

inexpensive alternative to multiquadrupole and multiselector instrumentation for the structural analysis of peptides and other biopolymers.

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The Unusual and the Unexpected in an Old Reaction. The Photochlorination of Alkanes with Molecular Chlorine in Solution¹

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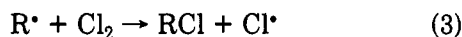
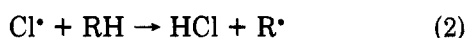
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The photochlorination of an alkane, RH, with molecular chlorine in solution has long been recognized to be a radical chain reaction:³

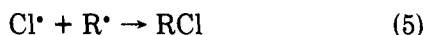
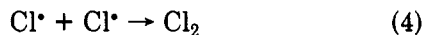
initiation



propagation



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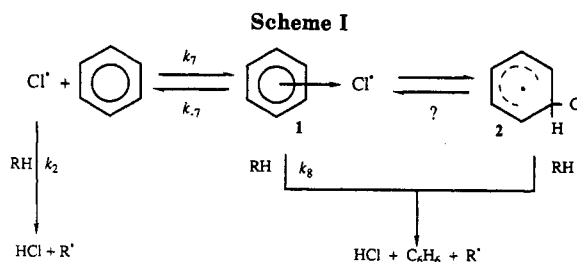
After reviewing the earlier literature,⁴ Haas, McBee, and Weber in 1936 provided more precise measurements of their own on some simple alkanes and formulated a series of important chlorination rules.^{4,5} In somewhat abbreviated form, the four main rules for solution chlorinations are as follows:

1. Carbon skeleton rearrangements do not occur, but every possible monochloride is always formed.
2. Hydrogen atoms are always substituted at rates that are in the order primary < secondary < tertiary.
3. At increasing temperatures, these relative rates approach 1:1:1.
4. Moisture, carbon surfaces, and light have no effect upon these product ratios.

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These rules are easy to understand. The first three imply that reactions 2 and 3 are fast and that the Cl[•] atom is a rather unselective hydrogen-abstracting agent while rule 4 is consistent with our expectations for a chain reaction that has a long chain length.

The Haas, McBee, and Weber chlorination rules remained unchallenged for over 20 years. Then, in 1957, Russell⁶ showed that whereas product ratios might not depend on moisture, carbon surfaces, or light, they certainly did depend on the solvent used for the photochlorination. Specifically, Russell⁶⁻⁸ showed that, in the photochlorination of 2,3-dimethylbutane (DMB), the tertiary/primary selectivity, S^m,⁹ could be increased by working in aromatic solvents (and in CS₂). For example,⁷ Russell found that at 25 °C S^m increased from 0.7 in pure liquid DMB to 10 for DMB in 8 M benzene. Russell proposed an equilibration between the "free" chlorine atom and a chlorine atom/arene π-complex,

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(3) In 1930, the photochlorination of CHCl₃ in CCl₄ was shown to have a very large quantum yield and a chain reaction involving Cl[•] and Cl₃C[•] was proposed; see: Schwab, G. M.; Heyde, U. *Z. Phys. Chem., Abt. B* 1930, 8, 147-158.

(4) Haas, H. B.; McBee, E. T.; Weber, P. *Ind. Eng. Chem.* 1935, 27, 1190-1195.

(5) Haas, H. B.; McBee, E. T.; Weber, P. *Ind. Eng. Chem.* 1936, 28, 333-339.

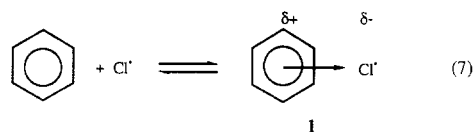
(6) Russell, G. A. *J. Am. Chem. Soc.* 1957, 79, 2977-2978.

(7) Russell, G. A. *J. Am. Chem. Soc.* 1958, 80, 4897-4996.

(8) Russell, G. A. *J. Am. Chem. Soc.* 1958, 80, 4997-5001.

(9) S^m refers to the molecular tertiary/primary chloride product ratio, i.e., S^m = [2-chloro-DMB]/[1-chloro-DMB].

the complex having the higher selectivity and its relative importance being increased by raising the concentration of the arene solvent. The aromatic compound acts as an electron donor to the chlorine atom, so the complex has a certain "charge-transfer" character.



Walling and Mayahi¹⁰ soon provided independent confirmation of Russell's major results and conclusions. Considerably later, during the pulse radiolysis of benzene in CCl_4 , a transient absorption having $\lambda_{\text{max}} \sim 490$ nm was obtained and identified as the $\text{Cl}^\bullet/\text{C}_6\text{H}_6$ charge-transfer complex, i.e., 1.^{11,12}

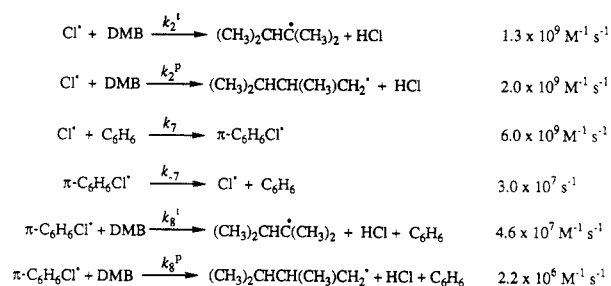
Nothing more was added to our understanding of this chemistry until 1983 when Skell, Baxter, and Taylor¹³ reinvestigated the photochlorination of DMB in the absence and presence of benzene. They made the very important new and extremely stimulating observation that S^m increased with a decrease in the concentration of DMB under conditions wherein the concentration of benzene was kept constant (at 4 M). They hypothesized that in addition to free Cl^\bullet atoms and the π -complex, 1, there was also a third hydrogen atom abstracting species, which was more selective than either of these. It was suggested that the third abstractor was the σ -complex, 2, i.e., the chlorocyclohexadienyl radical; see Scheme I.

Are There Two or Three Hydrogen Atom Abstractors?

An examination of Scheme I reveals that the increase in S^m with decreasing concentration of DMB at constant $[\text{C}_6\text{H}_6]$, which was discovered by Skell et al.,¹³ does not demand three hydrogen atom abstractors unless the free Cl^\bullet atom and its π -complex are in equilibrium. This appears to have been implicitly assumed,¹³ but it requires that k_7 (and k_{-7}) must be large relative to k_2 . However, the $k_7 \gg k_2$ inequality is highly improbable since it has long been known that the reaction of Cl^\bullet atoms with alkanes is extremely rapid and that k_2 may well approach the diffusion-controlled limit for a bimolecular reaction.¹⁴ It will be obvious that if k_7 and k_2 are of comparable magnitude, then some of the "nascent" Cl^\bullet atoms produced in reaction 3 will attack RH (=DMB) in competition with their attack on benzene. Furthermore, the fraction of nascent Cl^\bullet atoms that do react with the DMB will decrease as the $[\text{DMB}]/[\text{C}_6\text{H}_6]$ ratio decreases so that even with constant $[\text{C}_6\text{H}_6]$ the value of S^m will increase as $[\text{DMB}]$ is decreased. Hence, the results of Skell et al.¹³ can be explained with two, rather than with three, hydrogen atom abstracting species.

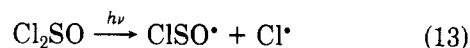
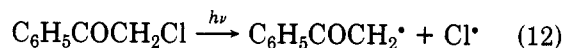
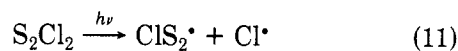
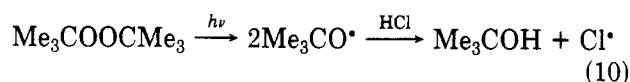
We decided that the most direct and simple method for determining whether or not three abstractors were required to explain the experimental results was to measure k_2 and k_7 by the technique of laser flash pho-

Scheme II



$$k_2^i/k_2^p = S^m_{\text{Cl}} = 0.66; \quad k_8^i/k_8^p = S^m_{\pi} = 21.0; \quad k_7/k_{-7} = 200 \text{ M}^{-1}$$

tolysis (LFP).¹⁵ Chlorine atoms were generated in solution at room temperature by 308- and/or by 337-nm LFP of five different molecular precursors:



In the presence of benzene, all five systems gave a transient spectrum (Figure 1) which showed a fairly strong and very broad band, $\lambda_{\text{max}} \sim 490$ nm ($\epsilon_{490} = 1800 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁶ essentially identical with that reported by earlier workers^{11,12,17,18} and assigned by them to the $\text{Cl}^\bullet/\text{C}_6\text{H}_6$ π -complex, 1. That this transient could be due to the postulated¹³ $\text{Cl}^\bullet/\text{C}_6\text{H}_6$ σ -complex, 2, is highly improbable since an authentic σ -complex, the cyclohexadienyl radical, exhibits a totally different transient absorption spectrum (see Figure 1).

Most of the rate constants required to provide a quantitative description of the effect of benzene on S^m for DMB were readily obtained by monitoring the 490-nm absorption at room temperature and at various benzene concentrations in CCl_4 (the inert diluent) both in the absence and presence of DMB (and some other alkanes).¹⁵ Careful measurements of the product ratio $[2\text{-chloro-DMB}]/[1\text{-chloro-DMB}] (=S^m)$ formed during the photochlorination of DMB in benzene/ CCl_4 mixtures were also carried out. Our experimental S^m values¹⁵ are shown in Figure 2. The curves on this figure have been calculated from the LFP derived rate constants and the six reactions shown in Scheme II. There is excellent agreement between the measured and calculated S^m values, and this agreement has been obtained with two hydrogen atom abstracting species, not three. A simple application of Occam's razor indicates that the benzene-modulated photochlorination of DMB in CCl_4 can and should be described in terms of two

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

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

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

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

(14) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; Chapter 8.

(15) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464-5472.

(16) McGimpsey, W. G.; Scaiano, J. C. *Can. J. Chem.* **1988**, *66*, 1474-1478.

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

(18) Aver'yanov, V. A.; Kirichenko, S. E.; Khudyakov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 274-279.

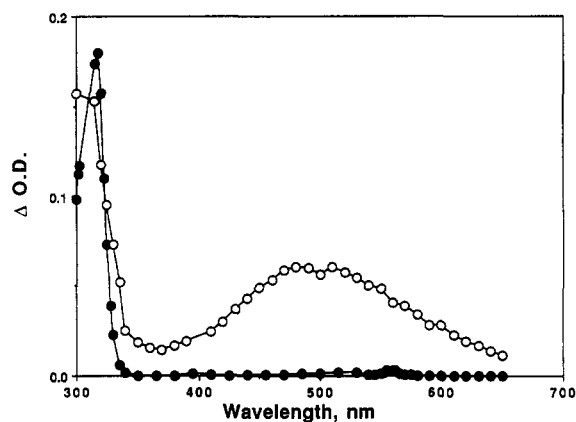


Figure 1. Transient spectra obtained by 308-nm excitation of solutions of di-*tert*-butyl peroxide (0.27 M) in HCl-saturated benzene (○) and 0.27 M di-*tert*-butyl peroxide in benzene containing 1.0 M 1,4-cyclohexadiene (●).

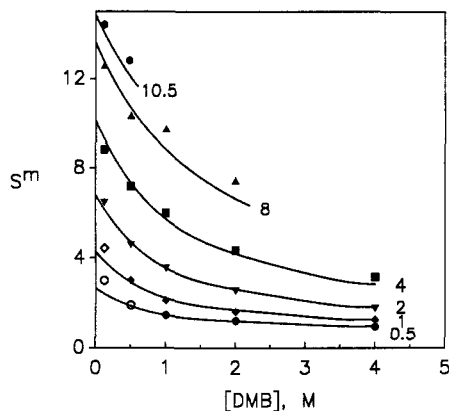


Figure 2. Dependence of S^m on DMB concentration for various benzene molarities (indicated on the right). Filled points correspond to data used for computing the curves (see ref 15). Open points refer to data with 15% or more polychlorination.

hydrogen abstractors, the free Cl^* atom and the $\text{Cl}^*/\text{C}_6\text{H}_6$ π -complex.

Subsequently, Skell et al.¹⁹ reported the results of various experiments that were asserted to demonstrate (i) that three hydrogen-abstracting species were present during the liquid-phase photochlorination of organic compounds in the presence of C_6H_6 and (ii) that the highly selective hydrogen abstractor was the σ -complex, 2, rather than the π -complex, 1 (the latter being assumed to have a selectivity only slightly larger than that of the free chlorine atom). However, none of these experiments provided convincing proof of either assertion, and most of them have been subjected to critical analyses.²⁰⁻²²

To complete this section, we note that other workers^{23,24} have confirmed our earlier report¹⁵ that free chlorine atoms react with many organic substrates in solution with rate constants close to the diffusion-controlled limit (see Table I). A transient absorption with $\lambda_{\text{max}} = 400$ nm formed by reaction of Cl^* atoms with dimethyl sulfoxide was employed to monitor the attack

(19) Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300-6311.

(20) Aver'yanov, V. A.; Ruban, S. G. *Kinet. Katal.* **1986**, *27*, 485-489.

(21) Walling, C. J. *Org. Chem.* **1988**, *53*, 305-308.

(22) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 3519-3524.

(23) Sumijoshi, T.; Katayama, M. *Chem. Lett.* **1987**, 1125-1126. Sumijoshi, T.; Miura, K.; Hagiwara, H.; Katayama, M. *Ibid.* **1987**, 1429-1430.

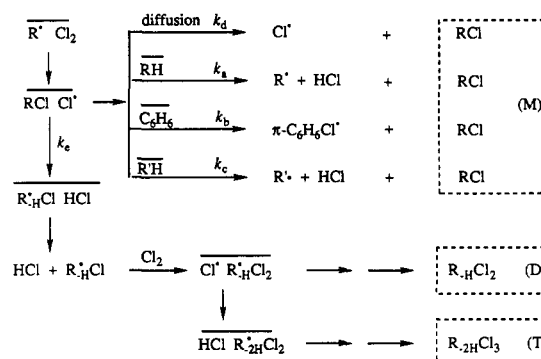
(24) Neta, P.; Mosseri, S.; Alfassi, Z. B. *J. Phys. Chem.* **1989**, *93*, 1380-1385.

Table I
Some Absolute Rate Constants for the Reactions of Cl^* in Solution at Ambient Temperatures

substrate	k , $\text{M}^{-1} \text{s}^{-1}$	ref
DMSO	7.0×10^9 ^a	23
CH_3OH	2.7×10^9 ^a	23
cyclohexene	1.2×10^{10} ^b	24
$\text{C}_6\text{H}_5\text{OH}$	2.5×10^{10} ^b	24
$\text{C}_6\text{H}_5\text{NH}_2$	4×10^{10} ^b	24
$(\text{CH}_3)_6\text{C}_6$	2.2×10^{10} ^b	24
CH_2Cl_2	9×10^6 ^b	24

^a In CCl_4 solvent. ^b In CH_2Cl_2 solvent.

Scheme III



of Cl^* atoms on a variety of substrates.

Polychlorination: Cl^* Atom/RCl Geminate Pairs and the Effect of Reactive "Cage Walls" on the Competition between Monochloride Rotation and Cl^* Atom Escape

A unique and unexpected observation of particular importance was reported by Skell and Baxter in 1985.²⁵ During alkane photochlorinations in inert perhalogenated solvents, these workers found that at low alkane concentrations there was a remarkably high yield of di- and trichlorinated compounds even at very low conversions (see also open symbols in Figure 2). This surprising result was attributed to a cage effect (see Scheme III, in which the bars above the reactants refer to caged species and molecules in the cage walls). That is, when an alkyl radical reacts with a Cl_2 molecule, they form a geminate pair of products, the alkyl (mono)chloride and a chlorine atom. The high reactivity of the Cl^* atom allows reaction with the molecules of the "cage wall" around the Cl^* to compete with its diffusion out of the cage. Since one component of the cage wall is the geminate alkyl chloride, a reaction of Cl^* with this monochloride will give a radical, $\text{R}'_1\text{Cl}$, which will subsequently become a dichloride (Scheme III). Furthermore, a second in-cage reaction of the $\text{Cl}^*/\text{R}'_1\text{Cl}_2$ geminate pair can produce trichlorides. Thus, dichlorides (and trichlorides) can be produced by routes other than a diffusive encounter between a Cl^* atom and a molecule of monochloride (or dichloride).

It will be obvious that the monochloride/(di- + trichloride) ($=[\text{M}]/([\text{D}] + [\text{T}])$) ratio must depend on the nature of the cage wall since this will affect the "escape"²⁶ of the Cl^* atom from in-cage RCl. Thus, at

(25) Skell, P. S.; Baxter, H. N., III. *J. Am. Chem. Soc.* **1985**, *107*, 3823-3824.

(26) "Escape" is used to describe all routes by which the Cl^* atom is removed from geminate RCl; these are diffusion from the solvent cage in which the Cl^* was formed plus its reaction with molecules other than RCl which formed a part of the cage wall.

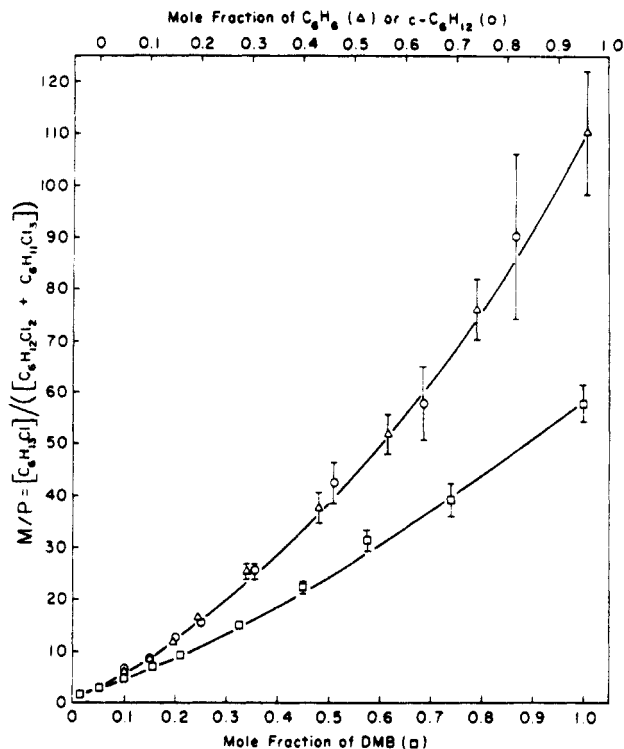


Figure 3. Photochlorination of DMB at room temperature. Monochloride/polychloride ratio as a function of the mole fraction of X, with CCl_4 as the inert diluent: \square , RH = DMB, X = DMB; Δ , RH = 0.5 M DMB, X = C_6H_6 ; \circ , RH = 0.5 M DMB, X = $c\text{-C}_6\text{H}_{12}$. Reprinted with permission from ref 22. Copyright 1988 American Chemical Society.

low RH concentrations in perhalogenated solvents, the only reactive wall component will be the geminate RCl, and polychloride formation will be extensive. Wall reactivity will increase and polychloride formation decrease as the concentration of RH is increased. Wall reactivity will also increase in the presence of benzene or a second hydrogen donor, R'H. A simple kinetic treatment of the reactions shown in Scheme III yields the relation²²

$$\frac{[M]}{[P]} = \frac{[M]}{[D] + [T]} = \frac{k_d + k_a[\text{RH}] + k_b[\text{C}_6\text{H}_6] + k_c[\text{R'H}]}{k_e[\text{RCl}]} \quad (\text{I})$$

According to eq I, for a single alkane, RH, and in the absence of benzene, the monochloride/polychloride ($= [M]/[P]$) ratio should increase linearly as the mole fraction of RH in an inert solvent is increased. However, for DMB (and for cyclohexane) this plot was found²² to have an upward curvature (Figure 3), and with a constant concentration of DMB (0.5 M), the replacement of the inert solvent CCl_4 by benzene²⁷ or by cyclohexane produced an even more pronounced upward curvature (Figure 3). Thus, the yield of polychloride decreases more rapidly than would be predicted as the overall system, including specifically the "cage walls", becomes more reactive. This has been

(27) The apparent absence of polychlorides at high benzene concentrations has been used to argue for a three abstractor photochlorination model¹⁹ (i.e., Cl^* , 1, and 2). However, it can be seen from Figure 3 that benzene behaves in a manner essentially identical with that of cyclohexane, a saturated hydrocarbon with a reactivity toward Cl^* that is comparable to that of benzene.

(28) Russell, G. A.; Ito, A.; Konaka, R. *J. Am. Chem. Soc.* 1963, 85, 2988-2991.

Table II
Sites of Attack as a Percentage of Total Attack on Chlorocyclohexane by Free (Diffusive) Chlorine Atoms and by In-Cage (Geminate) Chlorine Atoms^a

diffusive-pair chlorination, 0.5 M $c\text{-C}_6\text{H}_{11}\text{Cl}$ in CCl_4	geminate-pair chlorination	
	0.5 M $c\text{-C}_6\text{H}_{12}$ in CCl_4	neat $c\text{-C}_6\text{H}_{12}$
 14 ± 1 18 ± 1 32 ± 1 36 ± 1	 19 ± 1 27 ± 1 30 ± 1 24 ± 1	 17 ± 2 33 ± 1 29 ± 1 21 ± 1

^a Data presented here come from a more detailed investigation of these reactions than was reported in ref 22. Errors correspond to 2 standard deviations.

attributed²² to the fact that the in-cage reaction of Cl^* with molecules in the cage wall (other than the geminate RCl) that surrounds the geminate Cl^*/RCl pair competes with the (partial) rotation of the geminate RCl, and of course, at least some degree of rotation of this molecule relative to the Cl^* atom must occur if the RCl is to "present" a second H atom to the Cl^* atom. Thus, as the mole fraction of RH, C_6H_6 , or R'H increases, the cage walls become more and more reactive and rotation of the geminate RCl becomes more and more the rate-determining step for polychloride formation. For this reason, the $[M]/[P]$ ratio increases more rapidly than was predicted on the basis of a freely rotating geminate RCl,²² i.e., on the basis of eq I.

An interesting consequence of the above interpretation of $[M]/[P]$ ratios is that it leads to the prediction that the dichlorides formed by reaction of the Cl^*/RCl geminate pair should show a "pattern" that changes so that the two chlorine atoms in the dichlorides become closer together as the cage-wall reactivity increases (and the lifetime of the geminate Cl^*/RCl pair decreases). Furthermore, the geminate "pattern" of dichlorides formed even in an inert solvent is expected to have the two chlorine atoms closer together than for the diffusive Cl^*/RCl pair produced by photochlorinating RCl itself. Some data on cyclohexane and chlorocyclohexane that confirm this prediction are given in Table II. It can be seen that attack on the "remote" 4-position of chlorocyclohexane decreases while attack at the "close" 2-position increases along the series 0.5 M $c\text{-C}_6\text{H}_{11}\text{Cl}$ in CCl_4 , 0.5 M $c\text{-C}_6\text{H}_{12}$ in CCl_4 , neat C_6H_{12} .

The photochlorination of neopentane in the presence of a number of arenes yields plots of $[M]/[P]$ vs [arene] that are linear.²⁹ According to eq I, a comparison of the slopes of such plots for different arenes will yield the relative rates of reaction of the Cl^* atom with the arene. A table of relative rates for $\text{Cl}^* + \text{arene}$ obtained by this method has been compiled.²⁹ It would be interesting to compare these relative k 's with absolute k 's measured by LFP to check the validity of the kinetic assumptions built into both techniques.

Influence of Arene on S^m

Russell, who discovered the effect of arene solvents on S^m , demonstrated^{6,7} that arenes that were electron-poor relative to benzene produced lower S^m values than benzene and that certain electron-rich arenes produced S^m values greater than that found for benzene. Since he did not control his DMB concentration (and there-

(29) Tanko, J. M.; Anderson, F. E., III. *J. Am. Chem. Soc.* 1988, 110, 3525-3530.

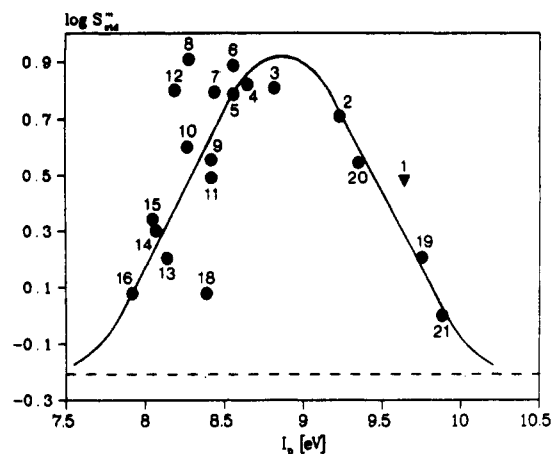


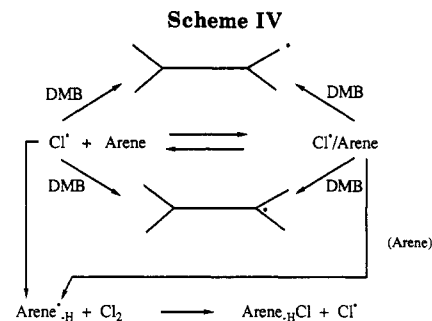
Figure 4. Plot of $\log S^m_{std}$ vs I_D of the arene. The arene numbering is as follows: 1, C_6H_5Cl ; 2, C_6H_6 ; 3, $C_6H_5CH_3$; 4, $C_6H_5C(CH_3)_3$; 5, 1,2- $(CH_3)_2C_6H_4$; 6, 1,3- $(CH_3)_2C_6H_4$; 7, 1,4- $(CH_3)_2C_6H_4$; 8, 1,4- $(C(CH_3)_3)_2C_6H_4$; 9, 1,2,3- $(CH_3)_3C_6H_3$; 10, 1,2,4- $(CH_3)_3C_6H_3$; 11, 1,3,5- $(CH_3)_3C_6H_3$; 12, 1,3,5- $(C(CH_3)_3)_3C_6H_3$; 13, 1,2,3,4- $(CH_3)_4C_6H_2$; 14, 1,2,3,5- $(CH_3)_4C_6H_2$; 15, 1,2,4,5- $(CH_3)_4C_6H_2$; 16, $(CH_3)_5C_6H$; 17, $(CH_3)_6C_6$; 18, $C_6H_5OCH_3$; 19, $C_6H_5CF_3$; 20, C_6H_5F ; 21, $C_6H_5NO_2$. The limiting S^m value obtained with free Cl^* atoms in the gas phase (0.62) is indicated by the dotted line. The curve is an artist's impression. Reprinted with permission from ref 30. Copyright 1989 American Chemical Society.

fore his S^m values, *vide supra*), we undertook the measurement of S^m values for DMB in a variety of aromatic solvents under *standard conditions*³⁰ (room temperature, [arene] = 2.0 M, [DMB] = 0.15 M in CCl_4). Where comparisons are possible, our results are generally in good agreement with Russell's. The expected monotonic increase in our standard selectivities, S^m_{std} , with an increase in the π -electron density in the aromatic ring³¹ (and hence, in the equilibrium favoring the $Cl^*/$ arene π -complex relative to the free Cl^* atom) did not materialize (see Figure 4). Instead, the largest S^m_{std} values were obtained with toluene, the dimethylbenzenes, and the *tert*-butyl-substituted benzenes, and the smallest S^m_{std} values were obtained with aromatics containing strongly electron withdrawing substituents (e.g., CF_3 , NO_2) and with highly methylated and other electron-rich arenes (see Figure 4).

Russell⁷ argued that complexes between Cl^* and an electron-deficient arene would be only slightly stabilized with respect to the free Cl^* atom and hence would be only slightly more selective in hydrogen abstraction than the Cl^* atom. Increasing the electron density on the arene³¹ should stabilize the complex and produce a species with increased selectivity. Although his results did not demonstrate that very electron rich arenes would reduce the selectivity of photochlorinations, he did predict that this would occur and provided two entirely reasonable explanations for the phenomenon.⁷ First, strong $Cl^*/$ arene complexes may be highly selective, but they will also be relatively unreactive; hence, most hydrogen abstraction from DMB will be carried out by free Cl^* atoms, and a low selectivity will be observed. Second, for arenes possessing abstractable hydrogens, a rapid, irreversible decomposition of the π -complex via such a reaction will form the side-chain-chlorinated arene. This will provide a mechanism for

(30) Raner, K. D.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* 1989, 111, 3652-3658.

(31) The π -electron density in the aromatic ring is expected to be related to the vertical ionization potential of the arene, I_D .



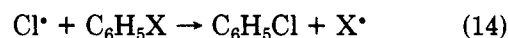
the conversion of the $Cl^*/$ arene complex back to free Cl^* atoms that does not involve DMB (see Scheme IV), and most importantly, it will reduce the yield of RCl and ensure that most of the RCl that is produced is formed via free Cl^* atoms. The yield of DMB chlorides as a percentage of the chlorides produced by a radical chain reaction³² varies from 100% for C_6H_6 , C_6H_5Cl , $C_6H_5CF_3$, etc., to $\leq 2\%$ for anisole and some highly methylated benzenes.³⁰ Indeed, for the latter compounds, the reactivities of the $Cl^*/$ arene complexes toward DMB are likely to be lower than their reactivities toward a second arene molecule so that much of the hydrogen abstraction from DMB must be due to the free Cl^* atom. The scatter in the S^m_{std} values at low arene ionization potentials, I_D (see Figure 4), appears to be due to changes in the relative amounts of abstraction by free vs complexed Cl^* so that, for example, the poly-*tert*-butylbenzenes have higher S^m_{std} values than the (more reactive) polymethylbenzenes of comparable I_D .

Bunce et al.³³ have shown that in (4 M) mono-, di-, or trifluorobenzene the S^m values increase as the DMB concentration decreases and that at a particular [DMB] the S^m values decrease with the extent of fluorination. By way of contrast, S^m was independent of [DMB] in hexafluorobenzene, as would be expected for a very electron deficient arene.

Of all the aromatics we examined, only pyridine yielded a higher S^m_{std} value than 1,4-di-*tert*-butylbenzene, viz., 8.5 vs 8.1.³⁰ However, pyridine ($I_D = 9.88$ eV) does not fit into the pattern shown in Figure 4 presumably because, in the Cl^*/C_5H_5N complex, the Cl^* is complexed to the nitrogen and lies in the plane of the aromatic ring,³⁴ i.e., the Cl^*/C_5H_5N complex is structurally quite different from the $Cl^*/$ arene complexes. It was not examined further.³⁰

Ips0 Substitution

The ipso substitution of Cl for Br or I during the reaction of Cl^* atoms with C_6H_5Br or C_6H_5I is well-known³⁵ and is thermodynamically favored. The



photochlorination of DMB in C_6H_5Br yields $S^m_{std} = 5.3$,³⁰ a value much greater than would be predicted for this electron-deficient arene ($I_D = 9.05$ eV). However,

(32) Electron-rich arenes also undergo electrophilic chlorination of the aromatic ring. Significant quantities of the available Cl_2 can be consumed in this way, e.g., 88% by anisole, 78% by pentamethylbenzene, etc.³⁰

(33) Bunce, N. J.; Joy, R. B.; Landers, J. P.; Nakai, J. S. *J. Org. Chem.* 1987, 52, 1155-1156.

(34) Breslow, R.; Brandl, M.; Hunger, J.; Turro, N.; Cassidy, K.; Krogh-Jespersen, K.; Westbrook, J. D. *J. Am. Chem. Soc.* 1987, 109, 7204-7206.

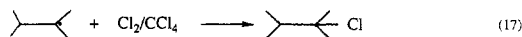
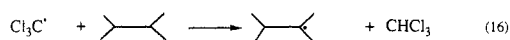
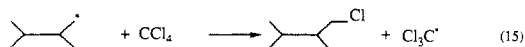
(35) Traynham, J. G. *Chem. Rev.* 1979, 79, 323-330.

C_6H_5Cl constitutes 63% of the products, so it is obvious that at least some of the Br atoms formed in reaction 14 abstract hydrogen from DMB, a process with a high preference (ca. 10^4 – 10^5) for the tertiary hydrogen. In C_6H_5I , the DMB chlorides constituted 47% and C_6H_5Cl 17% of the products and S^m_{std} was 23! Since I^* does not abstract hydrogen from DMB, we tentatively attribute the remarkable selectivity in this arene to abstraction by $C_6H_5\dot{I}Cl$.³⁰

Influence of Noncomplexing Solvents on S^m

Noncomplexing solvents can also influence S^m .³⁶ Thus, in the presence of an adequate supply of Cl_2 (e.g., continuous bubbling with pure Cl_2), the photochlorination of neat DMB yields $S^m = 0.64 \pm 0.01$ whereas with 0.5 M DMB in CCl_4 S^m is only 0.47.³⁶ The lower S^m value in CCl_4 has been traced to the fact that the in-cage chlorination (vide supra) of the tertiary chloride is faster than that of the primary chloride³⁶ and, of course, in-cage processes are more important in inert solvents (CCl_4) than in reactive solvents (neat DMB).

A second phenomenon we have observed³⁶ is that S^m values measured in the presence of "inert" CCl_4 can be increased by a factor of 3–4 by reducing the Cl_2 concentration. This is because CCl_4 and Cl_3C^* become important participants in the overall chain process. The Cl_3C^* radical is highly selective and essentially abstracts only the tertiary hydrogen from DMB. Chloroform was identified among the products.³⁶



A third phenomenon observed³⁶ is that even in the absence of CCl_4 the S^m values can be increased by up to a factor of 7 at very low Cl_2 concentrations because of residual oxygen. In this case, the DMB-derived radicals are converted (partially) to peroxy radicals and the latter (like Cl_3C^*) are highly selective for the tertiary hydrogen of DMB.

In the absence of these "complications", $S^m = 0.64$, a value that compares well with a value of 0.62, which we have measured in the gas phase.³⁶

UV/Visible Spectra of $Cl^*/$ Arene Complexes and Related π -Complexes

With the hope of obtaining more structural information about the Cl^*/C_6H_6 complex, we measured the UV/visible spectra for a large number of arene complexes of Cl^* , Br^* , I^* , Cl_2 , Br_2 , and I_2 .^{37,38} In all cases, charge-transfer⁴⁰ absorption spectra were observed in the visible region.³⁷ For a suitably restricted range of π -donors,⁴¹ the transition energies of the charge-transfer

(36) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Org. Chem.* 1988, 53, 5220–5225.

(37) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Phys. Chem.* 1989, 93, 564–570.

(38) Previous workers who have examined the $Cl^*/$ arene^{11,12} and $Br^*/$ arene³⁹ charge-transfer bands employed a more restricted range of arenes, which led to some incorrect conclusions.³⁹

(39) Bossy, J. M.; Bühler, R. E.; Ebert, M. *J. Am. Chem. Soc.* 1970, 92, 1099–1101.

(40) The appearance of a charge-transfer spectrum does not automatically imply that charge transfer plays a dominant, or even a significant, role in the binding together of the complex.⁴¹

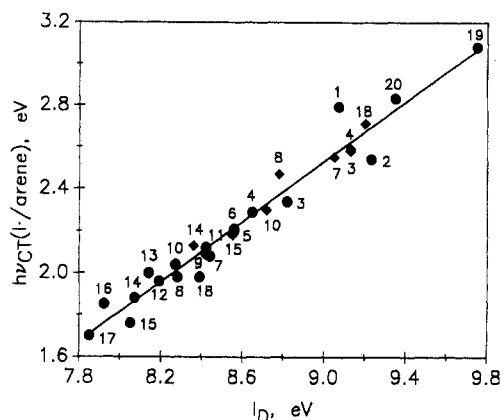


Figure 5. Plot of $h\nu_{CT}(I^*/\text{arene})$ against the first (●) and second (◆) ionization potential of the aromatic donor. For the identity of the arenes, see caption to Figure 4.

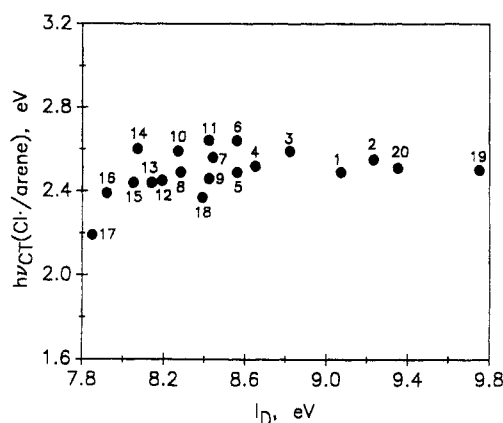


Figure 6. Plot of $h\nu_{CT}(Cl^*/\text{arene})$ against the first ionization potential of the aromatic donor. For the identity of the arenes, see caption to Figure 4.

absorption-band maxima, $h\nu_{CT}$, will normally correlate fairly well with the vertical ionization potentials of the aromatic donors, I_D .⁴² Such correlations for Cl_2 , Br_2 , and I_2 are rather poor,³⁷ but the "deviations" do appear to be consistent with steric effects due to the arene's substituents causing a change in the distance, r_{AD} , between the halogen acceptor and arene donor (as first discussed by Fukuzumi and Kochi⁴³). That is, the Mulliken theory⁴² states that the band energy is dependent on the acceptor's electron affinity, the donor's ionization potential, and r_{AD} . Despite the poor correlation of $h\nu_{CT}$ vs I_D for the molecular halogen/arene adducts, it is well established that these are π -molecular complexes.⁴²

Surprisingly, for $I^*/$ arenes, the plot of $h\nu_{CT}$ vs I_D gives an excellent straight line³⁷ (see Figure 5). This implies that steric effects are relatively unimportant for $I^*/$ arenes (i.e., constant r_{AD}) and that the I^* lies directly above the center of the ring, i.e., I^*/C_6H_6 is a classical, hexahapto complex. Even more surprisingly, for the $Cl^*/$ arene complexes (and the $Br^*/$ arene complexes), the $h\nu_{CT}$ values were almost independent of I_D and showed considerable scatter³⁷ (see Figure 6). It would appear that steric effects are more important for the arene complexes with the smaller Cl^* atom (and Br^* atom) than for the larger I^* atom.⁴⁴ It was concluded³⁷

(41) Dewar, M. J. S.; Thompson, C. C., Jr. *Tetrahedron* 1966, Suppl. 7, 97–114.

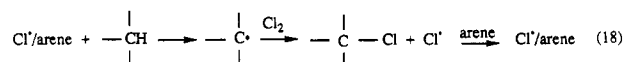
(42) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969.

(43) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* 1981, 46, 4116–4126.

that Cl[•]/arene (and Br[•]/arene) complexes are most likely to have structures similar to I[•]/arene, i.e., structure 1.

Effect of Oxygen on the Lifetimes⁴⁵ of Cl[•]/Arene Complexes

The lifetime⁴⁵ of the Cl[•]/C₆H₆ complex is the same in the presence and absence of oxygen.^{15,30} Since an authentic σ -complex, the cyclohexadienyl radical, C₆H₇[•], reacts very rapidly with O₂ ($k = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁴⁶ the very slow, or absent, reaction between the Cl[•]/C₆H₆ complex and O₂ provides strong evidence that this is a π -complex.¹⁵ Lifetimes of Cl[•] complexes with C₆H₅F, C₆H₅Cl, and C₆H₅CF₃ were likewise unaffected by O₂.³⁰ It was therefore with some surprise that we discovered that the lifetimes of the complexes formed between Cl[•] and 12 methyl-substituted benzenes, three *tert*-butyl-substituted benzenes, and anisole were significantly reduced by O₂.³⁰ Clearly this is not due to a direct reaction of these complexes with O₂ but rather to an indirect process related to the fact that these arenes contained abstractable hydrogen atoms. Hydrogen abstraction from the side chain of an arene does not significantly reduce the *observed* lifetime of the complex in the absence of O₂ because the complex is effectively "regenerated"¹⁵ by the reaction sequence



However, O₂ will scavenge the carbon-centered radical. This interferes with the regeneration process, and hence the observed lifetime of the complex is reduced.

Oxygen can also interfere with the "regeneration" process in the Cl[•]/C₆H₆/DMB system.³⁰ In the absence

(44) The atomic radii of Cl[•], Br[•], and I[•] are 1.80, 1.95, and 2.15 Å.

(45) "Lifetime" is the reciprocal of the (pseudo-) first-order rate constant for decay of the transient absorption.

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

of O₂, the addition of DMB produces only a small decrease in the Cl[•]/C₆H₆ complex's lifetime⁴⁷ because of regeneration.¹⁵ However, O₂ interferes with the regeneration process by trapping the carbon-centered radicals derived from DMB, which reduces the lifetime of the Cl[•]/C₆H₆ complex despite the fact that this complex is inert to oxygen.³⁰

Generally similar O₂-induced effects (or lack thereof) on lifetimes are observed with Br[•]/arene complexes.³⁰ The only notable difference is that O₂ has a negligible effect on the lifetimes of Br[•]/*tert*-butyl-substituted benzenes. This is simply a consequence of the very low reactivity of aliphatic methyl groups toward the Br[•] atom.

Conclusions

Studies on the influence of solvents on the selectivities of alkane photochlorinations have proved to be rich in surprises and have provided many new insights into the complexities that may be hidden in the words "a simple radical chain reaction". We wonder how many other "old" chain reactions will yield surprising chemistry when they are carefully reexamined by using modern, time-resolved kinetic procedures (such as LFP) in combination with spectroscopic techniques and detailed product analyses. Radical chemistry is not quite as simple as it may appear at first glance.

Note Added in Proof. Chateaufeuf has recently shown that "free" Cl[•] atoms in CCl₄ have a UV absorption ($\lambda_{\text{max}} = 330 \text{ nm}$) which he has utilized to measure rate constants for reactions of Cl[•] atoms with organic substrates directly, i.e., without an added "probe" molecule. See: Chateaufeuf, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 442-444.

Registry No. Cl, 7782-50-5.

(47) The total rate constant for DMB + Cl[•]/C₆H₆ is $4.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (see Scheme II).