

Table I. Photochlorinations of Cyclohexane at 20 °C

[cyclohexane], M	solvent	100[Cl ₂]/ [C ₆ H 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

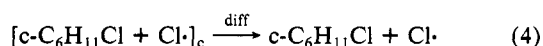
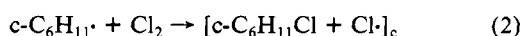
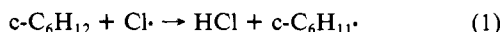
^a Polychlorides × 100 ÷ Σ monochlorides + polychlorides.

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 CCl₄ or CFCl₃, 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 Cl₂.

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 CFCl₃ solvent (10-mL solution) with 103 μmol of Cl₂ (0.01 M) produces 78 μmol of CH₂Cl₂. Similar experiments (1) with methylene chloride in CFCl₃ produce 83 μmol of CHCl₃ and (2) with ethyl chloride in CFCl₃ produce 90 μmol of C₂H₄Cl₂'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 Cl₂ 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.



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 CH₂Cl₂ and CHCl₃ 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 CH₃Cl, CH₂Cl₂, 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".

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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.

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

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This laboratory recently described¹ steady-state electron conduction through submicron films of electroactive polymeric transition-metal complexes sandwiched between two electrodes. Complexes like [Os(bpy)₂(vpy)₂](ClO₄)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 auxiliary electrodes. In this paper, we show that voltammograms with large limiting currents can be obtained for similarly prepared¹ Pt/poly[Os(bpy)₂(vpy)₂](ClO₄)₂/Au sandwiches *in the absence of an electrolyte solution*, bathed only in acetonitrile vapor or dry N₂ gas.

The essential features of the previous¹ 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 to 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

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(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

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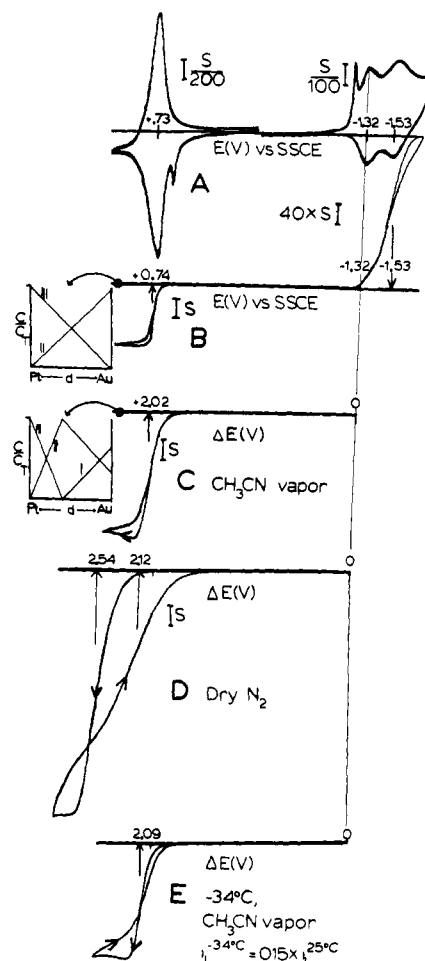


Figure 1. Voltammetry of Pt/poly[Os(bpy)₂(vpy)₂](ClO₄)₂/Au sandwich electrode in various media; $S = 31.2 \text{ mA/cm}^2$, $\Gamma_{\text{Os}} = 2.95 \times 10^{-8} \text{ mol/cm}^2$ (ca. 400-nm film). All voltammograms at 25 °C were obtained with the same electrode with a scan rate of 50 mV/s except as noted. The electrode was thoroughly rinsed with CH₃CN after electropolymerization, dried, and subjected to 10^{-7} -torr vacuum and moderate heating during Au evaporation. It was stored in a desiccator and then, in the order of the experiments, exposed to N₂ gas (D), CH₃CN vapor (C), and electrolyte solution (A and B). (A) i_{Pt} vs. E_{Pt} in 0.1 M Et₄NClO₄/CH₃CN; (B) i_{Pt} vs. E_{Pt} with $E_{\text{Au}} = 0 \text{ V}$ vs. SSCE in 0.1 M Et₄NClO₄/CH₃CN; (C) i vs. ΔE between Pt and Au electrodes in dry N₂ saturated with acetonitrile vapor; (D) i vs. ΔE in dry N₂ gas, scan rate = 2 mV/s; (E) i vs. ΔE in dry N₂ saturated with CH₃CN vapor at -34 °C using a different sandwich electrode.

hopping between Os(III) and Os(I) sites in the film¹ and is proportional to the electron diffusion coefficient $D_{\text{e(III/II)}}$ for the Os(III/II) couple and inversely proportional to film thickness d .

Figure 1C shows a Pt/poly[Os(bpy)₂(vpy)₂](ClO₄)₂/Au sandwich used as a two-electrode cell bathed in acetonitrile vapor (saturated, 25 °C). No current flows until the potential ΔE applied between the Pt and Au electrodes exceeds ca. 1.9 V. Then, a reproducible, steady-state voltammogram appears with an $E_{1/2} = 2.02 \pm 0.01 \text{ V}$ (for seven electrodes) which equals the difference between the formal potentials +0.73 and -1.32 V of the Os(III/II) and Os(II/I) couples appearing in Figure 1A,B.

We ascribe the electrical behavior in Figure 1C to the production of Os(III) and Os(I) sites at Pt and Au electrodes, respectively. Without a bathing electrolyte solution, charge conservation requires that for each Os(II) site oxidized to Os(III) at the Pt electrode, another must be reduced to Os(I) (releasing a ClO₄⁻ counterion) at the Au electrode. This can be called an *ion budget*, to emphasize the coupling of the redox chemistry of the film to its fixed but evidently quite mobile pool of electroinactive ClO₄⁻ counterions.

The limiting current $i_{\text{III/I}}$ in Figure 1C can be related to that of the Os(III/II) wave ($i_{\text{III/II}}$) in Figure 1B with simple electron

diffusion and charge conservation statements to give⁷

$$i_{\text{III/I}}/i_{\text{III/II}} = 1 + [D_{\text{e(II/I)}}/D_{\text{e(III/II)}}]^{1/2} \quad (1)$$

If the electron diffusion coefficients $D_{\text{e(III/II)}}$ and $D_{\text{e(II/I)}}$ for the Os(III/II) and Os(II/I) couples in Figure 1C are assumed to be the same as those in acetonitrile liquid bathed polymer in Figure 1B, this equation predicts that $i_{\text{III/I}}/i_{\text{III/II}} = 2.68$, which is fairly close to the ratio observed in Figure 1C and analogous experiments, 2.1 ± 0.4 (average of seven electrodes). Equation 1 seems thus to give a good first-order account of the vapor-bathed experiment. The same theory predicts that concentration profiles of Os(III), Os(II), and Os(I) sites in the film when the $i_{\text{III/I}}$ is flowing are as in the Figure 1C inset. The diagram contains the elements that Os(III) and Os(I) sites react quantitatively in the interior of the film to form Os(II) sites, whose position of maximum concentration is determined jointly by the ion budget and the relative values of $D_{\text{e(III/II)}}$ and $D_{\text{e(II/I)}}$ and occurs at $[D_{\text{e(III/II)}}]^{1/2}d/([D_{\text{e(III/II)}}]^{1/2} + [D_{\text{e(II/I)}}]^{1/2})$.

As discussed previously¹ for redox conductivity, eq 1 rests on electron conduction driven by *concentration gradients* of Os redox sites and not by trans-film potential gradients. The electron conduction in Figure 1C in this respect differs from that discussed previously for dry mixed-valent films.⁸ Also, we believe $i_{\text{III/I}}$ and the electron diffusion coefficients in eq 1 principally reflect electron rather than ionic mobilities in the polymer, and so $i_{\text{III/I}}$ is additionally different from currents in polymer electrolytes⁹ with ion-blocking electrodes. The Figure 1C experiment does find analogy to thin-layer electrodes containing solutions of redox species as described by Bard and co-workers.¹⁰

Voltammetry of the same Pt/poly[Os(bpy)₂(vpy)₂](ClO₄)₂/Au sandwich in dry N₂ gas shows (Figure 1D) a recognizable wave even though solvent has not been deliberately¹¹ added. The "dry" voltammogram shows significant differences from Figure 1C. First, there is hysteresis between currents recorded when ΔE is increasing vs. decreasing; this effect is less pronounced for slowly scanned ΔE . Apparently, ClO₄⁻ counterions are less mobile in the absence of acetonitrile vapor, and on the time scale of the ΔE scan do not move rapidly enough first toward and then away from the Os(III) side of the film (upon its oxidation and reduction, respectively) to achieve true steady-state currents and concentration profiles of Os sites. At the $i_{\text{III/II}}$ plateau, the ClO₄⁻ mobility should again become less significant in relation to the electron diffusion rate. Second, $E_{1/2}$ for both increasing and decreasing ΔE scans, $2.47 \pm 0.1 \text{ V}$ and $2.14 \pm 0.05 \text{ V}$ (average for eight electrodes), respectively, are larger than that (2.02 V) for the vapor-bathed film of Figure 1C. This suggests that one or both of the "dry" Os(III/II) and Os(II/I) formal potentials differs significantly from those of the vapor-solvated couples. Third, limiting currents $i_{\text{III/I}}$ in dry N₂ (Figure 1D) are 2.5 ± 0.6 (average of seven electrodes) times *larger* than those in acetonitrile vapor (Figure 1C). According to eq 1, this might occur either through an increase in $D_{\text{e(II/I)}}$ or a decrease in $D_{\text{e(III/II)}}$. Both effects have interesting connotations but further experiments must elucidate their origin(s).

Low-temperature voltammetry of a Pt/poly[Os(bpy)₂(vpy)₂](ClO₄)₂/Au sandwich electrode in acetonitrile vapor (Figure 1E) is similar to room temperature results (Figure 1C) except for a slight hysteresis indicating lowered ClO₄⁻ mobility and a depressed $i_{\text{III/I}}$ limiting current showing that electron hopping

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(11) While the films have not been analyzed, the procedure for making the Au electrode contact of the sandwich (see Figure legend) leads us to expect that after Au deposition the polymer contains little residual acetonitrile solvent.

is an activated process in the vapor-bathed film.

The significance of the experiments in Figure 1C-E is that voltammetry that can be understood (at least to a first order) with a simple electron diffusion model is observable in the absence of an electrolyte solution. This opens a variety of possibilities for probing how electron-transfer events depend on their environment. An obvious requirement of the experiment is that the electroactive

material be a good ionic conductor. However, two redox couples are not strictly required since one can, for instance, start with an Os(III/II) mixed-valent film.⁷

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Book Reviews*

Neurobiology of the Trace Elements. Volume 1. Trace Element Neurobiology and Deficiencies. Volume 2. Neurotoxicology and Neuropharmacology. Edited by Ivor E. Dreosti and Richard M. Smith (CSIRO, Adelaide, Australia). Humana Press, Inc., Clifton, NJ. 1983. Volume 1: xix + 354 pp. \$49.50. Volume 2: xix + 300 pp. \$49.50.

It is possible to distinguish among several classes of "essential" nutrients. At one extreme is O₂, so vital to our survival that intake occurs involuntarily, 24 h per day. At the other extreme are the required trace elements. Although essential, the consequences of a deficiency or excess of such a nutrient are slow to develop and proper intake appears to have been left to chance. We do not seem to be able to detect low dietary copper or high dietary lead and adjust our diets accordingly as we do for other essential elements of our diet, such as water or calories. A corollary of this is that it is difficult to determine a proper dietary level of such elements. Thus, it is fortunate that Drs. Dreosti and Smith have provided us with a comprehensive review of the current literature on the relationship between the trace elements and the nervous system. The two-volume work contains chapters on such elements as aluminum, cadmium, cobalt, copper, iodine, lead, manganese, mercury, selenium, and zinc. A chapter on lithium also is included because of the use of this element in pharmacotherapy for affective disorders. These chapters will serve as a useful resource for anyone wishing to explore the impact of a particular element on the functioning of the nervous system. The volume concludes with a helpful though all too brief attempt by the authors to provide a summary. Also noteworthy is the integration provided in the excellent chapter by Weiss on Behavioral Toxicology of Heavy Metals.

The authors of these chapters understandably focus on what is known—the roles of these trace elements in certain biochemical reactions and the overt consequences of too much or too little. However, as we move toward defining acceptable intake limits for these elements, we must pay some attention to what we do not know, as well. The nervous system has a facility for compensating for insults. Thus, many neurological disorders that appear late in life undoubtedly were initiated many years earlier but remained hidden from clinicians for years due to such compensation. A related problem, touched on by Weiss, is that imbalances that occur during development may not be manifest as overt dysfunction until later. These problems make the establishment of casual relationships difficult. If ingestion of a lead paint chip during infancy leads to a lowered IQ as measured 6 years later, how does one establish a safe exposure level? Hopefully, some of the future investigations into the neurobiology of trace metals that are stimulated by these volumes will help to shed light on such issues.

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Annual Reports on Analytical Atomic Spectroscopy. Volumes 10 and 12. Volume 10: Edited by M. S. Cresser (University of Aberdeen) and B. L. Sharp (Macaulay Institute). Royal Society of Chemistry: London. 1980. xii + 329. £36.00. Volume 12: Edited by M. S. Cresser (University of Aberdeen) and L. Ebdon (Plymouth Polytechnic). Royal Society of Chemistry: London. 1983. x + 404 pp. £45.00.

This book is the 12th in a series which review exhaustively the field of atomic spectroscopy. Volume 12 contains 2492 citations, including conference abstracts, published during 1982. Volume 10 (1980) has 1782 citations. The books are divided into four major chapters: Atomization and Excitation, Instrumentation, Methodology, and Applications. In addition, there are tables of New Books, Reviews, Meetings, Patents (Volume 10, only), References (complete citation plus the title and author's affiliation), Author, and Subject Indexes.

"ARAAS" is more than a mere listing of citations. The authors are remarkably well organized and provide cross-references to material which appears in other sections. The real value of "ARAAS", however, lies in

its style. The authors summarize research accomplishments in a clean, easy-to-read manner which could not be reproduced by any computerized data-base listing. The presentation and analysis allow the reader to determine the real value of the research with regard to his or her specific need. Major concepts are underlined in the text, and the "signal-to-noise" ratio is high—all the 1982 references in my subspecialty were cited.

The narrative portion of the book has been reproduced from type-written material (new in Volume 12), but the legibility is quite good. Many of the applications are presented in type-set tables sorted by matrix (primary key) and analyte (secondary key). These tables contain sufficient information for the practicing chemist to determine if the method is likely to be usable for the intended application.

"ARAAS" is highly recommended for researchers and industrial users. The cost is approximately the same as 2-3 computerized literature searches, but it is far more useful.

Scott R. Goode, *University of South Carolina*

Studies in Organic Chemistry. Volume 15. Ozone and its Reactions with Organic Compounds. By S. D. Razumovskii and G. E. Zaikov (Academy of Science of the USSR). Elsevier Science Publishers: Amsterdam and New York. 1984. xiv + 480 pp. \$100.00.

This monograph has two redeeming virtues. It brings notice to the extensive and often overlooked Soviet literature on ozone chemistry. It also devotes much attention to kinetic studies, as expected from the authors' research interests. These foci will be useful to an expert who can place the work into a large perspective. However, for a general reader, the monograph may be perilous. The survey of the non-Soviet literature is incomplete. Even some landmark reviews are not cited. The treatment of the solution ozonolysis reaction mechanism is some 10 years out of date. A section dealing with gas-phase kinetics mistakenly includes some liquid-phase reactions. In summary, this is a place to learn what the Soviet scientific community has done and thinks about organic ozone chemistry as of about 1975. However, it cannot be regarded as a comprehensive or critical survey.

The numerous typographical errors, spelling errors, punctuation errors, and the largely hand-drawn reaction equations in this photoreproduced volume give it an unprofessional and irritating appearance. It is apparent that the publisher undertook little editing (perhaps none), a circumstance that is unacceptable given the origin of the authors. It should be noted that this is the translation of "Ozon i Ego Reaktivnii c Organicheskimi Soedineniiemi". The translator is not identified and the date of the original work is not given.

Robert L. Kuczkowski, *University of Michigan*

Macromolecules. Volume 1. Structure and Properties. Volume 2. Synthesis, Materials and Technology. Second Edition. By Hans-Georg Elias (Michigan Molecular Institute, Midland, Michigan). Plenum Press: New York. 1984. xiii + 1342 pp. ISBN 030641077X. Volume 1: \$65.00. Volume 2: \$95.00. ISBN 0306410850.

The two volumes are a comprehensive introduction to polymer science suited to a graduate level course or for self-study as an introduction to the field. A good understanding of organic and physical chemistry at the undergraduate level is assumed.

The arrangement of the topics and their development is very organized. In Part 1 of Volume 1, on structure, there is an introductory chapter and following chapters on the constitution, configuration, and conformation of polymers. The final chapter in this part is on supermolecular structures. In this latter chapter, the techniques used to examine the crystalline and/or amorphous nature of polymers are discussed. Part 2 covers solution properties. The beginning chapters are theoretical, covering solution thermodynamics, transport phenomena, and molar mass distributions. The last and largest chapter in this part discusses techniques used to determine molar mass distributions. Part 3, the last part

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