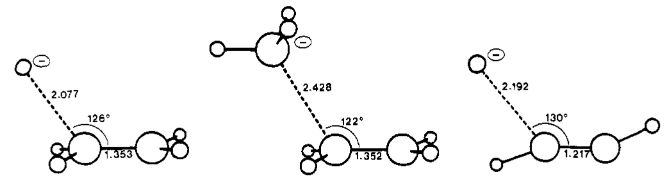

Figure 2. 3-21G geometries of transition structures for reactions of hydride with ethylene, methyl anion with ethylene, and hydride with acetylene.

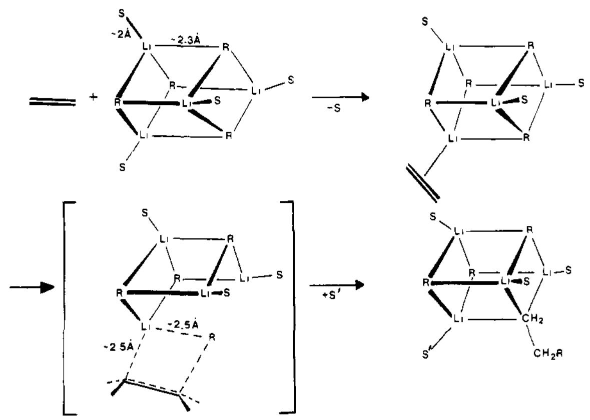

Figure 3. Possible mechanism for the addition of an alkyllithium tetramer to ethylene.

with some lateral displacement and a significant decrease of the $C^{\delta-}$–Li^+ distance.[17]

The angle of attack of H^- or Me^- on ethylene or acetylene is significantly larger than tetrahedral,[18] even though little CC bonding has developed in the transition structures. The presence of the Li^+ counterion decreases this angle slightly, as compared to isolated anion additions.

Activation energies and transition structures for additions to formaldehyde are not influenced significantly by dimerization of LiH or MeLi,[7] perhaps because the aggregation of organolithium compounds arises primarily from electrostatic effects.[19] A conceivable mechanism of addition of a solvated lithium tetramer to ethylene is shown in Figure 3. Displacement of solvent and coordination of ethylene should be slightly exothermic, since initial solvation energies of alkyllithium tetramers with THF are typically 7–8 kcal/mol, and 2–6 kcal/mol with ether.[20] Since the lone pair of the methyl anion is pointed toward the center of the lithium tetrahedron, two of the methyl-lithium bonds must be lengthened in order to allow rotation of the lone-pair to interact with the ethylene terminus. The activating effect of Lewis basic solvents upon the addition reaction[2a] may be due to greater ease of lengthening of these bonds when lithium is additionally coordinated in the transition state.

Acknowledgment. We are grateful to the National Science Foundation, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie for financial support of this research and to the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award to K.N.H.

Registry No. LiH, 7580-67-8; CH_3Li, 917-54-4; ethylene, 74-85-1; acetylene, 74-86-2.

Supplementary Material Available: Listings of geometries and energies (4 pages). Ordering information is given on any current masthead page.

(17) This motion in transition-metal complexes provides activation of alkenes toward nucleophiles: Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6149.
(18) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162.
(19) Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81. Kaufman, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856.
(20) Quirk, R. P.; Kester, D. E. *J. Organomet. Chem.* **1977**, *127*, 111.

Multiple Substitutions in Radical-Chain Chlorinations. A New Cage Effect

P. S. Skell* and H. N. Baxter III

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received December 3, 1984

It is widely agreed that radical-chain Cl_2 chlorinations of aliphatic systems in noncomplexing solvents or in gas phase are slower when electronegative substituents are present:[1a] For example, alkyl chlorides react less rapidly than the corresponding alkanes. Thus, the behavior we report here appears to be anomalous: In CCl_4 or $CFCl_3$ solvents, photochlorinations with low conversions of cyclohexane, isobutane, neopentane, or 2,3-dimethylbutane, with careful exclusion of O_2, result in formation of unexpectedly large proportions of multiply chlorinated products, resulting from further chlorination of the monochloro products. Although this is an effect which gives the appearance that the chloro derivatives are more reactive than the alkane, the dependence on alkane concentration leads us to a novel proposal, a type of elementary process which appears to have been unrecognized heretofore.

For example 1000 μmol of purified cyclohexane (purity 99.99%; 0.10 M) with 309 μmol of Cl_2 in CCl_4 (10 mL) shows no product formation in the dark, but on brief exposure to a tungsten lamp results in formation of 74 μmol of cyclohexyl chloride, 67 μmol of dichlorides, and 39 μmol of a mixture of trichlorides; *these are produced in the presence of more than 800 μmol of unreacted cyclohexane.* The composition of these multiply halogenated products is readily recognizable with GC–mass spectrum analysis. Thus, cyclohexyl chloride appears to be far more reactive than cyclohexane. The more usual behavior, cyclohexane more reactive than cyclohexyl chloride, is observed in chlorination of undiluted cyclohexane (18.5 mmol; no added solvent) with 483 μmol of Cl_2, resulting in formation of 460 μmol of cyclohexyl chloride and 15 μmol of dichlorides (no trichlorides).

With low conversion conditions we report here that the amount of polychlorinated product relative to the total amount of chlorinated product increases with decreasing concentration of cyclohexane. This can be seen in Table I. In the first four reactions, each starting with 10 mol % Cl_2 with respect to cyclohexane, the percentage of polychlorinated product increases from 6% in the photochlorination of neat cyclohexane to 56% in the reaction carried out with 0.030 M cyclohexane in CCl_4. The same increases in the percentage of polychlorinated product were observed in the reactions that initially contained 30 mol % Cl_2. Despite the 3-fold greater conversion of the cyclohexane, there is only a slightly increased percentage of polychlorinated product. This effect is independent of the Cl_2 concentration and is attributable to the change of cyclohexane concentration and to the percentage of its conversion. For example, a reaction of 0.020 M cyclohexane in CCl_4 in the presence of 0.031 M Cl_2, stopped early by quenching with corn oil, resulted in ~20% loss of the original 200 μmol of cyclohexane and production of 12.4 μmol of cyclohexyl chloride, 16.0 μmol of dichlorides, and 11.0 μmol of a mixture of trichlorides, 68% polychlorinated product. A reaction identical except for 0.006 M Cl_2 resulted in an identical product composition. Thus, the percentage of polychlorination is independent of $[Cl_2]$ and dependent on $[C_6H_{12}]$.

An analogous result is obtained with low conversion photochlorinations of 2,3-dimethylbutane (DMB). In pure DMB the two isomeric $C_6H_{13}Cl$'s are produced in ~100% yield; with 0.10 M DMB in $CFCl_3$ (10 mL), 102 μmol of Cl_2 produces 41 μmol of monochlorides and 24 μmol of dichlorides. This result is independent of either the presence of HCl produced in the reaction, or its presence initially at 0.5 M, or of scavenging of HCl by anhydrous K_2CO_3.

(1) Poutsma, M. L. In "Methods in Free-Radical Chemistry"; Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; (a) pp 138–163, (b) pp 84–87.

Table I. Photochlorinations of Cyclohexane at 20 °C

[cyclohexane], M	solvent	$100[Cl_2]/[C_6H_{12}]$	polychlorinated product, %[a]
9.2	none	10	6
1.0	CCl_4	9.7	29
0.10	CCl_4	10	53
0.030	CCl_4	11	56
3.0	CCl_4	32	20
1.0	CCl_4	30	33, 33
0.30	CCl_4	32	51
0.10	CCl_4	31	57, 59
0.050	CCl_4	30	63, 64
0.020	CCl_4	33	63, 64, 68
1.0	$CFCl_3$	34	33
0.10	$CFCl_3$	31	58
0.020	$CFCl_3$	33	63, 68, 70

[a] Polychlorides × 100 ÷ $\sum$monochlorides + polychlorides.

Low-conversion photochlorinations of 0.10 M neopentane or 0.10 M isobutane in inert solvents similarly result in formation of unexpectedly large amounts of the dichlorides.

But, if benzene is used as the solvent, in place of CCl_4 or $CFCl_3$, the anomalous behavior is *not* observed: Chlorination of 0.10 M cyclohexane or 0.10 M DMB results in nearly exclusive formation of monochlorides in excellent yields, based on Cl_2.

In contrast, "normal" behavior is observed with methyl chloride, methylene chloride, ethyl chloride, and 1,1-dichloroethane under all conditions. For example, chlorination of 1000 μmol of methyl chloride (0.10 M) in $CFCl_3$ solvent (10-mL solution) with 103 μmol of Cl_2 (0.01 M) produces 78 μmol of CH_2Cl_2. Similar experiments (1) with methylene chloride in $CFCl_3$ produce 83 μmol of $CHCl_3$ and (2) with ethyl chloride in $CFCl_3$ produce 90 μmol of $C_2H_4Cl_2$'s. With these compounds similar results are obtained at high concentrations of substrate. There is no concentration effect with these substrates such as that observed with alkanes.

These results are understandable if one recognizes a consequence of attributing an encounter-controlled rate constant to the reaction of Cl· with an alkane.[1b] The alkyl radicals react with Cl_2 to produce the alkyl chloride and a chlorine atom. These geminate reaction products are in the same solvent cage and react by transfer of a hydrogen atom from the alkyl chloride to the Cl·, thus leading ultimately to the dihalides etc.

$$\text{c-}C_6H_{12} + Cl\cdot \rightarrow HCl + \text{c-}C_6H_{11}\cdot \quad (1)$$

$$\text{c-}C_6H_{11}\cdot + Cl_2 \rightarrow [\text{c-}C_6H_{11}Cl + Cl\cdot]_c \quad (2)$$

$$[\text{c-}C_6H_{11}Cl + Cl\cdot]_c \rightarrow HCl + \text{c-}\dot{C}_6H_{10}Cl \quad (3)$$

$$[\text{c-}C_6H_{11}Cl + Cl\cdot]_c \xrightarrow{\text{diff}} \text{c-}C_6H_{11}Cl + Cl\cdot \quad (4)$$

Reaction of the cage partners accounts for the multiple chlorinations; escape of Cl· from the cage leads to monochlorides. This cage effect should be most notable at low concentrations of alkane in relatively inert solvents. With the alkane as the solvent, cage "walls" would also consist of alkane molecules which react faster than the alkyl chloride with the chlorine atom, thus giving a normal product distribution. The same result is obtained with any solvent for which the rate of reaction with Cl· is encounter controlled, as, for example, benzene.[2]

With low reactivity substrates, for which the rate constants for reaction with Cl· are substantially below the cage-escape rate, multiple consecutive cage chlorinations should not be important pathways. Substrates such as CH_2Cl_2 and $CHCl_3$ react with chlorine atoms at rates 1–2 orders of magnitude less than those of primary C–H's of alkanes,[1a,3] thus explaining the failure to observe the anomalous behavior with the substrates CH_3Cl, CH_2Cl_2, etc.

One can predict this anomalous effect, resulting from reactions of the geminate pair, will be observed when (1) the solvent is relatively inert, (2) the substrate concentration is low enough to make improbable that substrate and chlorination product molecules will be found in the same cage, and (3) the rate of reaction of the geminate pair is equal to or greater than the rate of cage escape of the smallest member of the pair.

We are seeking other instances of this "anomaly".

Acknowledgment. This work was carried out with financial assistance from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. DMB, 79-29-8; cyclohexane, 110-82-7; methyl chloride, 74-87-3; methylene chloride, 75-09-2; ethyl chloride, 75-00-3.

(2) (a) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987. (b) Soumillion, J. P. *Ind. Chim. Belge* **1970**, *35*, 1065. (c) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120.

(3) Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; pp 283–293.

Electrochemistry of Polymer Films Not Immersed in Solution: Electron Transfer on an Ion Budget

Joseph C. Jernigan, Christopher E. D. Chidsey,† and Royce W. Murray*

Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Received October 29, 1984

This laboratory recently described[1] steady-state electron conduction through submicron films of electroactive polymeric transition-metal complexes sandwiched between two electrodes. Complexes like $[Os(bpy)_2(vpy)_2](ClO_4)_2$ were electropolymerized[2,3] onto polished Pt and then overlaid with a porous film of evaporated Au, which was contacted by an electrolyte solution containing reference and auxillary electrodes. In this paper, we show that voltammograms with large limiting currents can be obtained for similarly prepared[1] $Pt/poly[Os(bpy)_2(vpy)_2](ClO_4)_2/Au$ sandwiches *in the absence of an electrolyte solution*, bathed only in acetonitrile vapor or dry N_2 gas.

The essential features of the previous[1] sandwich voltammetry in electrolyte solution are summarized in Figure 1A,B. Figure 1A is a cyclic voltammogram where only E_{Pt} is controlled (vs. SSCE) and shows waves for the Os(III/II), Os(II/I), and Os(I/0) (formal) couples. In Figure 1B, where both E_{Pt} and E_{Au} are controlled (vs. SSCE), E_{Au} at 0 V and E_{Pt} being varied, a steady-state current–potential wave appears when E_{Pt} passes each region of film electroactivity. In the wave at positive E_{Pt}, for instance, the limiting current ($i_{III/II}$) means that all of the polymer next to the Pt electrode is Os(III) and all that next t o the Au electrode is Os(II), with linear concentration gradients of Os(III) and Os(II) states in the interior of the film as in Figure 1B inset. This $i_{III}/_{II}$ limiting current is controlled by the rate of electron

† Present address: AT & T Bell Laboratoris, Murry Hill, N.J.

(1) (a) Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510. (b) Pickup, P. G.; Murray, R. W. *J. Electrochem. Soc.* **1984**, *131*, 833. (c) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991.

(2) bpy = 2,2′-bipyridine; vpy = 4-vinylpyridine.

(3) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151.

(4) Similar results are obtained in pure acetonitrile liquid but because of an ionic impurity the limiting currents were less reproducible upon successive potential scans.

(5) Electroneutrality will not rigorously apply at the interphases between phases at equilibrium or at steady state.[6] However, space charges will only lead to minor deviations from the predictions made here. These deviations will be examined thoroughly in a future report.[7]

(6) Buck, R. P. In "Ion-Selective Electrodesin Analytical Chemistry"; Freiser, H., Ed.; Plenum: New York, 1978; Vol. 1, Chapter 1.

