Competitive Cage Kinetics. Relative Rates of Complexation of Chlorine Atom by Various Arenes

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Abstract: When the free-radical chlorination of an alkane (RH_2) is conducted in an inert solvent at low [RH_2], in addition to the expected monochloride (RHCl), unexpectedly high yields of dichlorides (RCl_2) are produced. This polychlorination phenomenon arises because the chain-propagating step, $RH^\bullet + Cl_2 \rightarrow$, generates the geminate ($RHCl/Cl^\bullet$) pair, and H abstraction from RHCl is competitive with diffusion out of the cage. At high [RH_2], polychloride formation is unimportant. Under these latter conditions, RH_2 constitutes a major component of the cage walls, which effectively trap $Cl^\bullet$ before its reaction with RHCl. If photochlorination is carried out in the presence of a high concentration of a *third* reagent (S) that is extremely reactive toward $Cl^\bullet$, the ratio of mono- to polychlorides (M/P) is perturbed toward *higher* values. (S, being an important constituent of the cage walls, is able to scavenge $Cl^\bullet$ before its reaction with RHCl.) We have performed a detailed kinetic analysis of these competing processes and describe a novel approach (competitive cage kinetics) based on the discussion above, which allows relative reaction rates of $Cl^\bullet$ with a variety of substrates (S) to be determined. Furthermore, neither direct observation nor quantitation of the $Cl^\bullet$/S reaction product(s) is required. In this manner, the intrinsic rate of complexation of chlorine atom with various arenes was measured. From our results, the following reactivity order is derived: $C_6H_5C_6H_5$ (21) > $C_6H_5(C{=}O)C_6H_5$ (2.8) > $C_6H_5OC_6H_5$ (2.7) > C_6H_5F (2.2) > C_6H_6 [1.00] > C_6H_5CN (0.88) > $C_6H_5CF_3$ (0.79) > C_6F_6 (0.27).

The free-radical chlorination of alkanes (Scheme I) is a topic of renewed interest in the recent literature.[1-6] When carried out in the usual manner (i.e., neat, such that the alkane is both the solvent and substrate), quantitative yields of the corresponding monochloride are obtained.

Scheme I

$$Cl_2 \rightarrow 2Cl^\bullet \quad \textit{initiation}$$

$$Cl^\bullet + RH \rightarrow R^\bullet + HCl \quad \textit{propagation}$$

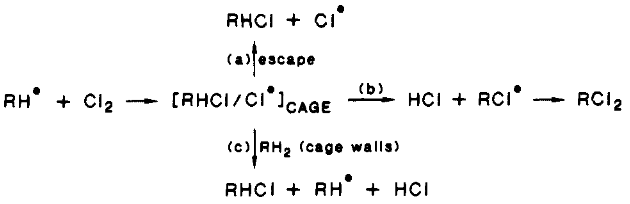
$$R^\bullet + Cl_2 \rightarrow RCl + Cl^\bullet$$

$$RH + Cl_2 \rightarrow RCl + HCl \quad \textit{overall}$$

Since $Cl^\bullet$ is an extremely reactive species, showing little selectivity toward primary, secondary, or tertiary hydrogens, regioselectivity is poor.[7] Absolute rate constants for hydrogen abstraction by $Cl^\bullet$, measured by laser flash photolysis (LFP), are at or near the diffusion-controlled limit.[3]

An intriguing consequence of the high reactivity of $Cl^\bullet$ has recently been discovered by Skell and Baxter.[2] When photochlorination was conducted in an inert solvent[8] at low alkane concentrations, in addition to the expected monochloride, an unexpectedly large amount of di- and trichlorides was produced. Since the reactions were run to low percent alkane conversion ($\leq$10%) and substitution of H by Cl tends to *decrease* the reactivity of an alkane toward $Cl^\bullet$, formation of polychlorides by further chlorination of the monochloride product in the usual sense (i.e., by diffusive encounter of $Cl^\bullet$ and monochloride) could be excluded.[2]

Scheme II



An alternate pathway to account for polychloride formation was proposed (Scheme II).[2] Reaction of an alkyl radical ($RH^\bullet$) with Cl_2 produces the $RHCl/Cl^\bullet$ geminate ("caged") pair.[9] Due to the exceptionally high reactivity of $Cl^\bullet$ and the "inertness" of the cage walls, abstraction of a second hydrogen from RHCl (path b) is competitive with cage escape (path a). At high RH_2 concentration, the cage walls are no longer inert, but comprised of RH_2 molecules, which effectively compete with RHCl for $Cl^\bullet$ (path c).[10] The relative rates of these competing reactions depend on the relative amounts of RHCl and RH_2 in the immediate proximity of $Cl^\bullet$ at the instant of its formation and the relative reactivity of RHCl and RH_2 toward chlorine atom.

Competitive Cage Kinetics

A. Effect of a *Third* Species (S) on the Mono-to Polychloride Ratio. In solution, a bimolecular reaction between a reactive intermediate (I) and substrate (S_i) irreversibly forming product P can be represented in two steps: diffusion of I and S_i together (k_{DIFF}), followed by reaction within the solvent cage with intrinsic rate constant $k_{o,i}$ (Scheme III).[11]

Scheme III

$$I + S_i \underset{k_{-d}}{\overset{k_{DIFF}}{\rightleftharpoons}} [I/S_i]_{CAGE} \xrightarrow{k_{o,i}} P$$

If $k_{o,i} \gg k_{-d}$, the observed rate constant for the reaction is equal to k_{DIFF} (i.e., diffusion is rate-limiting). For a series of high-reactivity substrates ($S_1, S_2, \ldots S_n$), it is possible that although their *intrinsic* rate constants ($k_{o,i}$) might vary, their *observed* rate

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

(2) Skell, P. S.; Baxter, H. N., III *J. Am. Chem. Soc.* **1985**, *107*, 2823.

(3) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

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

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

(6) Breslow, R.; Brandl, M.; Hunger, J.; Turro, N.; Cassidy, K.; Krogh-Jespersen, K.; Westbrook, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 7204. Breslow, R.; Brandl, M.; Hunger, J.; Adams, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 3799 and references therein.

(7) For a review of earlier work, see: Poutsma, M. L. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. 1, pp 79-193.

(8) A solvent with which $Cl^\bullet$ has no significant reactivity (e.g., CCl_4, CCl_2FCClF_2, etc.).

(9) A note on terminology: The diffusive $RHCl/Cl^\bullet$ pair arises from the reaction $RHCl + Cl^\bullet \rightarrow$, while the geminate pair arises from $RH^\bullet + Cl_2 \rightarrow$.

(10) Since the starting alkane possesses several abstractable hydrogens, analogous pathways would be written for the formation of trichlorides and higher order chlorides.

(11) Eigen, M. *Angew Chem., Int. Ed. Engl.* **1964**, *3*, 1.

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constants would be nearly identical, at the diffusion-controlled limit (ca. 10^9–10^{10} M^{-1} s^{-1}).[12]

The novelty of the "cage effect" in photochlorinations is that a highly reactive species ($Cl^•$) and substrate (RHCl) are formed directly as a caged pair. Our interest in this system centers on the potential application of the cage effect as a *kinetic* tool for studying the reaction of $Cl^•$ with various added substrates (S). For illustration, suppose the alkane photochlorination were carried out in the presence of a *third* species (S) that is not inert to $Cl^•$. As before, the reaction of $RH^•$ with Cl_2 produces the geminate $RHCl/Cl^•$ pair. However, if the bulk concentration of S were reasonably high, S would be an important component of the cage walls. If sufficiently reactive toward $Cl^•$,[13] reaction of S with $Cl^•$ would provide a *new* pathway for destruction of the geminate $RHCl/Cl^•$ pair and formation of monochloride. Furthermore, since S and $Cl^•$ are *already* in close promixity, their reaction should not be impeded by any diffusion-imposed barrier.[14] This hypothesis is illustrated in Scheme IV.

Scheme IV

$$(RHCl/Cl^•/RH_2/S)_{CAGE} \xrightarrow{k_{o,RHCl}} RCl^• + HCl + RH_2 + S$$

$$RCl^• + Cl_2 \rightarrow RCl_2 + \text{higher order chlorides}$$

$$(RHCl/Cl^•/RH_2/S)_{CAGE} \xrightarrow{k_{-d}} RHCl + Cl^• + RH_2 + S$$

$$(RHCl/Cl^•/RH_2/S)_{CAGE} \xrightarrow{k_{o,RH_2}} RHCl + HCl + RH^• + S$$

$$(RHCl/Cl^•/RH_2/S)_{CAGE} \xrightarrow{k_{o,s}} RHCl + Cl\text{–}S^• + RH_2$$

It is worth noting that *the time scale of the S/Cl• reaction must be on the same order of magnitude as the competing cage processes for perturbation of the M/P ratio to be detected.* Cast in a different light, in solution the reaction $Cl^• + S \rightarrow Cl\text{–}S^•$ must be diffusion-controlled. Therefore, perturbation of M/P at constant RH_2 provides a diagnostic tool for diffusion-controlled reactions.

The mono- to polychloride ratio (M/P = yield RHCl/yield RCl_2) is expressed by eq 1, where the $k_{o,X}[X]$ terms refer to rates of reactions within the cage and k_{-d} refers to the rate of cage escape. Assuming (a) that k_{-d} and $k_{o,RHCl}[RHCl]_{CAGE}$ ($=k_{o'}$)

$$\frac{M}{P} = \frac{k_{-d} + k_{o,RH_2}[RH_2]_{CAGE} + k_{o,S}[S]_{CAGE}}{k_{o,RHCl}[RHCl]_{CAGE}} \qquad (1)$$

are approximately constant for a given alkane/solvent combination and (b) that the concentrations of RH_2 and S comprising the cage walls are equal to their concentrations in bulk solution, eq 2 follows.

$$\frac{M}{P} = \frac{k_{-d} + k_{o,RH_2}[RH_2]_{BULK} + k_{o,S}[S]_{BULK}}{k_{o'}} \qquad (2)$$

Two important predictions arise: 1. In the absense of S, a plot of M/P vs $[RH_2]$ should yield a straight line whose slope is equal to $k_{o,RH_2}/k_{o'}$ and intercept to $k_{-d}/k_{o'}$. 2. At constant $[RH_2]$, a plot of M/P vs [S] should yield a straight line whose slope ($k_{o,S}/k_{o'}$) reflects the efficiency of S as a $Cl^•$ trap. If several substrates were studied, it would then be possible to assess their relative reactivities toward $Cl^•$.

B. Relative Rates of Chlorine Atom Complexation by Various Arenes. The kinetic treatment derived above suggests a powerful tool for ascertaining the relative reactivity of different substrates toward chlorine atom. Since the reactivity of $Cl^•$ toward S is gauged by the effect of [S] on the M/P ratio, unlike traditional techniques (e.g., direct competition kinetics), it is not necessary to isolate or quantitate the products of the S + $Cl^•$ reaction. As such, this procedure is attractive in cases where (a) the reaction $Cl^•$ S $\rightarrow$ Cl–$S^•$ is reversible or (b) the product is unstable and cannot be isolated. A series of substrates that possess these characteristics and, thus, appear particularly amenable to study by this approach are described below.

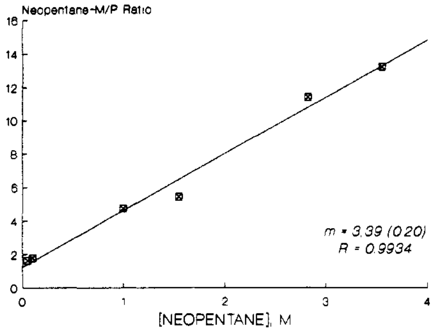

Figure 1. Effect of neopentane concentration on the neopentane M/P ratio.

As reported by Russell,[15] and shortly thereafter confirmed by Walling,[16] the high reactivity of $Cl^•$ in alkane chlorinations can be "moderated" by conducting the reaction in an aromatic solvent. Formation of an arene/$Cl^•$ complex (Scheme V) as the "high-selectivity" hydrogen abstractor is the universally accepted explanation for this phenomenon, although its precise identity (π complex[3,5,15,16] vs chlorocyclohexadienyl radical[1,4]) is uncertain.

Scheme V

$$Cl^• + RH \rightarrow R^• + HCl$$

$$Cl^• + PhH \rightleftarrows (Cl/PhH)^•$$

$$(Cl/PhH)^• + RH \rightarrow HCl + PhH + R^•$$

Products arising from reaction of $Cl^•$ with benzene (e.g., chlorobenzene, hexachlorocyclohexane) are generally not observed in alkane photochlorinations.[15,17] Yet, the existence of an arene/$Cl^•$ complex is clearly indicated by the altered selectivity.

Assuming that the arene/$Cl^•$ complex has a sufficient lifetime so as to allow its escape from the cage (>ca. 100 ps),[14] our procedure will provide a sensitive probe of the relative rate of $Cl^•$ complexation to various arenes. Since LFP experiments have demonstrated that the $Cl^•$/PhH complex has a lifetime on the order 2–7 μs,[3] our assumption appears reasonable.

Results

A. Neopentane Probe. 1. Effect of Neopentane Concentration on M/P. The first step in these studies was to examine the effect of $[RH_2]$ on M/P and, thus, the applicability of eq 2. Neopentane was the first alkane (RH_2) examined. The effect of neopentane concentration on M/P is depicted in Figure 1. These experiments were performed with 1,1,2-trichlorotrifluoroethane as the inert diluent, maintaining a $\gg$10:1 ratio of neopentane/Cl_2. M/P was measured by capillary GLC analysis.

Over the range of neopentane concentrations studied (0.05–3.6 M), the plot of M/P vs $[Me_4C]$ (Figure 1) was linear. A least-squares analysis yielded intercept = 1.2 (±0.6) and slope 3.39 (±0.20) M^{-1}, corresponding, in accordance with eq 2, to $k_{-d}/k_{o'}$ and $k_{o,RH_2}/k_{o'}$, respectively (R = 0.9934).

2. Relative Reactivity of Various Arenes toward Chlorine Atom: Neopentane Probe. By use of eq 2 and with the neopentane M/P

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[12] Bunnett has used an analogous argument as a diagnostic criterion for diffusion-controlled reactions; see: Gali, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140.

[13] "Sufficiently reactive" means that the bimolecular reaction between $Cl^•$ and S is at or near the diffusion-controlled limit. Otherwise, S will be "inert" toward $Cl^•$ within the time frame provided by the cage effect.

[14] In a discussion of geminate and diffusive encounters of A and B, Eisenthal has pointed out "... the diffusion coefficient in the usual description is assumed to be independant of the separation of A and B, which may be inappropriate for the processes considered here, since A and B are no more than a few molecular diameters apart...". See: Eisenthal, K. B. *Acc. Chem. Res.* **1975**, *8*, 118.

[15] Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987.

[16] Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485.

[17] Since our approach requires accurate measurement of the M/P ratio, this fact works to our advantage since the absolute yield of M and P is always high (virtually quantitative).

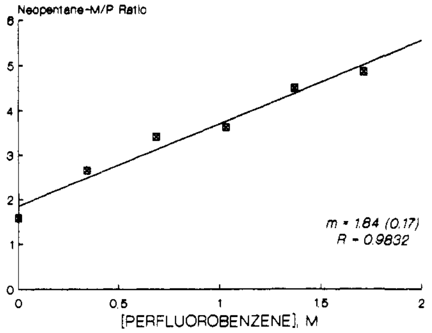


Figure 2. Effect of perfluorobenzene on the neopentane (0.10 M) M/P ratio.

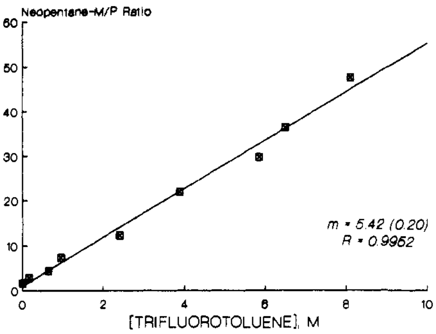


Figure 3. Effect of α,α,α-trifluorotoluene on the neopentane (0.10 M) M/P ratio.

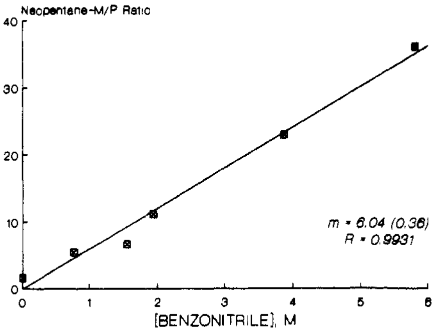


Figure 4. Effect of benzonitrile on the neopentane (0.10 M) M/P ratio.

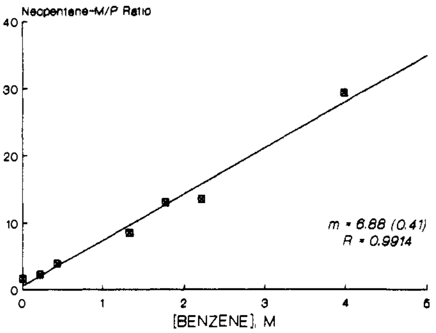


Figure 5. Effect of benzene on the neopentane (0.10 M) M/P ratio.

ratio as a probe, the relative reactivities of various arenes toward Cl• were assessed. Again, 1,1,2-trichlorotrifluoroethane was the diluent, *the neopentane concentration was maintained at a constant value of 0.10 M*, and a ratio of $[\mathrm{Me_4C}]:[\mathrm{Cl_2}] \gg 10:1$ was employed. For all arenes studied, the plots of M/P vs [arene] were linear. The data obtained from these experiments are presented in Figures 2–9. (Note: The slope m, the standard error in the slope Δm, and the correlation coefficient R are provided in the figures.) Reactivities for the various substrates studied, calculated relative to benzene, are compiled in Table I.

B. 2,3-Dimethylbutane (DMB) System. 1. Effect of [DMB] on M/P. In an effort to confirm the arene reactivity order reported

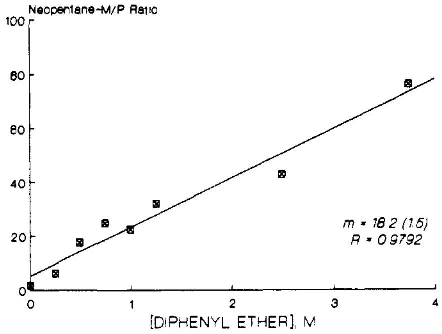


Figure 6. Effect of diphenyl ether on the neopentane (0.10 M) M/P ratio.

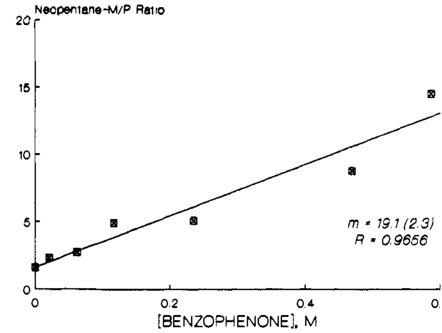


Figure 7. Effect of benzophenone on the neopentane (0.10 M) M/P ratio.

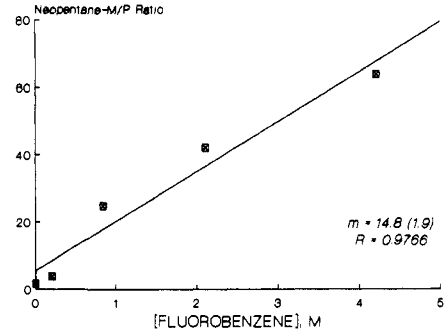


Figure 8. Effect of fluorobenzene on the neopentane (0.10 M) M/P ratio.

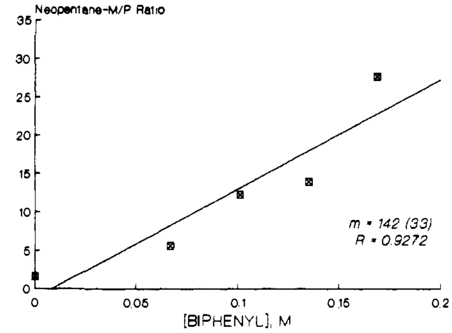


Figure 9. Effect of biphenyl on the neopentane (0.10 M) M/P ratio.

Table I. Relative Reactivities of Various Molecules toward Cl•

compound	relative reactivity	
	neopentane probe	DMB probe
C_6F_6	0.27 (±0.04)	0.22 (±0.06)
$(CH_3)_4C$	0.49 (±0.06)	
$C_6H_5CF_3$	0.79 (±0.08)	0.79 (±0.11)
DMB		0.79 (±0.11)
C_6H_5CN	0.88 (±0.10)	
C_6H_6	1.00	1.00
$(C_6H_5)_2O$	2.7 (±0.4)	2.3 (±1.5)
$(C_6H_5)_2C{=}O$	2.8 (±0.5)	
C_6H_5F	2.2 (±0.5)	1.2 (±0.3)
$C_6H_5C_6H_5$	21 (±6)	

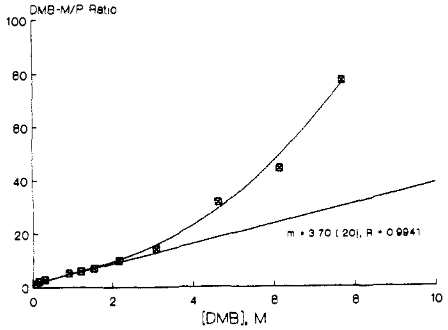


Figure 10. Effect of 2,3-dimethylbutane (DMB) concentration on the DMB M/P ratio.

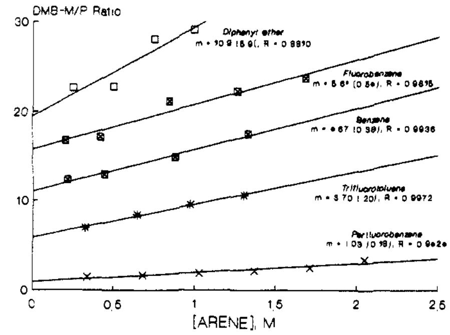


Figure 11. Effect of various arenes on the DMB (0.10 M) M/P ratio.

in the previous section with another alkane probe, the 2,3-dimethylbutane system was briefly examined. Upward curvature was exhibited by the plot of M/P vs [DMB] (Figure 10). Similar curvature in the M/P plots for DMB and cyclohexane has also been observed by Raner, Lusztyk, and Ingold in a related study of the cage effect.[18] The etiology of this phenomenon will be examined in the Dicussion.

2. Relative Reactivity of Various Arenes toward Chlorine Atom: DMB Probe. As mentioned above, strict adherence to eq 2 was not observed in the DMB system, thereby complicating the quantitative treatment of the data. By inspection of Figure 10, variation of M/P with increasing concentration appears roughly linear at low M/P (≤ 9). With the assumption that eq 2 is obeyed when the observed M/P ratio falls below this limit, the effect of various arenes on the DMB M/P ratio was examined (0.10 M DMB, 1,1,2-trichlorotrifluoroethane as diluent, and [DMB]:[Cl_2] $\gg$ 10:1).

The data are presented in Figure 11. The reactivity order obtained from the least-squares analysis of the data in accordance with eq 2 is summarized in Table I, alongside the results from the neopentane system. Despite the problems associated with curvature when the DMB is used, the two data sets are in reasonable agreement.

Discussion

A. Linearity vs Curvature in M/P Plots. In the neopentane system, all plots of M/P vs [RH_2] or [arene] were linear. In contrast, for DMB an upward curvature was noted. Analogous observations have been made by Raner, Lusztyk, and Ingold, who observed curvature in M/P plots for DMB and cyclohexane.[18] Their interpretation is that for the geminate RHCl/Cl$^\bullet$ pair, *abstraction of hydrogen from RHCl occurs on a time scale comparable to molecular rotation.* Put another way, for the geminate pair (RHCl/Cl$^\bullet$), RHCl must rotate in order to provide a hydrogen to Cl$^\bullet$ for abstraction. At very high [RH_2] or [PhH], the cage walls are highly reactive and consume Cl$^\bullet$ before rotation can occur, thereby yielding a higher M/P ratio than predicted from eq 2.[18] In a sense, the rate-limiting step for RCl$^\bullet$ formation changes from H abstraction (at low cage wall reactivity) to RHCl rotation (at high cage wall reactivity).

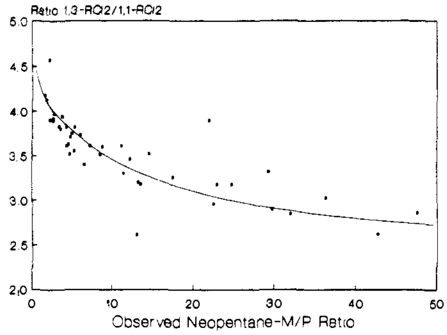
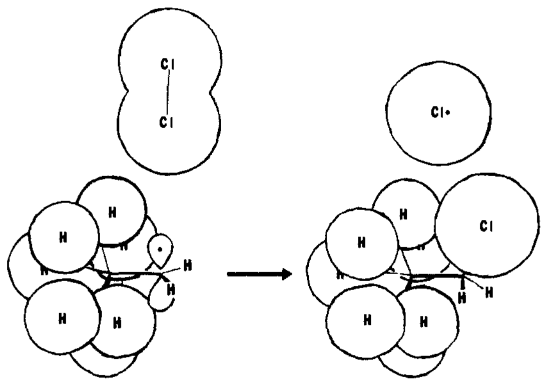


Figure 12. Effect of cage wall reactivity on the 1,3-RCl_2/1,1-RCl_2 ratio (neopentane system).

Scheme VI



If this hypothesis is correct, why was similar curvature not noted in the neopentane system? We suggest that for the geminate neopentylchloride/chlorine atom pair, very little rotation is required for hydrogen abstraction to occur. Assuming a linear transition state for abstraction of chlorine from Cl_2 by the neopentyl radical, the methyl hydrogens of the newly formed neopentyl chloride are *already* in close proximity to Cl$^\bullet$ (Scheme VI).

Evidence in support of this supposition can be derived by considering the ratio of the two dichlorides, 1,3-dichloro-2,2-dimethylpropane (1,3-RCl_2) and 1,1-dichloro-2,2-dimethylpropane (1,1-RCl_2), formed by diffusive and geminate encounter of neopentyl chloride and chlorine atom. Photochlorination of neopentyl chloride (neat) yields 1,3-RCl_2 and 1,1-RCl_2 in a ratio of 2.22 ($\pm$0.04):1. In Figure 12, utilizing the data from *all* our experiments with the neopentane probe, the ratio 1,3-RCl_2/1,1-RCl_2 is plotted as a function of the observed M/P ratio. Irrespective of the actual composition of the cage walls, the M/P ratio provides a good measure of cage wall reactivity under any given conditions. When M/P is low (i.e., the cage walls are inert, and consequently, the cage effect is most predominant) the 1,3-RCl_2/1,1-RCl_2 ratio is high (>4.5). As the M/P ratio increases (i.e., with increasing cage wall reactivity), the 1,3/1,1 ratio decreases and appears to approach a value of 2.2 (the experimentally observed value for the diffusive RHCl/Cl$^\bullet$ pair).

We suspect that under these latter conditions, the *diffusive* RHCl/Cl$^\bullet$ pair becomes a more important contributor to polychloride formation (i.e., the curvature suggests the onset of a different mechanism for polychloride formation). The fact that the 1,3/1,1 ratio appears to asymptotically approach the value observed for the diffusive pair would appear to support this hypothesis.

B. Reliability of the Kinetic Technique. This study has yielded data regarding Cl$^\bullet$ reactivity toward various substrates, which by other methods are either impractical or impossible to obtain. Consequently, there is not a plethora of existing data with which to compare our results. However, where data are available, our results compare favorably.

For instance, absolute rate constants (measured by LFP) have been reported for reactions of free chlorine atoms in CCl_4. For benzene and DMB, the rate constants are 6.0×10^9 and 3.3×10^9 M^{-1} s^{-1}, respectively[3] (i.e., PhH is 1.8 × more reactive). Using

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[18] Raner, K. D.; Lusztyk, J.; Ingold, K. U., preceding paper in this issue.

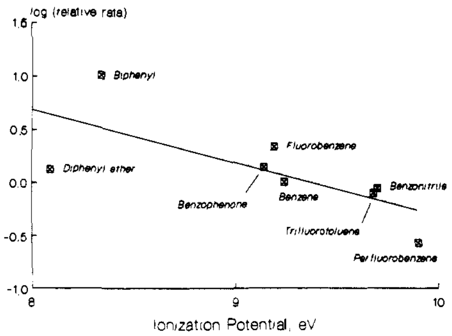
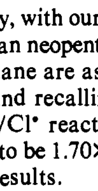


Figure 13. Relative rates of complexation of various arenes with chlorine atom as a function of their ionization potentials.[23]

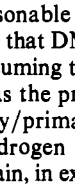
the data obtained with the DMB probe (Table I), we calculate PhH to be 1.3× more reactive, in reasonable agreement.

Similarly, with our procedure, we find that DMB is 1.61× more reactive than neopentane (Table I). Assuming that the hydrogens of neopentane are as equally reactive as the primary hydrogens of DMB and recalling that the tertiary/primary selectivity for the DMB/Cl• reaction is 4.2 (per hydrogen basis),[15] DMB is calculated to be 1.70× more reactive, again, in excellent agreement with our results.

C. Structure and Reactivity of the Arene/Cl• Complex. Regarding the precise structure of the PhH/Cl• complex, two formulations have been considered: a centrosymmetric π complex[3,5,15,16] and the 6-chlorocyclohexadienyl radical (or σ complex).[1,4]



π complex



6-chlorocyclohexadienyl radical (σ complex)

To what extent does our data shed light on this issue? Figure 13 is a plot of log (k_{rel}) for the various arenes studied vs their respective ionization potentials.[19] Generally, the more easily oxidized the arene, the faster the Cl• complexation. Such a trend would be expected for formation of a donor–acceptor type π complex.

However, consider hydroxyl radical (HO•), a species often compared with Cl•. The same general trend is observed,[20] and HO• is generally recognized to form a hydroxycyclohexadienyl radical in its reaction with benzene.[21] Consequently, we do not believe it possible to infer the structure of the complex from our reactivity data.

However, the data do provide some new information regarding its *reactivity*. We propose that the widely varying selectivity for alkane photochlorination conducted in different aromatic solvents[5,15] does not arise from vastly differing rates of complex formation. These rates are all on the same order of magnitude (vide supra). Instead, the variable selectivity must arise from differing *reactivities* of the complexes, once formed.

For example, consider the photochlorination of DMB in benzene and perfluorobenzene. In the absense of aromatic solvents, the perhydrogen selectivity (tertiary/primary) is 4.2.[15] In neat benzene (0.1 M DMB), the selectivity arises to ≃84![3,4] However, the observed selectivity in perfluorobenzene is virtually the same as the free (uncomplexed) chlorine atom.[5]

Our results indicate that the rate of Cl• complexation by C_6F_6 is only 3.7× smaller than C_6H_6! Thus, failure of C_6F_6 to alter Cl• properties cannot be attributed to a low rate of complexation. Clearly, either the C_6F_6/Cl• complex is short-lived, decomposing (C_6F_6/Cl• → C_6F_6 + Cl•) faster than it can abstract hydrogen from DMB, or the complex exhibits nearly the same selectivity as free chlorine atom. The former possibility seems more reasonable.

Summary

1. The approach described in this paper (competitive cage kinetics) provides a diagnostic tool for compounds whose bimolecular rate constants for reaction with Cl• are at or near the diffusion-controlled limit.

2. Application of eq 2 permits measurement of the relative reaction rates of various substrates with Cl•, without complications introduced by rate-limiting diffusion. Additionally, direct observation or detection of the reaction products is not required. Where comparison with existing literature data is possible, excellent agreement is found.

3. The following order for relative rates of complexation with Cl• was ascertained: $C_6H_5C_6H_5$ (21) > $C_6H_5(C{=}O)C_6H_5$ (2.8) > $C_6H_5OC_6H_5$ (2.7) > C_6H_5F (2.2) > C_6H_6 [1.00] > C_6H_5CN (0.88) > $C_6H_5CF_3$ (0.79) > C_6F_6 (0.27).

4. As hypothesized by Raner, Lusztyk, and Ingold,[18] abstraction of H by Cl• in the geminate RHCl/Cl• caged pair occurs within a time frame competitive with molecular rotation.

5. The reactivity data provide little evidence regarding the *structure* of arene/Cl• complexes. However, the data do support the notion that the previously observed variation of alkane photochlorination selectivity with the nature (identity) of the arene solvent[5,15] arises from differences in *reactivity* of the Cl•/arene complexes and not from differences in their rates of formation.

Experimental Section

A. General Methods. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5890A instrument equipped with a HP 3393A reporting integrator. Most analyses were accomplished with a Alltech RSL-200 (nonpolar) capillary column (30 × 0.25 mm). For reactions with neopentane in the presence of benzene, since neopentylchloride and benzene were coincident on the nonpolar column, a polar column (Alltech 30 × 0.25 mm Superox) was utilized.

For experiments with neopentane, products were identified by comparison of the retention times with that of authentic samples and quantitated vs a measured quantity of an appropriate internal standard. For the DMB system, authentic samples of the primary and tertiary RCl's were available for comparison. Di- and trichlorides were identified by GC–MS analysis.

B. Materials. The following materials were obtained from Aldrich Chemical Co. and used without purification: benzene (99.9%, HPLC grade); biphenyl (99%); 2,3-dimethylbutane (97%); diphenyl ether (gold label, 99+%); fluorobenzene (99%); hexafluorobenzene (99%); neopentylchloride (99%); 1,1,2-trichlorotrifluoroethane (HPLC grade, 99.9%); α,α,α-trifluorotoluene (99+%).

Benzonitrile (Aldrich gold label, 99+%) was stirred overnight over CaH_2 under N_2 and vacuum distilled prior to use. Chlorine (Matheson, UHP) was transferred to a glass pressure tube, degassed, and stored at 0 °C. Neopentane (Wiley Organics) contained a substantial quantity of olefinic impurities and was purified by treatment with Br_2, followed by distillation.[22]

C. General Procedure. The desired quantities of liquid or solid reagents were combined, and the resulting solution (5–10 mL) was transferred to a Pyrex pressure tube (equipped with a Teflon-coated magnetic stir bar and a Teflon needle valve). Gaseous reagents were measured manometrically and condensed into the pressure tube with a vacuum line. Reaction mixtures were degassed 3–4× by the freeze–pump–thaw method (freezing to −196 °C and thawing at room temperature). Cl_2 was measured with a calibrated gas pipet and purified immediately before use by condensation from a trap at −78 °C directly into the degassed reaction mixture. The pressure tube was sealed, placed in a thermostatically maintained water bath, and irradiated with a 150-W

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[19] Ionization potentials were obtained from: Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements, 1971–1981*; National Bureau of Standards Report No. NSRDS–NBS 71; U.S. Government Printing Office: Washington, D.C., 1982.

[20] Relative rates of reaction of HO• with substituted benzenes have been correlated by the Hammett equation, with $\rho = -0.41$. See: Anbar, M.; Meyerstein, D.; Neta, P. *J. Phys. Chem.* **1966**, *70*, 2660.

[21] For an excellent review, see: Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

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[23] For molecules with more than one aryl moeity, a statistical correction was applied (e.g., the "corrected" reactivity of biphenyl is $^1/_2$ times its observed reactivity, etc.).

tungsten lamp for 10–30 min. Afterward, a measured amount of an appropriate internal standard was added, and the reaction mixtures were analyzed directly by GLC (triplicate determinations). Tables containing the experimental data used to construct the figures are available as supplementary material.

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Registry No. DMB, 79-29-8; C_6F_6, 392-56-3; $C_6H_5CF_3$, 98-08-8; C_6H_5CN, 100-47-0; $(C_6H_5)_2O$, 101-84-8; $(C_6H_5)_2CO$, 119-61-9; C_6H_5-C_6H_5, 92-52-4; $(CH_3)_4C$, 463-82-1.

Supplementary Material Available: Tables on the effect of neopentane and various arenes on the neopentane M/P ratios (6 pages). Ordering information is given on any current masthead page.

Reactions of Alkylmercurials with Heteroatom-Centered Acceptor Radicals[1]

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Abstract: The relative reactivities of alkylmercury halides toward $PhS^\bullet$, $PhSe^\bullet$, or $I^\bullet$ decrease drastically from R = *tert*-butyl to R = *sec*-alkyl to R = *n*-butyl, indicative that $R^\bullet$ is formed in the rate-determining step in the attack of these radicals upon RHgCl. The alkyl radicals thus formed will enter into chain reactions in which a heteroatom-centered radical ($A^\bullet$) is regenerated from substrates such as RS–SR, ArSe–SeAr, ArTe–TeAr, PhSe–SO_2Ar, Cl–SO_2Ph; ZCH═CHA (A = Cl, I, SPh, SO_2Ph); or PhC≡CHA (A = I, SPh, SO_2Ph). *β*-Styrenyl (PhCH═CHA, Ph_2C═CHA) and *β*-phenethynyl (PhC≡CA) systems with A = I, Br, SO_2Ph also enter into chain reactions with mercury(II) salts with the ligands PhS, PhSe, $PhSO_2$, or $(EtO)_2PO$. The relative reactivities of a series of reagents toward *t*-$Bu^\bullet$ and of PhCH═CHA, Ph_2C═CHA, and PhC≡CA toward *c*-$C_6H_{11}^\bullet$ are reported as well as the regioselectivity of *t*-$Bu^\bullet$ attack observed for 1,2-disubstituted ethylenes (ZCH═CHA) with Z and A from the group Ph, Cl, Br, I, SO_2Ph, SPh, Bu_3Sn. Reactions of (*E*)- and (*Z*)-PhCH═CHI or MeO_2CCH═CHI with *t*-$Bu^\bullet$ or *c*-$C_6H_{11}^\bullet$ occurred in a regioselective and stereospecific (retention) manner. Reactions of (*E*)- and (*Z*)-ClCH═CHCl occurred in a nonstereospecific manner in which the *E*/*Z* product ratio increased with the bulk of the attacking radical. A similar effect on the *E*/*Z* product ratios was observed for (*Z*)-MeO_2CCH═CHCl.

Alkylmercurials (RHgX, R_2Hg) are recognized to undergo attack at mercury by halogen atoms to form alkyl radicals.[3–5] Reactions of alkylmercurials with halogen molecules yield the alkyl halides by both homolytic attack at mercury and electrophilic attack at carbon although in many cases it is possible to select conditions which will favor either the ionic or homolytic process.[3] The reactions between alkylmercurials and vicinal dihalides (e.g., C_2Cl_6) leads to dehalogenation by a free-radical chain process involving halogen atom abstraction by $R^\bullet$ followed by a *β*-elimination of a halogen atom which regenerates $R^\bullet$ by attack upon the mercurial.[6,7]

The reactions of alkylmercurials with disubstituted dichalcogenides (RSSR, ArSSAr, ArSeSeAr, ArTeTeAr) have been known for some time as thermal processes,[8] but only recently has it been recognized that these substitutions occur by a radical chain mechanism in which the chalcogenide-centered radical attacks RHgCl to form a primary, secondary, or tertiary alkyl radical.[9] The free-radical chain reactions of halogens or dichalcogenides with alkylmercurials involve the attack of an electron-accepting radical ($A^\bullet$ = $I^\bullet$, $Cl^\bullet$, $RS^\bullet$, etc.) at the mercury atom (reaction 1). The chain reaction propagates by reaction of the alkyl radical

$$A^\bullet + RHgX(R_2Hg) \rightarrow AHgX(RHgA) + R^\bullet \qquad (1)$$

$$R^\bullet + Y\text{–}A \rightarrow RY + A^\bullet \qquad (2)$$

thus formed with the substrate Y–A (e.g., I–I, RS–SR). Other reagents which will react with alkyl radicals to furnish a heteroatom-centered acceptor radical which will participate in reaction 1 are benzenethiol and the arylsulfonyl halides, sulfides, and selenides. With the sulfonyl derivatives, Reaction 2 yields the arylsulfonyl radical ($ArSO_2^\bullet$) which serves as $A^\bullet$ in reaction 1. *N*-Bromosuccinimide and arylsulfenyl halides might be expected to react with RHgCl by a radical chain reaction. However, electrophilic substitution processes occur so readily for these materials that no evidence for a free-radical process was observed at 30 °C in PhH or CH_2Cl_2 solution.

Another route to acceptor radicals involves the addition–elimination sequence of reactions 3 and 4[10] and the analogous processes

$$ZCH{=}CHA + R^\bullet \rightarrow Z\dot{C}H\text{-}C(H)(R)A \qquad (3)$$

$$Z\dot{C}H\text{-}C(H)(R)A \rightarrow ZCH{=}CHR + A^\bullet \qquad (4)$$

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