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Influence of Aromatic Solvents on the Selectivity for Photochlorination of 2,3-Dimethylbutane with Molecular Chlorine[1]

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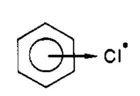
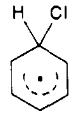
Abstract: The effect of benzene and a wide variety of substituted benzenes upon the photochlorination of 2,3-dimethylbutane (DMB) has been investigated under standard conditions (0.15 M DMB, 2.0 M arene in CCl_4 at room temperature). The standard selectivities, S^{m}_{std}, are given by the product ratios [2-ClDMB]/[1-ClDMB] under these conditions. For arenes which are less electron rich than benzene, log S^{m}_{std} values decrease monotonically with the increase in the arenes' ionization potentials and with the decrease in the arenes' π-basicities. For arenes which are more electron rich than benzene, S^{m}_{std} values are greater than for benzene only for the mono- and dialkylated benzenes and 1,3,5-tri-*tert*-butylbenzene. Chlorination in the presence of trimethylbenzenes, more highly methylated benzenes, and anisole afforded less selective mixtures of DMB chlorides than benzene. The reduced selectivities of the most electron-rich arenes is attributed to the low reactivities of their $Cl^{\bullet}$/arene π-complexes and the low yields of DMB chlorides, much of which are formed by hydrogen abstraction by the free $Cl^{\bullet}$ atom. Ipso substitution occurs with bromo- and iodobenzene and these two arenes are more selective than would be predicted. It has also been demonstrated by laser flash photolysis that $Cl^{\bullet}$/arene and $Br^{\bullet}$/arene π-complexes will appear to react with O_2 *only* if the arene contains substituents which can donate hydrogen to the halogen atom and/or complex, viz., CH_3, $C(CH_3)_3$, and OCH_3 substituents for chlorine but only CH_3 and OCH_3 for bromine. This apparent reaction is due to interference by O_2 in the process which otherwise would very rapidly "regenerate" the halogen atom/arene complex following such hydrogen abstraction.

It is well-established that the selectivities for alkane photochlorinations in solution using molecular chlorine can be dramatically increased by carrying out the reaction in a variety of aromatic solvents. This solvent effect on the products of a radical-chain reaction has most commonly been studied with 2,3-dimethylbutane (DMB) as the substrate and by measuring the selectivity, S^{m}, for its chlorination, where S^{m} is defined as being equal to the molar ratio of the two possible monochloride products: i.e., S^{m} = [2-chloro-2,3-dimethylbutane]/[1-chloro-2,3-dimethylbutane] = [2-ClDMB]/[1-ClDMB].[3-16] Russell,[3,4] who discovered this phenomenon, explained it in terms of an equilibrium between "free" (i.e., nonsolvated) chlorine atoms and π-molecular complexes formed between the chlorine atom and the arene. These $Cl^{\bullet}$/arene π-complexes were presumed to have a greater preference than a free $Cl^{\bullet}$ atom for abstracting a tertiary hydrogen atom from DMB relative to the primary hydrogen. As one might expect, the overall selectivity of the chlorination could be increased by increasing the concentration of the aromatic solvent since this would increase the relative importance of H atom abstraction by the $Cl^{\bullet}$/arene complex. An unexpected but important discovery made in 1983 by Skell et al.[7] was that S^{m} could also be increased while keeping the arene concentration unchanged simply by reducing the DMB concentration. We have confirmed this result[9] and a flurry of research activity in this area has ensued.[10-17] Most of this recent work[9,11-14,17] has provided additional support for Russell's original suggestion[3] that $Cl^{\bullet}$ atoms form a π-molecular complex with benzene, π, and that this $Cl^{\bullet}$/benzene complex is more selective in hydrogen abstraction from DMB than the free $Cl^{\bullet}$ atom. An alternative proposal[7,10] that the highly selective hydrogen atom abstracting species is a $Cl^{\bullet}$/benzene σ-molecular complex, σ, appears to lack a valid experimental foundation.[11,14]



π



σ

What are the effects on S^{m} induced by other aromatic solvents? Russell had demonstrated[3,4] that aromatics which were electron poor relative to benzene produced lower S^{m} values than benzene and that certain electron-rich aromatics produced S^{m} values greater than that found in benzene. However, Russell had not controlled his DMB concentrations and therefore his selectivities,[18] and their interpretations are at least open to question. We therefore undertook to measure S^{m} values for DMB in a variety of aromatic solvents under *standard* conditions (room temperature (22 ± 2 °C), [arene] = 2.0 M, [DMB] = 0.15 M, inert[16] diluent CCl_4). Where comparison is 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 ring[19] does not materialize. Instead, the largest S^{m}_{std} values are obtained with toluene, the dimethylbenzenes, and the *tert*-butyl-substituted benzenes and the smallest S^{m}_{std} values

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[16] (a) Under rather different conditions nonaromatic solvents such as CCl_4 can also influence S^{m} values for reasons that have nothing to do with the formation of a molecular complex between the chlorine atom and the solvent. (b) See: Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 5220–5225.

[17] Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1989**, *93*, 564–570.

[18] These were reported on a "per hydrogen" basis and must be divided by 6 in order to obtain S^{m}, the molecular selectivity for DMB. Most of Russell's measurements were made at 55 °C.

[19] (a) The π-electron density in the aromatic ring is expected to be related to the vertical ionization potential of the arene, I_D, and to the π-basicity of the arene. The latter has been determined by Brown and Brady[20] by measuring the solubility of HCl in 5 mol % solutions of arenes in *n*-heptane at −78.5 °C. (b) We are indebted to an unidentified referee for pointing out that because values of S^{m}_{std} are ratios of rate constants, dimensionally log S^{m}_{std} should be compared to energetic variations like I_D.

[20] Brown, H. C.; Brady, J. D. *J. Am. Chem. Soc.* **1952**, *74*, 3570–3582.

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Table I. Photochlorination of 0.15 M DMB, 2.0 M Arene in CCl_4 Using 7% Cl_2/93% N_2 at Room Temperature

			% chlorinated-product yields					
			DMB		arene			
no.[a]	arene	S^{m}_{std}	total[b]	(D)[c]	side chain[d]	ring[e]	I_D,[f] eV	relative π-basicity[g]
1	PhCl	3.0	100	(10)		0	9.07	0.47
2	PhH	5.1	100	(13)		0	9.23	(1.00)[h]
3	PhMe	6.4[i]	49[i]	(10)[i]	51	0	8.82	1.51
4	$PhBu^t$	6.6	62	(5)	38	0	8.65	2.23
5	1,2-$Me_2C_6H_4$	6.1	34	(*j*)	66	0	8.56	1.85
6	1,3-$Me_2C_6H_4$	7.7	33	(*j*)	64	3	8.56	2.07
7	1,4-$Me_2C_6H_4$	6.2	28	(*j*)	72	0	8.44	1.64
8	1,4-$Bu^t_2C_6H_4$	8.1	30	(6)	69	1	8.28	
9	1,2,3-$Me_3C_6H_3$	3.6	13	(3)	37	50	8.42	2.39
10	1,2,4-$Me_3C_6H_3$	4.0	5.0	(3)	65	30	8.27	2.23
11	1,3,5-$Me_3C_6H_3$	3.1	1.8	(*k*)	54	44	8.42	2.61
12	1,3,5-$Bu^t_3C_6H_3$	6.3	21	(5)	41	38	8.19	
13	1,2,3,4-$Me_4C_6H_2$	1.6	2.1	(*k*)	92	6	8.14	2.67
14	1,2,3,5-$Me_4C_6H_2$	2.0	0.68	(*k*)	24	75	8.07	2.74
15	1,2,4,5-$Me_4C_6H_2$	2.2	5.9	(2)	54	40	8.05	
16	Me_5C_6H	1.2	1.4	(*k*)	21	78	7.92	
17	Me_6C_6		≤0.05		100	0	7.85	
18	PhOMe	1.2	0.16	(*k*)	12	88	8.39	
19	$PhCF_3$	1.6	100	(7)		0	9.75	0.22
20	PhF	3.5	100	(3)		0	9.35	0.69
21	$PhNO_2$	1.0	100	(12)		0	9.88	
22	PhBr	5.3	See text				8.99	0.38
23	PhI	23	See text				8.75	0.37
DMB	(neat liquid)[l]	0.63	100	(1.7)				
DMB	(gas phase)[l]	0.62	100	(0)[m]				

[a] Arenes **1–18** have been numbered in the same way as in ref 17. Arenes **19–22** were not examined previously. [b] Combined yield of DMB mono- and dichlorides (D) as a percentage of the total yield of chlorinated products. [c] Percentage yield of DMB dichlorides (D) based on the total yield of DMB mono- and dichlorides. [d] Percentage yield of chlorinated aromatic products formed in the radical chain reaction by hydrogen atom abstraction from the substituents attached to the aromatic ring as identified by ^1H NMR, viz. (polymethyl)benzyl chlorides from (poly)methylbenzenes, (2-chloro-1,1-dimethylethyl)benzenes from the *tert*-butylbenzenes, and chloromethyl phenyl ether from anisole. [e] Percentage yield of chlorinated aromatic products formed by electrophilic chlorination of the aromatic ring as identified by ^1H NMR. [f] First vertical ionization potential of the arene. Data are from the literature cited in ref 17. [g] See ref 19a and 20. [h] Assumed. [i] To discriminate between the DMB monochlorides and the toluene, the GC analysis was carried out on a 10-m 20 M Carbowax column held at 70 °C for 6 min, the temperature was then increased at a rate of 5 °C/min to a final temperature of 180 °C. [j] Unknown because of incomplete resolution of the DMB dichlorides and the xylene. Since the percentage yield of dichlorides is probably only ca. 5%, they have been ignored in calculating the total yield of DMB chlorides and of arene chlorides. [k] Detectable amounts of dichlorides were formed but were too small to be worth quantifying. [l] Data are from ref 16b. [m] None detected.

are obtained with aromatics containing strongly electron-withdrawing substituents (e.g., $C_6H_5CF_3$ and $C_6H_5NO_2$) *and* with highly methylated and other electron-rich aromatics. Thus, plots of log S^{m}_{std} against two measures[19] of the arenes' π-electron density go throgh a maximum. Although Russell's original results[3,4] do not demonstrate that such plots would have a maximum, it is perfectly clear that he expected them to have a maximum since he provided two perfectly reasonable explanations for the occurrence of a maximum! We happily make use of both of Russell's explanations to interpret our results.[21]

Experimental Section

Chlorine (7% in N_2) was slowly bubbled through deoxygenated solutions containing 0.15 M DMB and 2.0 M arene in CCl_4 at room temperature, care being taken to prevent evaporative losses. The reaction was initiated with the light from a 100-W tungsten-filament lamp and the conversion of DMB to mono- and dichlorides was limited to ≤10%. The chlorinated products were analyzed in triplicate on a Varian 3700 gas chromatograph using, in general, a 100 m, 0.25-mm i.d. 007 methyl silicone column. The column temperature was held at 60 °C for the first 7 min and was then increased at 20 °C/min to a final temperature of 230 °C. The flow rate of helium through the column was 4 mL/min and the injector port and detector were held at 130 and 300 °C, respectively. The products formed from some of the arenes were identified by GC, GC/MS, and ^1H NMR spectroscopy, the last on a Varian 360 instrument. The experimental technique of laser flash photolysis (LFP) in photochlorination studies has been adequately described in earlier publications from this laboratory.[9,17]

Results

S^{m}_{std} for the Photochlorination of DMB. The major results of the present work are summarized in Table I. These include (i) S^{m}_{std} values for more than 20 arenes together with S^{m} values previously determined[16b] in neat liquid DMB and for DMB in the gas phase, (ii) the percentage yields of DMB mono- and dichlorides, and (iii) the percentage yields of chlorinated arene products. The arene chloride yields have been divided into those products which arise from the radical-chain chlorination of the aromatic side chain and those which arise from electrophilic chlorination of the aromatic ring. Table I also includes the arenes' vertical ionization potentials, I_D, and their relative π-basicities as measured by Brown and Brady.[20] The numbering of the first 18 arenes listed in Table I corresponds to that used in our earlier paper on the spectroscopy of $Cl^•$/arene molecular complexes.[17]

Alkane photochlorinations in CCl_4 are known to occur with a fairly high degree of polychlorination even at low conversions because of a solvent "cage" effect.[8,9,14] Since a significant fraction of each of the DMB monochlorides can be converted "in cage"[14] to polychlorides, the measured ratio, [2-ClDMB]/[1-ClDMB], does not necessarily reflect the relative rates of abstraction of the tertiary and primary hydrogen atoms of DMB.[14] Fortunately, with 2.0 M arene the "cage walls" are sufficiently reactive (maximum DMB polychlorination = 13%; see Table I) that we can safely assume that the S^{m}_{std} values listed in Table I are a reliable measure of the relative rates of tertiary to primary hydrogen abstraction from DMB.

As we have noted previously,[9] chlorobenzene is not formed in detectable amounts ($\leq 10^{-3}$ M) during the photochlorination of DMB in benzene under our conditions. Similarly, chlorobenzene could not be detected among the products formed during the photochlorination of DMB in toluene, *tert*-butylbenzene, anisole, or nitrobenzene. Ipso free radical aromatic substitution[22] of $Cl^•$ for $CH_3^•$, $(CH_3)_3C^•$, $CH_3O^•$, and $NO_2^•$ therefore does not occur to any significant extent with these particular arenes.

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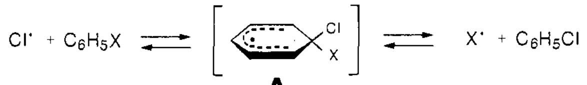
(21) We draw the reader's attention to footnote 55 in ref 9.

(22) Traynham, J. G. *Chem. Rev.* **1979**, *79*, 323–330 and references cited.

The proces of ipso substitution by Cl$^\bullet$ atoms is commonly *assumed* to proceed via an intermediate chlorocyclohexadienyl radical, A, but the species having this more-or-less symmetric structure may, of course, simply correspond to the transition state for loss of X$^\bullet$ or Cl$^\bullet$,[47] i.e.



A

For X = NO_2, ipso substitution by Cl$^\bullet$ is a known, but very slow, reaction.[22] Bond strength arguments would suggest that for X = CH_3, $(CH_3)_3C$, and CH_3O ipso substitution by Cl$^\bullet$ would be endothermic and, hence, would also be very slow. By way of contrast, chlorobenzene was produced with bromobenzene and iodobenzene. For X = Br and I, ipso substitution by Cl$^\bullet$ is well-known[22] and is, of course, thermodynamically favored. An interesting consequence of the ipso-substitution process with these two arenes is that it leads to the formation of H atom abstracting species which are very much more selective than the chlorine atom (vide infra). Bromobenzene and iodobenzene therefore gave "unexpectedly" high $S^{\rm m}_{\rm std}$ values. The results obtained with these two arenes are described below.

Bromobenzene (2.0 M) and DMB (0.15 M) in CCl_4 under our standard chlorination conditions yielded 2-ClDMB and 1-ClDMB in a ratio of 5.3. An $S^{\rm m}_{\rm std}$ value of this magnitude is at least twice as great as would be predicted from bromobenzene's ionization potential of 9.05 eV or its relative π-basicity of 0.38[20] (vide infra). The following halogenated organic products were formed in the yields indicated: 2-ClDMB, 25%; 1-ClDMB, 4.7%; 2-BrDMB, 2%; PhCl, 63%; 1,4-$Cl_2C_6H_4$, 5%.[23] The ipso substitution of bromobenzene by Cl$^\bullet$ atoms is clearly of major importance in this system. The Br$^\bullet$ atom formed in this process will not only react with molecular Cl_2 to form BrCl[24] and a Cl$^\bullet$ atom but will also abstract hydrogen from DMB with an extremely high ($\sim 10^4$–10^5) preference for a tertiary hydrogen atom. It is therefore easy to account for the elevated $S^{\rm m}_{\rm std}$ value found in bromobenzene.[25]

In order to investigate this ipso substitution process in more detail, we carried out 308-nm laser flash photolysis (LFP) experiments on Cl_2 in bromobenzene *and* on Br_2 in chlorobenzene as described previously.[17] *Both* systems yielded "instantaneously" (≤ 10 ns) a transient absorption identical in terms of $\lambda_{\rm max}$ = 539–541 nm, lifetime,[26] and the absence of a measurable reaction with molecular oxygen. Comparison can be made with the $\lambda_{\rm max}$ values for the following halogen atom/arene π-molecular complexes: Br$^\bullet$/PhF, $\lambda_{\rm max}$ = 529 nm; Br$^\bullet$/PhBr, $\lambda_{\rm max}$ = 543 nm; Cl$^\bullet$/PhF, $\lambda_{\rm max}$ = 494 nm; and Cl$^\bullet$/PhCl, $\lambda_{\rm max}$ = 498 nm. It is self-evident that the complex formed by LFP of the Cl_2/PhBr and Br_2/PhCl systems should be represented as the bromine atom/arene π-molecular complexes, Br$^\bullet$/PhBr and Br$^\bullet$/PhCl. Furthermore, the ipso substitution reaction of Cl$^\bullet$ with PhBr to form the Br$^\bullet$/PhCl complex must have a rate constant $\geq 10^8$ M^{-1} s^{-1}. The rapidity of this ipso substitution implies that there can be no hydrogen abstraction from DMB by a Cl$^\bullet$/PhBr complex. That is, the enhanced $S^{\rm m}_{\rm std}$ value found in bromobenzene cannot be attributed to an arene complexed chlorine atom but must be attributed instead to hydrogen abstraction by the liberated Br$^\bullet$ atom. It will require LFP studies on the picosecond time scale to determine whether a Cl$^\bullet$/PhBr complex is actually formed initially.

Iodobenzene (2.0 M) and DMB (0.15 M) in CCl_4 under our standard conditions yielded 2-ClDMB and 1-ClDMB in a ratio of 23:1 (= $S^{\rm m}_{\rm std}$·1) and in yields of 45% and 2%, respectively. Chlorobenzene was formed in 17% yield and there was a 36% yield of various unidentified, high-boiling materials, which may have included $PhICl_2$.[22] Since benzene might have been formed but have remained undetected because its GC retention time was virtually the same as that of CCl_4, we also used $CFCl_2CF_2Cl$ as a solvent in place of the CCl_4. Under otherwise standard conditions we obtained essentially the same [2-ClDMB]/[1-ClDMB] ratio and yields of DMB chlorides as in CCl_4, however, no benzene was detected.

Table II. Effect of 6.25 × 10^{-3} M O_2 on the Lifetimes, τ, of Cl$^\bullet$/Arene Complexes Formed from 5.9 × 10^{-2} M Cl_2 in CCl_4 at Room Temperature

no.[a]	arene	[arene], M	$\tau(N_2)$,[b] μs	$\tau(O_2)$,[c] μs	$10^{-7}k^{O_2}$-(apparent),[d] M^{-1} s^{-1}
1	PhCl	0.5	4.8	4.9	NR[e]
2	PhH	0.5	2.4	2.4	NR[e]
3	PhMe	0.5	3.6	2.4	1.7 ± 0.5
4	PhBu^t	0.5	2.9	1.3	6.8 ± 0.5
5	1,2-$Me_2C_6H_4$	0.5	4.0	1.3	6.1 ± 0.7
6	1,3-$Me_2C_6H_4$	0.5	9.4	8.4	0.2 ± 0.4
7	1,4-$Me_2C_6H_4$	0.5	5.6	2.4	3.5 ± 0.5
8	1,4-$Bu^t_2C_6H_4$	0.1	4.0	2.2	3.8 ± 0.6
9	1,2,3-$Me_3C_6H_3$	0.25	5.1	2.8	2.8 ± 0.5
10	1,2,4-$Me_3C_6H_3$	0.25	3.4	2.3	2.0 ± 0.2
11	1,3,5-$Me_3C_6H_3$	0.25	10.9	9.8	0.15 ± 0.3
12	1,3,5-$Bu^t_3C_6H_3$	0.01	12.0	5.7	1.6 ± 0.2
13	1,2,3,4-$Me_4C_6H_2$	0.25	2.0	1.4	2.7 ± 0.4
14	1,2,3,5-$Me_4C_6H_2$	0.25	4.3	3.9	0.4 ± 0.6
15	1,2,4,5-$Me_4C_6H_2$	0.25	4.3	3.3	1.8 ± 0.1
16	Me_5C_6H	0.05	3.7	2.8	1.4 ± 0.2
17	Me_6C_6	0.05	2.7	2.1	1.3 ± 0.4
18	PhOMe	0.05	3.8	2.3	3.3 ± 0.1
19	$PhCF_3$[f]	0.5	1.6	1.6	NR[e]
20	PhF[g]	0.5	2.2	2.2	NR[e]
22	PhBr[h]	0.5	1.3	1.3	NR[e]

[a] See footnote *a*, Table I. [b] Solution saturated with 760 Torr of N_2. [c] Solution saturated with 380 Torr of N_2 + 380 Torr of O_2. [d] Calculated apparent rate constant for reaction of Cl$^\bullet$/arene complex with O_2 ($\pm 2\sigma$), k^{O_2}(apparent) = $\{1/\tau(O_2) - 1/\tau(N_2)\}/[O_2]$. [e] No reaction, k^{O_2}(apparent) $\leq 1 \times 10^6$ M^{-1} s^{-1}. [f] Cl$^\bullet$/$PhCF_3$ has $\lambda_{\rm max}$ = 495 nm, $h\nu_{\rm CT}$ = 2.50 eV (cf. ref 17). [g] Cl$^\bullet$/PhF has $\lambda_{\rm max}$ = 494 nm, $h\nu_{\rm CT}$ = 2.51 eV (cf. ref 17). [h] The results with Cl_2 and PhBr were essentially identical with those obtained with Br_2 and PhCl (see text and Table IV).

No attempt was made to carry out LFP experiments on the Cl_2/PhI system because of the strong absorption by iodobenzene at 308 nm. We did not explore the iodobenzene system further but note that I$^\bullet$ does not abstract from DMB under our conditions.[27] The iodine atom cannot therefore be responsible for the high selectivities found in the presence of this arene. We tentatively attribute these high selectivities to hydrogen abstraction by the Ph$\dot{\rm I}$Cl radical formed in the reaction

$$\mathrm{Cl}^\bullet + \mathrm{PhI} \rightarrow \mathrm{Ph\dot{I}Cl}$$

Effect of Oxygen on the Lifetimes[26] of Cl$^\bullet$ Atom/Arene Complexes. The cyclohexadienyl radical, $C_6H_7^\bullet$, reacts very rapidly with molecular oxygen (k^{O_2} = 1.6 × 10^9 M^{-1} s^{-1} in benzene at room temperature).[28] This suggested to us during our original LFP studies of these systems[9] that O_2 might serve as a useful kinetic "probe" of the structure of the Cl$^\bullet$/C_6H_6 system. That is, we expected that the chlorocyclohexadienyl radical, σ (see the introduction), would react rapidly with O_2, whereas a Cl$^\bullet$/C_6H_6 π-molecular complex would react slowly. In the event,[9] the lifetime,[26] τ, of the Cl$^\bullet$/C_6H_6 complex generated by LFP of Cl_2 in 0.5 M C_6H_6 in CCl_4 was the same in the absence of O_2 as when the solution was saturated with 380 Torr of O_2 (= 6.25 × 10^{-3} M). It was therefore with some surprise that we discovered that the lifetimes of the complexes formed between Cl$^\bullet$ atoms and all

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(23) The formation of 1,4-$Cl_2C_6H_4$ during the ipso substitution of C_6H_5Br by Cl$^\bullet$ has been previously reported.[22]

(24) Skell, P. S.; Baxter, H. N., III; Tanko, J. M. *Tetrahedron Lett.* **1986**, *27*, 5181–5184.

(25) The photohalogenation of DMB with an equimolar mixture of Br_2 and Cl_2 (≡ BrCl) yields $S^{\rm m}$ values of 2.5–4.2 and 1.7–2.5 for chlorides and bromides, respectively, in $CFCl_3$ and 15 and 8.3–10 for chlorides and bromides, respectively, in 4 M benzene/$CFCl_3$.[24]

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

(27) Photolysis of DMB/I_2/Cl_2 in CCl_4 gave a ratio of [2-ClDMB]/[1-ClDMB] = 0.62, which is the selectivity found for the free chlorine atom.

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

Table III. Effect of DMB Concentration on the Room Temperature Lifetimes, τ, of the $Cl^\bullet/C_6H_6$ Complex Formed from 5.9×10^{-2} M Cl_2 and 0.5 M C_6H_6 in CCl_4 in the Absence of O_2 and in the Presence of 6.25×10^{-3} M O_2

[DMB], M	$\tau(N_2)$,[a] μs	$\tau(O_2)$,[b] μs	$10^{-9}k^{O_2}$- (apparent),[c] M^{-1} s^{-1}
0	2.4	2.4	
0.05	2.2	0.28	0.50 ± 0.05
0.13	1.8	0.13	1.1 ± 0.1
0.25	1.5	0.075	2.0 ± 0.2
0.5	1.1	0.052	2.9 ± 0.3
1.0	0.74	0.031	4.9 ± 0.5

[a] Solution saturated with 760 Torr of N_2. [b] Solution saturated with 380 Torr of N_2 + 380 Torr of O_2. [c] See footnote *d*, Table II.

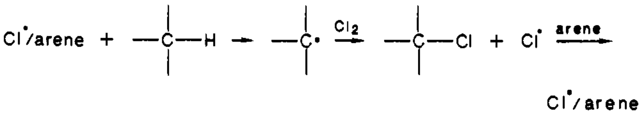
Table IV. Effect of 6.25×10^{-3} M O_2 on the Lifetimes, τ, of $Br^\bullet$/Arene Complexes Formed from 6.0×10^{-4} M Br_2 in CCl_4 at Room Temperature

no.[a]	arene	[arene], M	$\tau(N_2)$,[b] μs	$\tau(O_2)$,[c] μs	$10^{-7}k^{O_2}$- (apparent),[d] M^{-1} s^{-1}
1	PhCl	0.5	1.3	1.3	NR[e]
2	PhH	0.5	1.8	1.8	NR[e]
3	PhMe	0.5	0.38	0.25	18 ± 2
4	$PhBu^t$	0.5	5.1	4.8	0.2 ± 0.07[f]
5	$1,2\text{-}Me_2C_6H_4$	0.5	0.60	0.15	90 ± 17
6	$1,3\text{-}Me_2C_6H_4$	0.5	0.93	0.40	23 ± 4
7	$1,4\text{-}Me_2C_6H_4$	0.5	0.33	0.11	96 ± 16
8	$1,4\text{-}Bu^t{}_2C_6H_4$	0.1	9.5	9.3	*f*
9	$1,2,3\text{-}Me_3C_6H_3$	0.25	1.1	0.35	31 ± 8
10	$1,2,4\text{-}Me_3C_6H_3$	0.25	0.43	0.16	54 ± 3
11	$1,3,5\text{-}Me_3C_6H_3$	0.25	1.1	0.66	12 ± 1
12	$1,3,5\text{-}Bu^t{}_3C_6H_3$	0.05	6.1	6.0	*f*
18	PhOMe	0.1	1.7	0.57	19 ± 4
19	$PhCF_3$[g]	0.5	0.15	0.15	NR[e]
20	PhF[h]	0.5	1.9	1.9	NR[e]
22	PhBr[i]	0.5	1.0	1.0	NR[e]

[a] See footnote *a*, Table I. [b] Solution saturated with 760 Torr of N_2. [c] Solution saturated with 380 Torr of N_2 + 380 Torr of O_2. [d] Calculated apparent rate constant for reaction of $Br^\bullet$/arene complex with O_2 ($\pm 2\sigma$). [e] No reaction, $k^{O_2} \leq 1 \times 10^6$ M^{-1} s^{-1}. [f] No significant reaction; i.e., the small reduction in lifetime in the presence of O_2 is within our probable experimental error. [g] $Br^\bullet/PhCF_3$ has λ_{max} = 510 nm, $h\nu_{CT}$ = 2.43 eV (cf. ref 17). [h] $Br^\bullet$/PhF has λ_{max} = 529 nm, $h\nu_{CT}$ = 2.34 eV (cf. ref 17). [i] $Br^\bullet$/PhBr has λ_{max} = 543 nm, $h\nu_{CT}$ = 2.28 eV (cf. ref 17).

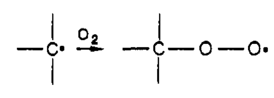
12 methyl-substituted benzenes, all three *tert*-butyl-substituted benzenes, and anisole were reduced significantly by the same concentration of oxygen (see Table II). The apparent rate constants for reaction of these 16 $Cl^\bullet$/arene complexes with O_2, k^{O_2}, lie in the range 10^6–7×10^7 M^{-1} s^{-1} (see Table II). However, there was no measurable reaction between O_2 and the $Cl^\bullet$ atom complexes formed with chlorobenzene, trifluoromethylbenzene, fluorobenzene, and of course, benzene (see Table II). We presume that there would be no measurable reaction between O_2 and the $Cl^\bullet$/nitrobenzene complex, but unfortunately, LFP experiments were not possible in the presence of this arene because it absorbs too strongly in the visible region.

Spectroscopic evidence[17] makes it highly unlikely that the structures of those $Cl^\bullet$/arene complexes that had shortened lifetimes in the presence of O_2 could be grossly different from the structures of those complexes for which the lifetimes were unchanged by O_2. This suggested that the reduction in lifetime in the presence of O_2 was *not* due to a reaction of the $Cl^\bullet$/arene complex with O_2. The arenes that form $Cl^\bullet$ atom complexes that appear to be reactive toward O_2 all have alkyl or alkoxyl substituents, while those that show no reactivity toward O_2 do not contain substituents having C–H bonds. For the former group of arenes any inter- or intramolecular abstraction of hydrogen from the side chain by the $Cl^\bullet$/arene complex does not significantly reduce the *observed* lifetime of the complex in the absence of oxygen because the complex is efficiently "regenerated"[9] by the reaction sequence



$$Cl^\bullet/\text{arene} + -\overset{|}{\underset{|}{C}}-H \longrightarrow -\overset{|}{\underset{|}{C}}{}^\bullet \xrightarrow{Cl_2} -\overset{|}{\underset{|}{C}}-Cl + Cl^\bullet \xrightarrow{\text{arene}} Cl^\bullet/\text{arene}$$

However, in the presence of oxygen the carbon-centered radical will be scavenged:



$$-\overset{|}{\underset{|}{C}}{}^\bullet \xrightarrow{O_2} -\overset{|}{\underset{|}{C}}-O-O^\bullet$$

This will interfere with the regeneration process and, in consequence, the observed lifetime of the complex will decrease.

If the foregoing explanation of the "oxygen effect" is correct, it implies that the effect of O_2 on lifetimes should not require that the alkyl or alkoxyl group be bonded to the arene. With this in mind, we measured the lifetimes of the $Cl^\bullet/C_6H_6$ complex formed by LFP of 0.059 M Cl_2 in the presence of 0.5 M C_6H_6 in CCl_4 containing various concentrations of DMB in the absence of O_2 and in the presence of 6.25×10^{-3} M O_2. In contrast to our earlier report,[9,29] we find that, in the absence of O_2, the DMB does reduce the lifetime of the $Cl^\bullet/C_6H_6$ complex (see Table III), the apparent rate constant for reaction of the complex with DMB being 1×10^6 M^{-1} s^{-1}. In the presence of O_2 the reduction in lifetime is much greater than in the absence of O_2 and this difference increases as the concentration of DMB increases (see Table III). The measured lifetimes in the absence and in the presence of oxygen yield apparent rate constants for the reaction of $Cl^\bullet/C_6H_6$ with O_2, k^{O_2} (apparent), which range from ca. 0.5×10^9 to 5.0×10^9 M^{-1} s^{-1}, increasing as the DMB concentration increases (see Table III). In the presence of O_2 the measured lifetimes at the different DMB concentrations yield an apparent overall rate constant for reaction of both the free $Cl^\bullet$ atom and the $Cl^\bullet/C_6H_6$ complex with DMB of ca. 3×10^7 M^{-1} s^{-1}. This is 30 times larger than the value found in the absence of O_2 but is still only ca. 50% of the global rate constant measured in our earlier work[9] at the same benzene concentration but with a photochemical source of $Cl^\bullet$ atoms for which there was no regeneration of the complex.

We conclude that the apparent reactivity toward oxygen of the complexes formed between $Cl^\bullet$ atoms and the alkylated arenes (and anisole) is due to the ability of O_2 to intercept carbon-centered radicals and thereby interfere with the process by which the complex is regenerated.

Effect of Oxygen on the Lifetimes of $Br^\bullet$/Arene Complexes. If carbon-centered radicals were, in fact, involved in the O_2-induced reductions in the lifetimes of the $Cl^\bullet$ atom complexes with alkylated benzenes and anisole, we reasoned that a similar phenomenon should be observed for the $Br^\bullet$ atom complexes with certain, but not all, alkylated benzenes. That is, the benzylic C–H bonds in toluene are known to be fairly reactive toward $Br^\bullet$ atoms whereas primary aliphatic C–H bonds are very unreactive.[30] We therefore anticipated that the $Br^\bullet$ atom complexes with the methyl-substituted arenes would have lifetimes which would be noticeably reduced by O_2, whereas the *tert*-butyl-substituted benzenes would have lifetimes which would be almost unaffected by O_2. Appropriate LFP experiments showed that this was indeed the case (see Table IV). The lifetimes of the $Br^\bullet$ atom complexes with

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(29) We reported[9] that "DMB (0.03 M ≤ [DMB] ≤ 0.4 M), had little or no effect on the lifetime of the signal (obtained with $[Cl_2]$ = 0.062 M)." These experiments were carried out with 0.0664 M benzene (rather than 0.5 M benzene, see Table III). On reexamination of the original data we found that DMB had had a small effect on τ that we had overlooked. This old data yielded an apparent rate constant for reaction of the $Cl^\bullet/C_6H_6$ complex with DMB of 1×10^6 M^{-1} s^{-1}; i.e., a value equal to the value found in the present work. We apologize for our misleading statement.

(30) The relative rates of hydrogen atom abstraction by $Br^\bullet$ from toluene and *tert*-butylbenzene can be estimated to be about 1:3 × 10^{-3} at 40 °C from data given in ref 31.

(31) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2.

Table V. Effect of DMB Concentration on the Room Temperature Lifetimes, τ, of the $Br^{\bullet}/C_6H_6$ Complex Formed from 9×10^{-4} M Br_2 and 0.5 M C_6H_6 in CCl_4 in the Absence of O_2 and in the Presence of 6.25×10^{-3} M O_2

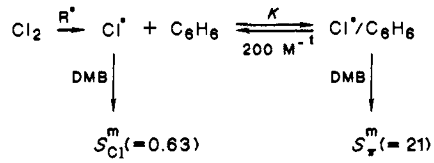
[DMB], M	$\tau(N_2)$,[a] μs	$\tau(O_2)$,[b] μs	$10^{-7}k^{O_2}$-(apparent),[c] $M^{-1}\ s^{-1}$
0	1.1	1.1	
0.05	1.0	0.89	2.0 ± 0.5
0.13	0.91	0.76	3.5 ± 0.7
0.25	0.86	0.70	4.3 ± 1.0
0.5	0.81	0.66	4.5 ± 1.0

[a] Solution saturated with 760 Torr of N_2. [b] Solution saturated with 380 Torr of N_2 + 380 Torr of O_2. [c] See footnote *d*, Table IV.

benzene, the halogenated benzenes, and (trifluoromethyl)benzene were also unchanged by oxygen (Table IV). DMB produced a relatively small reduction in the lifetime of the $Br^{\bullet}/C_6H_6$ complex, this effect being slightly larger in the presence of oxygen (see Table V).

Discussion

General. The selectivity for hydrogen atom abstraction from DMB by the free $Cl^{\bullet}$ atom, S^{m}_{Cl}, is ca. 0.63,[16b] while the selectivity for abstraction by the $Cl^{\bullet}/C_6H_6$ π-molecular complex, S^{m}_{π}, is ca. 21.[9] In the presence of benzene the measured selectivity, S^{m},



is not, however, determined by the *equilibrium* concentration and reactivities of the free $Cl^{\bullet}$ atom and the $Cl^{\bullet}/C_6H_6$ π-complex.[9] This is because the rates of reaction of the free $Cl^{\bullet}$ atom[32] and of the $Cl^{\bullet}/C_6H_6$ π-complex with DMB are appreciable, under normal experimental conditions, relative to the rates of the forward and reverse reaction of $Cl^{\bullet}$ with C_6H_6, reactions that would establish the equilibrium if given time to do so. That is, both sides of the $Cl^{\bullet}$ + C_6H_6 equilibrium are "bled-off" by reaction with DMB at rates comparable to those involved in the equilibrium.

It would seem reasonable to expect that arenes which form weaker π-complexes with $Cl^{\bullet}$ than benzene should have selectivities under our standard conditions that are lower than S^{m}_{std} for benzene. That is, for weaker complexes there will be a higher equilibrium concentration of free $Cl^{\bullet}$ atom and the complex itself will presumably be less selective than the $Cl^{\bullet}/C_6H_6$ complex; i.e., for a weaker complex than benzene, S^{m}_{π} would be expected to be less than the value of 21 found for benzene. In addition, the rate of complexation of $Cl^{\bullet}$ atoms by these arenes may be somewhat slower than that for complexation of $Cl^{\bullet}$ atoms by benzene,[33] in which case, the competition between the arene and DMB for free $Cl^{\bullet}$ atoms will become more favorable to DMB, with a consequent further decrease in S^{m}.

Similarly, for arenes that form stronger π-complexes with $Cl^{\bullet}$ atoms than benzene, it is reasonable to expect higher S^{m}_{std} values than for benzene because of a lower equilibrium concentration of free $Cl^{\bullet}$ atoms and a more selective complex than $Cl^{\bullet}/C_6H_6$. The percentage contribution of free $Cl^{\bullet}$ atoms to the measured selectivity would not be expected to become appreciably lower than for benzene because the rate constant for complex formation cannot, in principle, become much larger than the near diffusion limited value of 6.0×10^{9} $M^{-1}\ s^{-1}$ found for benzene.[9,34] Nevertheless, S^{m}_{std} values for arenes which form stronger complexes with $Cl^{\bullet}$ atoms than benzene can be *lower* than the S^{m}_{std} value for benzene for the two reasons pointed out by Russell.[4] First, "a complex might be so stable that the complexed chlorine atom would be unable to abstract a hydrogen atom from the hydrocarbon. In this case, only the chlorine atom in equilibrium with the complex[35] could attack the hydrocarbon and, although the rate of chlorination should be greatly depressed, the products of chlorination would not be affected".[4] Second, Russell pointed out that a rapid, *irreversible* decomposition of the π-complex involving $Cl^{\bullet}$ atom addition to or H atom abstraction from the organic moiety would mean that there would be "only a small amount of aliphatic substitution" and, since this would occur mainly via free $Cl^{\bullet}$ atoms, there should be "a very small solvent effect", i.e., a low S^{m}_{std} value.

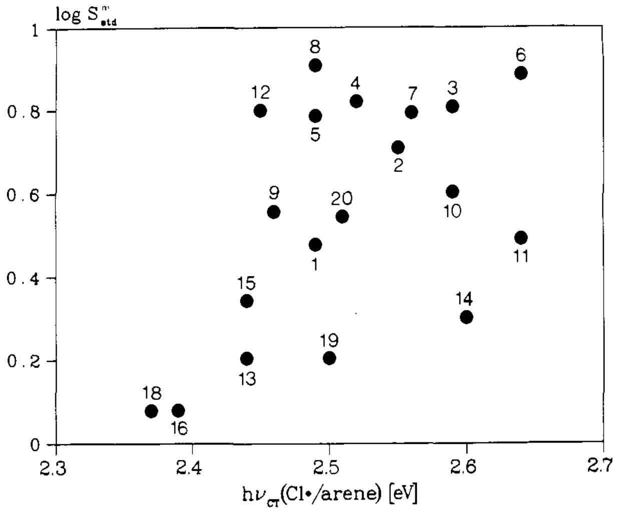
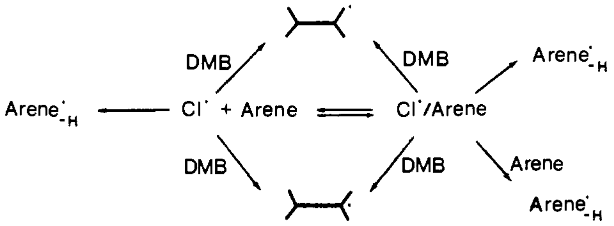


Figure 1. Plot of log S^{m}_{std} vs the energy of the charge transfer band, $h\nu_{CT}$, for $Cl^{\bullet}$/arene complexes.

Scheme I



The reactions which may be involved during the photochlorination of DMB in the presence of an arene containing alkyl or alkoxyl side chains and which are relevant to the measured magnitude of S^{m}_{std} are shown in Scheme I.

Standard Selectivities for the Photochlorination of DMB. The foregoing general discussion of the factors which can affect S^{m}_{std} values provides a suitable basis for interpreting the results summarized in Table I. A detailed analysis[36] would require, at a

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[32] These include (a) the de novo $Cl^{\bullet}$ atoms formed in the chain-propagating step $R^{\bullet} + Cl_2 \rightarrow RCl + Cl^{\bullet}$ and in the chain initiating step $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$ and (b) the $Cl^{\bullet}$ atoms formed by dissociation of the $Cl^{\bullet}/C_6H_6$ complex.

[33] Any such reduction in the rate of formation of $Cl^{\bullet}$/arene complexes is probably rather small (see ref 11 and 15).

[34] In practice, this is another matter. If we take[9] the overall rate constant for the reaction of $Cl^{\bullet}$ with DMB to be 3.3×10^{9} $M^{-1}\ s^{-1}$, our failure to detect DMB chlorides in the presence of hexamethylbenzene (yield ≤ 0.05%) translates into a rate constant for the reaction of $Cl^{\bullet}$ with Me_6C_6 that is $\geq 4.95 \times 10^{11}$ $M^{-1}\ s^{-1}$! While a rate constant of this magnitude might possibly be rationalized in terms of an initial electron transfer to form the $Cl^{-}/Me_6C_6^{\bullet+}$ ion pair, we are more attracted by a suggestion made by Skell et al.[10] which involves the direct formation during chain propagation of the $Cl^{\bullet}$/arene complex rather than the free $Cl^{\bullet}$ atom. That is, the Cl_2/Me_6C_6 complex may be sufficiently strong that there is little or no free Cl_2 and the attack of a carbon-centered radical on the Cl_2/Me_6C_6 complex might yield the $Cl^{\bullet}/Me_6C_6$ complex directly:

$$Me_5C_6CH_2^{\bullet} + Cl_2/Me_6C_6 \rightarrow Me_5C_6CH_2Cl + Cl^{\bullet}/Me_6C_6 \rightarrow HCl + Me_5C_6CH_2^{\bullet}$$

[35] The role played by de novo $Cl^{\bullet}$ atoms (see ref 32(a)) and by DMB in disrupting the equilibium was not recognized in this early work.

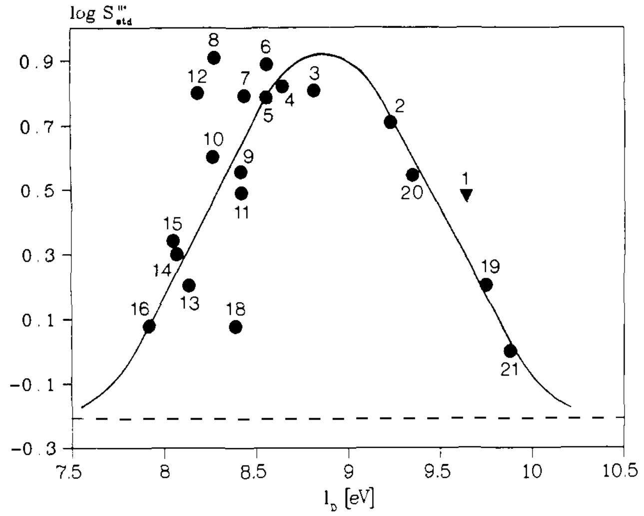

Figure 2. Plot of log S^{m}_{std} vs I_D of the arene. The limiting S^m value obtained with free Cl$^\bullet$ atoms in the gas phase (0.62) is indicated by the dotted line. The point for PhCl (**1**), ▼, has been plotted at the second ionization potential of this arene.[38a] The solid curve is only an "artist's impression".

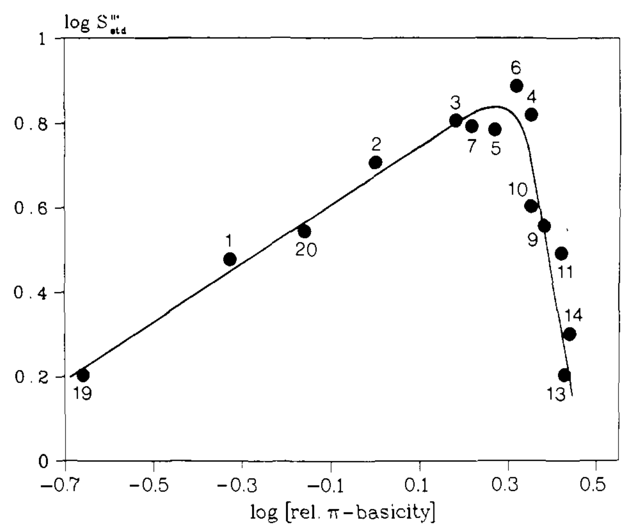

Figure 3. Plot of log S^{m}_{std} vs log [relative π-basicity] of the arene. The solid curve is only an "artist's impression".

minimum, knowledge of the equilibrium constants, K, for complex formation for each arene. Since this information is not available, we have to make use of other potential measures of the strengths of the Cl$^\bullet$/arene complexes.

These Cl$^\bullet$/arene complexes are π-molecular complexes in which there is an interaction between the acceptor (the electrophilic chlorine atom) and the donor (the π-electron system of the aromatic).[17] The strength of this acceptor–donor interaction should therefore increase as the π-electron density in the arene increases. These Cl$^\bullet$/arene complexes show charge-transfer (CT) bands in the visible spectrum but, as we have shown,[17] the energies of these CT bands, $h\nu_{CT}$, do not correlate with the I_D of the arene.[37] It is therefore not surprising that a plot of log S^{m}_{std} against $h\nu_{CT}$[19b] shows a "buckshot" pattern (see Figure 1).

By way of contrast, a plot of log S^{m}_{std} against I_D[19b] does show the general behavior expected, although it also shows quite a bit of "scatter", particularly for arenes having a relatively low I_D (see Figure 2). That is, this plot[38] shows that S^{m}_{std} values increase as the I_Ds of the arenes decrease from 9.88 eV ($PhNO_2$, **21**); they reach a maximum at ca. 8.8 eV and then decrease as the arenes' I_Ds fall to 8.0 eV and lower. The decrease in the S^{m}_{std} values for arenes having high I_Ds is easy to understand (vide supra), while the decrease in S^{m}_{std} values for arenes having low I_Ds can be readily explained in terms of strong complex formation and, *particularly*, the low yields of DMB chlorides. These low yields (see Table I) indicate that most of the radical-chain chlorination involves hydrogen abstraction from the side chain of the arene[40] rather than from the DMB. For the polymethyl-substituted benzenes and anisole the reactivities of the Cl$^\bullet$/arene complexes toward DMB are likely to be appreciably lower than their reactivities toward a second arene molecule.[41] This means that much of the hydrogen abstraction from the DMB must be by the free Cl$^\bullet$ atom with its low selectivity. For this reason the polymethyl-substituted benzenes and anisole produce a substantial decrease in the yields of DMB chlorides and in the S^{m}_{std} values. The Cl$^\bullet$ atom complexes of the *tert*-butyl-substituted benzenes will presumably be less reactive toward a second arene molecule[42] and hence yields of DMB chlorides and S^{m}_{std} values are relatively high in the presence of these arenes. Indeed, the scatter in the S^{m}_{std} values at low I_Ds is clearly due largely, if not entirely, to changes in the relative amount of abstraction by free vs complexed chlorine atoms, as indicated by the percentage yields of DMB chlorides. Consider, for example, the four arenes having I_Ds in the range 8.39–8.44 eV, viz., 1,4-$Me_2C_6H_4$ (**7**), 1,2,3-$Me_3C_6H_3$ (**9**), 1,3,5-$Me_3C_6H_3$ (**11**), and PhOMe (**18**), which show a monotonic decrease in S^{m}_{std} values along the series, viz., 6.2, 3.6, 3.1, and 1.2, as the percentage yields of the DMB chlorides decrease, viz., 28%, 13%, 1.8%, and 0.16% (see Table I). Similarly, the "unexpectedly" high S^{m}_{std} values of 8.1 and 6.3 found for 1,4-di-*tert*-butylbenzene (**8**, I_D = 8.28 eV)[44] and 1,3,5-tri-*tert*-butylbenzene (**12**, I_D = 8.19 eV), respectively, can be compared to S^{m}_{std} values of 4.0 and 1.6 found for 1,2,4-$Me_3C_6H_3$ (**10**, I_D = 8.27 eV) and 1,2,3,4-$Me_4C_6H_2$ (**13**, I_D = 8.14 eV), respectively. This can be attributed to the low reactivities of the Cl$^\bullet$ atom complexes toward the *tert*-butyl-substituted benzenes (DMB chloride yields of 30% for **8** and 21% for **12**) relative to the methyl-substituted benzenes (DMB chloride yields of 5.0% for **10** and 2.1% for **13**).

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(36) A kinetic analysis which allows for hydrogen atom abstraction from the arene and does not assume that the Cl$^\bullet$ atom and Cl$^\bullet$/arene complex are present at their equilibrium concentrations yields a kinetic equation that is too complex to be useful.

(37) The reason(s) for this lack of correlation may be associated with variations in the equilibrium distance which separates the Cl$^\bullet$ atom and the arene in the complex.[17]

(38) (a) Note that the point for chlorobenzene has been plotted against the *second* vertical ionization potential of this arene (9.64 eV) rather than the first I_D (9.07 eV). The first I_D has been assigned to photoejection of an electron from a $4b_1$ MO which involves a 3p lone pair on chlorine in an orbital which is perpendicular to the plane of the aromatic ring and the second I_D to a $1a_2$ MO that has a node at the chlorine atom.[39] Since the LUMO of Cl$^\bullet$ is a p orbital, symmetry considerations suggest that in the Cl$^\bullet$/C_6H_5Cl complex the Cl$^\bullet$ atom will interact with the $1a_2$ MO. (b) Bromobenzene has been excluded from this plot because the halogen atom/arene complex is Br$^\bullet$/C_6H_5Cl rather than Cl$^\bullet$/C_6H_5Br, vide supra.

(39) Klasinc, L.; Kovac, B.; Güsten, H. *Pure Appl. Chem.* **1983**, *55*, 289–298.

(40) Electrophilic chlorination of the arene serves only to deplete the supply of molecular chlorine.

(41) Or the same arene since an intramolecular hydrogen abstraction is also a distinct possibility.

(42) The much higher concentration of the arene permits even the *tert*-butylbenzenes to compete with DMB to some degree for the Cl$^\bullet$ atom complex. This competition will produce a small decrease in the yields of DMB chlorides and will also reduce the S^{m}_{std} values.[43] This provides, at least in part, an explanation for the fact that S^{m}_{std} is smaller for 1,3,5-tri-*tert*-butylbenzene, **12**, than for 1,4-di-*tert*-butylbenzene, **8**. Of course, the lower S^{m}_{std} value for **12** may also be due in part to steric factors since this arene may form a complex with Cl$^\bullet$ relatively slowly, and once formed, this complex may be less reactive toward hydrogen donors than would be expected from **12**'s I_D.

(43) Photochlorination of 0.15 M DMB, 0.50 M $(CH_3)_3CC(CH_3)_3$, and 2.0 M C_6H_6 in CCl_4 gave a DMB selectivity essentially equal to the S^{m}_{std} value for benzene, viz. 5.1. However, an increase in the tetramethylbutane concentration to 2.0 M reduced the selectivity to 3.4.

(44) Of the aromatic compounds we have examined, only pyridine yielded a higher S^{m}_{std} value than 1,4-di-*tert*-butylbenzene, viz. 8.5 vs. 8.1. However, pyridine (I_D = 9.88 eV) does not fit into the pattern shown in Figure 2, presumably because, in the Cl$^\bullet$/C_5H_5N complex, the chlorine is known to be complexed to the nitrogen atom and to lie in the plane of the ring.[45] The structure of the Cl$^\bullet$/C_5H_5N complex is therefore quite different from that of the Cl$^\bullet$/arene complexes considered in the present work and the effect of pyridine on the photochlorination of DMB was not examined further.

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

Russell[4] obtained a reasonably good though limited correlation between the logarithm of his arene selectivities and the logarithm of the relative π-basicity of the arene.[20] Our own log $S_{\mathrm{std}}^{\mathrm{m}}$ values also show an excellent correlation with log [relative π-basicity] for arenes that are less reactive than benzene[38b] (see Figure 3). However, at relative π-basicities $\gtrsim$2.0 the $S_{\mathrm{std}}^{\mathrm{m}}$ values fall abruptly for the two reasons outlined above. Although the points in Figure 3 show less scatter than those in Figure 2, this is probably due to there being somewhat fewer relative π-basicities available than I_{D}s.

Effect of Oxygen on the Lifetimes of Halogen Atom/Arene Complexes. Oxygen reduces the lifetimes of $\mathrm{Cl^{\bullet}}$/arene and $\mathrm{Br^{\bullet}}$/arene complexes whenever there are abstractable hydrogen atoms available either on the arene itself (see Tables II and IV) or because an alkane is present (see Tables III and V). We attribute this oxygen effect to a simple competition between the molecular halogen and the molecular oxygen for carbon-centered radicals.[46]

When carbon-centered radicals are trapped by the molecular halogen, a halogen atom is produced and, since this will react extremely rapidly with the arene, the halogen atom/arene complex is regenerated. In the absence of oxygen this regeneration is remarkably efficient. Of course, our results show that regeneration is not 100% efficient, but this is quite likely to be due to the presence of residual traces of oxygen. Moreover, if the O_2 were to be entirely eliminated, the complex would still decay even if the efficiency of regeneration were 100% because of radical-(atom)/radical(atom) chain-terminating events and because the molecular Cl_2 would itself be seriously depleted in the chain reaction initiated by the laser pulse.

When a carbon-centered radical is trapped by oxygen there will be no regeneration of the complex by that carbon-centered radical. The lifetime of the complex is therefore reduced by oxygen but regeneration will not be completely inhibited except at high $[O_2]/[Cl_2]$ ratios. It should even be possible to employ LFP and measure rate constants for reactions of $\mathrm{Cl^{\bullet}}$/arene complexes with alkanes and alkylarenes by employing molecular chlorine as the $\mathrm{Cl^{\bullet}}$ atom source and working at high $[O_2]/[Cl_2]$ ratios. Indeed this has been done in one instance.[45]

It is important to note that the rate constants calculated for the *apparent* reactions of the $\mathrm{Cl^{\bullet}}$/arene (Table II) and $\mathrm{Br^{\bullet}}$/arene (Table IV) complexes with O_2, k^{O_2}(apparent), have no intrinsic meaning since the species which actually reacts with the oxygen is an alkyl radical.[46] Nevertheless, the absence of any significant reaction between oxygen and the complexes formed by $\mathrm{Br^{\bullet}}$ atoms and the *tert*-butylbenzenes when compared with the large magnitudes of the k^{O_2}(apparent) values for the $\mathrm{Br^{\bullet}}$ atom complexes with the methyl benzenes certainly reflects the fact that there is relatively little hydrogen abstraction from the *tert*-butyl groups. That is, the regeneration of $\mathrm{Br^{\bullet}}$/arene complexes via reactions of carbon-centered radicals with Br_2 is very much more important for the methyl benzenes than for the *tert*-butyl benzenes,[30] and hence the oxygen-effect on lifetimes is greater for the former than for the latter. For the $\mathrm{Br^{\bullet}}/C_6H_6$/DMB system we presume that regeneration of the complex and the interruption of this process by oxygen involves abstraction of a tertiary hydrogen atom from DMB.

Summary

The selectivity, $S_{\mathrm{std}}^{\mathrm{m}}$, for the arene-modulated photochlorination of 2,3-dimethylbutane, DMB, has been measured under standard conditions (room temperature, [arene] = 2.0 M, [DMB] = 0.15 M in CCl_4) for a wide variety of arenes. Our principal findings are as follows.

(1) Electron-poor arenes that have higher ionization potentials, I_{D}, and lower π-basicities than benzene and that would therefore be expected to form weaker $\mathrm{Cl^{\bullet}}$/arene π-complexes than the $\mathrm{Cl^{\bullet}}/C_6H_6$ π-complex yield $S_{\mathrm{std}}^{\mathrm{m}}$ values lower than the $S_{\mathrm{std}}^{\mathrm{m}}$ value for benzene. Furthermore, for these arenes there is a monotonic correlation between log $S_{\mathrm{std}}^{\mathrm{m}}$ values and both the I_{D} and the logarithm of the relative π-basicity of the arene.

(2) Electron-rich arenes that have lower I_{D}s and higher π-basicites than benzene and that would therefore be expected to form stronger $\mathrm{Cl^{\bullet}}$/arene π-complexes than the $\mathrm{Cl^{\bullet}}/C_6H_6$ π-complex mostly yield $S_{\mathrm{std}}^{\mathrm{m}}$ values that are lower than the $S_{\mathrm{std}}^{\mathrm{m}}$ value for benzene. Following Russell,[4,21] we attribute the low $S_{\mathrm{std}}^{\mathrm{m}}$ values found for the majority of the electron-rich arenes to two factors: (i) the low reactivity of strong $\mathrm{Cl^{\bullet}}$/arene π-complexes and (ii) the low yields of DMB chlorides, a significant fraction of which are produced by free $\mathrm{Cl^{\bullet}}$ atoms. For the polymethylated benzenes and anisole the low yields of DMB chlorides can probably be largely attributed to the preference of the $\mathrm{Cl^{\bullet}}$/arene complex to react with arene rather than with DMB.

(3) Oxygen does not react with $\mathrm{Cl^{\bullet}}$/arene complexes at a measurable rate ($k^{O_2} < 10^6$ M^{-1} s^{-1}) though it may appear to do so if the arene contains a substituent bearing an abstractable hydrogen atom, viz., CH_3, $C(CH_3)_3$, and OCH_3. Oxygen does not react with $\mathrm{Br^{\bullet}}$/arene complexes though it may appear to do so if the arene contains CH_3 or OCH_3 substituents, but not if the arene contains $C(CH_3)_3$ substituents. The apparent reactivity of these halogen atom/arene complexes toward oxygen is an artifact which we attribute to the formation of carbon-centered radicals formed by hydrogen abstraction from the side chain of the arene. If such a carbon-centered radical reacts with the molecular halogen, it will form halide and a halogen atom; the latter will regenerate the complex. Oxygen interferes with this process by trapping the carbon-centered radical.

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Registry No. 1, 108-90-7; **2**, 71-43-2; **3**, 108-88-3; **4**, 98-06-6; **5**, 95-47-6; **6**, 108-38-3; **7**, 106-42-3; **8**, 1012-72-2; **9**, 526-73-8; **10**, 95-63-6; **11**, 108-67-8; **12**, 1460-02-2; **13**, 488-23-3; **14**, 527-53-7; **15**, 95-93-2; **16**, 700-12-9; **17**, 87-85-4; **18**, 100-66-3; **19**, 98-08-8; **20**, 462-06-6; **21**, 98-95-3; **22**, 108-86-1; **23**, 591-50-4; DMB, 79-29-8; 2-ClDMB, 594-57-0; 1-ClDMB, 600-06-6; 1,4-$Cl_2C_6H_4$, 106-46-7; $\mathrm{Br^{\bullet}}$, 10097-32-2; $\mathrm{Cl^{\bullet}}$, 22537-15-1; O_2, 7782-44-7.

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[46] As a referee pointed out, our k^{O_2}(apparent) values reflect in some way the relative rates of reaction of the carbon-centered radicals with Cl_2 and O_2. Unfortunately, the complexity of the kinetic situation defied out attempts to extract relative rate constants for these two reactions from our data. Absolute rate constants for both reactions are, of course, known.[9,16b,28]

[47] Crossed-beam scattering studies indicate that complexes analogous to A have extremely short lifetimes in the gas phase; see: Robinson, G. N.; Continetti, R. E.; Lee, Y. T. *J. Chem. Phys.* **1988**, *89*, 6226–6237.