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Selectivity in the Photochlorination of 2,3-Dimethylbutane with Molecular Chlorine in Noncomplexing Solvents[1]

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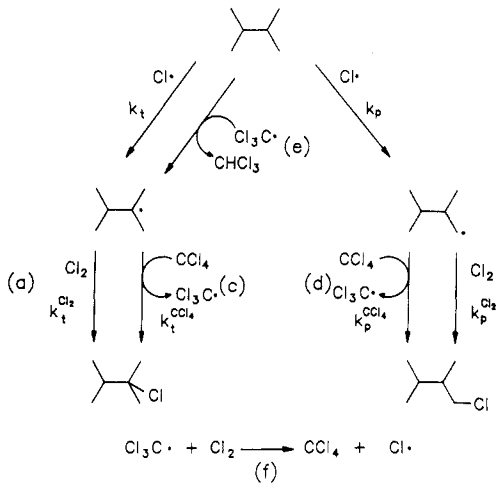
The factors affecting changes in the measured selectivity for the photochlorination of 2,3-dimethylbutane (DMB) in alkane solvents and in CCl_4 have been identified. At low chlorine concentrations in CCl_4 as solvent, the selectivities, S^m = [2-ClDMB]/[1-ClDMB], are dramatically enhanced because of CCl_4 and $Cl_3C^\bullet$ participation in the overall chain process. In the absence of CCl_4, the selectivities may also increase at very low chlorine concentrations because residual O_2 and peroxyl radicals participate in the overall chain process. In the absence of either of the above phenomena, S^m was calculated to be 0.64, a value that compares well with a value of 0.62, which we have measured in the gas phase.

2,3-Dimethylbutane (DMB) has been widely employed as a substrate in studies of photoinitiated, radical chain chlorinations of alkanes by molecular chlorine.[3–11] Its popularity in this respect arises from the fact that molecular regioselectivities, S^m,[8] for abstraction of a tertiary vs a primary hydrogen atom can be determined by measuring the relative yields of 2-chloro- and 1-chloro-2,3-dimethylbutane (2-ClDMB and 1-ClDMB, respectively), i.e., S^m = [2-ClDMB]/[1-ClDMB]. As was first demonstrated by Russell[3–5] and has been abundantly confirmed by others,[6–11] the values found for S^m for DMB in aromatic solvents[12] are much higher than the values found for S^m for neat DMB or for DMB in perhalogenated solvents. The higher values found for S^m in aromatic solvents have been attributed to the formation of arene/$Cl^\bullet$ complexes that are more selective in hydrogen atom abstraction than the "free", i.e., noncomplexed chlorine atom. In our own studies of DMB photochlorination,[8,11] we have repeatedly observed that S^m values in alkane solvents (neat DMB[8,11] and cyclohexane[11]) are not precisely equal to those obtained in CCl_4. Indeed, in 1985 we commented:[8] "Just because chlorine atoms are not "free" in aromatic (and certain other) solvents, we must not be blinded to the fact that they may not be "free" (in the gas-phase sense) in what are generally considered to be noncomplexing solvents. Alkanes and CCl_4 would normally be considered to be such solvents, but nevertheless the selectivities for DMB chlorination in the absence of benzene show a small but real difference between neat DMB and dilute solutions of DMB in CCl_4". The S^m values that were found[8] were 0.47 (0.125 M DMB in CCl_4), 0.58 (1.0 M DMB in CCl_4), and 0.66 (neat DMB). More recently, we obtained[11] S^m = 0.55 (0.5 M DMB in CCl_4), 0.63 (neat DMB), and 0.72 (0.5 M DMB in 7.5 M c-C_6H_{12} containing 1.22 M CCl_4 cosolvent). In the present paper we explore the origin of these differences and demonstrate that alkanes and CCl_4 are noncomplexing solvents insofar as the chlorine atom is concerned. "High" S^m values (e.g., 0.72 for 0.5 M DMB in c-C_6H_{12})[11] and "low" S^m values (e.g., 0.55 for 0.5 M DMB in CCl_4)[11] arise from other and different causes.

Scheme I



Results

It must be pointed out immediately that the S^m value for DMB in CCl_4 cannot be considered to be equal to the selectivity of monochloride *formation*. It is well known[8,9,11] that alkane photochlorinations in CCl_4 proceed with a high degree of polychlorination even at low conversions. Since a significant proportion of the monochlorides is converted "in cage"[11] to polychlorides (e.g., 26.6% for 0.5 M DMB in CCl_4),[11] the tertiary to primary ratio of the remaining monochlorides does not necessarily reflect their relative rates of formation from DMB. The S^m values found for DMB solutions containing large amounts of CCl_4 cannot therefore be meaningfully interpreted. However, solutions of DMB that contain mainly alkane and either no CCl_4 or only small amounts of CCl_4 can and do yield meaningful S^m values virtually "uncontaminated" by the effects of polychlorination (for neat DMB, only 1.7% of the monochlorides are further chlorinated "in cage").[11]

The previously reported[8,11] S^m values for neat DMB (0.63, 0.66) and 0.5 M DMB, 7.5 M c-C_6H_{12}, 1.22 M CCl_4 (0.72) show a small but significant difference. We have now measured the S^m values for 0.5 M DMB in neat c-C_6H_{12} and obtained 0.66. Since this value is in agreement with the value found for neat DMB, it would seem that the S^m value of 0.72 must have been due to the 1.22 M CCl_4 and not to the 7.5 M cyclohexane.

The most obvious explanation for differences in S^m values in the presence and absence of CCl_4 is that the CCl_4 actually becomes involved in the radical chain chlorination of DMB (Scheme I). Primary alkyl radicals abstract

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[12] Enhanced S^m values are also found in certain other solvents such as CS_2.

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Table I. Selectivities for the Photochlorination of DMB Solutions with Various Gas Mixtures

	neat DMB	0.5 M DMB in c-C_6H_{12}	0.5 M DMB in 7.5 M c-C_6H_{12}, 1.22 M CCl_4	0.5 M DMB in CCl_4
1% Cl_2–N_2	0.64	0.67	0.76	0.61
7% Cl_2–N_2	0.63	0.66	0.72	0.55
100% Cl_2	0.65	0.63	0.63	0.47

chlorine from CCl_4 fairly readily.[13] The resultant $Cl_3C^\bullet$ radical is rather unreactive but does appear to be highly selective in hydrogen atom abstraction reactions.[18-23] Thus, it has been reported that $Cl_3C^\bullet$ does not abstract primary hydrogen atoms from DMB[18,19] but that it does abstract the tertiary hydrogens from this molecule with a rate constant of ca. 68–80 $M^{-1}\ s^{-1}$ at 27 °C.[24,25] The rate constant for abstraction of secondary hydrogen atoms by $Cl_3C^\bullet$ is about 3 or 4 times smaller than for tertiary hydrogens, e.g., for cyclohexane a value of 21.4 $M^{-1}\ s^{-1}$ can be calculated at 27 °C from the Arrhenius parameters reported for this reaction.[20,26]

From Scheme I, it is clear that at sufficiently high concentrations of molecular chlorine all of the DMB radicals will be chlorinated by paths a and b while none should be chlorinated by paths c and d. High chlorine concentrations therefore yield a limiting value for S^{m}, which we represent by S^{m}_{∞}, and which must be equal to k_t/k_p, i.e.,

$$S^{m}_{\infty} = k_t/k_p$$

However, at low chlorine concentrations some of the DMB radicals can react by paths c and d (rate constants $k_t^{CCl_4}$ and $k_p^{CCl_4}$, respectively), processes which will produce $Cl_3C^\bullet$ radicals. Furthermore, at low $[Cl_2]$, abstraction of the tertiary hydrogen from DMB by $Cl_3C^\bullet$ (path e) should be able to compete favorably with the conversion of $Cl_3C^\bullet$ to CCl_4 (path f). Thus, S^{m} would be expected to *increase* as the chlorine concentration *decreases*.

Table II. DMB Selectivities for the Photochlorination of 6.91 M DMB, 0.98 M CCl_4 at Known Initial Chlorine Concentrations

$10^3[C_6H_{13}Cl]$,[a] M	S^{m}	X_{Cl_3C},[b] %	$10^3[Cl_2]_0^{calcd}$,[c] M
119	0.67	1.2	118
59.6	0.77	6.8	55.6
25.5	0.83	9.8	23.0
14.1	0.88	12	12.4
10.7	0.96	16	9.0
10.0	1.10	21	7.9
4.19	1.26	27[d]	3.1[e]
3.49	1.50	34[d]	2.3[e]
2.46	1.69	39[d]	1.5[e]
2.04	2.49	53[d]	1.0[e]
1.11	2.22	49[d]	0.6[e]

[a] $[C_6H_{13}Cl]$ = [1-ClDMB] + [2-ClDMB]. [b] X_{Cl_3C} is the fraction of hydrogen abstraction from DMB by $Cl_3C^\bullet$. [c] $[Cl_2]_0^{calcd}$ is equal to the sum of the concentrations of DMB monochlorides arising from reaction of $Cl^\bullet$ with DMB, i.e., $[Cl_2]_0^{calcd} = (1 - X_{Cl_3C})[C_6H_{13}Cl]$. [d] This value is overestimated as residual O_2 was participating in the chain process (see Scheme II and Table IV). [e] This value is underestimated as X_{Cl_3C} was overestimated.

Table III. DMB Selectivities for the Photochlorination of 0.48 M DMB, 6.88 M c-C_6H_{12}, 1.95 M CCl_4 at Known Initial Chlorine Concentrations

10^3-$[C_6H_{13}Cl]$,[a] M	10^3-[c-$C_6H_{11}Cl$], M	S^{m}	X_{Cl_3C},[b] %	10^3-$[Cl_2]_0^{calcd}$,[c] M
8.8	214	0.81	8.8	217
5.0	112	0.90	13	112
2.1	47.1	1.03	19	46.4
1.5	27.8	1.30	28	26.4
0.67	10.3	1.89	43	9.0
0.27	3.9	2.86	57[d]	3.1[e]

[a] $[C_6H_{13}Cl]$ = [1-ClDMB] + [2-ClDMB]. [b] X_{Cl_3C} is the fraction of hydrogen abstraction from DMB by $Cl_3C^\bullet$. [c] $[Cl_2]_0^{calcd}$ is equal to the sum of the concentrations of monochlorides arising from the reaction of $Cl^\bullet$ with DMB and with c-C_6H_{12}. The correction for monochloride formation by reaction of these hydrocarbons with $Cl_3C^\bullet$ is $7X_{Cl_3C}[C_6H_{13}Cl]$, see text; i.e., $[Cl_2]_0^{calcd} = (1 - 7X_{Cl_3C})[C_6H_{13}Cl] + [c\text{-}C_6H_{11}Cl]$. [d] This value is overestimated as residual O_2 was participating in the chain process (see Scheme II and Table IV). [e] This value is underestimated as X_{Cl_3C} was overestimated.

The "usual" conditions for alkane photochlorination in our laboratory[8,11] have involved bubbling 7% Cl_2 in N_2 through 1-mL samples with photolysis by exposure to normal laboratory light. To assess the dependence of S^{m} on $[Cl_2]$, we have now performed the chlorination of DMB in various solvent systems with not only 7% Cl_2 in N_2 but also 1% Cl_2 in N_2 and pure Cl_2 gas. The results of these experiments are listed in Table I.

First, it can be seen that with one exception, viz. 0.5 M DMB in CCl_4, at the highest Cl_2 concentrations (i.e., pure Cl_2) the S^{m} values are essentially identical (0.63–0.65) for neat DMB and for 0.5 M DMB in both c-C_6H_{12} and 7.5 M c-C_6H_{12}, 1.22 M CCl_4. Second, in the solutions that contain no CCl_4 (neat DMB, 0.5 M DMB in c-C_6H_{12}) there is a negligible dependence of S^{m} on $[Cl_2]$. Third, those solutions containing CCl_4 show a marked dependence of S^{m} on $[Cl_2]$, and this dependence is in the expected direction. (The actual S^{m} values are always lower in CCl_4 than in an alkane solvent under the same conditions, presumably because there is extensive polychlorination in CCl_4, vide supra.)[11]

Under the above-mentioned conditions in which there was continuous bubbling of chlorine containing gas, the true concentration of Cl_2 in the solution is, of course, unknown since the extreme rapidity of photochlorinations precludes the normal assumption that there will be complete equilibration between gas and liquid phases. To overcome this problem, solutions containing 6.91 M DMB

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(13) Rate constants for the reaction of primary alkyl radicals with CCl_4 have been variously estimated as: $1.2 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C;[14] $5.8 \times 10^4\ M^{-1}\ s^{-1}$ at 27 °C;[15] $7.2 \times 10^3\ M^{-1}\ s^{-1}$ at 25 °C;[16] and $1.2–2.4 \times 10^5\ M^{-1}\ s^{-1}$ at 50 °C.[17]

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(24) Values of 80 $M^{-1}\ s^{-1}$ in the gas phase[18] and 68 $M^{-1}\ s^{-1}$ in solution[19] can be calculated from the Arrhenius parameters given for the $Cl_3C^\bullet$ + DMB reaction.

(25) There must, of course, also be *some* abstraction of the primary hydrogens from DMB, but the rate constant for this process must be rather low. Indeed, for the radical chain chlorination of DMB at 40 °C in CCl_4 in the absence of molecular chlorine we have found a selectivity, $S^{m} = 165$. This indicates that the rate constant for attack on the primary hydrogens of DMB must be $<0.5\ M^{-1}\ s^{-1}$ at 27 °C.

(26) A rate constant of about half this magnitude can be calculated from the Arrhenius parameters reported for the $CCl_3^\bullet$ + c-C_6H_{12} reaction in the gas phase.[18,21]

with 0.98 M CCl_4 as cosolvent were prepared with initial chlorine concentrations, $[Cl_2]_0$, varying from ca. 1×10^{-1} M to ca. 1×10^{-3} M (see the Experimental Section). Similarly, solutions containing 0.48 M DMB and 6.88 M c-C_6H_{12} with 1.95 M CCl_4 as cosolvent were also prepared with $[Cl_2]_0$ varying from ca. 2×10^{-1} M to ca. 4×10^{-3} M. Photochlorinations were carried to completion and the measured S^m values are given in Tables II and III.

Since it was difficult to prepare solutions containing known concentrations of chlorine, the initial chlorine concentrations were calculated after the experiment from the absolute yields of monochlorides. (Polychloride formation did not exceed 2%, and thus di- and trichlorides could be ignored.) At low chlorine concentrations a large proportion of 2-ClDMB must arise from attack on DMB by $Cl_3C^\bullet$ and this must be considered when calculating the initial chlorine concentration. The available evidence[18,19,25] indicates that the abstraction of primary hydrogen from DMB by $Cl_3C^\bullet$ can be ignored at ambient temperatures. It follows, therefore, that 1-ClDMB can be considered to originate only from attack on DMB by $Cl^\bullet$ atoms. The amount of 2-ClDMB arising from attack on DMB by $Cl^\bullet$ atom is therefore given by (k_t/k_p)[1-ClDMB]. Taking $k_t/k_p = 0.65$ (the value obtained for neat DMB with constant bubbling of pure Cl_2 gas), the amount of monochlorides formed by the reaction of DMB with Cl_2 can be calculated. For the DMB (6.91 M)/CCl_4 (0.98 M) system (Table II) this is, of course, equal to the initial concentration of chlorine, $[Cl_2]_0$. However, for the DMB (0.48 M)/c-C_6H_{12} (6.88 M), CCl_4 (1.95 M) system (Table III), there will also be some chlorination of the cyclohexane arising via hydrogen abstraction from cyclohexane by $Cl_3C^\bullet$ radicals. The available rate constants for hydrogen abstraction by $Cl_3C^\bullet$ from DMB and from cyclohexane, viz., ca. 74 M^{-1} s^{-1} [18,19,24] and ca. 21 M^{-1} s^{-1} [20,26] at 27 °C, respectively, allows us to estimate that the DMB:c-C_6H_{12} relative reactivity toward the $Cl_3C^\bullet$ radical is roughly 3.5:1.0. In order to check this estimate we carried out a competitive, thermally initiated, radical chain chlorination of these two hydrocarbons in CCl_4 at 40 °C using the CCl_4 as the only chlorine source. This gave a DMB:c-C_6H_{12} relative reactivity toward the $Cl_3C^\bullet$ radical of 2.4:1.0, which is in satisfactory agreement with the estimated value of 3.5 and is certainly more reliable. With use of this ratio of 2.4 we calculate that with the [c-C_6H_{12}]/[DMB] molar ratio of 14.3 there will be roughly six times as much attack by $Cl_3C^\bullet$ on the cyclohexane as on the DMB. The initial chlorine concentrations given in Table III have therefore been calculated on this basis.

The S^m values listed in Tables II and III show that there is a very substantial increase in S^m as the initial chlorine concentration decreases. It is also evident that the S^m values for the DMB/c-C_6H_{12}/CCl_4 system are higher than those for the DMB/CCl_4 system at the same $[Cl_2]_0$. In the former system, DMB and cyclohexane are competing for reaction with $Cl^\bullet$ and since cyclohexane is both more reactive than DMB toward $Cl^\bullet$[11] and is present in a much greater amount, there is relatively less hydrogen abstraction from DMB by $Cl^\bullet$. However, $Cl_3C^\bullet$ radicals will be formed in large amounts by reaction of c-$C_6H_{11}^\bullet$ with CCl_4. A significant fraction (ca. $^1/_7$, vide supra) of these $Cl_3C^\bullet$ radicals will react with DMB to give the tertiary alkyl radical. Hence, there will be an enhanced yield of 2-ClDMB and an elevated S^m value in this system relative to that in the DMB/CCl_4 system at the same $[Cl_2]_0$.

A careful GC/MS analysis of the photochlorination products of the 6.91 M DMB, 0.98 M CCl_4 solution with $[Cl_2]_0 = 7.9 \times 10^{-3}$ M revealed the presence[27] of chloroform, as would indeed be expected (see Scheme I). Furthermore, photochlorination of 7.05 M c-$C_6D_{11}CD_3$, 0.98 M CCl_4 with the same initial chlorine concentration was found to yield a small amount of $CDCl_3$. These findings confirm that CCl_4 is directly involved in the radical chain chlorination of alkanes at low molecular chlorine concentrations.

Table IV. Selectivities for the Photochlorination of Neat DMB (7.68 M)

experimental conditions	$10^3[Cl_2]_0^{calcd}$, M	S^m
argon-purged	3.11	0.80
argon-purged	2.19	0.93
argon-purged	1.60	1.04
argon-purged	1.12	1.12
argon-purged	0.61	1.33
argon-purged	0.27	2.72
air-saturated	3.40	0.92
air-saturated	1.61	1.50
air-saturated	0.28	4.56
thoroughly degassed	2.84	0.67
thoroughly degassed	1.43	0.67
thoroughly degassed	0.39	0.76

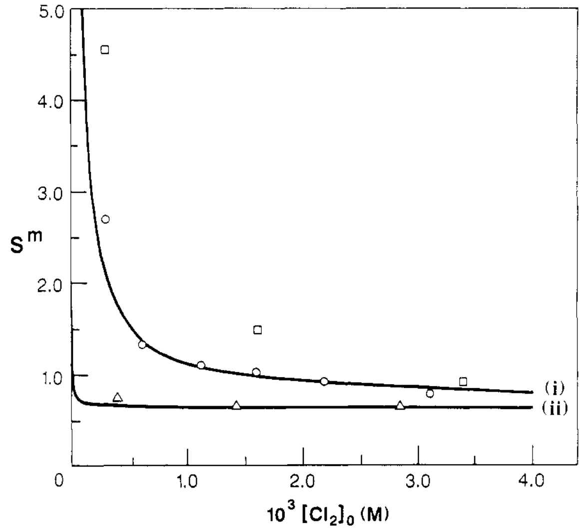

Figure 1. S^m as a function of the initial chlorine concentration, $[Cl_2]_0$ for the photochlorination of neat DMB at room temperature: purged with argon (○); saturated with air (□); and thoroughly degassed (△). Solid lines represent theoretical curves calculated from eq I with $k^{p\to t}/k_p^{Cl_2} = 1.3 \times 10^{-5}$ (i), 1×10^{-7} (ii).

There is also a second potential explanation for the variations in S^m with $[Cl_2]_0$. This involves a more direct "degradation" of primary DMB radicals to tertiary DMB radicals, i.e., reaction 1. At high concentrations of molecular chlorine the primary alkyl radicals must react mainly with Cl_2 to form 1-ClDMB, rate constant $k_p^{Cl_2}$. However, at a sufficiently low chlorine concentration the reaction of the primary alkyl radical with DMB to form the tertiary radical, rate constant $k^{p\to t}$, might begin to compete with the chlorination. Hence, as the Cl_2 concentration is decreased, the *apparent* selectivity for attack of $Cl^\bullet$ on DMB as measured by S^m *must* start to increase if reaction 1 is operative.

$$(CH_3)_2CHCH(CH_3)\dot{C}H_2 + DMB \xrightarrow{k^{p\to t}} DMB + (CH_3)_2CH\dot{C}(CH_3)_2 \quad (1)$$

Samples of neat DMB were purged with argon, and varying initial concentrations of chlorine were added in

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[27] It was not possible to analyze quantitatively for $CHCl_3$ because its GC retention time put it in the "tail" of the DMB peak and because it has a very poor response factor by FID.

the dark (see the Experimental Section). Photochlorinations were carried to completion and GC analyses yielded the S^m values given in the first section of Table IV. Again, there is a clear and dramatic increase in S^m as $[Cl_2]_0$ was decreased (see also Figure 1). However, in this system the dependence of S^m on $[Cl_2]_0$ only becomes evident at much lower initial chlorine concentrations than were required for photochlorination in the presence of CCl_4. This would suggest that the direct "degradation" of the primary to tertiary radical (reaction 1) is much slower than the pathway involving chlorine abstraction from CCl_4 (Scheme I). That is, $k^{p\to t}$[DMB] (reaction 1) must be much less than $(k_p^{CCl_4} + k_t^{CCl_4})[CCl_4]$ (Scheme I). Taking [DMB] = 7.68 M (Table IV and Figure 1) and $[CCl_4]$ = 0.98 M (Table II), an upper limit may be set for $k^{p\to t}$. Assigning $k_p^{CCl_4}$ and $k_t^{CCl_4}$ as 5.8×10^4 and 3.1×10^4 $M^{-1}\ s^{-1}$, respectively (the values for n-Bu$^\bullet$ and t-Bu$^\bullet$, respectively, at 27 °C),[15] $k^{p\to t}$ must be much less than $1 \times 10^4\ M^{-1}\ s^{-1}$.

The foregoing limit on the magnitude of $k^{p\to t}$ is consistent with the limited data available on alkyl radical/alkane reactions although this would appear not to contain information regarding the abstraction of tertiary hydrogens from alkanes by primary alkyl radicals in solution.[28,29] In order to remedy this deficiency and to obtain an actual value for $k^{p\to t}$ at ambient temperatures we resorted to a well-developed experimental procedure employing EPR spectroscopy.[31] Photolysis of pentanoyl peroxide in neat DMB directly in the cavity of a Varian E104 EPR spectrometer with UV light from a 1000-W high-pressure mercury lamp gave detectable signals from both the n-butyl radical and the 2,3-dimethylbut-2-yl radical at temperatures ranging from 293 to 353 K. Under the conditions of this experiment the overall reaction scheme can be represented as

$$(CH_3CH_2CH_2CH_2CO_2)_2 \xrightarrow{h\nu} 2CH_3CH_2CH_2CH_2^\bullet + 2CO_2$$

$$CH_3CH_2CH_2CH_2^\bullet + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{k^{p\to t}} CH_3CH_2CH_2CH_3 + (CH_3)_2CH\dot{C}(CH_3)_2$$

$$\left.\begin{array}{l} CH_3CH_2CH_2CH_2^\bullet + CH_3CH_2CH_2CH_2^\bullet \xrightarrow{2k_t} \\ CH_3CH_2CH_2CH_2^\bullet + (CH_3)_2CH\dot{C}(CH_3)_2 \xrightarrow{k_t} \\ (CH_3)_2CH\dot{C}(CH_3)_2 + (CH_3)_2CH\dot{C}(CH_3)_2 \xrightarrow{2k_t} \end{array}\right\} \text{nonradical products}$$

It is now firmly established[31,32] that simple, nonhindered alkyl radicals react with one another at the diffusion-controlled limit, i.e., the rate constants $2k_t$ in the above reaction scheme will all be equal. Under steady and continuous photolysis where the radical concentrations do not change significantly with time, a simple kinetic analysis yields the relation[31]

$$\frac{k^{p\to t}}{2k_t} = \frac{[(CH_3)_2CH\dot{C}(CH_3)_2]}{[DMB]}\left(1 + \frac{[(CH_3)_2CH\dot{C}(CH_3)_2]}{[CH_3CH_2CH_2CH_2^\bullet]}\right)$$

Table V. EPR Study of the Reaction of *n*-Butyl Radicals with DMB[a]

T, K	10^8-[n-Bu$^\bullet$], M	10^8-[2-DMB$^\bullet$], M	$10^8 k^{p\to t}/(2k_t)$	$10^{-9} 2k_t$,[b] $M^{-1}\ s^{-1}$	$k^{p\to t}$, $M^{-1}\ s^{-1}$
293	16	8.0	1.6	9.3	150
303	15	10	2.2	11	240
313	29	18	3.8	12	460
323	7.4	25	14	14	2000
333	2.8	31	8.5	15	1300
343	6.8	31	22	17	3700
353	6.0	41	42	19	8000

[a] Pentanoyl peroxide (0.37 M) in neat DMB (7.7 M). [b] Data for the *tert*-butyl radical bimolecular self-reaction in n-heptane from ref 32d corrected[33] for the difference in viscosity between n-heptane and DMB.

At a known concentration of DMB the measurement of the absolute concentrations of $(CH_3)_2CH\dot{C}(CH_3)_2$ and of $CH_3CH_2CH_2CH_2^\bullet$ under steady-state conditions, in the usual way by double integration of appropriate lines in their EPR spectra, will therefore yield $k^{p\to t}/2k_t$. These data are presented in Table V.

In order to calculate $k^{p\to t}$ we need to know the values of $2k_t$ at each temperature. Rather than measure these rate constants, we made use of Schuh and Fischer's[32d] very carefully determined values of $2k_t$ for the bimolecular self-reaction of the *tert*-butyl radical in n-heptane over a range of temperatures and applied a small correction for the slight difference in the viscosities of n-heptane and DMB.[33] The values of $2k_t$ estimated in this way and the values of $k^{p\to t}$ derived therefrom are also listed in Table V. These rate constants yield the Arrhenius relation

$$\log (k^{p\to t}/M^{-1}\ s^{-1}) = (12.0 \pm 1.0) - (13.6 \pm 1.5)/\Theta$$

where $\Theta = 2.3RT$ kcal/mol and the errors correspond to two standard deviations. The preexponential factor is certainly too high,[34] which probably reflects the difficulties encountered in measuring absolute radical concentrations. We therefore take a "normal" value[34] for this preexponential factor of $10^{8.5}\ M^{-1}\ s^{-1}$ and mean $k^{p\to t}$ values determined near the middle of our temperature range and calculate an activation energy of 8.0 kcal/mol, i.e., $\log (k^{p\to t}) = 8.5 - 8.0/\Theta$. From this Arrhenius equation we can calculate that $k^{p\to t} \simeq 450\ M^{-1}\ s^{-1}$ at 27 °C. This value for $k^{p\to t}$ is probably rather more reliable than the value of ca. 200 $M^{-1}\ s^{-1}$ that would be estimated by a simple interpolation between the $k^{p\to t}$ values measured at 20 °C and at 30 °C (see Table V).

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(28) For a comprehensive listing of alkyl radical/molecule reactions in solution, see: Asmus, K.-D.; Bonifačić, M. *Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part b.

(29) For general comparison, rate constants in the range 5×10^2 to $5 \times 10^3\ M^{-1}\ s^{-1}$ have been measured at room temperature for the reactions: $CH_3^\bullet + CH_3CH_2X \to CH_4 + CH_3\dot{C}HX$ (X = OH, CN, CO_2H, CO_2CH_3) in water.[28] From gas phase data,[30] we calculate room temperature rate constants of ca. 70 and 310 $M^{-1}\ s^{-1}$ for the reaction of $CH_3^\bullet$ with cyclohexane and isobutane, respectively.

(30) Tedder, J. M. *Tetrahedron* **1982**, *38*, 313–329; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 401–410.

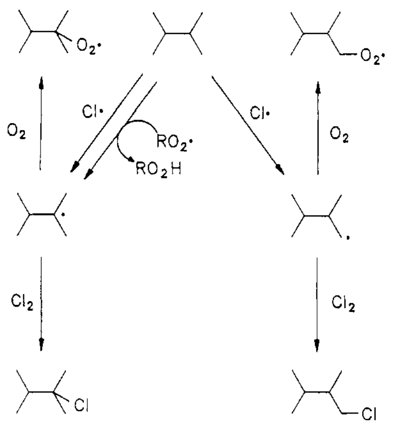
(31) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193–200 and references cited therein.

(32) (a) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491–494. (b) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1974**, *6*, 453–456. (c) Schuh, H.; Fischer, H. *Ibid.* **1976**, *8*, 341–356; (d) *Helv. Chim. Acta* **1978**, *61*, 2130–2164; (e) *Ibid.* **1978**, *61*, 2463–2481. (f) Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705–713. (g) Paul, H.; Segaud, C., *Ibid.* **1980**, *12*, 637–647. (h) Huggenberger, C.; Fischer, H., *Helv. Chim. Acta* **1981**, *64*, 338–353. (i) Münger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1984**, *16*, 1213–1226. (j) Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555–2559. (k) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200–206 and references cited therein.

(33) (a) At 30 °C, the viscosity of n-heptane can be calculated to be 0.367 cP from the reported[32d] parameters A_η and E_η. The viscosity of DMB, at this temperature, is 0.303 cP.[33b] Thus the ratio of viscosities for n-heptane to DMB is 1.2:1.0. This implies that $2k_t$ will be 1.2 times greater in DMB than in n-heptane at 30 °C. Since the "activation energies" for the viscosities of n-heptane[32d] and DMB[33b] are almost identical, viz. 1.8 and 1.9 kcal/mol, respectively, the ratio of viscosities was taken to be 1.2:1.0 at all temperatures. (b) Dobis, O. *J. Chem. Phys.* **1976**, *65*, 4264–4271.

(34) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

Scheme II



We can determine S^m_∞ by kinetic analysis of the data given in Tables II–IV. A plot of S^m vs $1/[Cl_2]_0$ yields S^m_∞ as the intercept because no carbon tetrachloride participation or radical degradation process can compete with chlorination at infinite $[Cl_2]_0$. Such plots give S^m_∞ values of about 0.64, which are consistent with the S^m values found for chlorination conducted by bubbling pure chlorine through neat DMB or DMB in cyclohexane (see Table I).

Kinetic analysis of the direct degradation process shown in reaction 1 yields the following integrated rate expression (see supplementary material):

$$S^m = \frac{S^m_\infty + (a[\mathrm{DMB}]/[Cl_2]_0)\ln(1 + [Cl_2]_0/(a[\mathrm{DMB}]))}{1 - (a[\mathrm{DMB}]/[Cl_2]_0)\ln(1 + [Cl_2]_0/(a[\mathrm{DMB}]))} \qquad (\mathrm{I})$$

where $a = k^{p\rightarrow t}/k_p^{Cl_2}$.

Taking $S^m_\infty = 0.64$, the data in the first section of Table IV obtained with argon-purged DMB can be fitted to eq I to give $k^{p\rightarrow t}/k_p^{Cl_2} = 1.3 \times 10^{-5}$ (see Figure 1). If we take $k^{p\rightarrow t} = 450\ M^{-1}\ s^{-1}$ (vide supra) we obtain $k_p^{Cl_2} = 3.5 \times 10^7\ M^{-1}\ s^{-1}$ at 27 °C. There would appear to be no reliable measurements of $k_p^{Cl_2}$ in solution[28,35] with which to compare this result. However, gas-phase studies[37] suggest that the reaction of molecular chlorine with alkyl radicals should occur at, or near, the diffusion-controlled limit in solution, i.e., $k_p^{Cl_2}$ would be expected to have a value of ca. $10^{10}\ M^{-1}\ s^{-1}$.[39] We therefore sought an alternative explanation for the higher values of S^m in neat DMB at low $[Cl_2]_0$.

If small amounts of residual oxygen were present in the solutions with low $[Cl_2]_0$, a competition between O_2 and Cl_2 for the DMB radicals would be established (Scheme II). Peroxyl radicals are highly selective hydrogen atom abstracting agents and hence any chain propagation by the peroxyl radicals would enhance S^m values.

Chlorination of neat, air-saturated DMB gave higher S^m values than had been obtained with argon-purged DMB (Table IV and Figure 1). Furthermore, very carefully degassed DMB (see the Experimental Section) gave S^m values that were lower than those obtained with the argon-purged DMB (Table IV and Figure 1). These last mentioned S^m values are consistent with the theoretical curve calculated from the integrated rate expression, I, taking $k^{p\rightarrow t}/k^{Cl_2} = 1 \times 10^{-7}$ (see Figure 1). Since $k^{p\rightarrow t} = 450\ M^{-1}\ s^{-1}$ (vide supra), $k_p^{Cl_2}$ can be calculated to be ca. $5 \times 10^9\ M^{-1}\ s^{-1}$, which confirms that the reaction of primary alkyl radicals with molecular chlorine proceeds at the diffusion-controlled rate. We conclude that at low chlorine concentrations S^m values can be strongly influenced by trace amounts of oxygen, i.e., enhanced S^m values arise from the reactions shown in Scheme II and not from the direct degradation process of reaction 1. Indeed, it would take extremely thorough deoxygenation and extremely low chlorine concentrations for reaction 1 to have a significant influence on S^m.

Discussion

Our results show that measured selectivities, S^m, for the photochlorination of DMB are not necessarily equal to the limiting value, S^m_∞, corresponding to the ratio of the rate constants for abstraction of tertiary and primary hydrogens from DMB by a "free" chlorine atom in "noncomplexing" solvents. Instead, S^m can be *greater* than S^m_∞ both because of CCl_4 and O_2 participation in the chain reaction at low chlorine concentrations. Furthermore, values of S^m can be lower than S^m_∞ when working with low concentrations of DMB in the "inert" (to $Cl^\bullet$) solvent, CCl_4 because of a selective loss of 2-ClDMB by "in-cage" (geminate) chlorination,[11] i.e., $Cl^\bullet$/2-ClDMB geminate pairs must react more rapidly than the $Cl^\bullet$/1-ClDMB geminate pairs. Reliable values of S^m_∞ can be most readily obtained from measured [2-ClDMB]/[1-ClDMB] ratios by working with deoxygenated, neat DMB and high concentrations of chlorine.

Finally, the rather remote possibility that the chlorine atom might be complexed, and hence more selective, in alkane solvents was explored by measuring the value of S^m in the gas phase. The photoinitiated chlorination of 30 Torr DMB containing ca. 1 Torr Cl_2 at room temperature gave, on complete reaction, S^m values in the range 0.61–0.62. Such a gas-phase S^m value is not sensibly different from the value of 0.64 deduced for S^m_∞ from the chlorination of neat DMB. We conclude, therefore, that chlorine atoms either are not complexed in alkane solvents or, that if they are complexed, such complexation has little effect on their selectivity as hydrogen abstractors.

Experimental Section

Commercially available materials were purified by normal procedures before use. Solutions were deoxygenated by bubbling with argon for 30 min, unless otherwise specified. GC analyses were performed in triplicate on a Varian 3700 gas chromatograph fitted with a 100 m, 0.25 mm i.d. 007 methyl silicone column. The exact conditions have been described previously.[11]

Reactions with Known Initial Concentrations of Chlorine. CCl_4 was saturated with Cl_2 (1.69 M) by bubbling with 100% Cl_2 for 15–30 min at room temperature. Aliquots of this solution were diluted with additional argon-purged CCl_4 to obtain solutions containing a range of Cl_2 concentrations. For the photochlorination of 6.91 M DMB (Table II), samples of one of these solutions of Cl_2 in CCl_4 (0.10 mL) were added to argon-purged DMB (0.90 mL), and the resultant mixture was exposed to ambient light at room temperature. After complete consumption of the chlorine, the reaction products were analyzed by GC. For

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(35) The only alkyl radical/Cl_2 rate constant listed in ref 28 is almost certainly too low, viz.[36] $1.5 \times 10^6\ M^{-1}\ s^{-1}$ for $c\text{-}C_6H_{11}^\bullet + Cl_2$.

(36) Kosorotov, V. I.; Dzhagatspanyan, R. V. *Kinet. Katal.* **1978**, *19*, 1123–1126.

(37) For the reaction of Cl_2 with $CH_3^\bullet$, $CH_3CH_2^\bullet$, $(CH_3)_2CH^\bullet$, and $(CH_3)_3C^\bullet$, the rate constants at 25 °C are 1.2×10^9, 1.1×10^{10}, 3.4×10^{10}, and $2.7 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively.[38a] Somewhat lower values for the reactions of Cl_2 with $CH_3^\bullet$ and $CH_3CH_2^\bullet$, have also been reported, viz 2.90×10^8 and $2.73 \times 10^9\ M^{-1}\ s^{-1}$, respectively, at 25 °C.[38b]

(38) (a) Timonen, R. S.; Gutman, D. *J. Phys. Chem.* **1986**, *90*, 2987–2991. (b) Timonen, R.; Kalliorinne, K.; Koskikallio, J. *Acta Chem. Scand. A* **1986**, *40*, 459–466.

(39) The reactions of alkyl radicals with I_2 certainly are diffusion-controlled.[28,40] The reaction of the cyclopropylcarbinyl radical with Br_2 has been recently estimated to be $2.2 \times 10^{10}\ M^{-1}\ s^{-1}$ at 15 °C.[41]

(40) Foldiak, G.; Schuler, R. H. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1983**, *38A*, 1154–1155.

(41) Tanko, J. M.; Skell, P. S.; Seshadri, S. *J. Am. Chem. Soc.* **1988**, *110*, 3221–3225.

the photochlorination of 0.48 M DMB in 6.88 M c-C_6H_{12} (Table III), the procedure involved the addition of a solution of Cl_2 in CCl_4 (0.20 mL) to argon-purged cyclohexane (0.80 mL) containing DMB (0.066 mL), followed by reaction and GC analysis. The photochlorination of neat DMB was carried out by bubbling 7% Cl_2–N_2 through argon-purged DMB (2 mL) for a short time (2–30 s) in the dark, sealing the tube and then allowing the reaction to proceed to completion in the presence of light. In all these systems, the initial concentration of chlorine was calculated from the measured total yields of monochlorides. The data presented in Tables II and III have been corrected to allow for the 2-ClDMB that was formed by reaction of $Cl_3C^•$ radicals with DMB.

The photochlorination of thoroughly degassed DMB was accomplished in the following way. Neat DMB (10 or 50 mL), together with a glass-coated magnet were introduced into a Pyrex reaction vessel containing a break-seal. The DMB was degassed on a high-vacuum line by six freeze–thaw cycles and sealed under vacuum. Chlorine gas was measured (manometer with no exposed mercury) and sealed into a 1.0-mL tube separated from the DMB by the glass break-seal. This was then broken (in the dark), and the resulting Cl_2/DMB solution was stirred to ensure homogeneity. The photochlorination and analysis were carried out in the usual way. The yield of DMB chlorides agreed, within experimental error, with the calculated amount of chlorine added.

Relative Reactivities of DMB and Cyclohexane toward the Trichloromethyl Radical. *n*-Decanoyl peroxide (20 mg, 0.058 mmol) was dissolved in a deoxygenated mixture of DMB (0.25 mL, 1.92 mmol), cyclohexane (0.25 mL, 2.30 mmol), and carbon tetrachloride (0.50 mL). The solution was maintained at 40 °C for 17 days and was then analyzed by GC. From the relative yields of DMB monochlorides and cyclohexyl chloride, the relative reactivity of the two alkanes toward $Cl_3C^•$ was calculated. The selectivity for the DMB chlorination, under these conditions, was also measured.[25]

EPR Measurements. Deoxygenated solutions of DMB (0.40 mL) containing *n*-pentanoyl peroxide (30 μL) were photolyzed in the cavity of a Varian E104 EPR spectrometer with a 1000-W high-pressure mercury lamp. Relative concentrations of *n*-butyl and tertiary DMB radicals were determined by manual double integration of appropriate lines in the first-derivative EPR spectrum. Absolute radical concentrations were calibrated against DPPH,[42] with all measurements being made in the same tube.

Gas-Phase Chlorination. A 1-L reaction bulb on a specially constructed vacuum line (no greased stopcocks, no exposed mercury) was evacuated and filled with DMB vapor at 30 Torr. A small quantity (ca. 1 Torr) of Cl_2 was delivered to this bulb from a reservoir at 100 Torr. The reaction bulb was irradiated for 48 h, and the products were then condensed and subjected to GC analysis.

Acknowledgment. We thank Professor G. A. Russell for some extremely helpful comments that led us to initiate the present work.

Registry No. DMB, 79-29-8; 2-DMB$^•$, 24436-98-4; CCl_4, 56-23-5; c-C_6H_{12}, 110-82-7; $Cl_3C^•$, 3170-80-7; $(CH_3CH_2CH_2CH_2CO_2)_2$, 925-19-9; $CH_3CH_2CH_2CH_2^•$, 2492-36-6.

Supplementary Material Available: Derivation of the integrated rate expression, I (2 pages). Ordering information is given on any current masthead page.

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[42] Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* 1971, *93*, 903–908.

β-Scission of 8-Hydrindanoxyl and Related Free Radicals

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The β-scission of alkoxyl free radicals prepared from thermolysis (77 °C) of the in situ generated hypoiodite derived from structurally related hydrindan-8-ol and hydrinden-8-ol systems was examined. The course of alkoxyl radical β-scission was sensitive to changes in alkyl substitution at the ring junction site and olefin introduction in the hydrindan skeleton. Thus, the cleavage pattern must reflect the interplay of multiple thermodynamic and kinetic factors.

Alkoxyl free radicals undergo a variety of synthetically useful intramolecular hydrogen abstraction and β-scission processes. We have been examining the potential of β-scission reactions of alkoxyl free radicals, situated at ring fusion sites, for the synthesis of medium- and large-ring systems via selective carbon–carbon bond cleavage.[1] Our initial studies on the course of alkoxyl radical β-scission in 9-decalinoxyl and several structurally related free radicals demonstrated that the mode of alkoxyl fragmentation in these systems is highly sensitive to changes in the molecular geometry of the precursor alcohol. The mode of β-scission in unsymmetrical alkoxyl free radicals[2,3] has been rationalized by considerations of the relative stabilities of the resultant carbon-centered free radical and carbonyl[4] or cyclic ketone components,[5] by analysis of stereoelectronic factors,[6] and by frontier molecular orbital theory.[7]

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[2] For reviews of alkoxy radical β-scission, see: (a) Ramaiah, M. *Tetrahedron* 1987, *43*, 3541. (b) Brun, P.; Waegell, B. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, pp 367. (c) Kochi, J. K. *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, p 665. (d) Minisei, F.; Citterio, A. *Advances in Free Radical Chemistry*; Williams, C. H., Ed.; Heyden: London, 1980; Vol. 6, p 128.

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[6] (a) Brun, P.; Waegell, B. *Tetrahedron* 1976, *32*, 517. (b) Bensadoun, N. I.; Brun, P.; Casanova, J.; Waegell, B. *J. Chem. Res., Synop.* 1981, 236 and references therein.

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