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JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY

VOL. 100　　JANUARY 4, 1978　　NO. 1

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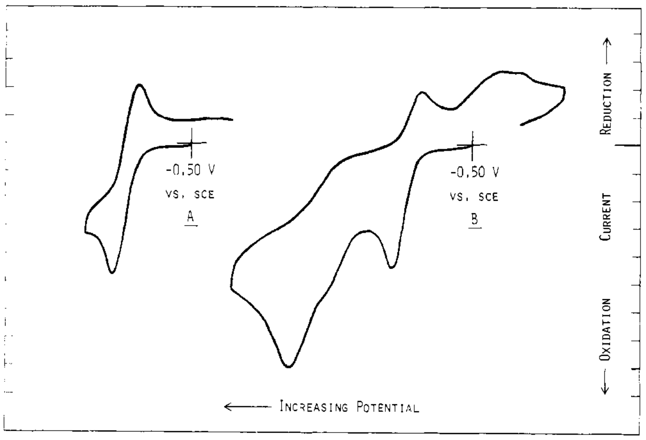

Figure 1. Cyclic voltammograms of uranocene in C_6H_5CN, 0.1 M (n-Bu)$_4N^+PF_6^-$, at a Pt disk electrode (area = 0.21 cm^2). Conditions: sweep rate, 0.8 V/s; 6 °C; switching potentials,0.232 (A),1.167 (B). Abscissa: 20 μA/division.

shown that no more than 1/3 of all the COT ligand is liberated as free COT. Subtraction of both the electrolyte and the solvent bands from the FT IR spectrum of the product solution left bands at 810 (w), 774-780 (m), 758 (w), 719 (w), 644-650 (m), and 608 (w) cm^{-1}, which are in the region characteristic for π-COT complexes to lanthanides and actinides.[19b] The solution is paramagnetic (Gouy balance) and no peaks in the NMR spectrum were observed which one might attribute to the product. The visible spectrum of a typical THF solution showed bands at 659 ($\epsilon \simeq 222$), 637 ($\epsilon \simeq 253$), 540 ($\epsilon \simeq 113$), 490 ($\epsilon \simeq 136$, sh), 478 ($\epsilon \simeq 149$), and 410 nm ($\epsilon \simeq 264$).[20] The same product is formed in both benzonitrile and tetrahydrofuran which appears to rule out solvent molecule incorporation in the structure.

Since at most 1/3 of all COT is liberated in the oxidation and the n value is fractional, a dimeric or cluster product cation is indicated.[21] Strikingly, this substance is air stable, unlike most organouranium compounds, suggesting that the uranium atoms are effectively shielded from attack by O_2 as is the case for both tetra-π-cyclopentadienyluranium(IV)[22a] and di-π-tetraphenylcyclooctatetraenyluranium(IV).[22b]

In summary, the uranocene monocation has been shown to be a short-lived species, thus making a detailed test of Streitwieser's model impossible. It appears, however, that the removal of a 5f electron weakens the metal-ligand bond in uranocene, leading to structural changes and irreversible electrochemistry.[23] The electrochemistry of thoracene (both oxidation and reduction) should also be interesting, but, owing to its insolubility in most solvents, a direct comparison with the uranocene electrochemistry will be difficult.[24] It is clear that electrochemistry, and electrosynthesis in particular, has a valuable role to play in the area of organoactinide chemistry.[25]

Acknowledgments. We thank Dr. Robert Compton and Dr. John Bloor for providing the use of an inert atmosphere box and Dr. William Bull for the use of his Gouy balance. This work was supported by a grant from the Research Corporation and by the University of Tennessee. The FT NMR and IR spectrometers were purchased with National Science Foundation funds. We are grateful to the Tennessee Eastman Co. for fellowship support of J.A.B.

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(4) See R. G. Hays and N. Edelstein, *J. Am. Chem. Soc.*, **94,** 8688 (1972), for a molecular orbital calculation on uranocene and related species.

(5) The U(IV) character of the metal is established by its magnetic moment and by Mössbauer spectroscopy of the analogous neptunium compound.[3]

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(7) Positive and negative ions have been generated in the gas phase by mass spectrometry: A. D. Williamson, R. N. Compton, J. A. Butcher, Jr., J. E. Bloor, and R. M. Pagni, unpublished results.

(8) Of course, if the 5f orbitals on thorium are not sufficiently close in energy to the ligand orbitals, an ionic structure for **2** is certainly reasonable.

(9) Attempted oxidation with Ag^+, NO^+, Cu^{2+}, Cu^+, Sn^{2+}, Cd^{2+}, CH_3NO_2, TCNQ, $(C_6H_5)_3C^+$, and $HFSO_3$ resulted in disruption of the complex and the formation of inorganic products.

(10) There is some evidence that either (n-Bu)$_4N^+ClO_4^-$ or a trace impurity in it participates in the chemical reactions in this system as witnessed by a large and variable reduction wave observed in CVs in the presence of this electrolyte.

(11) Cyclic voltammograms in THF, CH_2Cl_2, and CH_3CN (pulse voltammogram) were qualitatively similar to those in benzonitrile.

(12) The current function of this wave ($i_p/\sqrt{v}$) is proportional to U(COT)$_2$ concentrations, independent of sweep rate, and corresponds approximately to a one-electron process. The peak current ratio, i_p^c/i_p^a, attains a maximum value of 0.6 at a sweep rate of 1 V/s.

(13) IP = 6.20,[6a,b] 6.15,[6c] and 6.20 eV.[7]

(14) (a) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37,** 916 (1972); (b) $E_{1/2}$ vs. Ag = 0.89 IP − 6.04 leads to $E_{1/2} = -0.57$ vs. Ag using IP = 6.2 eV, which is identical with the $E_{1/2}$ obtained in acetonitrile.

(15) O. Hammerlich and V. D. Parker, *Electrochim. Acta*, **18,** 537 (1973).

(16) The uranocene appeared to react with the alumina and decreased in concentration rapidly. The alumina turned a yellow-brown color and a large COT wave appeared in the CV. This was in spite of vacuum drying the alumina at 150 °C overnight and breaking vacuum to Ar.

(17) A Pt gauze electrode passivated under these conditions. The RVC electrode was connected by a carbon rod above the solution level. If contact was made by either a Pt wire or carbon in the solution, the point of contact passivated as well. Other workers in this department have used RVC electrodes successfully. See V. E. Norvell and G. Mamantov, *Anal. Chem.*, **49,** 1470 (1977).

(18) Owing to the high solution resistance and porous nature of the working electrode, constant potential electrolysis conditions were not achieved with the potentiostat (P.A.R. Model 173)-cell configuration. The RVC electrode potential was initially at the foot of the oxidation wave and became more positive as the electrolyses proceeded.

(19) (a) Although the material was air stable, it was sensitive to water and changes in the polarity of the THF solution. Standard methods—chromatography, fractional crystallization, dialysis, adding nucleophyles, electrochemical reduction, and sublimation—were of no avail. Either no separation from the electrolyte was achieved or precipitation of an inorganic degradation product resulted. (b) 900 (m), 787 (w), 772 (w), 741 (m), 594 (s) cm^{-1} for uranocene from ref 3. See also ref 2c.

(20) These ϵ values are calculated for a diuranium cluster and are approximate. The uranocene concentration prior to electrolysis (visible spectrum using published ϵ values for uranocene[3]) was assumed to be equal to the total uranium concentration in the postelectrolysis solution.

(21) For example, the ion could be $U_2COT_3^{3+}$ if n = 1.5 and 1/4 of all COT is liberated. See S. R. Ely, T. E. Hopkins, and C. W. DeKock, *J. Am. Chem. Soc.*, **98,** 1624 (1976), for a lanthanide example: $Nd_2COT_3 \cdot 2THF$.

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(23) Structural changes leading to irreversible steps in metallocene electrochemistry have been observed: J. D. L. Holloway, W. L. Bowden, and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **99,** 7090 (1977).

(24) We have recently found that thoracene in HMPA yields a solution which exhibits cyclic voltammetry consistent with that expected for thoracene based on Miller's correlation:[14] E_p = 0.11 vs. SCE. Unfortunately corresponding measurements on uranocene cannot be made in this solvent since U(COT)$_2$ decomposes in HMPA, as reported in ref 3 and verified in this laboratory.

(25) Electron spin resonance and field ionization mass spectrometry experiments are now in progress on the product of the bulk electrolysis.

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Synthesis of Highly Conducting Films of Derivatives of Polyacetylene, (CH)$_x$

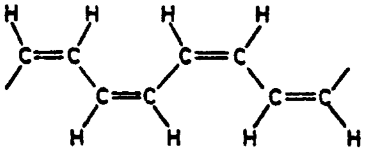
Sir:

We have recently reported[1-3] that, when flexible, crystalline, silvery films of the semiconducting *cis*-(CH)$_x$ (1) or *trans*-

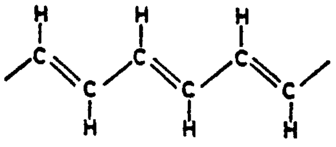
Table I. Conductivity of Polycrystalline Polyacetylene and Derivatives (As-Grown Films)

Material	Conductivity, σ (Ω^{-1} cm^{-1}) (25 °C)
cis-$(CH)_x$[a,b]	1.7×10^{-9}
trans-$(CH)_x$[a,b]	4.4×10^{-5}
trans-$[(CH)(HBr)_{0.04}]_x$	7×10^{-4}
trans-$(CHCl_{0.02})_x$	1×10^{-4}
trans-$(CHBr_{0.05})_x$[c]	5×10^{-1}
trans-$(CHBr_{0.23})_x$[b,c]	4×10^{-1}
cis-$[CH(ICl)_{0.14}]_x$	5.0×10^{1}
cis-$(CHI_{0.25})_x$	3.6×10^{2}
trans-$(CHI_{0.22})_x$[b,c]	3.0×10^{1}
trans-$(CHI_{0.20})_x$[b]	1.6×10^{2}
cis-$[CH(IBr)_{0.15}]_x$	4.0×10^{2}
trans-$[CH(IBr)_{0.12}]_x$	1.2×10^{2}
trans-$[CH(AsF_5)_{0.03}]_x$	7×10^{1}
trans-$[CH(AsF_5)_{0.10}]_x$[b]	4.0×10^{2}
cis-$[CH(AsF_5)_{0.14}]_x$	5.6×10^{2}
trans-$[Na_{0.28}(CH)]_x$	8×10^{1}

[a] H. Shirakawa, T. Ito, and S. Ikeda, unpublished results; see ref 1-3. [b] Composition obtained by chemical analysis from Galbraith Laboratories, Inc. (sum of all elements is ~99.8-100.1%). [c] See ref 1-3.



(1)



(2)

$(CH)_x$ (**2**) polymer were doped with controlled amounts of electron-attracting species such as chlorine, bromine, iodine, or AsF_5, their electrical conductivity could be systematically and controllably varied over a wide range, with up to 10^{11} overall increase in conductivity. The most highly conducting films exhibited a conductivity at room temperature of several hundred Ω^{-1} cm^{-1}—by far the highest conductivity observed for any covalent organic polymer. The $(CH)_x$ polymer films used in the studies were prepared using the techniques developed previously by Shirakawa et al.[4]

We wish to report that this doping phenomenon, previously studied primarily with *trans*-$(CH)_x$, also occurs, possibly to an even greater extent, with *cis*-$(CH)_x$, and that for both isomers significantly higher conductivities than those previously observed can now be obtained (Table I). New electron-attracting dopants which give remarkably high conductivites with both isomers have been identified and studied (Table I). In addition, we have succeeded in making conducting films with an electron donor such as sodium as dopant.

Four platinum wires were attached to films of *cis*- or *trans*-$(CH)_x$ by means of Electrodag and were connected to an apparatus for measuring their dc conductivity by the four-probe method. The films were then treated with the vapor of the dopant at room temperature in vacuo for 3-4 h, and their resistance was monitored at intervals. Final compositions of the doped $(CH)_x$ were determined either by the elemental analysis of a piece of reference film placed just below the film whose conductivity was being measured and/or by the increase in weight of the reference film during doping. The Na-doped films were prepared by treating the polymers with a solution of sodium naphthalide, $Na^+(C_{10}H_8)^{-}\cdot$, in THF, whereupon electron transfer from the naphthalide radical anion to the $(CH)_x$ occurred. The results of a number of experiments are given in Table I.

Table II. Conductivity, σ (Ω^{-1} cm^{-1}), at Room Temperature

Compd	Polycrystalline (compressed pellets), σ_{av} of $\sigma_{\parallel}$ and $\sigma_{\perp}$)	Single crystal
$(SN)_x$	~20	$\sigma_{\parallel} = 3.7 \times 10^{3}$
$(SNBr_{0.4})_x$	~30-300	$\sigma_{\parallel} = 3.8 \times 10^{4}$
(TTF)(TCNQ)	~10	$\sigma \sim 3\text{-}7 \times 10^{2}$
cis-$[CH(AsF_5)_{0.14}]_x$	5.6×10^{2} (as-grown film)	Unknown

The more recent iodination experiments involving *trans*-$(CH)_x$ yield significantly improved electrical properties (σ = 160 Ω^{-1} cm^{-1}) as compared with earlier results (σ = 30 Ω^{-1} cm^{-1}). This increase may be related to a slower rate of iodination which might be expected to lead to more uniform doping throughout the films. Detailed studies of the effects of film thickness, reaction rate, etc., are underway.

The conductivity of iodinated films is electronic. No evidence of any significant increase in the resistance of a film was observed even after passing enough current through the sample over a time period such that the integrated charge exceeded by a factor of 10 the amount needed to cause complete polarization, if conduction were by an ionic mechanism. Preliminary experiments indicate no significant change in the conductivity of the two films tested to date, $[(CH)I_{0.19}]_x$ and $[CH(AsF_5)_{0.10}]_x$, when they were held in vacuum at room temperature for 1 week. The conductivity of films decreases in air during several days.

Electrical and optical studies[2] indicate that $(CH)_x$ films can be chemically doped with electron-attracting (acceptor) or electron-donating (donor) species in a manner analogous to that found for simple classical semiconductors such as silicon. The conductivity progressively increases with doping. With certain dopants, e.g., I_2, AsF_5, etc., a semiconductor-metal transition occurs at a few mole percent dopant concentration to give flexible films of organic metals having a very high room temperature conductivity (Table I).[2]

As a result of the extreme sensitivity of "pure" $(CH)_x$ to impurities, we expect that the intrinsic conductivity of both the cis and trans isomers is probably considerably smaller than the values given in Table I. This is supported by the observation that exposure of *trans*-$(CH)_x$ to vapor of the donor, NH_3, causes the conductivity to fall more than four orders of magnitude (to $<10^{-9}$ Ω^{-1} cm^{-1}) without detectable weight increase. Subsequent reaction of the compensated film with AsF_5 brings the conductivity back up to metallic levels.

It has been known for some time that treatment of a fairly wide variety of compounds such as $(CH)_x$ powder,[5] polyphenylacetylene,[6] polycyclic hydrocarbons,[7] glyoximate,[8] and phthalocyanine[9] metal complexes, $(SN)_x$,[10] etc., with an electron-withdrawing species, usually iodine, may result in an increase of conductivity of many orders of magnitude, but the final room temperature conductivity obtained with most single crystals and with all polycrystalline material, with the exception of $(SN)_x$ derivatives, is still very small. From Table I it can be seen that, when $(CH)_x$ is doped with a number of different species, extraordinarily large increases in conductivity

Table III. Conductivity Adjusted for Density

Material	Density, d (g cm^{-3})	Conductivity (vol), σ (Ω^{-1} cm^{-1}) (25 °C)	Conductivity (wt), σ/d (cm^2 Ω^{-1})-(g^{-1})) (25 °C)
Cu	8.92	5.8×10^5	6.5×10^4
Au	19.3	4.1×10^5	2.1×10^4
$(SNBr_{0.4})_x$	2.67	3.8×10^4	1.4×10^4
Fe	7.86	1.0×10^5	1.3×10^4
$(SN)_x$	2.30	3.7×10^3	1.6×10^3
Hg	13.6	1.0×10^4	7.4×10^2
cis-$[(CH)(AsF_5)_{0.14}]_x$	0.8	5.6×10^2	7.0×10^2

are observed in certain cases—ca. 10^{11} increase when *cis*-$(CH)_x$ is converted to *cis*-$[(CH)(AsF_5)_{0.14}]_x$. Furthermore, *surprisingly large room temperature conductivities are obtained with several dopants.* Some of the $(CH)_x$ derivatives, even in the form of polycrystalline, *un*compressed, *non*aligned films, have an electrical conductivity much greater than polycrystalline *compressed* pellets of $(SN)_x$,[11] (TTF)(TCNQ),[12] etc. (Table II). Indeed, the conductivity of *cis*-$[(CH)(AsF_5)_{0.14}]_x$ is identical with that commonly found for *single* crystals of (TTF)(TCNQ) (Table II). This strongly suggests that aligned films of $(CH)_x$ derivatives should have still higher conductivities.

The highly conducting polymers formed from $(CH)_x$ and electron-withdrawing species may be charge-transfer π complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.[13] These latter observations suggest that the substances formed from $(CH)_x$ and electron-attracting species may consist of a positively charged $(CH)_x$ chain acting as a polycation with appropriate halogen, etc., anions situated at intervals adjacent to the chain.

Although the resistivity (ρ) of a material is usually defined on a volume basis, it can also be defined on a mass basis (ρd) where d is the density. Since the bulk density of the $(CH)_x$ derivatives obtained from the dimensions and weight of a film is considerably smaller (~0.5–1 g cm^{-3}) than that of most metals, the conductivity adjusted for density of a material such as *cis*-$[(CH)(AsF_5)_{0.14}]_x$ is comparable with that of many metals (Table III).

Films of *cis*-$(CH)_x$ doped with AsF_5 have been used as ubstitute "wires" in simple electrical circuits. For example, such films with contacts ~1 cm apart having a weight of ~10 mg will carry sufficient current to cause a flashlight bulb to glow brightly when connected to two 1.5-V flashlight batteries.

Considering possible polyacetylene derivatives, replacement of some or all of the hydrogen atoms in $(CH)_x$ with organic or inorganic groups, copolymerization of acetylene with other acetylenes or olefins, and the use of different dopants should lead to the development of a large new class of conducting organic polymers with electrical properties that can be controlled over the full range from insulator to semiconductor to metal.

Acknowledgment. This work was supported by the Office of Naval Research.

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Received September 6, 1977

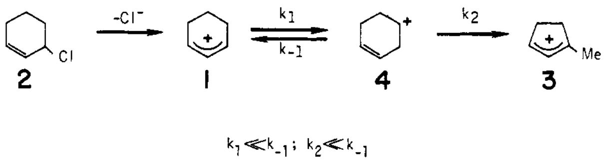
Protonation and Ionization of 4-Chlorocyclohexene in Superacid. A Fast 1,2-Hydride Shift in the 4-Cyclohexenyl Cation

Sir:

Recently we reported the ring contraction of the 3-cyclohexenyl cation (**1**), generated from 3-chlorocyclohexene (**2**), to the 1-methylcyclopentenyl cation (**3**) and measured the rate of this transformation in FSO_3H-SbF_5 (4:1)-SO_2FCl solution.[1] It is conceivable that the first step of this reaction is the formation of the 4-cyclohexenyl cation (**4**) from **1**, by a 1,2-hydride shift. This same transformation is involved in the isotope scrambling observed in a sample of **1** labeled with deuterium.[2] The scrambling occurred at a temperature (−65 °C) much lower than that at which the rate of ring contraction (**1** → **3**) becomes reasonably fast (−20 °C); by extrapolation it was estimated that $k_{-1} \approx 10^4 k_2$ (Scheme I). At the same time, since none of the homoallylic ion **4** was ever evidenced[1-3] in equilibrium with **1**, it follows that, in Scheme I, $k_{-1} \gg k_1$.

Generation of the 4-cyclohexenyl cation (**4**) from various precursors (**5**) in superacid solutions has been attempted before.[3] In each case, the ring-contracted isomer **3** was the only

Scheme I



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