

Free Radical Chlorinations in Halogenated Solvents: Are There Any Solvents Which Are Truly Noncomplexing?†

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The free radical chlorination of alkanes was examined in several solvents. The results of these experiments suggest that Cl• forms complexes with halogenated solvents and that these complexes exhibit higher selectivity in hydrogen abstractions than “free” chlorine atom. The observed selectivity decreases with increasing Cl-content of the solvent (paralleling the increase in the ionization potential of the solvent), and selectivity is greater in bromoalkane solvents compared to chloroalkanes, suggesting that these are donor/acceptor-type complexes.

I. Introduction

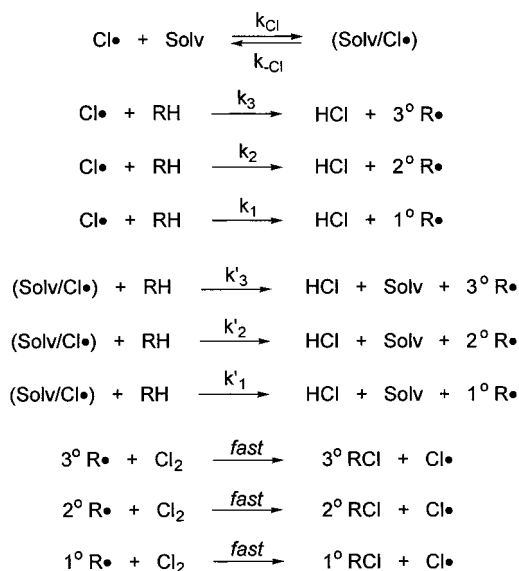
In 1957–1958, Russell demonstrated that the observed selectivity in the free radical chlorinations is significantly increased when the reaction is conducted in an aromatic solvent.¹ For example, in the chlorination of 2,3-dimethylbutane (23DMB), the 3° vs 1° selectivity of Cl• on a per-hydrogen basis, $S(3°/1°)$,² is 4.2:1 when the reaction is conducted in neat 23DMB. In 8 M benzene, the selectivity increases to 59:1. Russell suggested that in aromatic solvents, two hydrogen abstractors are in equilibrium: “Free” chlorine atom and a complex between chlorine atom and the aromatic solvent (Scheme 1, Solv = C₆H₆). The conclusion that these two species were in equilibrium was based on the fact that $S(3°/1°)$ did not appear to vary with [23DMB]. These conclusions were subsequently confirmed by Walling and Mayahi.³

In 1983, Skell found that in contrast to Russell’s initial observations, $S(3°/1°)$ did vary as a function of [23DMB].⁴ (These workers examined a much broader range of concentrations than Russell and Walling.) Specifically, it was found that at high 23DMB concentrations the selectivity approached that of free Cl atom, while at lower alkane concentrations, selectivity varied with concentration in a nonlinear fashion. Based upon Scheme 1, a kinetic expression (eq 1, where $S_0 = k_3/k_1$ and $S_X = k'_3/k'_1$) can be written which expresses the observed selectivity as a function of the pertinent rate constants. All experimental results are consistent with this kinetic scheme.

$$S(3°/1°) = 6 \frac{[3°\text{RCl}]}{[1°\text{RCl}]} = 6 \frac{\left[S_0 \frac{k_{-Cl}}{K_1} + S_0(S_X + 1)[\text{RH}] + S_X \frac{k_{Cl}}{K_1} [\text{Solv}] \right]}{\left[\frac{k_{-Cl}}{K_1} + (S_X + 1)[\text{RH}] + \frac{k_{Cl}}{K_1} [\text{Solv}] \right]} \quad (1)$$

In 1985, in addition to confirming the experimental observations of Skell regarding the effect of alkane

Scheme 1



concentration, employing laser flash photolysis, Ingold et al. recorded the UV/vis spectrum of the PhH/Cl• complex and reported absolute rate constants for all of the kinetically significant steps in Scheme 1 ($k_3 + k_1 = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k'_3 + k'_1 = 4.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{Cl} = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{Cl}/k_{-Cl} = 200 \text{ M}^{-1}$ for RH = 23DMB and Solv = C₆H₆).⁵

There has been considerable discussion in the recent literature regarding the precise structure of the chlorine atom/benzene complex (i.e., a hexahapto π -complex vs a 6-chlorocyclohexadienyl radical or σ -complex). However, this debate over structure has not been satisfactorily resolved and, moreover, is not germane to this paper.⁶

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(2) $S(3°/1°) = 6([3°\text{RCl}]/[1°\text{RCl}])$.

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† This paper is dedicated to Prof. Glen A. Russell (1925–1998).

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Table 1. Chlorine Atom Selectivity ($3^\circ/1^\circ$ and $2^\circ/1^\circ$) in Several Chlorinated and Brominated Solvents at 20°C

solvent ^a	$S(2^\circ/1^\circ)$	$S(3^\circ/1^\circ)$
CCl_4^b	1.81 ± 0.03	3.0 ± 0.1
$\text{CHCl}_2\text{CCl}_3$	1.81 ± 0.02	3.1 ± 0.1
CHCl_3	1.94 ± 0.02	3.3 ± 0.1
$\text{CCl}_3\text{CH}_2\text{Cl}$	1.97 ± 0.03	3.4 ± 0.1
$\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$	1.98 ± 0.03	3.5 ± 0.1
$\text{CHCl}_2\text{CHCl}_2$	1.98 ± 0.04	3.5 ± 0.2
$\text{CHCl}_2\text{CH}_2\text{Cl}$	2.11 ± 0.04	3.7 ± 0.1
CH_2Cl_2	2.13 ± 0.05	3.6 ± 0.1
$\text{CH}_2\text{ClCH}_2\text{Cl}$	2.76 ± 0.04	5.2 ± 0.2
$(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$	3.11 ± 0.06	6.2 ± 0.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	3.32 ± 0.06	6.8 ± 0.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	3.45 ± 0.07	7.1 ± 0.2
$\text{CH}_3\text{CH}_2\text{Cl}$	3.56 ± 0.06	7.8 ± 0.2
$\text{CH}_3\text{CHClCH}_2\text{CH}_3$	3.62 ± 0.05	7.9 ± 0.1
$\text{CH}_3\text{CHClCH}_3$	3.70 ± 0.07	8.2 ± 0.2
$(\text{CH}_3)_3\text{CCl}$	3.91 ± 0.06	8.9 ± 0.3
$\text{CH}_3\text{CH}_2\text{Br}$	8.81 ± 0.12	38.0 ± 1.0

^a Substrate concentration = 0.64 M; solvent concentration = 7.0 M. ^b $[\text{CCl}_4] = 8.6\text{ M}$.

In addition to complexes between $\text{Cl}\cdot$ and aromatic solvents, other halogen atom/solvent complexes have been reported which result in enhanced selectivities: $\text{Cl}\cdot/\text{CS}_2$,^{1,7} $\text{Cl}\cdot/\text{pyridine}$,^{8,9} and $\text{Br}\cdot/\text{CS}_2$.¹⁰ It has generally been assumed that nonaromatic solvents have no pronounced effect on chlorine atom selectivity. However, in a preliminary report,¹¹ we noted that enhanced selectivities were observed when the chlorination is conducted in chlorinated solvents and that the observed selectivity increases as the number of chlorine atoms in the solvent decreases. In this paper, we expand this study in an attempt to elucidate the origin of this solvent effect.

II. Results and Discussion

The selectivity of $\text{Cl}\cdot$ toward 3° vs 1° hydrogens on a per-hydrogen basis, $S(3^\circ/1^\circ)$, was determined in several chlorinated and brominated solvents by using 23DMB as a substrate. Similarly, $S(2^\circ/1^\circ)$ was determined by utilizing *n*-hexane, *n*-heptane, and *n*-octane as substrates. The selectivity was calculated by determining the relative amounts of monochlorides ($3^\circ/1^\circ$ or $2^\circ/1^\circ$) produced under conditions where $[\text{RH}]_{\text{init}}/[\text{Cl}_2]_{\text{init}} > 10$ (i.e., less than 10% alkane conversion). Reactions were carried out in sealed ampules at 20°C and were photo-initiated. Product yields were determined by GLC. For the calculation of $S(2^\circ/1^\circ)$, the total quantity of secondary monochlorides was used because the reactivities of the different secondary C–H bonds are nearly equal. The results are summarized in Table 1.

Additional evidence for enhanced selectivity in haloalkane solvents was provided by kinetic isotope effects, $k_{\text{H}}/k_{\text{D}}$, which were measured for cyclohexane and cyclohexane- d_{12} chlorination via competition reactions vs 23DMB. The

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Table 2. Chlorination of *n*-Hexane with Molecular Chlorine in the Presence of Molecular Bromine

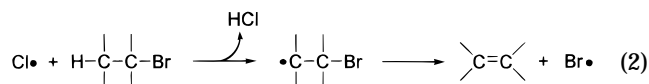
$[\text{Br}_2]_{\text{init}}/[\text{Cl}_2]_{\text{init}}$	$S(2^\circ/1^\circ)$	$\Sigma[\text{RBr}]/\Sigma[\text{RCl}]^a$
0.000	1.83 ± 0.03	0.00
0.020	2.13 ± 0.04	0.03 ± 0.005
0.045	2.36 ± 0.05	0.07 ± 0.01
0.077	2.49 ± 0.04	0.15 ± 0.01
0.123	2.60 ± 0.06	0.31 ± 0.04
0.185	2.90 ± 0.05	0.48 ± 0.05

^a Ratio of monobromides to monochlorides produced.

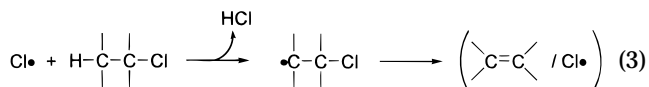
rate constant ratio $k_{\text{H}}/k_{\text{D}}$ was found to be 1.09 (± 0.05) in the absence of haloalkane and 1.74 (± 0.10) in the presence of 10 M bromoethane.

The results in Table 1 demonstrate that chlorine atom selectivity varies significantly in chlorinated solvents, with selectivity decreasing with increasing chlorine content of the solvent. Even greater selectivity was found in brominated solvents. This variation in selectivity does not correlate with any “normal” solvent property (e.g., dielectric constant, viscosity, or internal pressure).

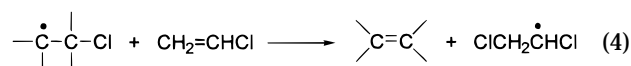
A. β -Hydrogen Abstraction from Solvent as an Explanation for Enhanced Selectivity. It is plausible that the exceptionally high selectivities observed in the monohalogenated solvents may arise from competing chains involving intermediates produced from β -hydrogen abstraction from solvent by $\text{Cl}\cdot$. For brominated solvents, β -hydrogen abstraction could lead to $\text{Br}\cdot$ via β -scission of β -bromoalkyl radicals (eq 2).¹² Bromine atom is documented to exhibit exceptionally high selectivities in hydrogen abstractions from alkanes.¹³



For monochlorinated solvents, it is conceivable that β -hydrogen abstraction could lead to a $\text{Cl}\cdot$ /olefin complex as illustrated in eq 3 and that this complex is a more selective hydrogen abstractor than free $\text{Cl}\cdot$.



Starnes has provided kinetic evidence for complexes of this type formed in the polymerization of vinyl chloride (eq 4).¹⁴ Whether these $\text{Cl}\cdot$ /olefin complexes are β -chloroalkyl radicals or $\text{Cl}\cdot$ /alkene π -complexes is unclear; however, Starnes' results do demonstrate that these complexes participate in bimolecular reactions ($\text{Cl}\cdot$ transfer) rather than release free $\text{Cl}\cdot$.



To examine the potential importance of $\text{Br}\cdot$ chains in bromoalkane solvents, the chlorination of hexane in CCl_4 was examined in the presence of Br_2 at several $\text{Br}_2:\text{Cl}_2$ ratios (Table 2). As expected, in the presence of Br_2 ,

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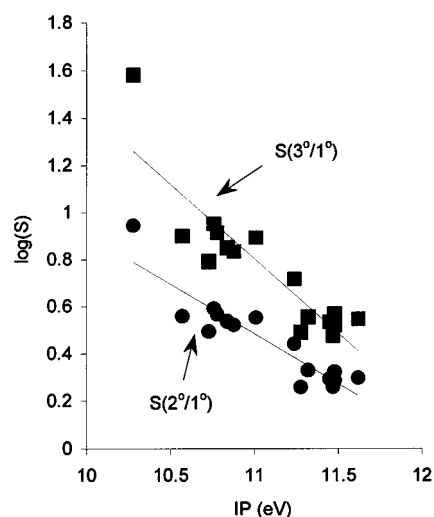
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Table 3. Chlorination of 23DMB in Neopentyl Bromide^a

[C ₅ H ₁₁ Br], M	<i>S</i> (3°/1°)
0.00	3.00 ± 0.10
2.65	20.8 ± 2.0
3.97	25.6 ± 1.8
5.30	33.4 ± 1.9
6.62	31.9 ± 2.7
7.28	34.2 ± 3.0

^a [23DMB] = 0.64 M, 25 °C, CCl₄ as diluent solvent.**Table 4. Chlorination of 23DMB in Neopentyl Chloride^a**

[C ₅ H ₁₁ Cl], M	<i>S</i> (3°/1°)
0.00	3.00 ± 0.10
2.71	4.5 ± 0.2
4.06	5.2 ± 0.3
5.42	5.8 ± 0.5
6.77	6.2 ± 0.6
7.45	6.3 ± 0.5

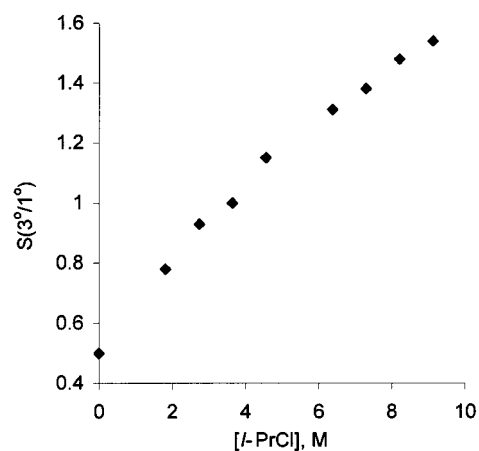
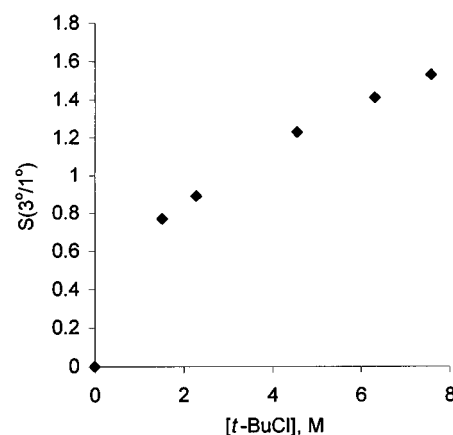
^a [23DMB] = 0.64 M, 25 °C, CCl₄ as diluent solvent.**Figure 1.** Variations in selectivity for chlorination of alkanes in haloalkane solvents as a function of the ionization potential of the solvent.

significant quantities of alkylbromides are formed.¹⁵ However in all cases, Cl• selectivity is observed. These observations demonstrate that Br• is an ineffective chain carrier in these reactions.

Even more compelling evidence against β-hydrogen abstraction from solvent as the etiology for enhanced selectivity was obtained by conducting the chlorinations in haloalkane solvents which do not possess β-hydrogens (Tables 3 and 4). For chlorinations in both neopentyl chloride and bromide solvents, high selectivities were observed.

B. Complexation between Chlorine Atom and Halogenated Solvents as an Explanation for Enhanced Selectivity. Using the data in Table 1, a good correlation is found between selectivity (or more appropriately, log(*S*)) and the vertical ionization potential (IP) of the solvent (Figure 1). This observed variation of selectivity with IP is consistent with the proposition that chlorine atom forms a donor/acceptor complex with halogenated molecules,¹⁶ and that this complex exhibits higher selectivity in hydrogen abstractions than “free”

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**Figure 2.** Chlorination of 23DMB in isopropyl chloride: Variation of *S*(3°/1°) with solvent concentration (0.64 M 23DMB, 20 °C, CCl₄ as diluent solvent).**Figure 3.** Chlorination of 23DMB in *tert*-butyl chloride: Variation of *S*(3°/1°) with solvent concentration (0.64 M 23DMB, 20 °C, CCl₄ as diluent solvent).

chlorine atom. (For chlorinations in aromatic solvents, both the selectivity¹⁷ and rate¹⁸ of formation of Cl•/arene complexes also vary with the ionization potential of the solvent).

To provide further evidence for complex formation, 23DMB chlorination selectivity was examined over a wide range of solvent and hydrocarbon concentrations for selected haloalkane solvents. The results are summarized in Figures 2–4. Over the range of haloalkane and 23DMB concentrations studied, the plots of *S*(3°/1°) vs [Solv] or vs [23DMB] were hyperbolic, in direct analogy to what is found for chlorination in aromatic solvents, where complex existence is clearly established. A similar concentration dependence for the chlorination of *n*-heptane and *n*-hexane was reported earlier.¹¹ On the basis of these observations, we suggest that a donor/acceptor complex is produced between chlorine atom and

(16) A common criteria for the assignment of charge-transfer complexes is linearity in the plot of the charge-transfer energy of several complexes with the same acceptor against the vertical ionization potential of the donor, see Bühler, R. E.; Ebert, M. *Nature* **1967**, 214, 1220. Bühler, R. E. *Radiat. Res. Rev.* **1972**, 4, 233.

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Table 5. Kinetic Parameters for Chlorination of Alkanes in Haloalkane Solvents^a

solvent/substrate	K_3/K_1 or K_2/K_1	k_{Cl}/k_1	k_{-Cl}/K_1
(CH ₃) ₂ CHCl/ <i>n</i> -hexane (ref 11)	8.3 ± 0.5 (6.2 ± 0.4)	1.1 ± 0.1 (6.6 ± 0.6)	4.3 ± 1.2 (25 ± 7)
(CH ₃) ₂ CHCl/23DMB	3.7 ± 0.6 (22.1 ± 3.6)		
(CH ₃) ₃ CCl/23DMB	4.7 ± 0.9 (28.4 ± 5.1)		
CH ₃ CH ₂ Br/ <i>n</i> -heptane (ref 11)	28.3 ± 2.7 (17.0 ± 1.6)	4.2 ± 0.6 (25.4 ± 3.4)	27 ± 7.3 (160 ± 44)
CH ₃ CH ₂ Br/23DMB	22.2 ± 2.7 (133 ± 16)	1.9 ± 0.1 (22.9 ± 1.0)	19.6 ± 5.3 (235 ± 64)
C ₆ H ₆ /23DMB (refs 4 and 5)	22.3 ± 6.7 (134 ± 40)	2.7 ± 0.2 (32.4 ± 2.4)	19.6 ± 4.5 (235 ± 56)

^a Values in parentheses represent relative rate constants on a *per hydrogen* basis

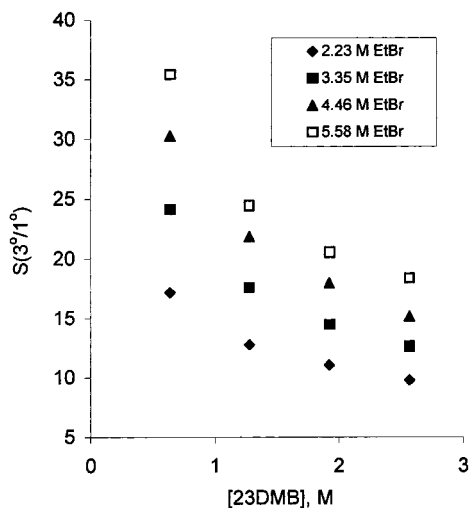


Figure 4. Chlorination of 23DMB in ethyl bromide: Variation of $S(3^\circ/1^\circ)$ with [23DMB] and [CH₃CH₂Br] at 20 °C.

bromo- or chloroalkane molecule and that this species is responsible for enhanced selectivity in these solvents.

The selectivity data in the alkane/haloalkane/Cl₂ system are consistent with the existence of two hydrogen abstractors: Free chlorine atom and a chlorine atom/haloalkane complex in direct analogy to Scheme 1 and eq 1.¹⁹

The rate constant ratios K_3/K_1 , k_{Cl}/k_1 , and k_{-Cl}/k_1' may be obtained from effect of substrate and solvent concentration on observed selectivity via nonlinear regression analysis. In terms of physical significance, k_3/k_1 represents the selectivity for 3° vs 1° hydrogen atom abstraction by free chlorine atom (*per molecule basis*) and it is equal 0.5 experimentally, K_3/K_1 represents the intrinsic selectivity of the (Solv/Cl•) complex, k_{Cl}/k_1 is the relative rate constant for two competing reactions of free chlorine atom, complex formation (k_{Cl}) vs primary hydrogen atom abstraction from 23DMB (k_1), and k_{-Cl}/k_1' represents the relative rate constant for two competing pathways for (Solv/Cl•) consumption, complex dissociation (k_{-Cl}) and

(19) Hydrogen abstraction from the solvent by free Cl• will have no effect on selectivity. However, hydrogen abstraction from the solvent by Solv/Cl• may diminish the observed selectivity. Modification of Scheme 1 and eq 1 to account for hydrogen abstraction from the solvent by free Cl• and by Solv/Cl•, k^S_{Cl} and $k^S_{Solv/Cl}$, respectively, results in the following expression:

$$S(3^\circ/1^\circ) = [S_0(k_{-Cl}/K_1) + S_0(S_X + 1)[RH] + (S_X(k_{Cl}/k_1) + (k^S_{Solv/Cl}/K_1)S_0)[Solv]] / [(k_{-Cl}/K_1) + (S_X + 1)[RH] + ((k_{Cl}/k_1) + (k^S_{Solv/Cl}/K_1))[Solv]]$$

Estimating the upper limit for $k^S_{Solv/Cl}/K_1$ as k^S_{Cl}/K_1 which equals 0.14 for CH₃CH₂Br and 0.23 for (CH₃)₂CHCl (i.e., assuming that (Solv/Cl•) abstracts hydrogen from solvent with a rate constant less than or equal to that for free Cl•), it is apparent that hydrogen abstraction from solvent has only a negligible effect on selectivity in these experiments.

primary hydrogen abstraction by “complexing” chlorine atom (K_1). These rate constant ratios for the various systems reported in this paper and for the chlorine atom–benzene complex are compiled in Table 5. It should be particularly emphasized that all three above-mentioned parameters, K_3/K_1 , k_{Cl}/k_1 , and k_{-Cl}/K_1 , completely define the kinetics of this system.

The absolute rate constant $k_{Cl} = 5.4 (\pm 2.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for formation of the chlorine atom/benzene complex was calculated by using values of k_{Cl}/k_1 (Table 5) and the reported value for abstraction of a 1° hydrogen abstraction from 23DMB by free Cl•, $k_1 = 2.0 (\pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁵ This derived value compares favorably to $k_{Cl} = 6.0 (\pm 1.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, measured directly by Ingold et al. via laser flash photolysis.⁵ The similarity of the results obtained by these two methods demonstrates that the relative rate constants derived from the nonlinear regression analysis are reliable.

We similarly calculated k_{Cl} values for complex formation with bromoethane ($k_{Cl} = 3.8 (\pm 1.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and 2-chloropropane ($k_{Cl} = 2.2 (\pm 0.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). It is apparent that the rate constants for complexation of Cl• with these solvents are comparable to the rate constant for complexation with benzene.

There is literature precedent for complex formation between halogen atoms and bromo- and chloroalkanes. Neta detected complexes of Br• with bromoethane, CH₂Br₂, CHBr₃, and CBr₄.²⁰ He also remarked in this work that a short-lived species was produced from Cl• and CCl₄ during CCl₄ radiolysis. This latter species was detected in the other work,²¹ and was suggested to be a donor/acceptor complex.

Complex stability and concomitantly selectivity increase with increasing electron density at the chlorine atom in the solvent molecule. As a result, both complex stability and selectivity are expected to decrease from monochloroalkanes to polychloroalkanes (attributable to the polar effect of the other chlorine atoms) and increase from primary to secondary and tertiary chloroalkanes (because of the polar effect of alkyl groups). It is also reasonable to expect that complex stability will be even greater for bromoalkanes and that intrinsic selectivities will be higher for these complexes. This analysis is consistent with the observed variation of selectivity with ionization potential for these solvents.

As the data in Table 5 reveal, C₆H₆/Cl• and C₂H₅Br/Cl• complexes have comparable intrinsic selectivities. Because a good correlation often exists between radical stability and selectivity, we suggest that these two complexes may also have similar stabilities.

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III. Conclusions

The results presented herein demonstrate that $\text{Cl}\cdot$ forms complexes with halogenated solvents resulting in higher selectivity in hydrogen abstractions. Selectivity decreases with increasing Cl content of the solvent (paralleling the increase in the ionization potential) and selectivity is greater in bromoalkane vs chloroalkane solvents. This variation in selectivity with ionization potential provides a good indication that the primary interaction between $\text{Cl}\cdot$ and the haloalkane is charge transfer (i.e., these are donor/acceptor type complexes).

IV. Experimental Section

General. All solvents were obtained from commercial sources and purified by normal procedures. 2,3-Dimethylbutane (Aldrich) was distilled before use. Gas chromatographic analyses were performed on the Chrom-4 chromatograph with a 3-m column of SE-54 on Chromaton-N Super.

Chlorination of Alkanes (Typical Procedure). CCl_4 was saturated (2.0 M) by bubbling with Cl_2 at room temperature. Aliquots of this solution were diluted with additional

argon-purged CCl_4 . The appropriate hydrocarbon, with or without internal standard, and haloalkane solvent (CCl_4 as cosolvent) were deoxygenated by bubbling with argon for 5–15 min. In the absence of light, an aliquot of this solution and an aliquot of 1 M solution of Cl_2 in CCl_4 were added to each glass ampule. (An aliquot of 0.5 M Br_2 in CCl_4 was added for chlorination in the presence of molecular bromine.) The reaction ampules were filled to 95–98% of volume, sealed, equilibrated at 20 °C, and irradiated with a UV lamp for 10–15 min. After the reactions were complete, the product mixtures were analyzed by GLC. All experiments were performed in triplicate.

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