**Figure 1.** Cyclic voltammogram of 5.0×10^{-3} M $(OC)_5ReRe(CHO)$-$(CO)_4^-$ (I) in acetonitrile containing 0.1 M TEAP at a scan rate of 200 mV s^{-1} at 25 °C. Parts 2 and 3, in the presence of 3 and 10 equiv dihydroanthracene, respectively. II is the CV wave of $(OC)_5ReRe$-$(H)(CO)_4^-$.

quantum yield for the photoinitiated conversion to II was found to be $\Phi > 400$. Importantly, this value was markedly decreased in the presence of 1 equiv of dihydroanthracene.[10]

The long kinetic chain lengths arising from free radical and photochemical initiation indicate an efficient propagation sequence which we ascribe to the following mechanism:

Scheme I

$$HC(=O)(re) + re\cdot \rightarrow OC(re)\cdot + H(re) \qquad (2)$$

$$OC(re)\cdot \rightarrow CO + re\cdot \text{ etc.} \qquad (3)$$
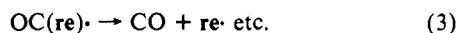
where $re = (OC)_5ReRe(CO)_4^-$. Precedent for both steps derives from the studies of Brown and co-workers,[11] who demonstrated the ability of carbonylrhenium radicals (i) to abstract hydrogen atoms from various donors as in eq 2 and (ii) to undergo facile exchange of carbonyl ligands as in eq 3.

Initiation of the radical chain by AIBN homolysis affords $(CH_3)_2\dot{C}CN$, which abstracts hydrogen from I to produce directly the carbonyldirhenate radical re· for Scheme I. Photochemical initiation derives from Re–Re bond scission[12] of I to generate two carbonylrhenium radicals, each capable of hydrogen abstraction from I.[13] Carbonylrhenium radicals can also be generated electrochemically. For example, the galvanostatic reduction of I (2.0×10^{-2} M) in acetonitrile containing 0.1 M TEAP consumed 0.035 F mol^{-1} (turnover number $\simeq$ 30) to yield essentially quantitative yields of II.[6] The rapidity of the electrocatalytic process is revealed in the cyclic voltammogram in Figure 1 showing (a) the cathodic current for the irreversible wave of I at E_p –2.1 V to be only 20% of that expected for a one-electron reduction (based on ferrocene calibration) and (b) the simultaneous appearance of II by comparison of the CV wave at E_p –2.6 V with that of an authentic sample. The occurrence of a chain decomposition was also evident by the marked increase in the cathodic current for I and concomitant decrease of II by incremental additions of dihydroanthracene in Figure 1, parts 2 and 3.[14] We

propose that electroinitiation proceeds via carbonylrhenium radicals formed by dissociative electron attachment[15] of I and is followed by the propagation mechanism in Scheme I. Indeed, an equivalent catalytic process can be induced chemically by reducing agents. For example, the addition of 10 mol % sodium anthracene to a 10^{-1} M THF solution of I was sufficient to effect conversion to II in 75% yield within 10 min. Thus it is not surprising that anthracene (5 mol %) promotes the electrocatalytic conversion of I to II in quantitative yield at potentials >300 mV more positive than E_p –2.1 V for I in acetonitrile (note, for anthracene E^0 –2.03 V).

We are examining the behavior of other formylmetal complexes in order to stabilize unpersistent ones and to test the generality of the radical chain mechanism.

(10) E.g., $\tau_{1/2}$ of I increased from 30 min to >10 h in the presence of 1 equiv of dihydroanthracene.

(11) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, 2, 775 and references cited therein.

(12) Cf.: Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, 92, 3653. Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 89 ff. Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, 105, 822. Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *Ibid.* **1982**, 104, 1842. It is also possible that photochemical irradiation generates re· directly from I.

(13) See ref 11 and Byers and Brown [Byers, B. L.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, 99, 2527] for the homolytic reactivity of carbonylrhenium radicals.

(14) (a) Cf.: Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, 104, 3034. (b) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *Ibid.* **1981**, 103, 3161. (c) However, saturation of the dihydroanthracene effect suggests the presence of a competing electrocatalytic pathway (Narayanan, B. A.; Amatore, C.; Kochi, J. K., manuscript in preparation).

(15) Cf.: Lemoine, P.; Giraudeau, A.; Gross, M. *Electrochim. Acta* **1976**, 21, 1, for:

$$\text{I} \xrightarrow{+e} [(OC)_5Re\cdot + (OC)_4ReCHO^{2-}] \text{ or } [(OC)_5Re^- + (OC)_4ReCHO^-\cdot]$$
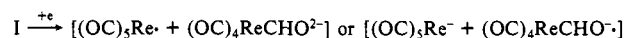
Preparation and Reactions of Cr⁻. The Cr–H Bond Strength

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Recent studies of the chemistry of gaseous atomic metal ions have provided a valuable new source of information about metal–ligand bond strengths[1,2] as well as an opportunity to observe the reactivity of metal ions in the absence of solvation, counterions, and ligand-field perturbations.[1–3] While atomic transition-metal cations can be generated for gas-phase studies via surface ionization,[4] laser desorption,[5] and electron-impact ionization of volatile inorganic complexes such as metal carbonyls,[6] the corresponding atomic metal anions are not normally observed under these conditions,[7] and hence, their chemical reactivity has remained largely unexplored. We now wish to report that atomic transition-metal anions can be produced in good yields in a Fourier transform mass spectrometer (FTMS) utilizing collision-induced dissociation (CID) of anionic metal carbonyl complexes. We present here the results of our initial studies of the gas-phase reactivity of Cr⁻, including a determination of its proton affinity and the Cr–H bond dissociation energy.

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(2) Jones, R. W.; Staley, R. A. *J. Am. Chem. Soc.* **1982**, 104, 2296–2300 and references cited therein.

(3) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, 104, 5944–5950. Allison, J.; Ridge, D. P. *Ibid.* **1979**, 101, 4998–5009. Halle, L. F.; Armentrout, P.; B.; Beauchamp, J. L. *Organometallics* **1982**, 1, 963–968.

(4) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, 74, 2819–2826.

(5) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spec. Ion Phys.* **1980**, 33, 37–43. Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, 103, 4360–4367.

(6) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, 101, 1332–1333.

(7) Atomic metal anions are occasionally observed in low abundance from laser desorption–ionization of metal targets. Most previous studies of atomic negative ions have utilized sputter-type ion sources, cf.: Corderman, R. R.; Engelking, P. C.; Lineberger, W. C. *Appl. Phys. Lett.* **1980**, 36, 533–535.

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J. Am. Chem. Soc., Vol. 105, No. 20, 1983 6353
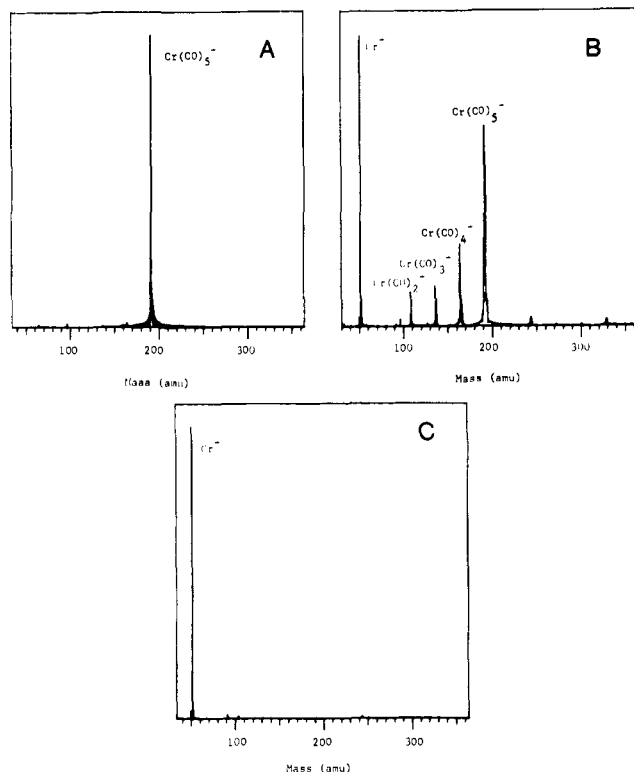
Figure 1. Fourier-transformed mass spectra illustrating generation of Cr^- from (A) electron-impact ionization of $Cr(CO)_6$, (B) irradiation of $Cr(CO)_5^-$ at its cyclotron frequency with an 18.5-V 0.100-ms CID pulse in the presence of 6×10^{-6} torr of Ar, and (C) double-resonance ejection of all ions from the cell except Cr^-.
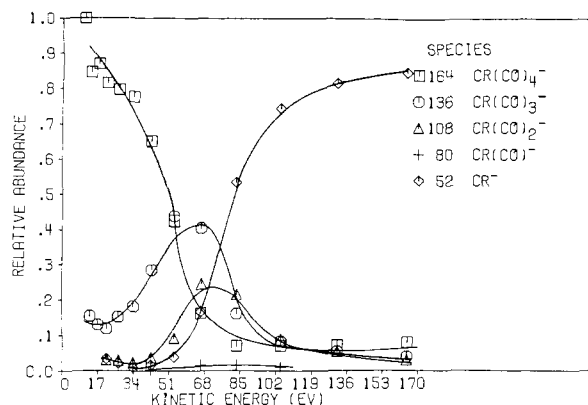
Figure 2. Product ion distribution vs. parent ion kinetic energy for collision-induced dissociation of $Cr(CO)_5^-$. Ion translational energies calculated by the methods described in ref 9.

The experiment utilizes a Nicolet FTMS 1000 with a modified 5.2-cm cell as described previously.[8,9] $Cr(CO)_5^-$ was formed by a 12.9-eV, 150-ms electron beam pulse on $Cr(CO)_6$ at ca. 5×10^{-8} torr (Figure 1A). After 100 ms, an 18.5-V CID pulse was applied for 0.100 ms, and a 100-ms CID interaction time was allowed for collisional dissociation against Ar at 6×10^{-6} torr (Figure 1B). The excitation energy delivered to $Cr(CO)_5^-$ was varied, and a plot illustrating its effect on fragmentation ion yields is shown in Figure 2. The extent of carbonyl loss sequentially increases as the parent ion kinetic energy is increased. Interestingly, the $CrCO^-$ intensity remains nearly zero for the entire range of CID energies applied to $Cr(CO)_5^-$. We view this as a manifestation of a relatively weak Cr–C bond in $CrCO^-$, which reflects the inherent stability of the $3d^5 4s^2$ Cr^- fragment.[10]

(8) Cody, R. B.; Freiser, B. S. *Int. J. Mass. Spec. Ion Phys.* **1982**, *41*, 199–204.

(9) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96–101.

Table I. Proton Affinity of Cr^- Bracketed with Acids of Known Gas-Phase Acidity[a]

reference acid	ΔH_{acid} (300 K)	proton abstraction by Cr^- observed?
HCOOH	345.2 ± 2	no
$CH_3COCH_2COCH_3$	343.7 ± 2	no
p-$H_2NC_6H_4COOH$	341.1 ± 2[b]	no
5,5-dimethylcyclohexane-1,3-dione (dimedone)	338.9 ± 2	yes
C_6H_5SH	338.9 ± 3.5	yes
CF_3COOH	322.7 ± 2	yes

[a] Acidities and estimated uncertainties (kcal mol^{-1}) taken from ref 17. [b] ΔH_{acid}(300 K) assumed equal to ΔG_{acid}(600 K), see: McMahon, T. B.; Kebarle, P. J *J. Am. Chem. Soc.* **1977**, *99*, 2222–2230.

Ejection of all ions from the FTMS cell except Cr^- (Figure 1C) permits the examination of its bimolecular ion–molecule reactions with neutral substrates added to the system via leak valves, pulsed inlets,[11] or a solid probe. Two products of roughly equal abundance arise from the reaction between Cr^- and the parent chromium hexacarbonyl (eq 1). Double resonance clearly identifies Cr^- as

$$Cr^- + Cr(CO)_6 \xrightarrow{a} Cr(CO)_5^- + Cr + CO$$
$$\xrightarrow{b} Cr_2(CO)_5^- + CO$$

$$(1)$$
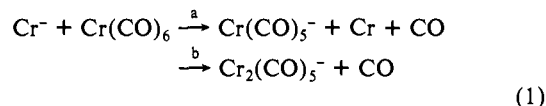
a precursor for both products, although a small amount of the observed $Cr(CO)_5^-$ also derives from ionization of $Cr(CO)_6$ by trapped thermal electrons. Path a represents a dissociative charge transfer, and path b may be viewed as an adduct formation with subsequent loss of CO. The occurrence of path b implies that $D[Cr(CO)_5^- - Cr] \geq EA(Cr) + D[Cr(CO)_5 - CO] - EA[Cr(CO)_5]$. By analogy with $Fe(CO)_5^{12,13}$ and $Ni(CO)_4^{13,14}$ we assume that the last two terms in this expression are roughly equal, which leads to an estimated lower limit to $D[Cr(CO)_5^- - Cr]$ equal to $EA(Cr)$ (15.4 ± 0.2 kcal mol^{-1}).[15] That the chromium atom is relatively *weakly* bound in $Cr_2(CO)_5^-$ is demonstrated by the fact that *Cr loss and not CO loss* is the primary fragmentation pathway when $Cr_2(CO)_5^-$ is subjected to low-energy CID excitation.[16]

The reactions of Cr^- with Brønsted acids are of particular interest since a determination of its proton affinity can provide a measure of the Cr–H bond dissociation energy. The results of our bracketing experiments with reference acids of known gas phase acidity (ΔH_{acid})[17] are summarized in Table I. Double-resonance responses indicate that proton abstraction by Cr^- occurs with CF_3COOH, PhSH, and dimedone, while no reaction occurs with simple aliphatic carboxylic acids, 2,4-pentanedione, and p-aminobenzoic acid. From these results we assign the proton affinity of Cr^- equal to 340 ± 3 kcal mol^{-1}.[18] Combining this value with the measured electron affinity of Cr (15.4 ± 0.2 kcal mol^{-1})[15] and the ionization potential of hydrogen (313.6 kcal mol^{-1})[19] yields a Cr–H bond energy of 41.8 ± 3 kcal mol^{-1}. This

(10) Moore, C. E. "Atomic Energy Levels". *Nat. Bur. Stand. (U.S.) Circ.* **1952**, No. 467.

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(16) The $Cr_2(CO)_5^-$ ion also exhibits interesting bimolecular gas-phase reactions with a variety of substrates. Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S., manuscript in preparation.

(17) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, **1979**; Vol. 2, chapter 11.

(18) Estimate of error based upon uncertainties in ΔH_{acid} values (ref 17) plus the uncertainty inherent in bracketing measurements, cf.: Mautner, M. *J. Chem. Soc.* **1982**, *104*, 5–10.

value is in accord with an experimentally determined upper limit of 45 kcal mol^{-1} reported by Kant and Moon[20] and a theoretical value of 46 kcal mol^{-1} calculated by Das.[21]

By use of the technique described above, Fe$^-$, Co$^-$, Mo$^-$, and W$^-$ also have been generated in our laboratory and are presently under investigation. The details of their preparation and their gas-phase reactivity will be reported in forthcoming publications.

Registry No. Cr(CO)$_5^-$, 51222-95-8; Cr$^-$, 19498-56-7; CF$_3$COOH, 76-05-1; PhSH, 108-98-5; Cr(CO)$_6$, 13007-92-6; dimedone, 126-81-8.

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(21) Das, G. *J. Chem. Phys.* **1981**, *74*, 5766–5774.

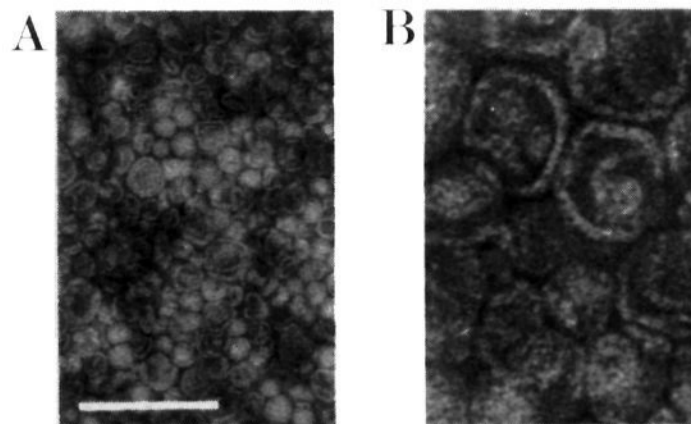### Polymerized–Depolymerized Vesicles. A Reversible Phosphatidylcholine-Based Membrane[1]

Steven L. Regen,* Kazuo Yamaguchi,[2] N. K. P. Samuel, and Maninder Singh

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Milwaukee, Wisconsin 53233*
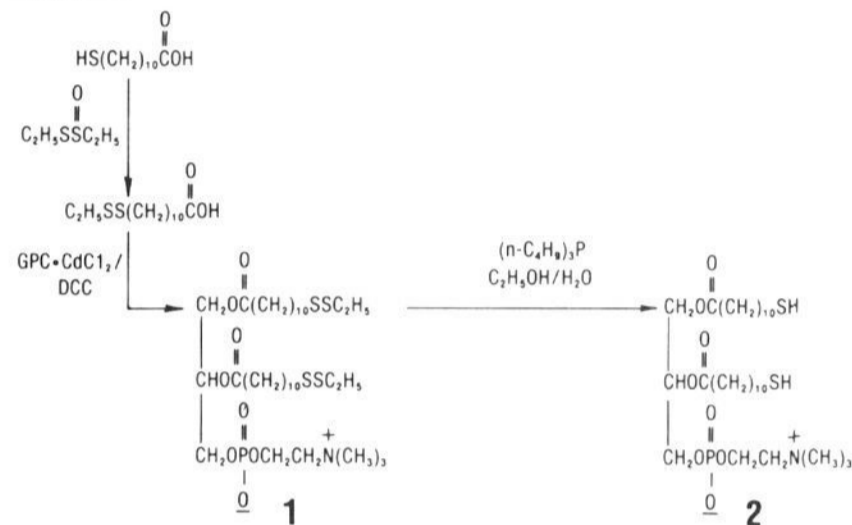
Received June 30, 1983

In this communication we report the synthesis and preliminary characterization of a phospholipid vesicle membrane that can be "switched on" (polymerized) and "switched off" (depolymerized) via oxidation and reduction, respectively. This membrane is based on the thiol-bearing lipid 1,2-bis(11-mercaptoundecanoyl)-*sn*-glycero-3-phosphocholine (**2**) whose synthesis is also described herein.

Polymerized forms of phospholipid bilayer vesicles represent a new and unique class of organic polymers that may find broad use as models for biological membranes and as carriers of drugs.[3–9] They have a close similarity to conventional liposomes in terms of their gross morphology, entrapment ability, permeability, and membrane structure but are substantially more stable. If polymerized vesicles could be depolymerized, in a reversible manner, their utility as a membrane model would be significantly increased. Biochemical studies could then be carried out either in the "on" (polymerized) or "off" (nonpolymerized) mode; they could also

be conducted during or between a series of "on–off" cycles. In the "on" position, lateral diffusion within the membrane (a parameter of central importance to many biomembrane problems) should be greatly reduced or eliminated. Moreover, the ability to depolymerize a vesicle network would allow one to take apart and recover key components, e.g., membrane proteins.[10] Polymerized vesicles that are susceptible to depolymerization in vivo might also be ideally suited as time-release carriers of drugs. Motivated by these ideas and by the intriguing structural features expected for an ordered network of monomers capable of reversible polymerization, we have begun to focus our efforts on the synthesis of polymerizable–depolymerizable vesicles. In the following report we present preliminary results obtained with the first representative example, a phosphatidylcholine-based membrane, whose reversibility derives from a thiol–disulfide redox cycle.[11]

The synthetic route used for the preparation of **2** is outlined in Scheme I. Oxidation of 11-mercaptoundecanoic acid with ethyl ethanethiosulfinate in chloroform produced an 80% isolated yield of 11-ethyldithioundecanoic acid;[12–14] subsequent esterification with *sn*-glycero-3-phosphocholine–CdCl$_2$ (GPC·CdCl$_2$) furnished a 91% isolated yield of 1,2-bis(11-(ethyldithio)undecanoyl)-*sn*-glycero-3-phosphocholine (**1**). Treatment of **1** in C$_2$H$_5$OH–H$_2$O (1/1)[15,16] with tri-*n*-butylphosphine afforded a 95% isolated yield of **2**.[15,16]

Figure 1. Electron micrographs of UV-polymerized vesicles of **2**. Bar represents 2000 Å; (B) is a 3.9 × magnification of (A).

Scheme I

(1) Supported by the National Science Foundation (Grant CHE-8103083) and by PHS Grant CA 28891, awarded by the National Cancer Institute, DHHS.
(2) On leave from the Department of Polymer Science, Tokyo Institute of Technology, Tokyo, Japan.
(3) Regen, S. L.; Singh, A.; Oehme, G.; Singh, M. *J. Am. Chem. Soc.* **1982**, *104*, 791. Kusumi, A.; Singh, M.; Tirrell, D.; Oehme, G.; Singh, A.; Samuel, N. K. P.; Hyde, J. S.; Regen, S. L. *Ibid.* **1983**, *105*, 2975.
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(14) Thin-layer chromatography was carried out under nitrogen using silica gel and CHCl$_3$–CH$_3$OH–H$_2$O (65/25/4) as the eluting solvent.
(15) Humphrey, R. E.; Potter, J. L. *Anal. Chem.* **1965**, *37*, 164.
(16) Lipid 2: ^{1}H NMR (CDCl$_3$) δ 1.27 (br s, 32 H, CH$_2$), 2.0–2.75 (m, 8 H, HSCH_2 and CH$_2$C=O), 3.35 (s, 9 H, NCH$_3^+$), 3.65–4.5 (m, 8 H, CH$_2$O and CH$_2$N$^+$), 5.15 (m, 1 H, > CHO); IR (neat) $\nu_{C=O}$ 1730 cm^{-1}, $\nu_{N(CH3)3}^+$ 1090, 1060, 970 cm^{-1}. Anal. Calcd for **2**, C$_{30}$H$_{60}$O$_8$NS$_2$P: N, 2.13; S, 9.75; P, 4.71. Found: N, 1.92; S, 8.38; P, 4.87.