'}, 1. \text{ mole}^{-1} \text{ sec}^{-1}) = 9.13 - 17.3/\theta$$

The A factor for (15') is in good agreement with the estimate above, and $E_{15'}$ leads to a stabilization energy for the cyclohexadienyl radical of 25.5 kcal/mole, if $E_{16'} = 2$ kcal/mole.[30,31] This, too, is in good agreement with the chlorination data.

Reaction 19 would be expected to have a kinetic isotope effect of $k_{19}(H)/k_{19}(D) \cong 2$. The reported[24,32] value of 1.4 for benzene-1,3,5-d_3 is consistent with this mechanism, as is the isotope effect of about 1.5 for benzene and benzene-d_6.[32]

The detailed analysis of the isomeric distribution of the product would be very complex. However, qualitatively one would expect the distribution to be essentially temperature independent and statistical with the exception that $ortho$ substitution might show a steric effect and be lower than expected ($ortho$ substitution

requires abstraction of a hydrogen atom in (19) adjacent to the X group). This is essentially consistent with the observations.[24,25,33] The nonstatistical $meta/ortho$ ratio, generally about 4 to 6, suggests such a steric effect.

The addition mechanism is also consistent with the generally accepted reactions of free radicals with aromatic compounds[34] and has been shown to account for the kinetics of hydrogenation of toluene and xylene.[35]

Appendix

The rate constants k_{17} and k_{19} may be estimated from analogous reactions in the literature;[36,37] thus, on a per site basis

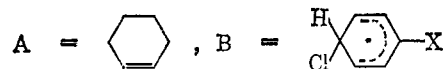$$\log (k_{17}, 1. \text{ mole}^{-1} \text{ sec}^{-1}) \sim 9.0 - 3/\theta$$

and

$$\log (k_{19}, 1. \text{ mole}^{-1} \text{ sec}^{-1}) \sim 10 - 3/\theta$$

k_{18} may be taken similar to k_{19}.
The heat of reaction 15 is given by

$$\Delta H_{15,16}° = D_\pi°(A) + SE°(C_6H_5X) - DH°(C-Cl) - SE°(B)$$

in which the π bond in benzene has been equated to the π bond in cyclohexene, $D_\pi°(A)$, and $SE°(C_6H_5X)$ and $SE°(B)$ are the stabilization energies of benzene and the cyclohexadienyl radical, respectively.

To evaluate these quantities, it is assumed that the bond dissociation energy $DH°(C-X)$ in cyclohexane is the same as in CH_3–CHX–CH_3. Therefore[38] $D_\pi°_{298}$ (cyclohexene) = 56.4 kcal/mole, $DH°_{298}(C-Cl) = 81.0$, and $SE°_{298}$(benzene) = 36.5.

(29) S. Levine and R. M. Noyes, $J. Am. Chem. Soc.$, 80, 2401 (1958).
(30) R. M. Noyes, R. G. Dickinson, and V. Schomaker, $ibid.$, 67, 1319 (1945).
(31) S. W. Benson, K. W. Egger, and D. M. Golden, $ibid.$, 87, 469 (1965).
(32) E. C. Kooyman, $Pure Appl. Chem.$, 7, 193 (1963).
(33) J. W. Engelsma, E. C. Kooyman, and J. R. Van der Bij, $Rec. Trav. Chim.$, 76, 325 (1957).
(34) See, for example, C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1958: (a) p 156; (b) pp 308–310; (c) 482–485; (d) pp 496–497.
(35) S. W. Benson and R. Shaw, to be published.
(36) P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hearst, $Trans. Faraday Soc.$, 58, 295 (1962).
(37) G. C. Fettis and J. H. Knox, $Progr. Reaction Kinetics$, 2, 3 (1964).
(38) S. W. Benson, $J. Chem. Educ.$, 42, 502 (1965).