

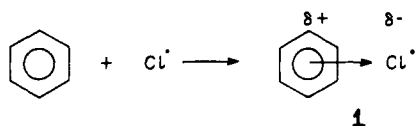
# Kinetic Study of the Photochlorination of 2,3-Dimethylbutane and Other Alkanes in Solution in the Presence of Benzene. First Measurements of the Absolute Rate Constants for Hydrogen Abstraction by the "Free" Chlorine Atom and the Chlorine Atom-Benzene $\pi$ -Complex. Identification of These Two Species as the Only Hydrogen Abstractors in These Systems<sup>1</sup>

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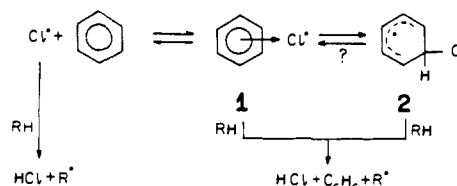
**Abstract:** Five photochemical sources have been employed to generate chlorine atoms in solution in the presence of benzene at room temperature. The chlorine atoms react with benzene ( $k_3 = 6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) to form a species which is firmly identified as the  $\text{C}_6\text{H}_6\text{Cl} \cdot \pi$ -complex, **1**. Laser flash photolytic techniques have been employed to measure absolute rate constants for hydrogen atom abstraction from various alkanes by **1**. This species proved to have a reactivity less than that of the "free" chlorine atom but greater than that of the *tert*-butoxyl radical. These absolute rate constants are in satisfactory agreement with the results of competitive chlorinations of certain alkanes in benzene solvent. Absolute rate constants were also measured for the reaction of the "free" chlorine atom with 2,3-dimethylbutane (DMB). A reasonably comprehensive study of the tertiary/primary selectivity for chlorination of DMB over a range of concentrations and in a variety of benzene/ $\text{CCl}_4$  mixtures has been carried out. It is shown that this DMB selectivity data can be quantitatively described by a kinetic scheme which involves hydrogen abstraction by *only* two species, "free" Cl $\cdot$  atoms and **1**.

In 1955 Russell and Brown<sup>3</sup> suggested that organic photochlorinations carried out in the presence of aromatic compounds would involve an attack on the substrate not by chlorine atoms but by a chlorine atom-aromatic  $\pi$ -complex, and that this complex would exhibit a selectivity different from that of a (free) chlorine atom. This suggestion was soon to be brilliantly confirmed by Russell<sup>4-6</sup>—at least insofar as selectivity was concerned. For example,<sup>5</sup> Russell found that at 25 °C with 2,3-dimethylbutane as substrate, which is referred to hereafter as DMB, the tertiary-to-primary selectivity on a per hydrogen basis,  $S$ ,<sup>7</sup> increased from 4.2 in the pure liquid alkane to 59 in 8 M benzene. Russell proposed an equilibration between the free chlorine atom and a chlorine atom-aromatic  $\pi$ -complex, the complex having the higher selectivity and its relative importance being increased by raising the concentration of the aromatic solvent. The aromatic compound acts as an electron donor and the chlorine atom as an electron acceptor, and so the complex has a certain "charge-transfer" character.



Russell assumed, quite reasonably, that the increase in selectivity brought about by the addition of benzene was accompanied by a decrease in reactivity; i.e., he assumed that the complex **1** was less reactive in hydrogen atom abstractions than a chlorine atom. However, no rate data supporting this assumption have, heretofore, been reported.

Scheme I



Walling and Mayahi<sup>8</sup> soon provided excellent and independent confirmation of Russell's major results and of his conclusions regarding the formation of **1** as a second hydrogen abstracting species.<sup>9</sup> Somewhat later, a transient absorption having  $\lambda_{\text{max}} \sim 490 \text{ nm}$ , which was obtained by the pulse radiolysis of benzene in carbon tetrachloride, was identified as the chlorine atom-benzene charge-transfer complex, i.e., **1**.<sup>10,11</sup> The same species has also been observed in a  $\gamma$ -irradiated benzene/ $\text{CCl}_4$  matrix at 77 K.<sup>12,13</sup>

Essentially nothing more was added to our understanding of this chemistry until 1983 when Skell, Baxter, and Taylor<sup>14</sup> reinvestigated the photochlorination of DMB in the absence and presence of benzene.<sup>15</sup> They made a new observation: to wit,

(8) Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485-1489.

(9) The senior author appears, however, to have had some second thoughts. See: Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368-3375.

(10) Bühler, R. E.; Ebert, M. *Nature (London)* **1967**, *214*, 1220-1221.

(11) Bühler, R. E. *Helv. Chim. Acta* **1968**, *51*, 1558-1571.

(12) Louwrier, P. F. W.; Hamill, W. H. *J. Phys. Chem.* **1969**, *73*, 1707-1711.

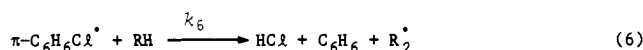
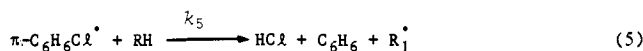
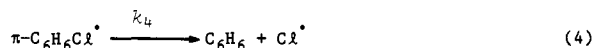
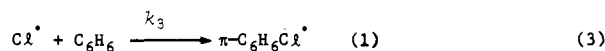
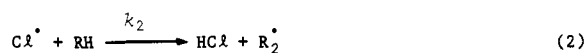
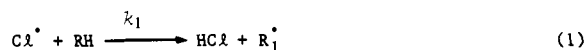
(13) For generally related optical studies of the bromine atom and iodine atom charge-transfer complexes with benzene, see: Yamamoto, N.; Kajikawa, T.; Sato, H.; Tsubomura, H. *J. Am. Chem. Soc.* **1969**, *91*, 265-267. Strong, R. L.; Rand, S. J.; Britt, J. A. *Ibid.* **1960**, *82*, 5053-5057. For other related work see: Bossy, J. M.; Bühler, R. E.; Ebert, M. *Ibid.* **1970**, *92*, 1099-1101. Bossy, J. M.; Bühler, R. E. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 85-94, 95-116. Fox, M.-A.; Nichols, W. C., Jr.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 8164-8166. Edwards, J.; Hills, D. J.; Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1974**, 556-557. Sergeev, G. B.; Pukhovskii, A. V.; Smirnov, V. V. *Zh. Fiz. Khim.* **1983**, *57*, 977-980.

(14) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120-121.

(15) The results of chlorinations in  $\text{CS}_2$ , which shows a strong solvent effect on selectivity,<sup>5</sup> were also reported.<sup>14</sup>

(1) Issued as NRCC No. 24331.  
 (2) (a) University of Guelph. (b) National Research Council of Canada.  
 (c) NRCC Research Associate 1982-85.  
 (3) Russell, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 4031-4035.  
 (4) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 2977-2978.  
 (5) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987-4996.  
 (6) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997-5001.  
 (7) Throughout this paper  $S^m$  refers to the molecular tertiary-to-primary ratio of chlorides produced from 2,3-dimethylbutane, while  $S$  refers to this ratio on a per hydrogen basis, i.e.,  $S = 6S^m$ .

## Scheme II



the selectivity,  $S$ , increased with a decrease in the concentration of DMB under conditions where the concentration of benzene was kept constant (at 4 M). They hypothesized that in addition to free chlorine atoms and the  $\pi$ -complex **1**, there was also a third hydrogen atom abstracting species which was more selective than either of these. It was suggested that this third abstractor was the  $\sigma$ -complex, **2**, i.e., the chlorocyclohexadienyl radical (see Scheme I).

In this paper we report the results of a reexamination of the question of complexation effects in the chlorination of alkanes in the presence of benzene. We have combined conventional<sup>3-6,8,14</sup> intra- and intermolecular selectivity measurements with laser flash photolysis studies. The latter have allowed us to address directly, in time-resolved experiments, the questions of complexation, of reactivity, and of the number and properties of the hydrogen abstracting agents that are required to explain the experimental data. We conclude that it is not necessary to invoke more than two abstractors, which we identify as the free chlorine atom and the  $\pi$ -complex, **1**. That is, for an alkane such as DMB which has two types of reactive hydrogen, Scheme II is sufficient to explain the observed selectivities and reactivities. We further note that our experimental results do not show significant discrepancies with those of earlier workers. Rather, our new experiments provide a better, more complete and properly quantitative understanding of the reaction mechanism.

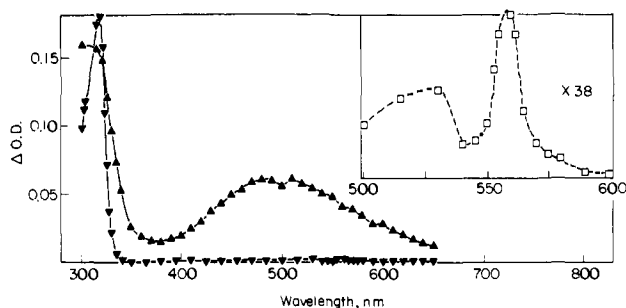
## Results

The laser flash photolytic experiments have been carried out under conditions which permit adequate comparison with the results of product studies. Unless otherwise indicated, experiments were carried out under oxygen-free conditions at room temperature (27 °C for the laser experiments and ca. 22 °C for product studies). Several alkanes have been examined, but a considerable fraction of our attention has focused on DMB which has been at the center of several earlier studies.<sup>5,8,14</sup> This section has been divided according to the experimental technique employed.

**A. Laser Flash Photolysis.** These experiments were carried out using the pulses from a nitrogen (337 nm) or excimer (308 nm) laser for excitation.

**Characterization of the Chlorine Atom-Benzene Complex.** Some of the spectral characteristics of this complex, particularly at  $\lambda > 400$  nm, are well established.<sup>10-12</sup> The spectrum (see Figure 1) shows a broad band,  $\lambda_{\text{max}}$  490 nm, which, on the basis of fairly compelling evidence,<sup>10-13</sup> has always been attributed to the charge-transfer,  $\pi$ -complex, **1**. There is also a second, stronger absorption in the UV. We have been able to generate this species using five independent sources of chlorine atoms. Though each system is best suited to a particular type of study they lead, overall, to a clear and unequivocal picture of the spectroscopic and kinetic properties of the complex.

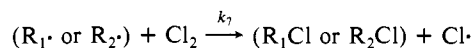
**System 1. Photodecomposition of Molecular Chlorine.** Laser photodecomposition of  $\text{Cl}_2$  in solutions containing benzene leads to the rapid formation of absorption bands at 490 nm and  $\lambda < 330$  nm. The UV absorption is about three times as intense as the visible band; the latter is identical with that previously assigned<sup>10-12</sup>



**Figure 1.** Transient spectra obtained by 308-nm excitation of solutions of di-*tert*-butyl peroxide (0.27 M) in HCl saturated benzene (▲) and 0.27 M di-*tert*-butyl peroxide in benzene containing 1.0 M 1,4-cyclohexadiene (▼). The expansion (top right) corresponds to a detail ( $\times 38$ ) of the cyclohexadienyl radical spectrum.

to the  $\pi$ -complex. In an inert solvent ( $\text{CCl}_4$ ,  $\text{CF}_2\text{ClCFCl}_2$ , etc.) and in the presence of very low concentrations of benzene ( $\leq 5 \times 10^{-3}$  M), the formation of this complex is not instantaneous on our nanosecond time scale. Growth of the signal follows pseudo-first-order kinetics, which allowed us to measure  $k_3$  of Scheme II (vide infra).

Decay of the signals obtained using system 1 are of limited kinetic utility. Typical lifetimes for the complex are in the range 2–7  $\mu\text{s}$  and are usually dominated by second-order kinetics. Alkanes, such as DMB ( $0.03 \text{ M} \leq [\text{DMB}] \leq 0.4 \text{ M}$ ), had little or no effect on the lifetime of the signal (obtained with  $[\text{Cl}_2] = 6.2 \times 10^{-2} \text{ M}$ ). At first glance one could have concluded that the observed complex did not react with alkanes, and the opportunity which the laser gives to carry out quantitative kinetic measurements would have been abandoned. As we show below, the complex certainly does react with alkanes, its reactivity being even greater than that of a *tert*-butoxyl radical.<sup>16</sup> What is actually occurring in system 1 is that the alkyl radicals  $\text{R}_1\cdot$  and  $\text{R}_2\cdot$  formed by hydrogen abstraction from RH by the complex (see  $k_5$  and  $k_6$  in Scheme II) react rapidly with molecular chlorine to regenerate a chlorine atom.



These chlorine atoms react with benzene ( $k_3$  of Scheme II) to "regenerate" the  $\pi$ -complex. Because these processes are extremely rapid there is no net loss of complex. In other words, when the complex is formed using molecular chlorine, reactions that it undergoes with alkanes are kinetically "invisible" by the laser technique we employ. While our data cannot yield a value for  $k_7$ , analysis of the reagent concentrations and the rates required to make regeneration an efficient process on our time scale indicate that  $k_7$  must be  $\gg 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . Such a large value is fully consistent with the value of  $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  that can be calculated<sup>17</sup> for the reaction:  $\text{C}_2\text{H}_5\cdot + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}\cdot$ , in the gas phase.

**System 2. Reaction of *tert*-Butoxyl Radicals with Hydrogen Chloride.** Photolysis of di-*tert*-butyl peroxide in the presence of HCl yields chlorine atoms.<sup>18</sup> In the presence of benzene this system yields exactly the same spectrum as is formed in system 1; i.e., the  $\pi$ -complex is formed according to the reactions in Scheme III, part A.<sup>19</sup> The time required to generate the complex is limited by the reactivity of *tert*-butoxyl toward HCl ( $k_8$ ) and by the solubility of HCl in the solvent, which was usually benzene in these experiments. In benzene saturated with HCl gas at 760 torr (corresponding to  $[\text{HCl}] \sim 0.46 \text{ M}$ ), the overall formation

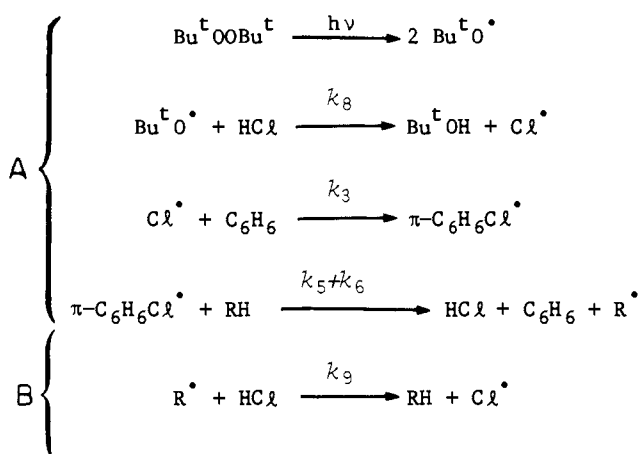
(16) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(17) Kerr, J. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973: (a) Vol. 1, Chapter 1. (b) Table 5.

(18) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6715–6720. Chen, K. S.; Elson, I. H.; Kochi, J. K. *Ibid.* **1973**, *95*, 5341–5349. Edge, D. J.; Kochi, J. K. *Ibid.* **1972**, *94*, 6485–6495.

(19) In this scheme, only a single radical is, for simplicity, indicated as being produced from RH.

## Scheme III



of the complex occurs with a lifetime  $\leq 15$  ns, as judged by the rate of formation of the 490-nm signal.

The "noninstantaneous" formation of chlorine atoms in this system makes it unsuitable for the study of very fast processes such as the formation of the  $\pi$ -complex. However, it is an excellent system both from a spectroscopic point of view (see Figure 1) and for the study of certain slower processes, such as  $\pi$ -complex decay and quenching. The spectrum of the complex that is shown in Figure 1 has been overlaid with the spectrum of the cyclohexadienyl radical,  $\text{C}_6\text{H}_7^\bullet$ . The  $\pi$ -complex was made by photolysis of  $\text{Bu}^t\text{OOBu}^t/\text{HCl}$  in benzene, and the  $\text{C}_6\text{H}_7^\bullet$  radical by photolysis of  $\text{Bu}^t\text{OOBu}^t/1,4$ -cyclohexadiene in benzene in a pair of carefully matched experiments. Under conditions where the only important reaction of  $\text{Bu}^t\text{O}^\bullet$  is H-atom abstraction from the substrate, the yields, and therefore the concentrations of the two radicals, should be approximately equal. The enlargement of the 500–600-nm region shows in more detail the weak band of  $\text{C}_6\text{H}_7^\bullet$ , that is a characteristic feature in the spectra of authentic cyclohexadienyl radicals.<sup>20</sup> The obvious differences between the two spectra are (i) the strong, broad band in the visible region of the  $\pi$ -complex's spectrum which is absent in the cyclohexadienyl radical, and (ii) the broad UV band of the  $\pi$ -complex which contrasts with the sharp UV band of the cyclohexadienyl.

System 2 proved suitable for measuring the absolute rate constants for reaction of the  $\pi$ -complex with alkanes having secondary and/or tertiary hydrogens. The observed rate constant for  $\pi$ -complex decay,  $k_{\text{decay}}$ , is related to its rate constant for hydrogen abstraction from the alkane,  $k_{\text{RH}}^1$ , according to:

$$k_{\text{decay}} = k_0 + k_{\text{RH}}^1[\text{RH}]$$

In this equation  $k_0$  is the rate constant for decay of the complex in the absence of RH; it incorporates all modes of first-order (or pseudo-first-order) decay. It should be noted that  $k_{\text{RH}}^1$  will be equal to  $k_5 + k_6$  (see Scheme II) provided the reaction with RH of free chlorine atoms in equilibrium with the complex does not contribute significantly to the decay of the complex (vide infra). This appears to be a good approximation in benzene as solvent (i.e., at high benzene concentrations), at least for the abstraction of secondary and tertiary hydrogens.<sup>21</sup>

Kinetic measurements were generally made by monitoring the absorption at 490 nm, or occasionally at 550 nm. Figure 2 shows

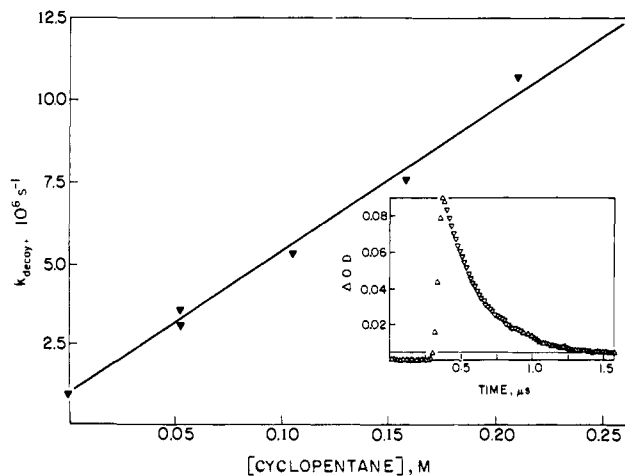


Figure 2. Plot of  $k_{\text{decay}}$  vs. [cyclopentane] for the reaction of the  $\pi$ -complex generated from  $\text{HCl}/\text{Bu}^t\text{OOBu}^t$ , and (inset) decay trace obtained at 490 nm in the presence of 0.053 M cyclopentane.

Table I. Absolute Rate Constants for the Reaction of the  $\pi$ - $\text{C}_6\text{H}_6\text{Cl}$ -Complex with Hydrogen Donors at 27 °C in Benzene as Solvent

substrate	system	Cl $\cdot$ source	$k_{\text{RH}}^1$ ( $\text{M}^{-1} \text{s}^{-1}$ )
DMB	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$4.6 \times 10^7$ <sup>a</sup>
cyclopentane	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$4.4 \times 10^7$
	3	$\text{S}_2\text{Cl}_2$	$4.4 \times 10^7$
cyclooctane	4	$\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$	$4.0 \times 10^7$
	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$1.2 \times 10^8$
<i>n</i> -heptane	4	$\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$	$1.2 \times 10^8$
	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$5.8 \times 10^7$ <sup>b,c</sup>
<i>n</i> -heptane- <i>d</i> <sub>16</sub> ( $\text{CH}_3$ ) <sub>3</sub> CC( $\text{CH}_3$ ) <sub>3</sub>	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$3.2 \times 10^7$ <sup>b,c</sup>
	(2)	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$> 1 \times 10^6$ <sup>d</sup>
1,4-cyclohexadiene	3	$\text{S}_2\text{Cl}_2$	$5.3 \times 10^6$
	4	$\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$	$5.8 \times 10^6$
	2	$\text{Bu}^t\text{OOBu}^t + \text{HCl}$	$2.2 \times 10^9$

<sup>a</sup> Rate constant for attack on the two tertiary hydrogens only; see text. <sup>b</sup>  $k_{\text{H}}/k_{\text{D}} = 1.8$ . <sup>c</sup> Rate constant for attack on secondary hydrogens only. <sup>d</sup> Preliminary value; see text for discussion of errors in this system.

our kinetic data ( $k_{\text{decay}}$  vs. [RH]) for cyclopentane in benzene solvent, together with a representative decay trace (inset). Cyclopentane is kinetically well behaved, as are all the other alkanes except 2,2,3,3-tetramethylbutane, which has the distinction of containing only primary hydrogen atoms. The primary alkyl radical produced from 2,2,3,3-tetramethylbutane caused "regeneration" problems similar to those encountered with all alkanes when the complex was generated from molecular chlorine. We attribute "regeneration" of the complex to the final reaction in Scheme III (labeled B).<sup>22</sup>

The conditions for the rate of reaction of the complex with an alkane to be measurable when using the  $\text{Bu}^t\text{OOBu}^t/\text{HCl}$  system is:

$$k_9[\text{R}^\bullet][\text{HCl}] \ll (k_5 + k_6)[\text{C}_6\text{H}_5\text{Cl}][\text{RH}]$$

If this condition is met, there will be no regeneration of complex on the time scale of our experiments. Both in principle and in practice it is possible to "adjust" [RH] and [HCl] so that this condition is met and, indeed, preliminary values for reaction of the complex with 2,2,3,3-tetramethylbutane were obtained in this way that were in reasonable agreement with values subsequently obtained using systems 3 and 4 (vide infra).

Rate constants,  $k_{\text{RH}}^1$ , obtained using system 2 are listed in Table I, which also includes  $k_{\text{RH}}^1$  values obtained in the other systems. It is important to note that with system 2 all values for alkanes having secondary and tertiary hydrogens were independent of changes in the HCl concentration provided this exceeded 25% of the 760-torr saturation limit.<sup>23</sup> The necessary condition for

(22) A rate constant of  $8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C can be calculated for the gas-phase reaction:  $\text{CH}_3^\bullet + \text{HCl} \rightarrow \text{CH}_4 + \text{Cl}^\bullet$ ; see ref 17a, Table 4.

(20) (a) Shida, T.; Hanazaki, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 646–651. (b) Jordan, J. E.; Pratt, D. W.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 5588–5590. (c) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *Ibid.* **1980**, *102*, 6063–6068.

(21) Primary, secondary, and tertiary hydrogens have roughly comparable reactivities toward free chlorine atoms (see footnote 46). However, primary hydrogens are significantly less reactive than secondary, which are in turn less reactive than tertiary hydrogens toward **1** (see Table I). The interference to the measured kinetics from reaction of RH with those free Cl $\cdot$  that are in equilibrium with **1** is therefore greatest for substrates having only primary hydrogen atoms and least for substrates containing tertiary hydrogens.

reliable kinetic data was therefore met. For DMB under the conditions used, we believe that the experimental  $k_{RH}^1$  value corresponds to reactions at tertiary sites only; i.e., reaction at primary sites leads to regeneration of the complex and hence is "invisible" to our technique.

**System 3. Photolysis of Sulfur Monochloride.** It has been reported<sup>24</sup> that the photolysis of  $S_2Cl_2$  yields chlorine atoms and, presumably, the  $ClS_2\cdot$  radical.<sup>25</sup> We find that photodecomposition (308 or 337 nm) of  $S_2Cl_2$  in benzene yields the  $\pi$ - $C_6H_6Cl\cdot$  complex in an essentially instantaneous process; the observable spectrum shows an overlap of the bands obtained in system 1 or 2 with the characteristic bands of  $S_3$  and  $S_4$  which are produced in the decomposition of  $S_2Cl_2$ .<sup>25</sup>

This source of the  $\pi$ -complex is suitable for kinetic studies, and values of  $k_{RH}^1$  were determined for cyclopentane (the "reference" alkane) and 2,2,3,3-tetramethylbutane (see Table I). At the low concentrations of  $S_2Cl_2$  employed ( $<10^{-3}$  M), this compound does not moderate the reactivity of the  $\pi$ -complex since the  $k_{RH}^1$  value for cyclopentane agrees well with the value obtained using system 2.

**System 4. Photolysis of  $\alpha$ -Chloroacetophenone.** Laser excitation (308 or 337 nm) of  $C_6H_5COCH_2Cl$  (typically  $\sim 1 \times 10^{-2}$  M) in benzene gave the expected  $\pi$ -complex in a not-quite instantaneous process. The chlorine atom precursor must be the ketone in its triplet state since the production of  $\pi$ - $C_6H_6Cl\cdot$  (monitored at 490 nm) could be quenched by 1,3-pentadiene.<sup>26</sup> A Stern-Volmer analysis of this quenching suggests a triplet lifetime of ca. 50 ns.<sup>27</sup> Kinetic measurements in this system were limited to experimental conditions where the lifetime of the  $\pi$ -complex was  $>200$  ns (i.e., [2,2,3,3-tetramethylbutane]  $<0.6$  M; [cyclopentane]  $<0.1$  M; [cyclooctane]  $<0.04$  M), in order to avoid any problems arising from the noninstantaneous nature of the chlorine atom generating process. Values of  $k_{RH}^1$  obtained with these three alkanes in this system under these limiting conditions are listed in Table I. They are in good agreement with values obtained using other systems.

**System 5. Photolysis of Thionyl Chloride.** Photodecomposition (308 nm) of  $Cl_2SO$  ( $10^{-2}$ – $10^{-3}$  M) in benzene yields the strong absorption band at 490 nm that is characteristic of the  $\pi$ - $C_6H_5Cl$  complex. Decay of the  $\pi$ -complex leaves some ( $\sim 20\%$ ) of residual absorption at  $\lambda <330$  nm, which indicated that other species (which presumably result from the photodecomposition of thionyl chloride) have overlapping absorptions in this spectral region. Unfortunately, system 5 proved to be unsatisfactory for kinetic purposes since the measured rate constants were somewhat lower than those obtained with other chlorine atom sources. For example, with cyclopentane  $k_{RH}^1 = 2.2$ – $2.5 \times 10^7$   $M^{-1} s^{-1}$  in system 5 vs. ca.  $4.0 \times 10^7$   $M^{-1} s^{-1}$  for systems 2, 3, and 4 (see Table I). We are inclined to believe that in this system we are faced with a "partial regeneration" of the  $\pi$ - $C_6H_6Cl\cdot$  complex via the reaction sequence:



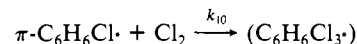
This suggestion is supported by the fact that when  $k_{RH}^1$  was measured for cyclopentane under conditions where oxygen at 760 torr was bubbled continuously through the solution, a value of  $3.1 \times 10^7$   $M^{-1} s^{-1}$  was obtained. Under these conditions the oxygen will undoubtedly scavenge many of the alkyl radicals, thus hampering the regeneration process.

**Effect of Oxygen on  $\pi$ - $C_6H_6Cl\cdot$ .** For systems 3 and 5 there was no detectable difference in the yield of complex nor in the kinetics of its decay between completely deaerated solutions and solutions saturated with oxygen at 760 torr by continuous bubbling. When

the same experiments were repeated in the presence of alkane, no effect of oxygen was observed in system 3, while in system 5 oxygen reduced "regeneration" problems and actually gave  $k_{RH}^1$  values in better agreement with those obtained in other systems (vide supra). Similarly, oxygen had no effect on either the yield or lifetime of the  $C_6H_6Cl\cdot$  complex in system 1 (comparison of results obtained by continuous bubbling into 0.5 M benzene in  $CCl_4$  of a gas mixture, 3.5/46.5/50.0:  $Cl_2/N_2/O_2$  (v/v), with a gas mixture, 3.5/96.5:  $Cl_2/N_2$  (v/v), both at 760 torr). The same was true of system 2 (comparison of results obtained by continuous bubbling into 0.24 M  $Bu^1OOBu^1$  in benzene of a gas mixture, 50/50:  $HCl/O_2$  (v/v), with a gas mixture, 50/50:  $HCl/N_2$  (v/v), both at 760 torr), and in this system oxygen was also shown to have no effect on the  $k_{RH}^1$  value for cyclopentane. The assessment of the effect of oxygen on the  $C_6H_6Cl\cdot$  complex in system 4 was complicated by the fact that the  $\alpha$ -chloroacetophenone triplet is itself rapidly quenched by oxygen. However, very careful comparisons of the traces obtained from samples that had been deaerated with those saturated by bubbling with oxygen at 760 torr, both in the absence and in the presence of an alkane, showed that the only changes were limited to those short time scales which can be associated with the unquenched  $\alpha$ -chloroacetophenone triplet.

It is clear from the foregoing that oxygen does not react at a measurable rate with the species responsible for the 490-nm band, i.e., with  $\pi$ - $C_6H_6Cl\cdot$ .

**Effect of Molecular Chlorine on the  $C_6H_6Cl\cdot$  Complex.** In contrast to the absence of an effect with  $O_2$ , we find that the lifetime of the  $\pi$ - $C_6H_6Cl\cdot$  complex in system 1 is influenced by the concentration of  $Cl_2$  employed. The lifetime of the complex decreases as  $[Cl_2]$  is increased, which implies (i) that the complex is quenched by  $Cl_2$ , and (ii) that this quenching does not produce a chlorine atom<sup>28</sup> (since such a reaction would merely "regenerate" the complex, vide supra). Our product studies, carried out under conditions where the dependence on  $[Cl_2]$  is observable in the laser experiments, do not show any dependence of  $S^m$  (the tertiary/primary selectivity for DMB<sup>7</sup>) on chlorine concentration. Therefore, it is extremely improbable that the intermediate formed by reaction of the  $\pi$ -complex with  $Cl_2$ , which we will represent for convenience as  $(C_6H_6Cl_3\cdot)$ , i.e.:



could be involved in the benzene moderated chlorination of alkanes. It seems much more likely that this reaction is the second step (initial step is  $k_3$ ) in the free-radical polychlorination of benzene which leads ultimately to hexachlorocyclohexane.<sup>29-31</sup>

By saturating benzene with various  $Cl_2/N_2$  mixtures of known composition and using the known<sup>32</sup> solubility of chlorine in benzene at 760 torr, we have been able to estimate that  $k_{10} \approx 2 \times 10^6$   $M^{-1} s^{-1}$  from the dependence of the decay rate of  $\pi$ - $C_6H_6Cl\cdot$  on the  $Cl_2$  concentration.

**Kinetics of Free Chlorine Atom Reactions.** Measurements of the absolute rate constants for reactions of free chlorine atoms are rather difficult because the high reactivity of  $Cl\cdot$  tends to make its chemical reactions occur on a very short time scale. In addition, the choice of "inert" solvents is rather limited and they must be purified extremely carefully. We have found  $CCl_4$  to be the most convenient solvent.

We have employed the "probe" technique<sup>16</sup> to measure a limited number of free chlorine atom rate constants. As our probe we

(28) As suggested in Scheme I of ref 14.

(29) Smith, H. P.; Noyes, W. A., Jr.; Hart, E. J. *J. Am. Chem. Soc.* **1933**, *55*, 4444–4459, and references cited.

(30) For a concise review of the photochlorination of benzene, see: Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; pp 308–313.

(31) The photochlorination of benzene is high order in  $Cl_2$  and has a negative temperature coefficient which suggests the intermediacy of a reversibly formed addition species which can react with  $Cl_2$ . These are precisely the conditions which were not used in our experiments. We thank Professor Walling for drawing these facts to our attention.

(32) Gerrard, W. "Gas Solubilities: Widespread Applications"; Pergamon: Oxford, 1980; p 135.

(23) At lower HCl concentrations the generation of  $Cl\cdot$  was not "instantaneous", and for this reason growth of the  $\pi$ - $C_6H_6Cl\cdot$  complex became observable. Such a grow-in of the signal interferes with the measurement of its decay as it undergoes reaction with the alkane.

(24) Braithwaite, M.; Leone, S. R. *J. Chem. Phys.* **1978**, *69*, 839–845.

(25) Casal, H. L.; Scaiano, J. C. *J. Photochem.*, in press.

(26) Dienes are well-known triplet quenchers; see, e.g.: Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238.

(27) This could include some self-quenching since the effect of changes in the  $C_6H_5COCH_2Cl$  concentration on triplet lifetime was not examined.

**Table II.** Absolute Rate Constants for Some Reactions of Free Chlorine Atoms in CCl<sub>4</sub> at 300 K

reaction	method <sup>a</sup>	$k$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>
Cl· + C <sub>6</sub> H <sub>6</sub> $\xrightarrow{k_3}$	D + S	$(6.0 \pm 1.5) \times 10^9$
Cl· + Cl <sub>2</sub> $\xrightarrow{k_{11}}$	B	$(5.3 \pm 2.0) \times 10^8$ <sup>c</sup>
Cl· + DMB $\xrightarrow{(k_1 + k_2)}$	S	$(2.6 \pm 0.8) \times 10^9$

<sup>a</sup>D = direct monitoring of growth of C<sub>6</sub>H<sub>6</sub>Cl· product. B = benzene probe with Stern–Volmer monitoring of growth of C<sub>6</sub>H<sub>6</sub>Cl·. S = benzene probe with Stern–Volmer analysis. <sup>b</sup>The quoted errors are far larger than the statistical errors. They are largely based on our experience as to the normal magnitude of the probable errors in measurements of this type and of this level of difficulty. “True” errors may be considerably smaller than quoted. <sup>c</sup>Note:  $\pi$ -C<sub>6</sub>H<sub>6</sub>Cl· + Cl<sub>2</sub> → (C<sub>6</sub>H<sub>6</sub>Cl<sub>3</sub>)·,  $k = 2 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>; see text.

chose benzene and the 490-nm band of the C<sub>6</sub>H<sub>6</sub>Cl· complex, using molecular chlorine as our chlorine atom source. By using very low concentrations of benzene in very carefully purified CCl<sub>4</sub> and a “double flow” system (to minimize contact time between Cl<sub>2</sub> and hydrocarbons before the laser excitation; see Experimental Section), we could obtain measurable *growth* lifetimes for the complex under a limited number of experimental conditions. For example, for 3.5% Cl<sub>2</sub>/96.5% N<sub>2</sub> at 760 torr the growth occurred with  $k_{\text{exptl}} = 5.8 \times 10^7$  s<sup>-1</sup> for 0.0029 M benzene. At the same time, the total signal observed at 490 nm ( $A_{490}$ ) is a function of the benzene concentration that can be described by:<sup>33</sup>

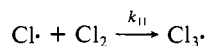
$$\frac{1}{A_{490}} = \alpha + \alpha \frac{k_0}{k_3} \frac{1}{[C_6H_6]}$$

At a given benzene concentration the rate of growth is given by:<sup>33</sup>

$$k_{\text{exptl}} = k_0 + k_3[C_6H_6]$$

where  $k_0$  includes all pseudo-first-order modes of chlorine atom decay in this system *including* reaction with molecular chlorine (vide infra) and trace impurities in the solvent. From the analysis of the data using these equations we obtain  $k_3 = (6.0 \pm 1.5) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> (see Table II).

Somewhat to our surprise, growth lifetimes were dependent on the chlorine concentration, becoming shorter as the chlorine concentration was increased. The only conceivable chemical reaction is:



The rate constant for this reaction was obtained using known chlorine concentrations (saturation of the CCl<sub>4</sub><sup>32</sup> with Cl<sub>2</sub>/N<sub>2</sub> mixtures of precisely known composition) and with benzene at  $2.7 \times 10^{-3}$  M as the probe. The results of these experiments are presented graphically in Figure 3 and the derived rate constant in Table II.

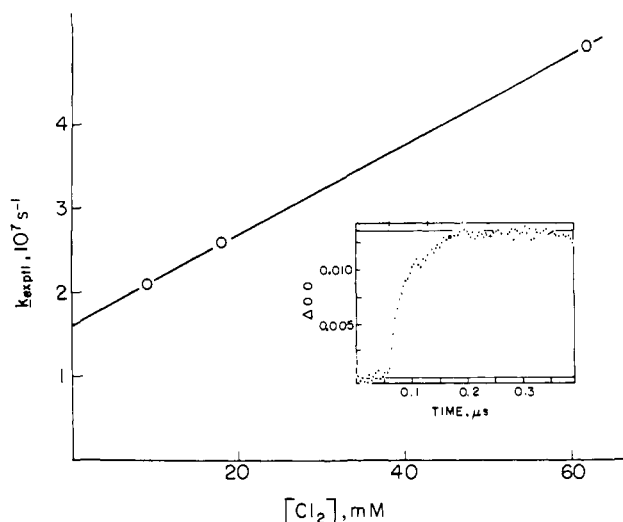
The fate of Cl<sub>3</sub>· was not examined in this work. However, we note that at the concentrations of chlorine, benzene, and alkane used for the determination of intra- and intermolecular selectivities (vide infra) this reaction does not play any significant role. The same appears to be true of the earlier work by Russell,<sup>3-6</sup> Walling,<sup>8</sup> and Skell,<sup>14</sup> but not of some recent Russian work<sup>34-36</sup> (see Discussion).

We also applied the benzene “probe” to measure the rate constant for the reaction of free chlorine atoms with DMB. Because low concentrations of reagents were employed and because the time scale of these experiments was very short (<100 ns), the “regeneration” of  $\pi$ -C<sub>6</sub>H<sub>6</sub>Cl· referred to earlier did not appear to cause any problems. Growth rates were too fast to measure

(33) As in any system where the measured kinetics corresponds to the approach to an equilibrium, the back reaction,  $k_4$ , is included within  $k_0$ .  
(34) Kosorotov, V. I.; Kolesnichenko, A. F.; Dzhagatspanyan, R. V.; Krishtal, N. F. *Kinet. Katal.* **1976**, *17*, 316–320.

(35) Sergeev, G. B.; Pukhovskii, A. V.; Smirnov, V. V. *Dokl. Akad. Nauk SSSR* **1981**, *258*, 685–688. Sergeev, G. B.; Pukhovskii, A. V. Abstracts of Third All-Union Scientific Conference “Present State and Development Prospects of the Theoretical Principles of Manufacture of Organic Chlorine Products” (in Russian), Baker, 1981, p 82, as quoted in ref 36.

(36) Sergeev, G. B.; Smirnov, V. V.; Pukhovskii, A. V.; Porodenko, E. V. *Kinet. Katal.* **1983**, *24*, 1046–1050.



**Figure 3.** Effect of Cl<sub>2</sub> on the rate of buildup ( $k_{\text{exptl}}$ ) of the 490-nm signal, and (inset) representative trace for  $[Cl_2] = 0.018$  M and  $[C_6H_6] = 0.0026$  M.

reliably,<sup>37</sup> and for this reason a Stern–Volmer type of analysis was employed in which the magnitude of the 490-nm absorption,  $A_{490}$ , was determined at various alkane concentrations after the growth of this signal to its maximum and before significant decay of  $\pi$ -C<sub>6</sub>H<sub>6</sub>Cl· (the “plateau” region):

$$A_{490}^0/A_{490} = 1 + (k_1 + k_2)\tau^0[DMB]$$

In this equation the superscript 0 refers to the absence of DMB ( $\tau^0 = 2.5$  ns at the benzene concentration ( $6.6 \times 10^{-2}$  M) employed).

The analysis yielded an “overall” rate constant for 2,3-dimethylbutane,  $(k_1 + k_2) = 2.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> (see Table II). Absolute rate constants for the reactions of free chlorine atoms with a variety of alkanes and other organic substrates can be readily calculated from literature data on competitive chlorinations in “inert” solvents.<sup>6,8,38</sup> It should be noted that if some complex were to be regenerated by the further reaction of R· and Cl<sub>2</sub>, then the true value of  $(k_1 + k_2)$  would be even higher than the value given above. Our complete kinetic analysis of the DMB chlorination (vide infra) does indeed suggest that the true value of  $(k_1 + k_2)$  is  $3.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, i.e., is slightly higher than the measured value. Certainly, we do not see any reasonable source of error that could have led us to overestimate  $(k_1 + k_2)$ . (See Discussion for the significance of a “high” value for  $(k_1 + k_2)$  in relation to other purported measurements of  $k$ 's for reaction of free chlorine atoms with alkanes in solution.)

**B. Product Studies.** These were carried out by measuring the relative yields of monochlorides formed by reaction of a large excess of alkane with chlorine. The solvent composition, whether neat alkane, alkane in benzene, or alkane in benzene/CCl<sub>4</sub> mixtures, was carefully controlled. Reactions were initiated by exposure to daylight and the products were examined by gas chromatography after total consumption of the chlorine. Unless otherwise indicated all experiments were carried out under vacuum or under an inert (nitrogen or argon) atmosphere. As would be expected from the earlier work of Russell<sup>5</sup> and Skell,<sup>14</sup> the main organic product was always alkyl chloride even at high (8 M) benzene concentrations, and there was no detectable ( $\leq 10^{-3}$  M) yield of chlorobenzene. The yields of alkyl chloride (based on our best estimate of the initial chlorine concentration) were somewhat lower for reactions that were run in solvents which had not been deaerated, e.g., for 0.5 M DMB in 4 M benzene ca. 75%

(37) Of course, both Cl<sub>2</sub> and alkane increase the growth rate as their concentration is increased which makes the rates harder to measure. However, with Cl<sub>2</sub> this disadvantage is offset by the increased intensity of the 490-nm signal. With alkane the disadvantage is augmented by a decrease in the intensity of this signal.

(38) Bunce, N. J.; Hadley, M. *J. Org. Chem.* **1974**, *39*, 2271–2276.

**Table III.**  $S^m$  Values for Photochlorination of DMB in the Presence of Benzene at ca. 22 °C<sup>a</sup>

DMB (M)	benzene (M)						
	0	0.5	1.0	2.0	4.0	8.0	10.5
0.125	0.47 <sup>b</sup>	2.99 <sup>b</sup>	4.42 <sup>b</sup>	6.45	8.82	12.61	14.40
0.5		1.89 <sup>b</sup>	3.00	4.57	7.18	10.36	12.81 <sup>c</sup>
1.0	0.58 <sup>b</sup>	1.45	2.11	3.53	5.99	9.77	
2.0		1.20	1.60	2.52	4.33	7.45	
4.0		0.94	1.24	1.75	3.14		
7.7 <sup>d</sup>	0.66						

<sup>a</sup>The inert diluent was CCl<sub>4</sub>. All values are averages of between two and six individual measurements. <sup>b</sup>Polychlorinated material exceeded 15% of monochlorides. <sup>c</sup>[DMB] = 0.48 M. <sup>d</sup>Neat DMB.

**Table IV.** Relative Rates of Photochlorination of Some Alkanes in >90% v/v Benzene as Solvent as Determined by Product Analysis. Comparison with the Ratio of the Absolute Rate Constants for Reactions of These Alkanes with the  $\pi$ -C<sub>6</sub>H<sub>6</sub>Cl<sup>+</sup> Complex As Given in Table I

alkane	product ratio <sup>a</sup>	$k_{RH}^1/k_{C_6H_6Cl}^1$
DMB	1.47	1.12 <sup>b</sup>
cyclopentane	(1.0)	(1.0)
cyclooctane	2.89	2.90
cyclohexane	1.27 <sup>c</sup>	
cyclohexane- <i>d</i> <sub>12</sub>	0.78 <sup>c</sup>	
(CH <sub>3</sub> ) <sub>3</sub> CC(CH <sub>3</sub> ) <sub>3</sub>	0.16	0.13

<sup>a</sup>Normalized to equimolar substrate. <sup>b</sup>Since only the tertiary hydrogens can be seen to react in system 1, we added  $k_6$  for DMB derived from Scheme IV, i.e.,  $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  to the measured value of  $k_{DMB}^1$ . The alternative correction for the primary hydrogens corresponding to the addition of  $2/3 k_{(CH_3)_3CC(CH_3)_3}^1$  would raise this ratio to 1.13. <sup>c</sup> $k_H/k_D = 1.6$ , cf. footnote *b* in Table I.

alkyl chlorides in a nondegassed sample vs. ca. 80% in a degassed sample.<sup>39</sup> However, the measured ratio of the yields of tertiary chloride to primary chloride,  $S^m$ ,<sup>7</sup> was quite unaffected by whether or not the sample had been degassed. This was shown to be true for a rather wide range (0–8) of benzene/DMB ratios.

Values of  $S^m$  for certain selected DMB concentrations in selected mixtures of benzene and CCl<sub>4</sub> are given in Table III.<sup>7</sup> Where comparison is possible<sup>41</sup> our  $S^m$  values are in good to excellent agreement with  $S^m$  values reported in the literature.<sup>4,5,8,14</sup> It should be noted that even at extremely low conversions the yield of dichlorinated and more highly chlorinated DMB relative to the yield of monochlorinated DMB is quite significant at low benzene and low DMB concentrations.<sup>42</sup> Selectivities measured under conditions where the yield of polychlorinated DMB was >15% of the yield of monochlorinated DMB have been clearly indicated in Table III. Data with over 15% polychlorination have also been identified in Figure 4. They have not been used to calculate kinetic parameters (vide infra).

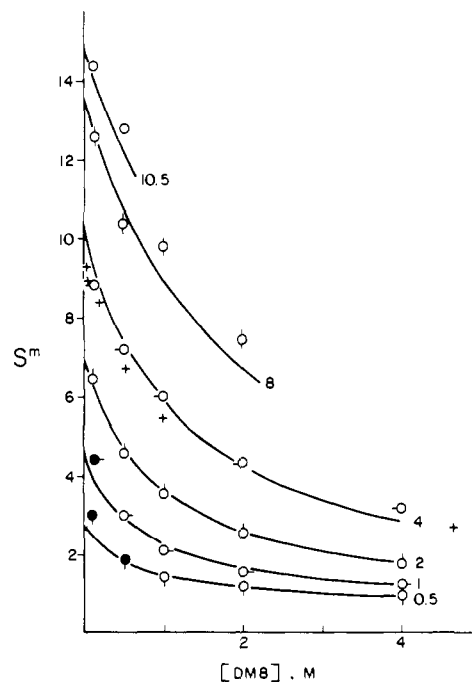
We have also carried out a certain number of competitive intermolecular chlorinations in solvent mixtures that contained >90% benzene, using cyclopentane as the reference alkane. The total alkane concentration in these experiments was in the range 0.65–1.24 M. Relative reactivities, normalized to cyclopentane,

(39) In this experiment the air-saturated solvent would have contained initially ca.  $2 \times 10^{-3} \text{ M}$  [O<sub>2</sub>] (see ref 40) and  $3.9 \times 10^{-2} \text{ M}$  [Cl<sub>2</sub>]. It is not, therefore, surprising to find that deoxygenating the solvent had little effect on the product yield.

(40) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(41) Very many measurements of  $S^m$  (quoted sometimes as *S*) have been made in the presence of benzene.<sup>4,5,8,14</sup> However, with one notable exception,<sup>14</sup> the precise concentrations of DMB and benzene have rarely been given. Moreover, many measurements (including the majority of our own initial measurements but excluding those in ref 14) were made under conditions where  $S^m$  changes very little with a change in DMB or benzene concentration. Such data are of little or no use when it comes to refining the precise, quantitative reaction scheme. Many of our own data have therefore had to be relegated to our files.

(42) Polychlorination under conditions of low alkane and low (or no) benzene concentrations is the subject of a communication in press (P. S. Skell, private communication).



**Figure 4.** Dependence of  $S^m$  on DMB concentration for various benzene (indicated on right) molarities. Open points correspond to data used for the calculations according to eq 1, with the ties indicating different benzene concentrations. Full points refer to data points with 15% or more polychlorination (see text). Also included are the data (+) from Skell et al.<sup>14</sup> for 4 M benzene.

are given in Table IV. Although a not insignificant fraction of the products will be formed from free chlorine atoms under these conditions (vide infra), the relative reactivities calculated from the products show the same trend as do the relative reactivities calculated from the measured absolute rate constants,  $k_{RH}^1$ , for reaction of the  $\pi$ -C<sub>6</sub>H<sub>6</sub>Cl<sup>+</sup> complex with the individual alkanes in benzene solvent that were presented in Table I (see Table IV).

## Discussion

**Background.** In the 1950's Russell<sup>3–6</sup> discovered that the photochlorination of alkanes in benzene (and in certain other solvents) occurred with greatly increased selectivity. He proposed that this was due to the formation of the  $\pi$ -complex, **1**, between the chlorine atom and benzene, the complex being more selective and, presumably, less reactive than the free chlorine atom. Russell adduced a wealth of chemical evidence in support of his suggestion that the C<sub>6</sub>H<sub>6</sub>Cl<sup>+</sup> adduct was a  $\pi$ -complex rather than a  $\sigma$ -complex, the latter being, of course, the chlorocyclohexadienyl radical, **2**. Russell's results and conclusions were confirmed by Walling.<sup>8</sup> The existence of a C<sub>6</sub>H<sub>6</sub>Cl<sup>+</sup> complex, which was assigned the  $\pi$ -structure, was later confirmed by spectroscopic procedures.<sup>10–13</sup> Then, in 1983 Skell et al.<sup>14</sup> reported the results of a very careful reexamination of the benzene (and CS<sub>2</sub>) moderated photochlorination of DMB. These workers suggested that their results could best be explained by invoking a third, even more selective hydrogen atom abstracting agent—which was presumed to be the  $\sigma$ -complex. The basis for Skell's<sup>14</sup> proposal was that selectivity at high benzene concentrations continued to increase as the concentration of DMB was progressively decreased. It was, however, assumed that all of the chlorine atoms that actually react with DMB would be fully equilibrated with the  $\pi$ -complex at high benzene and low DMB concentrations. This is not the case (vide infra).

Although we certainly do not claim that the advent of time-resolved kinetic techniques has made conventional, competitive selectivity studies obsolete, we do wish to emphasize that when they are employed alongside conventional competitive kinetic procedures they provide a very direct and unequivocal method for answering questions such as that posed in the provocative title of Skell's communication, viz., " $\pi$ -Complexing of Chlorine Atoms:

Is That All There Is?" Our results not only allow us to answer this question with a resounding YES, but they also allow us to place reliable rate constants on all the elementary reactions involved and, hence, to give a precise, quantitative description of the benzene<sup>43</sup> moderated photochlorination of alkanes. The evidence in support of this statement is presented below under a variety of headings.

**Spectral Assignment for C<sub>6</sub>H<sub>6</sub>Cl· Complex.** (i) *Could there be two species?* Figure 1 shows that two absorption bands are formed by the interaction of chlorine atoms with benzene. Are these due to a single species or are there two species present?

The two bands are always formed concurrently and at the same rate which requires that they have the same precursors, viz., Cl· and C<sub>6</sub>H<sub>6</sub>. In addition, the two bands decay with identical lifetimes regardless of the quencher used and its concentration.<sup>44</sup> These facts make us confident that the two bands are not due to two independent species. Therefore, if the band at λ < 340 nm were actually due to the chlorocyclohexadienyl radical, **2**, then this radical would have to be in complete equilibrium with the species responsible for the 490-nm absorption.

In order to test this "equilibrium" hypothesis, we examined the relative intensities of the two bands as a function of temperature using molecular chlorine as the chlorine atom source. Between -14 and +57 °C there was no significant change in the OD<sub>325</sub>/OD<sub>490</sub> ratio, which remained equal to 1.89 ± 0.15. If these two bands were to be assigned to different species, the upper limit for the enthalpy change for their interconversion would be ±0.2 kcal/mol. This provides a very strong indication that the two bands belong to a single species.

(ii) *Could this single species be the chlorocyclohexadienyl radical (σ-complex), **2**?* No, not unless **2** has properties that are totally unlike those of every other known cyclohexadienyl. These properties would have to include: (i) the shape of the UV band (cf. band due to C<sub>6</sub>H<sub>6</sub>Cl· vs. band due to C<sub>6</sub>H<sub>7</sub>· in Figure 1); (ii) the insensitivity of C<sub>6</sub>H<sub>6</sub>Cl· toward oxygen (note that C<sub>6</sub>H<sub>7</sub>· reacts with O<sub>2</sub> with a rate constant of 1.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> in benzene at room temperature<sup>40</sup>); and (iii) the gross difference between the spectra of C<sub>6</sub>H<sub>6</sub>Cl· and C<sub>6</sub>H<sub>7</sub>· in the 350–650-nm region (see Figure 1; note also that the weak, but well-resolved, band in the 530–590-nm region of the C<sub>6</sub>H<sub>7</sub>· spectrum is very characteristic for cyclohexadienyl radicals<sup>20</sup>). We rule out **2** as the species responsible for the observed absorptions because the degree of "special pleading" that would be required is outrageous.

(iii) *Could a small concentration of chlorocyclohexadienyl radical, **2**, be present in the system, even though its presence is not revealed by spectroscopic or other studies?* Yes, but small means very small. The sharp cyclohexadienyl band at 560 nm is too weak to be helpful in this regard. It is not identifiable in the C<sub>6</sub>H<sub>6</sub>Cl· absorption spectrum, which limits the concentration of **2** to less than 30% that of **1**. (Additional details of the C<sub>6</sub>H<sub>6</sub>Cl· spectrum in the 500–600-nm region are available as supplementary material.) A better limit on the possible relative concentration of **2** can be obtained from the UV region of the C<sub>6</sub>H<sub>6</sub>Cl· spectrum. We estimate that the sharp and strong UV absorptions common to cyclohexadienyl radicals should allow us to detect **2** if it were present in excess of 10% of the total C<sub>6</sub>H<sub>6</sub>Cl· complex. The lack of detectable oxygen quenching allows us to reduce this limit to ≤1%. It should be noted that such a low fraction for **2** also allows us to rule out the remote possibility that the observed decay of the complex, **1**, actually occurs by reaction of "invisible" σ-complex that exists in equilibrium with the π-complex. The measured rate constant of 2.2 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> found for reaction of the complex with 1,4-cyclohexadiene (specifically chosen for this experiment because it is such a good hydrogen donor)<sup>20c,45</sup> is far too large for

**Table V.** Comparison of Absolute Rate Constants for H-Atom Abstraction by Some Reactive Radicals at Room temperature<sup>a</sup>

substrate	"Free" Cl·	π-C <sub>6</sub> H <sub>6</sub> Cl·	Me <sub>2</sub> CO·
2,3-dimethylbutane	3.3 × 10 <sup>9</sup> <sup>b</sup>	4.8 × 10 <sup>7</sup> <sup>d</sup>	5.8 × 10 <sup>5</sup> <sup>f</sup>
cyclopentane	4.7 × 10 <sup>9</sup> <sup>c</sup>	4.3 × 10 <sup>7</sup> <sup>e</sup>	8.8 × 10 <sup>5</sup> <sup>g</sup>
<i>n</i> -heptane	7.0 × 10 <sup>9</sup> <sup>c</sup>	5.9 × 10 <sup>7</sup> <sup>d</sup>	1.3 × 10 <sup>5</sup> <sup>f</sup>
2,2,3,3-tetramethylbutane	3.1 × 10 <sup>9</sup> <sup>c</sup>	5.5 × 10 <sup>6</sup> <sup>e</sup>	1.3 × 10 <sup>5</sup> <sup>f</sup>
1,4-cyclohexadiene		2.2 × 10 <sup>9</sup> <sup>e</sup>	5.4 × 10 <sup>7</sup> <sup>g</sup>

<sup>a</sup>Rate constants are given in M<sup>-1</sup> s<sup>-1</sup> units; they refer to the entire molecule. <sup>b</sup>Value calculated from best fit analysis of DMB chlorination products (see Scheme IV and text). <sup>c</sup>Calculated from our value for 2,3-dimethylbutane and data given in ref 6 taking *k*/prim H, *k*/acyclic sec H, *k*/cyclopentyl H, and *k*/tert H to be 1.7, 6.0, 4.7, and 6.5 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. <sup>d</sup>Based on measured (secondary or tertiary only, Table I) *k*<sub>RH</sub> and *k*<sup>1</sup>/prim H = 1.8 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> derived from *k*<sub>6</sub> in Scheme IV. <sup>e</sup>From Table I. <sup>f</sup>Calculated from the cyclopentane *k* given in ref 16 and additional data given in: Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231–3232 (see footnote 25). Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49–51. Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208–211. The calculation is based on *k*/prim H, *k*/acyclic sec H, and *k*/tert H values of 7.0 × 10<sup>3</sup>, 7.0 × 10<sup>4</sup>, and 2.7 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. <sup>g</sup>Reference 16.

the complex to be decaying by a route that involves a species in equilibrium with it but that has a concentration ≤1% of [**1**]. That is, if a σ-complex, **2**, were responsible for the observed decay, then the rate constant for reaction of **2** with 1,4-cyclohexadiene would have to be ≥2.2 × 10<sup>11</sup> M<sup>-1</sup> s<sup>-1</sup> which is faster than the diffusion-controlled limit for a bimolecular reaction.

In summary, we assign both bands to the π-complex, **1**. Neither the spectroscopic nor the kinetic data (vide infra) require that we invoke the chlorocyclohexadienyl radical, **2**. The absence of chlorobenzene among the reaction products is also consistent with noninvolvement of **2** in the overall reaction.

*Why is **2** either not formed or formed in unimportant amounts relative to **1**?* We do not know the answer to this question and pose it only to draw the problem to the attention of theoretical chemists.

**Absolute Rate Constants (*k*<sub>RH</sub>) for the π-C<sub>6</sub>H<sub>6</sub>Cl· + RH Reactions.** (i) **Reactivity of the π-Complex.** Absolute rate constants for hydrogen atom abstraction by this species from a few alkanes are compared in Table V with the rate constants for abstraction by the free chlorine atom and the *tert*-butoxyl radical. The π-complex has a reactivity that is intermediate between these two reagents and must therefore be counted as a very active hydrogen abstracting agent. We note that photochlorination in CS<sub>2</sub> as solvent is an even more selective process than that in benzene.<sup>5,6,8,14</sup> It seems likely that the abstracting species formed from Cl· and CS<sub>2</sub> will be less reactive than π-C<sub>6</sub>H<sub>6</sub>Cl·.

(ii) **Comparison of Relative *k*<sub>RH</sub> Values with Relative Rates for Photochlorination at High Benzene Concentrations.** The relatively good agreement between these two quantities (see Table IV) provides justification for our assumption that the process being monitored in the laser flash photolysis experiments in which the quenching of the π-C<sub>6</sub>H<sub>6</sub>Cl· signal in benzene solvent by alkanes was followed does indeed correspond in the main to the process that is probed by product studies at high benzene concentrations.

**Reactivity of "Free" Chlorine Atoms.** The data in Table II show clearly that the "free" chlorine atom (i.e., Cl· in CCl<sub>4</sub> as solvent) is a highly reactive species, just as nearly everybody has always assumed. Rate constants for chlorine atom reactions with alkanes in the gas phase indicate that with the exception of methane hydrogen atom abstraction occurs on nearly every collision.<sup>46</sup>

(43) The study of other solvent systems (e.g., CS<sub>2</sub>) and also of temperature effects would certainly be interesting, but is beyond the scope of the present paper.

(44) There was on some occasions residual absorption in the UV region. This is a fairly common occurrence in laser flash photolytic experiments and is attributed to reaction products.

(45) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 785–792. Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.*, in press.

(46) From data given in Table 3 of ref 17a, we calculate that at 300 K the rate constants for the abstraction of a single H atom in the reaction Cl· + RH → HCl + R· are: 1.1 × 10<sup>7</sup>, 3.5 × 10<sup>9</sup>, 9.2 × 10<sup>9</sup>, and 1.7 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> for R = Me and for a primary, secondary, and tertiary hydrogen, respectively. See also: Knox, J. H.; Nelson, R. L. *Trans. Faraday Soc.* **1959**, *55*, 937–946. Knox, J. H.; Trotman-Dickenson, A. F. "Reactions of Free Radicals in the Gas Phase", Special Publication No. 9; The Chemical Society: London, 1957; pp 35–47.



Since the selectivities observed for attack of chlorine atoms and alkanes in the vapor phase and in noncomplexing solvents were very similar, Russell et al.<sup>47</sup> made the very reasonable assumption that the rate constants for H-atom abstraction were the same in noncomplexing solvents as in the vapor. This assumption was challenged in 1976 by Kosorotov et al.<sup>34</sup> who had carried out some measurements of overall rates of chlorination in a flow system in CCl<sub>4</sub> solvent. They concluded that the rate constant for Cl + C<sub>2</sub>H<sub>6</sub> → HCl + C<sub>2</sub>H<sub>5</sub>· was some four orders of magnitude smaller in CCl<sub>4</sub> than in the gas phase. This conclusion was based on some very questionable assumptions.<sup>36,48</sup> Furthermore, the [Cl<sub>2</sub>]/[C<sub>2</sub>H<sub>6</sub>] ratio was ca. 5 which would imply that the Cl + Cl<sub>2</sub> → Cl<sub>3</sub>· (k<sub>11</sub>) reaction (vide supra) should be important and could have provided a hydrogen abstracting agent other than Cl·. Unfortunately, the idea that chlorinations in CCl<sub>4</sub> are much slower than in the gas phase appears to have caught on. Subsequent measurements<sup>35</sup> of overall rates of chlorination<sup>48</sup> of methane in CF<sub>2</sub>Cl<sub>2</sub> using a static system, but still under conditions ([Cl<sub>2</sub>]/[CH<sub>4</sub>] = 0.3–0.1 initially) where Cl<sub>3</sub>· might play an important role, led to a rate constant for hydrogen abstraction from methane of 5 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> at 293 K (cf. <sup>46</sup> a value of ca. 4 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> in the vapor). Further competitive studies against methane<sup>36</sup> yielded, for example, rate constants for hydrogen abstraction from ethane of 4 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> (cf. <sup>46</sup> ca. 2 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> in the vapor), and from cyclohexane of 1.3 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.

Our measured rate constant for chlorine atom attack on 2,3-dimethylbutane, viz., 2.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (which can only be on the low side; vide supra and infra), not only shows that none of the above-mentioned<sup>34–36</sup> rate constants refer to the purported reactions, but they also show that Russell's hypothesis<sup>47</sup> was not too far from the truth. That is, using Knox et al.'s data<sup>46</sup> we calculate a rate constant for hydrogen abstraction from DMB in the gas phase of ca. 7.6 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> at ambient temperatures. It should be noted that our absolute rate constant for DMB can be used to calculate absolute rate constants for hydrogen abstraction by "free" chlorine atoms from other organic substrates using the compilations of relative reactivities that are available in the literature.<sup>38,47,49</sup>

Just because chlorine atoms are not "free" in aromatic (and certain other) solvents, we must not be blinded to the fact that they may not be "free" (in the gas-phase sense) in what are generally considered to be noncomplexing solvents. Alkanes and CCl<sub>4</sub> would normally be considered to be such solvents, but nevertheless the selectivities for DMB chlorination in the absence of benzene show a small but real difference between neat DMB and dilute solutions of DMB in CCl<sub>4</sub> (see Table III).

**Kinetic Analysis of Scheme II: The Quantitative Picture.** Essentially all the rate constants for the chlorination of DMB by free chlorine atoms and by the C<sub>6</sub>H<sub>6</sub>Cl· π-complex would appear to be available from the laser experiments. We therefore carried out a detailed analysis of our laser flash and product<sup>41</sup> data for this alkane in order to establish if Scheme II could provide a quantitative description of the chlorination of DMB in CCl<sub>4</sub>, in benzene, and in mixtures of these two solvents.

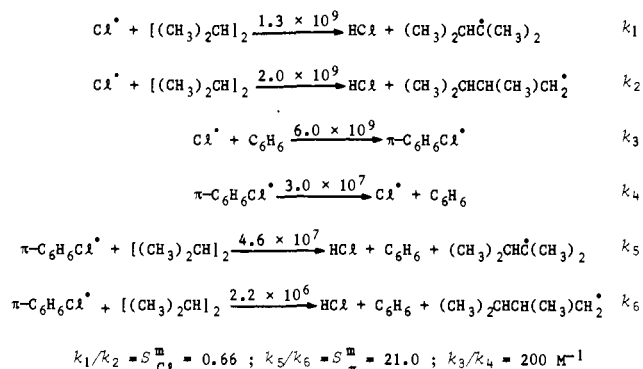
From Scheme II:

$$S^m = \frac{k_1[\text{Cl}\cdot] + k_5[\pi\text{-C}_6\text{H}_6\text{Cl}\cdot]}{k_2[\text{Cl}\cdot] + k_6[\pi\text{-C}_6\text{H}_6\text{Cl}\cdot]}$$

Application of the steady-state approximation to π-C<sub>6</sub>H<sub>6</sub>Cl· leads to:

$$S^m = \frac{S_{\text{Cl}}^m(k_4/k_6) + S_{\text{Cl}}^m(S_{\pi}^m + 1)[\text{DMB}] + S_{\pi}^m[\text{C}_6\text{H}_6](k_3/k_2)}{k_4/k_6 + (S_{\pi}^m + 1)[\text{DMB}] + [\text{C}_6\text{H}_6](k_3/k_2)} \quad (\text{I})$$

**Scheme IV.** Photochlorination of DMB in Benzene/CCl<sub>4</sub> Solvent Mixtures at Room Temperature (Rate Constants Are in M<sup>-1</sup> s<sup>-1</sup> and s<sup>-1</sup> Units)



In this equation, selectivities are on a molecular base<sup>7</sup> and rate constants are on a molar base; i.e., neither type of quantity has been statistically corrected for the number of primary and tertiary hydrogens in DMB. S<sup>m</sup> is the overall molecular selectivity, S<sub>π</sub><sup>m</sup> is the molecular selectivity of the π-complex (i.e., S<sub>π</sub><sup>m</sup> = k<sub>5</sub>/k<sub>6</sub>), and S<sub>Cl</sub><sup>m</sup> is the molecular selectivity of the free chlorine atom (i.e., S<sub>Cl</sub><sup>m</sup> = k<sub>1</sub>/k<sub>2</sub>).

It is interesting to examine eq I under different limiting conditions. For the case, [C<sub>6</sub>H<sub>6</sub>] → 0, we find that S<sup>m</sup> → S<sub>Cl</sub><sup>m</sup>, as expected. However, for the case, [DMB] → 0, we find that S<sup>m</sup> does not extrapolate to S<sub>π</sub><sup>m</sup>. This is due to the fact that when [DMB] → 0 no chlorine atoms react with DMB before equilibration with the π-complex. However, following equilibration the fraction of free chlorine atoms reacting with DMB is determined only by the benzene concentration; i.e., it is independent of [DMB].

Although eq I is quite useful for the above type of intellectual analysis, it is poorly suited to a multiple regression treatment. It was therefore rearranged into the form:

$$S^m = S_{\pi}^m - \frac{k_2[\text{DMB}]}{k_3[\text{C}_6\text{H}_6]} (S_{\pi}^m + 1)(S^m - S_{\text{Cl}}^m) - \frac{k_2k_4(S^m - S_{\text{Cl}}^m)}{k_3k_6[\text{C}_6\text{H}_6]} \quad (\text{II})$$

which has the advantage (vide infra) that S<sub>Cl</sub><sup>m</sup> appears only in (S<sup>m</sup> - S<sub>Cl</sub><sup>m</sup>) terms.

Although the value of S<sub>Cl</sub><sup>m</sup> is readily available from the literature,<sup>3–6,8,14</sup> we have found that it actually depends on the DMB/CCl<sub>4</sub> ratio (vide supra and Table III). A single fixed value for S<sub>Cl</sub><sup>m</sup> should, therefore, probably not be employed in the kinetic calculations. Fortunately, the precise value chosen for S<sub>Cl</sub><sup>m</sup> does not have much effect on the other numbers used to describe the reaction because, under most conditions, S<sup>m</sup> ≫ S<sub>Cl</sub><sup>m</sup>. For our calculations we chose to stay with the well-established value for neat hydrocarbon: S<sub>Cl</sub><sup>m</sup> = 0.66 (i.e., S = 3.96).

Equation II was fitted to the data in Table III (excluding only those measurements in which the yield of polychlorinated DMB was >15% of the monochlorinated product<sup>42</sup>). A multiple regression treatment was used with S<sub>Cl</sub><sup>m</sup> = 0.66 as the only fixed quantity, all other coefficients being allowed to float to their best fit. This procedure yielded: k<sub>2</sub>/k<sub>3</sub> = 0.327, k<sub>4</sub>/k<sub>6</sub> = 13.8 M, and k<sub>5</sub>/k<sub>6</sub> = S<sub>π</sub><sup>m</sup> = 21.0 (r = 0.899).<sup>50</sup> These data have been used to construct the calculated curves shown in Figure 4. Introducing, k<sub>3</sub> = 6.0 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> leads to k<sub>2</sub> = 1.96 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, and since k<sub>1</sub>/k<sub>2</sub> = 0.66, we obtain (k<sub>1</sub> + k<sub>2</sub>) = 3.25 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. This last value is in good agreement with the value obtained in the laser experiments, i.e., (k<sub>1</sub> + k<sub>2</sub>) = 2.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. In order to put k<sub>4</sub> and k<sub>6</sub> on an absolute scale, we combine the values of k<sub>4</sub>/k<sub>6</sub> and k<sub>5</sub>/k<sub>6</sub> given above with k<sub>5</sub> = 4.6 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> (from the top line of Table I). The rate constants obtained using the above

(47) Russell, G. A.; Ito, A.; Hendry, D. G. *J. Am. Chem. Soc.* **1963**, *85*, 2976–2983.

(48) How can chain propagation rate constants be calculated from measured rates of the overall reaction when the rate of chain initiation is unknown or, at best, ill-defined?

(49) Hendry, D. G.; Mill, T.; Piszkiwicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937–978.

(50) The rather small effect produced by changes in S<sub>Cl</sub><sup>m</sup> can be illustrated by the fact that if the value of 0.58 found for 1.0 M [DMB] (see Table III) was employed, then k<sub>2</sub>/k<sub>3</sub> = 0.288, k<sub>4</sub>/k<sub>6</sub> = 15.1 M, and k<sub>5</sub>/k<sub>6</sub> = S<sub>π</sub><sup>m</sup> = 20.14 (r = 0.914). This produced, k<sub>2</sub> = 1.73 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and (k<sub>1</sub> + k<sub>2</sub>) = 2.7 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>.



procedures are given in Scheme IV.<sup>51,52</sup>

The excellent agreement between measured  $S^m$  values and the calculated curves, as well as that between the  $(k_1 + k_2)$  value derived from the laser data alone and the value obtained by combining  $k_3$  with the product data, provides convincing proof that there are *only* two hydrogen atom abstracting species present in the benzene-moderated photochlorination of DMB, viz., the free chlorine atom and the  $C_6H_6Cl \cdot \pi$ -complex.<sup>53</sup> It should also be noted that  $S^m$  data from the literature, for which both the DMB and benzene concentrations were actually defined,<sup>41</sup> fit these curves rather well. Although most of the literature data are not especially diagnostic, the results of Skell et al.<sup>14</sup> at low DMB and high (4.0 M) benzene concentrations fit our quantitative kinetic model extremely well and have been included in Figure 4.

Before concluding we wish to point to two simple predictions that arise from our kinetic analysis. First, our specific rate and equilibrium constants imply that even in 11.1 M benzene (neat benzene = 11.2 M) containing 0.1 M DMB, some 0.4% of the DMB products will come from reaction of DMB with free chlorine atoms before equilibration and 2.5% after equilibration. Second, at a constant benzene concentration, not only is  $S^m$  reduced by an increase in the DMB concentration, but also there will be an approximately equal reduction in  $S^m$  if the total alkane concentration is increased by the addition of a different alkane, such as cyclopentane, the DMB concentration being held constant. This has actually been observed by Skell<sup>54</sup> and indications of this effect were already evident from Russell's work.<sup>5,6</sup>

### Conclusion

The photochlorination of alkanes with molecular chlorine in benzene/ $CCl_4$  solvent mixtures can be quantitatively described (see Scheme IV) by invoking *only* two hydrogen atom abstracting species, the "free" chlorine atom and the  $C_6H_6Cl \cdot \pi$ -complex.<sup>55</sup>

We have measured the first absolute rate constants for the reaction of the free chlorine atom in solution and the first absolute rate constants for reactions of the  $C_6H_6Cl \cdot \pi$ -complex. We do not envisage undertaking further work on this topic.<sup>43</sup>

### Experimental Section

**Materials.** Benzene (Aldrich) was purified by washing with  $H_2SO_4$  and distillation.  $CCl_4$  (Fisher Scientific) was freed from hydrocarbon

impurities by prolonged photolysis with benzophenone and distillation. Other chemicals were used as received.

**Laser Flash Photolysis.** Our laser flash photolysis apparatus was described previously.<sup>56</sup> A double-flow system was used for the experiments in which molecular chlorine was involved. Two streams, one carrying solvent saturated at 760 torr with a  $Cl_2/N_2$  mixture of known composition, another a deoxygenated mixture of solvent, benzene, and (for quenching experiments) hydrocarbon, were mixed in a T-piece, just before entering the photolysis cell. A double-head peristaltic pump was used to move the two streams. Teflon tubing was used everywhere except for the pump heads in which we used Viton washed with  $CCl_4$ . Other laser flash experiments were carried out in static systems with samples contained in Suprasil cells. These were usually deoxygenated by bubbling with oxygen-free nitrogen.

In the laser experiments that were carried out to check the effect of oxygen on the kinetic behavior of  $\pi$ - $C_6H_6Cl \cdot$ , the oxygen concentration was maintained at a high and constant value by continuous bubbling of gas at 760 torr through the reactants: system 1, 3.5%  $Cl_2$ , 46.5%  $N_2$ , 50%  $O_2$ ; system 2, 50%  $HCl$ , 50%  $O_2$ . Control experiments were always run in which  $O_2$  was replaced by  $N_2$ .

Since most of our kinetic analyses rely on processes that can be analyzed in terms of first- (or pseudo-first-) order kinetics, laser dose attenuation experiments (with neutral density filters) were routinely carried out. In this way we ensured that second-order (transient-transient) reactions were not involved to any significant extent.

**Product Analysis.** All the data in Table III were obtained by bubbling mixtures of  $Cl_2/N_2$  (for most experiments, 7%  $Cl_2$  in  $N_2$ ) through deoxygenated mixtures of benzene, usually an inert solvent  $CCl_4$ , and DMB during exposure to daylight. In addition, some data points were checked by preparing samples by the additions of deoxygenated DMB to a solution of benzene and solvent saturated with the  $Cl_2/N_2$  mixture and were only then exposed to daylight. For all the data listed in Table III, the conversion of the DMB was never allowed to exceed 10%. The products were analyzed by gas chromatography, and all measurements were repeated from two to six times in independent experiments. The GC analysis was carried out either on 100-m, 0.25-mm i.d. 007 Methyl Silicone column or 12-m, 0.22-mm i.d. BPI column using either Varian 3700 or Perkin-Elmer 8320 gas chromatographs.

For the product ratios listed in Table IV and for the product experiments carried out in nonde-aerated solvents, the hydrocarbon conversions were kept below 20%. The reactions in nonde-aerated solvents were carried out in screw-cap vials without mechanical agitation.

**Acknowledgment.** We thank Professor Cheves Walling for some perspicacious and extremely helpful comments on the initial version of this manuscript.

**Registry No. 1,** 16992-22-6; DMB, 79-29-8;  $CH_3(CH_2)_3CH_3$ , 142-82-5;  $CD_3(CD_2)_3CD_3$ , 33838-52-7;  $(CH_3)_3CC(CH_3)_3$ , 594-82-1;  $C_6H_6$ , 71-43-2;  $Cl_2$ , 7782-50-5;  $Cl \cdot$ , 22537-15-1; *t*-BuO $\cdot$ , 3141-58-0;  $HCl$ , 7647-01-0;  $S_2Cl_2$ , 10025-67-9;  $PhC(O)CH_2Cl$ , 532-27-4;  $Cl_2SO$ , 7719-09-7; *t*-BuOOBu-*t*, 110-05-4; cyclopentane, 287-92-3; cyclooctane, 292-64-8; 1,4-cyclohexadiene, 628-41-1.

**Supplementary Material Available:** Figure 5 giving detailed spectral data for  $\pi$ - $C_6H_6Cl \cdot$  and  $C_6H_7 \cdot$  in the 500–600 nm range (2 pages). Ordering information is given on any current masthead page.

(51) The equilibrium constant for the  $\pi$ -complex, i.e.,  $200 M^{-1}$ , is smaller than the value of  $>1000 M^{-1}$  previously estimated by Bühler.<sup>11</sup>

(52) A reasonable estimate of true error limits in  $k_5/k_6$  is probably  $21.0 \pm 4.0$ . Unfortunately, the only obvious way to reduce this uncertainty would be to approach experimentally the selectivity of  $\pi$ - $C_6H_6Cl \cdot$  by increasing the benzene concentration, but, of course, this cannot be increased beyond that for pure benzene (11.25 M). These errors will, of course, be carried into the  $k_4/k_6$  terms, and thus into  $k_4$  and hence into the equilibrium constant.

(53) Russell<sup>4,5</sup> reported that plots of  $S^m$  vs.  $[C_6H_6]$  were curved in that direction that would imply that  $S_m \rightarrow \infty$  as  $[C_6H_6] \rightarrow \infty$  and  $[RH] \rightarrow 0$ . He therefore suggested that a third abstracting species, formulated as  $(C_6H_6)_2Cl \cdot$ , was involved. Our own data show that at constant [DMB] all plots of  $S^m$  vs.  $[C_6H_6]$  curve in the opposite direction, i.e.,  $S^m \rightarrow S^m_\infty$  as  $[C_6H_6] \rightarrow \infty$ .

(54) Skell, P. S., private communication.

(55) Hats off to Glen Russell!

(56) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.