

Kinetic Evidence for Chlorine Atom Complexes in “Noncomplexing” Solvents†

John E. Chateaufneuf‡

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, and the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

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Introduction

In a recent issue of *J. Org. Chem.*, Dneprovskii, Tanko, and co-workers¹ present an article that describes the results of product analysis of hydrocarbon free radical chlorination reactions in halogenated solvents and ask the question “Are there any solvents which are truly noncomplexing?”. This question is asked in light of the pioneering work of Russell,² who observed dramatic increases in selectivity in tertiary to primary ($3^\circ/1^\circ$) mono-photochlorination of 2,3-dimethylbutane (DMB) in complexing solvents such as benzene, certain arenes, and CS₂. Other solvents such as CCl₄, CHCl₃, CH₂Cl₂, and CH₃CN were considered to be noncomplexing or nonselective solvents since the $3^\circ/1^\circ$ selectivity in these solvents was comparable to selectivity observed in neat liquid hydrocarbons, e.g., DMB, *n*-hexane, and cyclohexane. Since Russell’s work there have been numerous investigations of DMB photochlorination selectivity, and these investigations have revealed interesting complexities in an apparently simple free radical chain reaction.^{3,4}

Photochlorinations of DMB are typically performed in CCl₄ or other “inert” noncomplexing perhalogenated solvent containing DMB and often with an added complexing cosolvent. In 1985 Ingold and co-workers^{3c} observed that DMB chlorination selectivities, S^m ,^{5a} in alkane solvents were not precisely equal^{5b} to those obtained in CCl₄ and commented “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”. In a subsequent paper describing the investigation^{3f} of these different S^m values, the authors reverse themselves with

regard to CCl₄ and report “alkanes and CCl₄ are non-complexing solvents as far as the chlorine atom is concerned” and that different S^m values “arise from other and different causes”. The reported causes specifically involved contributions from cage reactions,^{3e} the influence of CCl₄ (actually, $\cdot\text{CCl}_3$), and the participation of O₂ in the photochlorination chain reaction at low [Cl₂].^{3f} While these contributions are indeed very important mechanistic aspects of the photochlorination reaction, they do not exclude the possibility of chlorine atom/CCl₄ complexation. In fact, the kinetic data presented in this report combined with the results of Dneprovskii, Tanko, and co-workers¹ provide very strong evidence that chlorine atoms (Cl \cdot) do complex or associate with halogenated solvents and that this association influences both rates of chlorine atom reactivity and selectivity.

Results and Discussion

Dneprovskii et al.¹ report the free radical chlorination of alkanes, including DMB, in 17 different halogenated solvents and found selectivity in Cl \cdot hydrogen atom abstraction to increase with a decrease in the ionization potential (IP) of the solvent. Values of Cl \cdot selectivity for DMB, reported on a per-hydrogen basis ($S(3^\circ/1^\circ) = S^m \times 6$), increased from 3.0 for CCl₄ to 38.0 for bromoethane. The increase in hydrogen atom abstraction in the halogenated solvents, compared with “free Cl \cdot ”, was attributed to formation of charge-transfer donor/acceptor complexes. This assignment is in complete agreement with the previously reported⁶ charge-transfer (CT) absorption spectra of chlorine atoms in halogenated solvents. Laser flash photolysis (LFP) of Cl₂ in several halogenated solvents of differing IPs resulted in transient absorption signals and absorption band maxima that correlate well with the IPs of the solvent; see Table 1. A plot of $h\nu$ (eV) versus IP (eV)⁷ gave a slope of 0.83 (± 0.09), corr coeff = 0.991. In accordance with Mulliken’s resonance structure theory,⁸ the transitions were assigned to 1:1 solvent to Cl \cdot donor–acceptor CT spectra.

The evidence is clear that there is sufficient Cl \cdot interaction with solvent to exhibit CT transitions in halogenated solvents. Until now, the unanswered question has been: Are these interactions sufficiently strong to influence reaction rate constants and selectivity? The newly reported¹ $S(3^\circ/1^\circ)$ values strongly suggest the interactions do influence hydrogen abstraction selectivity. It would be gratifying, however, to verify these results with direct kinetic data. The data present in Table 2 corroborate the results of Dneprovskii et al. and demonstrate that Cl \cdot complexation with halogenated solvent does influence measured rate constants for hydrogen atom abstraction. (It should be noted that the actual kinetics of complexation are not being measured in this work; see discussion below and refs 3c, 9, and 10.) Unfortunately, it is impossible to measure the *absolute* reactivity of Cl \cdot with DMB due to chain reactivity^{3c,9} (vide

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

‡ Send correspondence to the author at Western Michigan University.

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(2) (a) Russell, G. A. *J. Org. Chem.* **1957**, *22*, 2977. (b) Russell, G. A. *J. Org. Chem.* **1958**, *23*, 4987. (c) Russell, G. A. *J. Org. Chem.* **1958**, *23*, 4997.

(3) (a) Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485. (b) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120. (c) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszytk, J.; Scaliano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464. (d) Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300. (e) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 3519. (f) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 5220. (g) Raner, K. D.; Luszytk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 3652.

(4) For a review of photochlorinations, see: Ingold, K. U.; Luszytk, J.; Raner, K. D. *Acc. Chem. Res.* **1990**, *23*, 219.

(5) (a) DMB chlorination selectivity is typically reported as the molar chloride product ratio (S^m), where $S^m = [2\text{-Cl DMB}]/[1\text{-Cl DMB}]$. (b) For example, values of $S^m = 0.47$ (0.125M DMB) in CCl₄ and 0.66 in neat DMB are reported in ref 3c.

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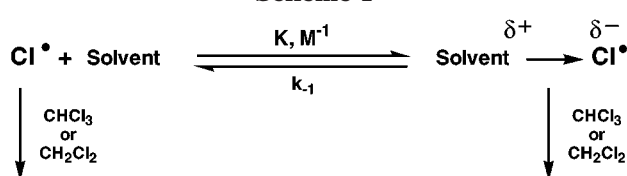
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Table 1. Chlorine Atom Charge-Transfer Maxima in Halogenated Solvents of Various Ionization Potentials^a

solvent	IP (eV)	λ_{\max} (nm)
C ₇ F ₁₄	13.2	235
CFCl ₂ CF ₂ Cl (Freon 113)	11.99	280
CFCl ₃	11.77	300
CHCl ₃	11.42	330
CCl ₄	11.47	330
CH ₂ Cl ₂	11.35	335
CHCl ₂ CHCl ₂	11.10	340
CHBrCl ₂	10.88	365

^a Data from ref 6.**Table 2. Bimolecular Rate Constants for Chlorine Atom Hydrogen Abstraction from CH₂Cl₂ and CHCl₃ in Halogenated Solvents of Various Ionization Potentials^a**

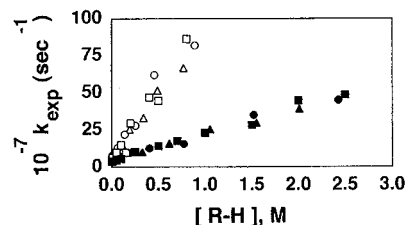
solvent	IP (eV)	CH ₂ Cl ₂	CHCl ₃
Freon 113	11.99	$(2.6 \pm 0.3) \times 10^8$	$(6.0 \pm 0.2) \times 10^7$
CFCl ₃	11.77	$(1.4 \pm 0.1) \times 10^8$	$(4.1 \pm 0.4) \times 10^7$
CCl ₄	11.47	$(8.2 \pm 0.8) \times 10^7$	$(1.4 \pm 0.1) \times 10^7$
CH ₂ Cl ₂ (ref 11)	11.35	9×10^6	

^a Errors represent $\pm 2\sigma$.**Scheme 1**

infra); therefore, CHCl₃ and CH₂Cl₂ were chosen as reactants and Freon 113, CFCl₃, and CCl₄ as nonreactive solvents. Cl[•] was generated by 355 nm LFP of Cl₂. Observed Cl[•] reactivity (k_{obs}) was monitored at the respective solvent CT maxima with changes in reactant concentration, [R-H]. Bimolecular rate constants (k_{bi}), M⁻¹ s⁻¹, were obtained according to $k_{\text{obs}} = k_0 + k_{\text{bi}}[\text{R-H}]$, where k_0 represents all modes of decay of reactant in the absence of R-H.

As expected, Cl[•] reactivity was found to be greater toward CH₂Cl₂ than CHCl₃ in each solvent investigated. More importantly, however, is that k_{bi} measured for Cl[•] reactivity toward each substrate was found to decrease with a decrease in IP of the solvent, see Table 2. Since the reactions were performed in each solvent under otherwise identical reaction conditions, the differences in k_{bi} are attributed to solvent interaction. That is, the rate constants do not reflect free Cl[•] reactivity with CH₂Cl₂ and CHCl₃; instead they reflect the combined reactivity of the Cl[•] complex (solvent → Cl[•]), free Cl[•], and the association constant of the complex (K , M⁻¹);^{3c,9,10} see Scheme 1.

Consistent with these findings is $k_{\text{bi}} = 6 \times 10^9$ M⁻¹ s⁻¹, reported by Alfassi et al.¹¹ for Cl[•] + CH₂Cl₂ (Table 2) in CH₂Cl₂ as solvent. These combined results demonstrate that a near 30-fold difference in reactivity may be observed for a single hydrogen abstraction reaction by varying the IP and, in turn, the degree of complexation of the solvent. Also of interest is a kinetic analysis of Forgeteg and Berces,¹² who use Cl[•]/arene reactivity to extract k_{bi} for Cl[•] + hydrogen donors. They report $k_{\text{bi}} =$

**Figure 1.** Chlorine atom quenching plots with added CH₂Cl₂ (open symbols) and CHCl₃ (closed symbols) by pulse radiolysis of CCl₄ (○, ●), 266 nm LFP of CCl₄ (□, ■), and 355 nm LFP of Cl₂ (△, ▲).

2.7×10^8 and 2.0×10^8 M⁻¹ s⁻¹ for “free” Cl[•] + CH₂Cl₂ and CHCl₃, respectively.

The rate constants reported in the present work could be obtained by minimizing the importance of free radical chain interference by using perhalogenated solvents containing no abstractable hydrogens and using substrates that generate relatively unreactive free radicals. Assurance that the k_{bi} were not influenced by the chain process, or other complexities^{3,4} associated with Cl₂ as the Cl[•] precursor, is attained by using two other Cl[•] sources that do not involve chain processes. The k_{bi} for Cl[•] with CH₂Cl₂ and CHCl₃ were also obtained from the CT absorption of Cl[•] in CCl₄ following either pulse radiolysis or 266 nm photodissociation of CCl₄.^{9,13} Values of (8.9 ± 1.7) and $(1.2 \pm 0.3) \times 10^7$ M⁻¹ s⁻¹ from pulse radiolysis and (7.2 ± 0.8) and $(1.8 \pm 0.1) \times 10^7$ M⁻¹ s⁻¹ from 266 nm LFP compare well with (8.2 ± 0.8) and $(1.4 \pm 0.1) \times 10^7$ M⁻¹ s⁻¹ from Cl₂ LFP for k_{bi} with CH₂Cl₂ and CHCl₃, respectively; see Figure 1.

There is now direct evidence that Cl[•] does indeed complex with halogenated solvents and that this complexation may influence photochlorination reactivity and selectivity.¹

Experimental Section

LFP experiments, either 355 or 266 nm, were performed using a Quanta Ray DCR-1 Nd:YAG (8 mJ, 6 ns pulse width) for laser excitation and a 1000 W pulsed xenon lamp as the monitoring source. Pulse radiolysis experiments were performed using a 10 ns pulse of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (LINAC). The pulse radiolysis and LFP apparatus have previously been described.⁹

Samples were prepared using halogenated solvents that were presaturated with nitrogen; then Cl₂ (Matheson, high-purity) concentrations were adjusted to 0.8 optical density at the 355 nm laser excitation wavelength and jacketed with a nitrogen atmosphere. Typically, only one laser shot was required for each kinetic trace. Methylene chloride (Fisher) and 1,1,2-trichlorotrifluoroethane (Freon-113) (Aldrich, Gold Label) were passed through neutral, activated aluminum oxide (Aldrich) and distilled. Carbon tetrachloride (Fisher) and chloroform (Aldrich) were also distilled from K₂CO₃ (35 cm Vigreux column) prior to use. Fluorotrichloromethane (Aldrich, NMR grade) was used as received.

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