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Kinetic Analysis of Alkane Polychlorination with Molecular Chlorine. Chlorine Atom/Monochloride Geminate Pairs and the Effect of Reactive "Cage Walls" on the Competition between Monochloride Rotation and Chlorine Atom Escape[1]

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Abstract: The free-radical chlorination of alkanes produces polychlorides even at low conversions. These are formed by reaction of chlorine atom/monochloride (or dichloride) geminate pairs. This process has been studied in detail in various solvent systems, and a kinetic scheme has been proposed. Deviations from this scheme have been rationalized as being due to competition between monochloride rotation and reaction of the chlorine atom with reactive molecules in the "cage walls" surrounding the chlorine atom/chloride geminate pair. Analysis of the dichloride products supports the suggestion that monochloride rotation is not completely "free" within the lifetime of the geminate pair.

Frank and Rabinowitsch's's[3] concept of a "cage" effect on the combination of radical pairs in solution is well established, although "the precise definition of the dimensions or other characteristics of this solvent property remains a problem today".[4] A necessary requirement for the experimental observation of a cage effect is that the cage contains two nonconnected[5] entities that can react with one another on a time scale comparable to the diffusion of one entity out of the cage. In order to achieve the necessary high mutual reactivity virtually all previous work has been concerned with radical pairs.[6] In 1985 Skell and Baxter[7] reported an unusual and extremely interesting example of a non-radical-pair cage effect in the radical-chain chlorination of alkanes by molecular chlorine in inert perhalogenated solvents. At low alkane concentrations rather high yields of di- and trichlorides were produced even at very low conversions, a result that was rationalized[7] as a cage effect arising from the high reactivity of the free chlorine atom (see Scheme I). The high reactivity of $Cl^{\bullet}$ allows reaction with the "cage wall" to compete with diffusion. One component of this wall is the monochloride RCl formed in step (i). Reaction "in-cage" of the $Cl^{\bullet}/RCl$ "geminate pair" leads to the formation of dichloride $R_{-H}Cl_2$, while a second in-cage reaction of the $Cl^{\bullet}/R_{-H}Cl_2$ geminate pair can yield trichloride, $R_{-2H}Cl_3$. Dichlorides (and trichlorides) can therefore be formed under conditions where the overall consumption of RH is negligible. That is, dichlorides (and trichlorides) can be produced by routes other than a diffusive encounter of a "free" chlorine atom with a molecule of monochloride (or dichloride), i.e., by routes that do not involve a $Cl^{\bullet}/RCl$ (or $Cl^{\bullet}/R_{-H}Cl_2$) "diffusive pair".

It is obvious that the monochloride/polychloride (=M/P) ratio [where P = dichloride (D) + trichloride (T)] must depend on the nature of the cage wall, since this will affect the "escape"[1b] of the $Cl^{\bullet}$ atom from in-cage RCl. That is, the precise nature of the medium in which RH is being chlorinated must influence the extent to which the $Cl^{\bullet}/RCl$ geminate pairs formed in step (i) react with one another. Thus, at low RH concentrations in perhalogenated solvents the only reactive wall component will be the geminate RCl (or $R_{-H}Cl_2$). However, wall reactivity must increase as the concentration of RH increases. It will also increase in the presence of benzene[8,9] or a second H-atom donor, R'H. Under such conditions the M/P ratio will have a higher value than at low [RH] in an unreactive solvent. If we assume that the reactions shown in Scheme I are irreversible (on a cage time scale), a simple kinetic analysis[10] yields eq 1, where the bars above the reactants refer to cage wall concentrations, not to bulk concentrations.

$$\frac{[M]}{[D]+[T]} = \frac{[M]}{[P]} = \frac{k_d + k_a[\overline{RH}] + k_b[\overline{C_6H_6}] + k_c[\overline{R'H}]}{k_e[\overline{RCl}]} \tag{1}$$

Our interest[8] in these unusual cage reactions was further stimulated by a report[9] "that benzene precludes multiple chlorinations", there being "no detectable polychloride formation" upon photochlorination of 0.1 M 2,3-dimethylbutane (DMB) in "benzene (2.5–11 M) as solvent".[11] This result is inconsistent with Scheme I and eq 1, and we therefore decided to reinvestigate the effect of benzene on M/P ratios. As we report herein, we have discovered not only that polychlorides are indeed produced at $[C_6H_6] > 2.5$ M but also that a much more interesting phenomenon occurs. According to eq 1, in an inert diluent at a constant substrate concentration ($\equiv$[RH] = constant) and with no second H donor ([R'H] = 0), a plot of M/P vs the mole fraction of C_6H_6 ($\equiv[C_6H_6]$) should be linear. This was not the case. Less polychlorinated products were formed at high $[C_6H_6]$ than would have been predicted by extrapolation from low $[C_6H_6]$. The same phenomenon was observed if [RH] was increased in the absence of C_6H_6 and R'H; i.e., the M/P ratio increases more rapidly with an increase in [RH] than predicted by extrapolation from low [RH]. These unexpected results and our explanation of them are described below.

Experimental Section

General Procedures. Chlorine (7% in nitrogen) was bubbled through deoxygenated solutions of the alkane being investigated at room tem-

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[1] (a) NRCC No. 28740. (b) "Escape" is used to describe diffusion from the cage in which the $Cl^{\bullet}$ atom is formed and its reaction while still in this solvent cage with molecules other than the monochloride that form a part of the "cage wall".

[2] NRCC Research Associate 1986–1987.

[3] Franck, J.; Rabinowitsch, E. *Trans. Faraday Soc.* **1934**, *30*, 120–131.

[4] Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 4.

[5] I.e., not biradicals, for example.

[6] For studies on caged radical pairs in which rotation competes with combination, see, e.g.: Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371–2386. Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867–874. Koenig, T.; Owens, J. M. *Ibid.* **1973**, *95*, 8484–8486. Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *Ibid.* **1977**, *99*, 2622–2627. Doering, W. v. E.; Birladeanu, L. *Ibid.* **1986**, *108*, 7442–7444; **1987**, *109*, 1286. For related studies in which rotation affects the combination to disproportionation ratio for caged radical pairs, see: Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463–2481. Lehni, M.; Fischer, H. *Int. J. Chem. Kinet.* **1983**, *15*, 733–757. Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555–2559.

[7] Skell, P. S.; Baxter, H. N., III *J. Am. Chem. Soc.* **1985**, *107*, 2823–2824.

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[9] Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300–6311.

[10] Trichloride does not appear on the right-hand side of this equation because it is formed at the expense of dichloride. The quantity of trichlorides plus the quantity of dichlorides together constitute P.

[11] Under the same conditions in $CFCl_3$ there was a 40% yield of mono- and a 60% yield of dichlorides.[9]

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Scheme I

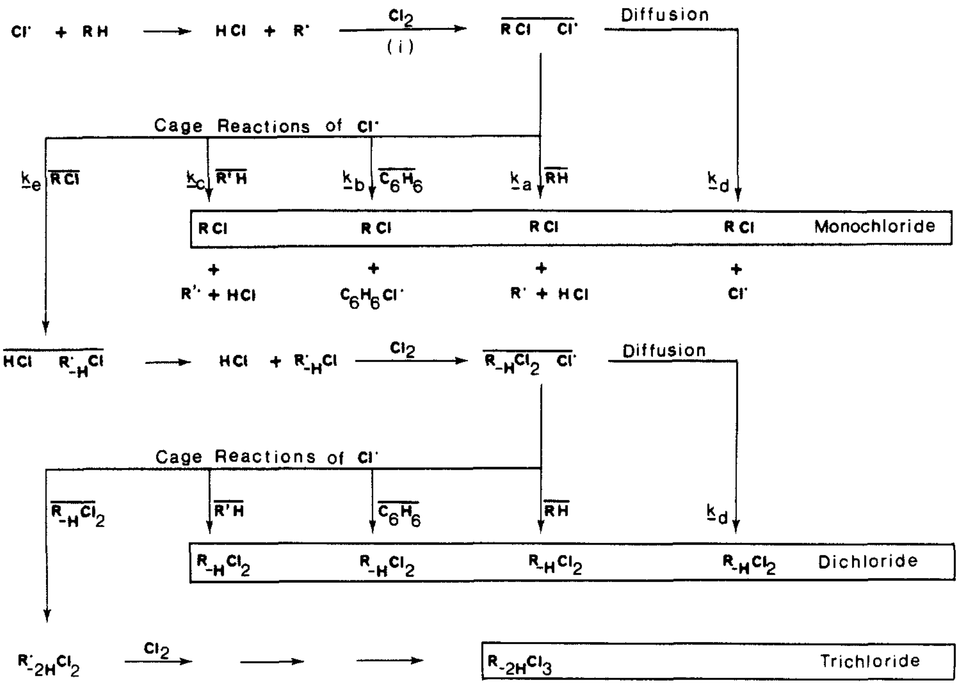

Table I. GC Retention Times and Some Representative Relative Yield Data Showing the Patterns of Di- and Trichloride Products Formed by In-Cage Polychlorination of 2,3-Dimethylbutane

		product pattern			
product	GC retn time,[a] min	0.5 M DMB in CCl_4	neat DMB	0.5 M DMB in 7.5 M c-C_6H_{12}	0.5 M DMB in C_6H_6
		Monochlorides			
2-ClDMB	10.57	0.55	0.63	0.72	9.94
1-ClDMB	11.64	(1.00)	(1.00)	(1.00)	(1.00)
		Dichlorides			
2,3-Cl_2DMB	13.90	0.44	0.70	0.89	3.04
1,1-Cl_2DMB[b] 1,2-Cl_2DMB[b]	14.85	(1.00)	(1.00)	(1.00)	(1.00)
1,3-Cl_2DMB	15.56	1.02	0.81	0.96	1.06
1,1'-Cl_2DMB	16.32	0.37	0.34	0.34	*c*
dl-1,4-Cl_2DMB[d]	16.90	0.30	0.18	0.28	*c*
meso-1,4-Cl_2DMB[d]	16.93	0.47	0.45	0.37	*c*
100D/(M + D + T)[e]		23.4%	1.7%	1.1%	0.9%
		Trichlorides			
	17.93	0.24	*c*	*c*	*c*
	18.05	0.26	*c*	*c*	*c*
1,2,3-Cl_3DMB	18.41	(1.00)	*c*	*c*	*c*
	18.83	0.80	*c*	*c*	*c*
	19.01	0.74	*c*	*c*	*c*
100T/(M + D + T)[f]		3.2%	<0.05%	<0.05%	<0.05%
100(M + D + T)/(RH + M + D + T)[g]		3.2%	0.9%	10.0%	9.7%

[a] For GC conditions see Experimental Section. [b] GC peaks due to these two compounds could not be resolved. It is likely that the main (possibly sole) isomer in this pair is 1,2-Cl_2DMB (see ref 15). [c] Too small to detect. [d] Peaks due to these two compounds were not easy to resolve. [e] Percentage yield of dichlorides (relative to total chlorides). [f] Percentage yield of trichlorides (relative to total chlorides). [g] Percentage conversion of DMB calculated from the relative amounts of RH, M, D, and T at the end of the reaction.

perature and with exposure to ambient light. The inert diluent was CCl_4 in all cases, and care was taken to prevent evaporative losses. The conversion of the alkane was limited to ≤10%. Products were analyzed in triplicate on a Varian 3700 gas chromatograph fitted with 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, generally at 20 °C/min to a final temperature of 230 °C. However, in order to resolve the peaks due to *trans*-1,4- and *cis*-1,3-dichlorocyclohexanes, it was necessary after the initial 7 min at 60 °C to increase the temperature by only 5 °C/min to a final temperature of 140 °C (under these conditions the trichlorocyclohexanes were not eluted from the column). In all cases, the flow rate through the column was 4 mL/min and the injector port and detector were held at 130 and 300 °C, respectively.

Two alkanes, RH, were chlorinated: 2,3-dimethylbutane (DMB) and cyclohexane. With DMB we could observe GC peaks due to the two monochlorides, to six (or seven)[12] out of seven possible dichlorides, and to five trichlorides. With cyclohexane we could observe GC peaks due

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[12] 1,1-Cl_2DMB and 1,2-Cl_2DMB were found to have identical GC retention times. Since the chlorine atom in, e.g., $CH_3CH_2CH_2CH_2Cl$ makes the hydrogens in the CH_2Cl group less reactive toward an attacking Cl· atom than those in the CH_3 group,[13] it is probable that 1,2-Cl_2DMB is the predominant component of this GC peak. This conclusion receives additional support from the study of Everly et al.[14] of the photochlorination of 1-chloro-2,3-dimethylbutane in CCl_4 at 30–40 °C. In order of increasing GC retention times: 1,2-, 1,3-, and 1,4- (shown to be a mixture of *meso* and *dl* isomers) dichlorides of DMB were obtained in the proportions 3:4:5, respectively, together with two other minor products presumed to be isomeric dichlorides. Separation of the products by preparative GC followed by ^{1}H NMR apparently did not reveal any 1,1-Cl_2DMB as an "impurity" in the 1,2-Cl_2DMB.

Table II. GC Retention Times and Some Representative Relative Yield Data Showing the Patterns of Di- and Trichloride Product Formed by In-Cage Polychlorination of Cyclohexane

		product pattern			
product	GC retn time,[a] min	0.5 M c-C_6H_{12} in CCl_4	neat c-C_6H_{12}	0.5 M c-C_6H_{12} in DMB	0.5 M c-C_6H_{12} in C_6H_6
		Monochloride			
c-$C_6H_{11}Cl$	13.63 (15.79)				
		Dichlorides			
1,1-$C_6H_{10}Cl_2$	16.20 (20.46)	0.18	0.14	0.17	0.33
trans-1,2-$C_6H_{10}Cl_2$	17.33 (22.78)	(1.00)	(1.00)	(1.00)	(1.00)
trans-1,3-$C_6H_{10}Cl_2$	17.56 (23.26)	0.52	0.25	0.30	0.75
trans-1,4-$C_6H_{10}Cl_2$	17.64 (23.38)	0.28	0.14	0.22	0.81
cis-1,3-$C_6H_{10}Cl_2$	17.64 (23.46)	0.74	0.60	0.85	1.38
cis-1,4-$C_6H_{10}Cl_2$	18.18 (24.65)	0.27	0.08	0.16	0.57
cis-1,2-$C_6H_{10}Cl_2$	18.31 (24.94)	0.07	0.03	0.05	0.12
100D/(M + D + T)[b]		24.8%	1.0%	3.9%	1.4%
		Trichlorides			
	18.94	0.30	[c]	[c]	[c]
	19.32	0.18	[c]	[c]	[c]
	19.68	0.15	[c]	[c]	[c]
	19.96	(1.00)	[c]	[c]	[c]
	20.19	0.20	[c]	[c]	[c]
	20.27	0.35	[c]	[c]	[c]
100T/(M + D + T)[d]		4.5%	<0.05%	<0.05%	<0.05%
100(M + D + T)/(RH + M + D + T)[e]		4.3%	1.2%	8.2%	9.2%

[a] For GC conditions see Experimental Section. The numbers in parentheses refer to the slower rate of temperature increase of the column (5 °C/min). [b] Percentage yield of dichlorides (relative to total chloride). [c] Too small to detect. [d] Percentage yield of trichlorides (relative to total chlorides). [e] Percentage conversion of c-C_6H_{12} calculated from the relative amounts of RH, M, D, and T at the end of the reaction.

to the monochloride, to all seven possible dichlorides, and to six trichlorides.

The DMB dichlorides and one of the DMB trichlorides (1,2,3-) were identified by comparison of their GC retention times (see Table I) with those of synthesized authentic materials.

Four of the seven cyclohexane dichlorides were identified by comparison of their GC retention times with those of authentic materials obtained from commerical sources (cis-1,2 and cis- and trans-1,4) or synthesized (trans-1,2). Of particular help in identifying the other dichlorocyclohexanes was a detailed report by Russell et al.[15] on the photochlorination of chlorocyclohexane. All seven dichlorides were unequivocally identified. In order of increasing GC elution times, on two different columns run under different conditions, they were 1,1-, *trans*-1,2-, *trans*-1,3-, *trans*-1,4-, *cis*-1,3-, *cis*-1,4-, and *cis*-1,2-dichlorocyclohexanes.[15] The order of GC retention times in our own experiments is identical (see Table II).

Synthesis of DMB Dichlorides. 2,3-Cl_2DMB was prepared by photochlorination of 2-ClDMB[16] in benzene by bubbling 7% Cl_2 in N_2 through the solution while irradiating with a tungsten filament lamp. The ^1H NMR spectrum was identical with that reported.[17]

1,1-Cl_2DMB was synthesized as follows: 2,3-Dimethylbut-1-ene was converted to the epoxide with *m*-chloroperbenzoic acid, and the epoxide was then rearranged to 2,3-dimethylbutanal by treatment with boron trifluoride etherate in CH_2Cl_2 at room temperature: ^1H NMR ($CDCl_3$) δ 0.80 (3 H, d, J = 7 Hz, CH_3), 0.96 (3 H, d, J = 7 Hz, CH_3), 1.00 (3 H, d, J = 7 Hz, CH_3), 1.6–2.2 (2 H, m, CHCH), 9.53 (1 H, d, J = 2 Hz, CHO). The aldehyde was converted to 1,1-Cl_2DMB by treatment with PCl_5 at room temperature: ^1H NMR (CCl_4) δ 0.8–1.0 (9 H, br, 3 CH_3), 1.5–2.0 (2 H, m, CHCH), 5.53 (1 H, d, J = 6 Hz, $CHCl_2$).

1,2-Cl_2DMB was prepared by addition of Cl_2 to 2,3-dimethylbut-1-ene. The ^1H NMR spectrum was identical with that reported.[14]

1,3-Cl_2DMB was prepared by a literature procedure[18] and had the appropriate ^1H NMR spectrum.

1,1'-Cl_2DMB was prepared by treating the corresponding diol[19,20] with thionyl chloride and pyridine in CCl_4 at reflux for 10 h: ^1H NMR ($CDCl_3$) δ 0.92 (6 H, d, J = 6 Hz, $C(CH_3)_2$), 1.60 (2 H, m, CHCH), 3.65 (4 H, m, $C(CH_2Cl_2)_2$).

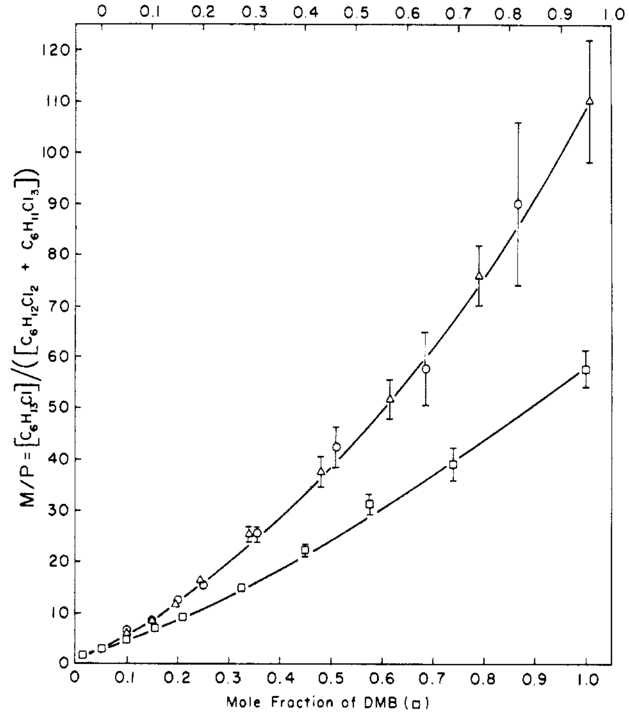

Figure 1. Photochlorination of 2,3-dimethylbutane at room temperature. Monochloride/polychloride ratio as a function of the mole fraction of X, with CCl_4 as the inert diluent. □, RH = DMB, X = DMB; △, RH = 0.5 M DMB, X = C_6H_6; ○, RH = 0.5 M DMB, X = c-C_6H_{12}. See also footnote 22. The error bars were calculated assuming a 0.1% error (based on total chloride yields) in the yields of mono-, di-, and trichlorides.

***meso*-1,4-Cl_2DMB** was prepared from *meso*-2,3-dimethylsuccinic acid[21] and had the appropriate ^1H NMR spectrum.

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(13) See, e.g.: Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 15.

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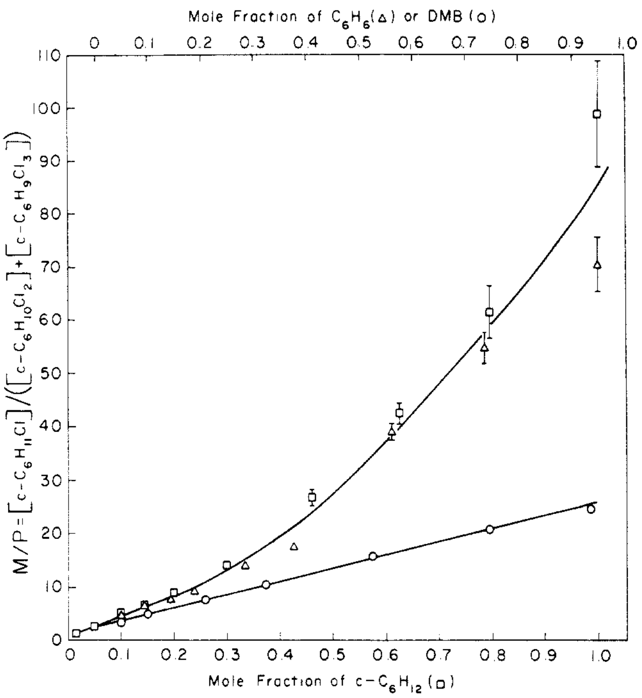

Figure 2. Photochlorination of cylohexane at room temperature. Monochloride/polychloride ratio as a function of the mole fraction of X, with CCl_4 as the inert diluent. □, RH = c-C_6H_{12}, X = c-C_6H_{12}; O, RH = 0.5 M c-C_6H_{12}, X = DMB; Δ, RH = 0.5 M c-C_6H_{12}, X = C_6H_6. See also footnote 22. The error bars were calculated assuming a 0.1% error (based on total chloride yields) in the yields of mono-, di-, and trichlorides.

***dl*-1,4-Cl_2DMB,** the remaining DMB dichloride, was assumed to be responsible for the remaining GC peak on the basis of its retention time (almost identical with that of *meso*-1,4-Cl_2DMB, see Table I) and of the proof of Everly et al.[14] that the photochlorination of 1-ClDMB yields a mixture of *meso*- and *dl*-1,4-dichlorides that were not resolved under their GC conditions.[12]

Synthesis of 1,2,3-Cl_3DMB. This trichloride was synthesized by the photochlorination (7% Cl_2 in N_2, tungsten lamp) of 2,3-Cl_2DMB in CCl_4: ^{1}H NMR (CCl_4) δ 1.80 (9 H, br, 3 CH_3), 3.83 (1 H, d, J = 12 Hz, one of CH_2Cl), 4.07 (1 H, d, J = 12 Hz, one of CH_2Cl).

Results

Plots of the M/P ratios obtained with 0.5 M DMB in the presence of varying mole fractions of benzene with CCl_4 as the inert diluent and of M/P ratios obtained in the absence of benzene at various DMB mole fractions in CCl_4 (up to and including neat DMB) show pronounced curvature (see Figure 1).[22] Similarly, plots of the M/P ratios obtained with cyclohexane (0.5 M c-C_6H_{12}/C_6H_6/CCl_4 and c-C_6H_{12}/CCl_4 systems) also show pronounced curvature (see Figure 2).[22] The curvature of such plots is not, however, necessarily confined to the effects induced by increasing concentrations of C_6H_6 or of the substrate itself. Thus, with 0.5 M DMB the addition of cyclohexane produced a curve that is essentially identical with that produced by benzene (see Figure 1).[22] However, with 0.5 M c-C_6H_{12} the addition of DMB produced an essentially linear increase in the cyclohexane M/P ratio (i.e., in [c-C_6H_{11}Cl]/([c-$C_6H_{10}Cl_2$] + [c-$C_6H_9Cl_3$]) (see Figure 2).[22] This last system was, therefore, the only one studied that actually obeyed eq 1. The experimental data from which Figures 1 and 2 were constructed are available as supplementary material.

Discussion

We first address the question of whether Scheme I can account in a general way for our experimental results by considering the initial slopes of the plots of M/P vs mole fraction of the added reactant X from Figures 1 and 2. These slopes correspond to k_x/k_e[RCl], with the magnitude of the denominator dependent on the nature of RCl (and, hence, on the nature of RH). Ratios of initial slopes therefore yield the relative reactivities of different molecules in the cage wall of the geminate Cl$^\bullet$/RCl pair. These relative reactivities are not expected to differ greatly from relative reactivities of the same compounds reacting with Cl$^\bullet$ atoms in diffusive encounters in bulk solution. For X = DMB, C_6H_6, and c-C_6H_{12} the initial slopes[23] are 39, 60, and 60 (RH = DMB, Figure 1) and 24, 38, and 36 (RH = c-C_6H_{12}, Figure 2), respectively, corresponding to relative reactivities of 1.0:1.5:1.5 and 1.0:1.6:1.5. Our earlier direct measurements of the absolute rate constants for reaction of free Cl$^\bullet$ atoms with DMB and C_6H_6 yield[8] a relative reactivity of 3.3×10^9:6.0×10^9 = 1.0:1.8, which we consider to be in satisfactory agreement with the 1.0:1.5–1.6 ratio measured from cage wall products, considering the difficulties involved in both experiments. Competitive chlorination of DMB/c-C_6H_{12} mixtures in the absence of any cosolvent gave a relative reactivity of 1.0:1.9 for the formation of monochlorides.

What of the curvature in the M/P vs X mole fraction curves that is seen at higher concentrations of X? A possibility considered when we first discovered the phenomenon was that k_d increased as [X] increased. However, such an effect would appear to be too small to account for the magnitude of the upward curvature. Thus, calculation of the diffusion coefficient of Cl$^\bullet$ gave essentially the same value in CCl_4 at room temperature[24] as in DMB. Furthermore, it is difficult to see why, when X = DMB, a strong upward curvature would be produced for RH = DMB (Figure 1) but there would be no curvature for RH = c-C_6H_{12} (Figure 2).

We propose that the principal reason[26] for the nonlinearity of the plots of M/P vs X mole fraction is a direct consequence of the similar time scales that are involved for (1) the in-cage reaction of Cl$^\bullet$ with molecules of X in the cage walls that confine the Cl$^\bullet$/RCl geminate pair and (2) the (partial) rotation of the geminate chloride molecule RCl ($R_{-H}Cl_2$). A partial rotation of the in-cage geminate chloride relative to the newly formed chlorine atom is, of course, essential if this molecule is to "present" a second H atom to the chlorine atom. Thus, at high [X] the reaction of Cl$^\bullet$ with X in the walls of the geminate pair cage becomes competitive with rotation of geminate RCl. The proportion of Cl$^\bullet$ attack on geminate RCl, and hence on the yield of polychlorides, is reduced to a greater extent by added X than would have been the case if RCl had had sufficient time to rotate before the Cl$^\bullet$ atom reacted. At a given mole fraction of X, the degree of deviation from linearity of the M/P vs [X] plots will depend on the time required for (partial) rotation of the geminate RCl, the reactivity of the geminate RCl, and the reactivity of X. Some information regarding the first two factors can be derived from the ratio of the initial slopes[23] of the M/P vs [X] curves for RH = DMB/RH = c-C_6H_{12} for X = DMB, C_6H_6, and c-C_6H_{12}; these ratios, which correspond to $k_e[\overline{\text{c-}C_6H_{11}Cl}]/k_e[\overline{C_6H_{13}Cl}]$, are 1.63, 1.58 and 1.67, respectively. The geminate monochloride from cyclohexane is therefore converted to dichlorides ca. 1.6 times as rapidly as the geminate monochlorides from DMB are converted to dichlorides. This rate difference, combined with a rate difference of 1.5–1.6 (vide supra) favoring Cl$^\bullet$ atom attack on cage-wall cyclohexane over cage-wall DMB, provides a simple explanation for the smaller deviation from linearity of the plot

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[22] Note that the point representing 0.05 mol fraction (i.e., 0.5 M) of the alkane for which the M/P ratios are being measured coincides with the points corresponding to zero mol fraction of benzene and zero mol fraction of the second alkane. For this reason, Figures 1 and 2 have two mole fraction scales. Note also that each point in these two figures was constructed from data as detailed as that contained in each of the four experiments listed in Tables I and II.

[23] Calculated by linear regression using the first four data points.

[24] The value obtained, viz., 5×10^{-5} cm^2 s^{-1}, is virtually identical with the experimentally measured diffusion coefficient for argon in CCl_4: viz.,[25] 4.85×10^{-5} cm^2 s^{-1}. The calculation was made with a conventional molecular dynamics simulation, by monitoring the mean squared displacement of the chlorine radical as a function of time.

[25] Hildebrand, H.; Lamoreaux, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3321–3324.

[26] I.e., changes in k_d may make a minor contribution to the curvature.

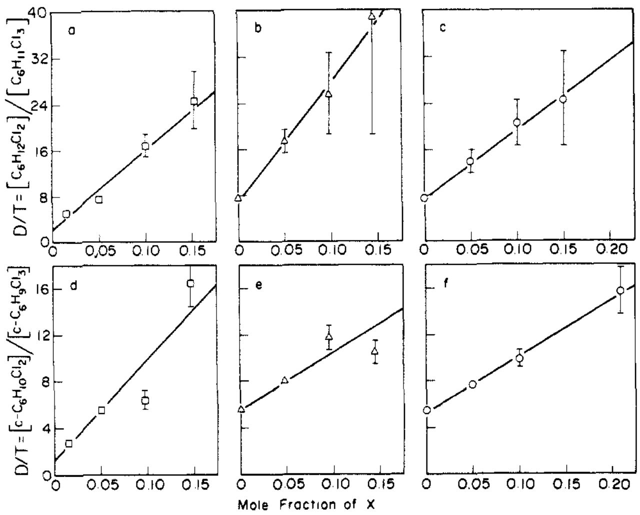


Figure 3. Dichloride/trichloride ratio as a function of the mole fraction of X, with CCl_4 as the inert diluent, for room-temperature photochlorinations: (a) RH = DMB, X = DMB; (b) RH = 0.5 M DMB, X = C_6H_6; (c) RH = 0.5 M DMB, X = c-C_6H_{12}; (d) RH = c-C_6H_{12}, X = c-C_6H_{12}; (e) RH = 0.5 M c-C_6H_{12}, X = C_6H_6; (f) RH = 0.5 M c-C_6H_{12}, X = DMB. The error bars were calculated assuming a 0.1% error (based on total chloride yields) in the yields of di- and trichlorides.

for RH = C_6H_{12}, X = DMB than for any of the other plots shown in Figures 1 and 2. That is, in this last system the geminate c-$C_6H_{11}Cl$ in the cage wall can compete effectively for the geminate Cl• with the cage wall DMB even at high DMB mole fractions.

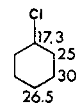
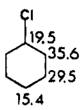
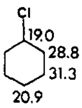
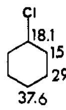
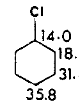
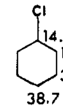
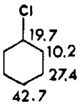
One would anticipate that the "second" set of cage processes shown in Scheme I (which leads to trichlorides) should show much the same features as the "first" set of cage processes (which leads to dichlorides). This is the case, as can be seen in Figure 3 in which the ratio of trichlorides T to dichlorides D has been plotted against the mole fraction of X. (The D/T ratios from which these plots were constructed are available as supplementary material.) Unfortunately, it is not possible to plot D/T vs X to mole fractions of X ≥ ca. 0.15–0.20 because the trichloride yields become too small to measure, and even over this range of X values, the errors in D/T are much greater than the errors in M/P (cf., Figures 1 and 2). Nevertheless, the slopes of the lines in Figure 3 indicate that the cage-wall reaction that converts dichlorides to trichlorides occurs more rapidly (mean value = 2.3) for the cyclohexyl dichlorides than for the DMB dichlorides.

The simple idea that a chlorine atom is so extremely reactive that it can abstract hydrogen from the alkanes and the chloroalkane which form the cage wall surrounding it on a time scale comparable to that required for the molecules in the cage wall to reorient themselves leads to the interesting prediction that attack of Cl• on RCl in the Cl•/RCl geminate pair should give a "pattern" of dichlorides which differs from the pattern of dichlorides obtained in the reaction of a Cl•/RCl diffusive pair. This is because the RCl in the Cl•/RCl geminate pair does not have sufficient time to rotate freely before the Cl• atom escapes[1b] from the cage in which it and RCl were formed. As a consequence, the pattern of dichlorides formed by the geminate pair should show a tendency for the two chlorine atoms in the product molecules to be closer to one another than would be the case for dichlorides formed from a diffusive encounter between a free chlorine atom and an RCl molecule under otherwise similar conditions. Our experimental results support this prediction.

Thus, if we examine cyclohexane (where the situation is somewhat simpler than with DMB because cyclohexane yields only a single monochloride), it is clear from Table II that while there is considerable "freedom" of rotation for chlorocyclohexane in the cage wall the dichloride patterns do differ from one solvent to another. The more reactive hydrogen atoms in chlorocyclohexane and those hydrogen atoms that are "closer" to the geminate chlorine atom will be attacked preferentially in the systems with the shorter in-cage lifetimes for the chlorine atom. Since cyclohexyl radicals invert very rapidly,[27] it seems reasonable to assume that the chlorocyclohexyl radicals will adopt their preferred conformations before they react with a chlorine molecule (since $[Cl_2]$ was always <0.1 M). If this assumption is valid, the cis/trans ratio of dichlorides does not reflect the conformational preference for the abstraction of specific cis or trans hydrogen atoms from the geminate chlorocyclohexane, but rather, it would reflect the conformational preference of the transition state for reaction of the chlorocyclohexyl radical with chlorine:

$$c\text{-}C_6H_{10}Cl^\bullet + Cl_2 \rightarrow c\text{-}C_6H_{10}Cl_2 + Cl^\bullet$$

Table III. Sites of Attack as a Percentage of Total Attack by In-Cage Chlorine Atoms on Chlorocyclohexane under the Conditions Listed in Table II and for Free Chlorine Atom Attack on Chlorocyclohexane (Values Calculated Per Available Hydrogen[28])

<table>
<tr><th colspan="12">GEMINATE PAIR CHLORINATION</th></tr>
<tr>
<td colspan="3">0.5M c-C_6H_{12} in CCl_4

Cl 17.3 25.8 30.4 26.5</td>
<td colspan="3">neat c-C_6H_{12}

Cl 19.5 35.6 29.5 15.4</td>
<td colspan="3">0.5M c-C_6H_{12} in DMB

Cl 19.0 28.8 31.3 20.9</td>
<td colspan="3">0.5M c-C_6H_{12} in C_6H_6

Cl 18.1 15.3 29.0 37.6</td>
</tr>
<tr><th colspan="12">DIFFUSIVE PAIR CHLORINATION</th></tr>
<tr>
<td colspan="4">0.5M c-$C_6H_{11}Cl$ in CCl_4

Cl 14.0 18.4 31.8 35.8</td>
<td colspan="4">c-$C_6H_{11}Cl$ in CCl_4 at 40° (ref. 15)

Cl 14.0 16.8 30.5 38.7</td>
<td colspan="4">0.5M c-$C_6H_{11}Cl$ in C_6H_6

Cl 19.7 10.2 27.4 42.7</td>
</tr>
</table>

In Table III is shown the percentage of geminate attack at each position of chlorocyclohexane *per available hydrogen* at that position (viz., one at the 1-, four at the 2- and 3-, and two at the 4-position).[28] For 0.5 M c-C_6H_{12} in CCl_4 there would, at first sight, appear to be essentially complete freedom for the rotation of in-cage chlorocyclohexane. [The (partial) rotation of RCl in the cage wall will be referred to hereafter as its freedom to rotate, in order to emphasize the relationship between the time required for rotation of RCl and the time required for escape[1b] of the Cl• atom from the cage.] It can be seen that the hydrogens at positions 2–4 are attacked about equally, only the hydrogen at position 1 showing deactivation by the *gem*-chlorine atom. However, this evidence is misleading, as can be seen from results obtained by ourselves[29] and by Russell et al.[15,30] for the photochlorination of chlorocyclohexane in CCl_4, i.e., for the reaction of Cl•/c-$C_6H_{11}Cl$ diffusive pairs (see Table III). These results show that the percentage of attack at both the 1- and 2-position of chlorocyclohexane is lower for Cl•/c-$C_6H_{11}Cl$ diffusive pairs than for Cl•/c-$C_6H_{11}Cl$ geminate pairs. We conclude, therefore, that in the geminate Cl•/c-$C_6H_{11}Cl$ pair in 0.5 M c-C_6H_{12}/CCl_4 there is a preference for attack at the hydrogen atoms that are closer to the newly formed chlorine atom. This preference for the closer hydrogens is enhanced as the in-cage lifetime of the Cl•/c-$C_6H_{11}Cl$ geminate pair is reduced by using DMB as solvent and is even

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(27) At room temperature, the rate constant for cyclohexyl radical inversion is 1.4×10^9 s^{-1}. See: Ogawa, E. Fessenden, R. W. *J. Chem. Phys.* **1964**, *41*, 994–998.

(28) This method of presentation was chosen so that the 4-position of chlorocylohexane would not appear to be unduly unreactive.

(29) Photochlorination of 0.5 M chlorocyclohexane in neat CCl_4 gave the dichlorides (in percentages) noted: 1,1 (4.9%); trans-1,2 (22.6%); trans-1,3 (13.8%) trans-1,4 (13.5%); cis-1,3 (30.6%); cis-1,4 (11.5%); and cis-1,2 (3.1%).

(30) For comparison with the data shown in Table II the results of Russell et al.[15] at 40 °C give the following, normalized, yields of 1,1-, *trans*-1,2-, *trans*-1,3-, *trans*-1,4-, *cis*-1,3-, *cis*-1,4-, and *cis*-1,2-dichlorocyclocyclohexanes: 0.23, (1.00), 1.10, 0.66, 0.88, 0.59, and 0.09, respectively. The chlorocyclohexane concentration was not specified in this work.

Table IV. Geminate Pair and Diffusive Pair Sites of Attack as a Percentage of Total Attack by Chlorine Atoms on 1-Chloro-2,3-dimethylbutane

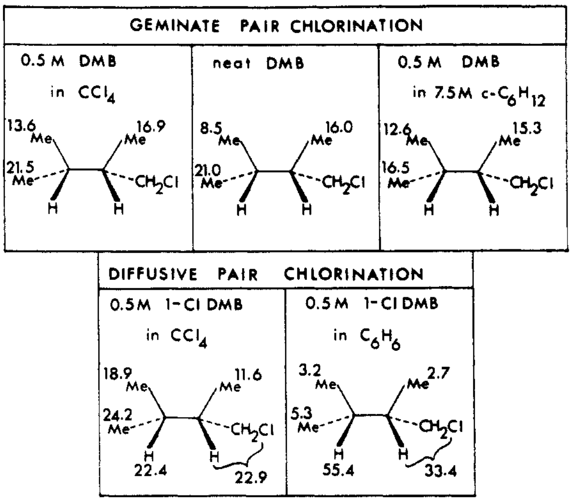
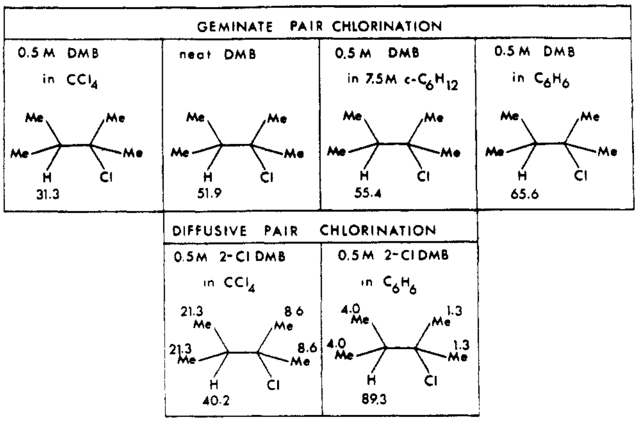


Table V. Geminate Pair and Diffusive Pair Sites of Attack as a Percentage of Total Attack by Chlorine Atoms on 2-Chloro-2,3-dimethylbutane



further enhanced by using cyclohexane as the solvent (see Table III).[31] The dichloride patterns obtained by the photochlorination of 0.5 M c-C_6H_{12} in C_6H_6 and of 0.5 M chlorocyclohexane in benzene[32] are also shown in Table III.

For DMB the nature of the dichloride patterns is complicated by the fact that these compounds are produced from two monochlorides and that only five out of the seven dichlorides are derived from a specific monochloride. That is, 1-ClDMB is the only precursor for 1,1-Cl_2DMB, 1,1′-Cl_2DMB, and the two 1,4-Cl_2DMBs, while 2-ClDMB is the only precursor for 2,3-Cl_2DMB. The two remaining dichlorides, viz., 1,2-Cl_2DMB and 1,3-Cl_2DMB, can be formed from either monochloride. The yields of these last two dichlorides cannot, therefore, be apportioned between the two monochloride precursors. Within the limits imposed by this restriction, the dichloride yields given in Table I have been utilized to assign sites of attack as a percentage of total attack in the Cl•/1-ClDMB geminate pairs (Table IV) and in the Cl•/2-ClDMB geminate pairs (Table V). The two monochlorides of DMB (0.5 M) were also photochlorinated in CCl_4 and in benzene in order to obtain comparable data for Cl•/1-ClDMB and Cl•/2-ClDMB diffusive pair reactions. These results are included in Tables IV and V.

The interpretation of the reactivity patterns exhibited by the geminate pair reactions, as summarized in Tables IV and V, is complicated by the necessary absence of data regarding the yields of 1,2-Cl_2DMB and 1,3-Cl_2DMB. The data for the 1-ClDMB geminate pair may be complicated further if there is a solvent effect on the preferred conformation of the 2,3-dimethylbutyl radical[33] because, in the Cl•/1-ClDMB geminate pair, this could change the relative distances from the geminate Cl• atom to the tertiary H at position 3 and the two methyl groups attached to the 3-carbon. For these reasons, discussion of the data contained in Tables IV and V will be confined to two points. First, comparison of the diffusive pair dichloride yields for 0.5 M 1-ClDMB in CCl_4 with the geminate pair dichlorides derived from 1-ClDMB during the photochlorination of 0.5 M DMB in CCl_4 shows that there is a significantly greater percentage of Cl• attack on the 1′-CH_3 group in the geminate pair (16.9%) than in the diffusive pair (11.6%). Presumably, this reflects the fact that the 1′-CH_3 group is closer to the geminate Cl• atom than the other two CH_3 groups. Second, for the Cl•/2-ClDMB geminate pair the percentage of attack at the 3-position increases as the lifetime of the caged geminate pair decreases.

In conclusion, we note that benzene appears to be neither qualitatively nor quantitatively different as an "X" from any other compound that is highly reactive toward free Cl• atoms [cf., X = C_6H_6 and c-C_6H_{12} for both RH = DMB (Figure 1) and RH = c-C_6H_{12} (Figure 2)]. The effect of benzene on M/P ratios does not, therefore, yield any information regarding the structure of the $C_6H_6Cl^•$ complex and/or the presence of a third chlorinating species in benzene-containing systems.[35]

Acknowledgment. We thank Dr. R. W. Impey and Dr. M. L. Klein for their calculation of Cl• diffusion coefficients and Dr. J. C. Scaiano for pointing out that reactive cage walls might reduce caged Cl• atom lifetimes to values comparable to molecular rotation times.

Registry No. DMB, 79-29-8; cyclohexane, 110-82-7.

Supplementary Material Available: Tables VI and VII giving percentage yields of mono-, di-, and trichloride products together with M/P ratios for each point shown in Figures 1 and 2 and D/T ratios for each point shown in Figure 3 (2 pages). Ordering information is given on any current masthead page.

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(31) These results are quite consistent with our earlier statement that the nonlinearity observed in the M/P plots (Figures 1 and 2) is due to there being insufficient time available for completely free rotation of the monochlorides. The formation of 1,3- and 1,4-dichlorocyclohexanes does, however, imply that there is a remarkable freedom of rotation of at least some of the geminate c-$C_6H_{11}Cl$ in the cage wall. Perhaps these dichlorides are produced primarily from a small fraction of geminate c-$C_6H_{11}Cl$ that, for strictly "local" reasons, has adequate freedom to rotate.

(32) Photochlorination of 0.5 M chlorocylohexane in neat benzene gave the dichlorides (in percentages) noted: 1,1 (7.7%); trans-1,2 (14.2%); trans-1,3 (17.1%); trans-1,4 (18.7%); cis-1,3-(25.8%); cis-1,4 (14.7%); and cis-1,2 (1.8%).

(33) The gauche and anti rotational isomers of DMB are present in the statistical ratio of 2:1 at −180 °C in Freon solvents, and the free energy of activation for the anti–gauche interconversion is 4.3 kcal/mol.[34] With such a high barrier, any 1-ClDMB that reacts in-cage with the geminate Cl• atom to form dichlorides is unlikely to relax from the conformation in which it was formed.

(34) Lunazzi, L.; Macciantelli, D.; Bernardi, F.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4573–4576.

(35) A controversy surrounds the number (two[8,36,37] or three[9,38]) and structure (π or σ) of the chlorinating agents involved in photochlorinations in the presence of benzene. It has been argued[9] that a two-intermediate system could be ruled out because, in such a system, "*multiple chlorination should have been observed*" in the presence of benzene.

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

(37) Walling, C. *J. Org. Chem.* **1988**, *53*, 305–308.

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