obscuronatin (**4**) and its rearrangement product **5** from soft corals of the genus *Xenia*. Kalihinol-A (**1**) is the most richly functionalized example of this skeletal type.

Acknowledgment. We thank Drs. C. Ireland and G. R. Schulte for collection of the animal, Professor P. Bergquist for identification, and the National Science Foundation and the Sea Grant College Program for financial support. C.W.J.C. thanks the University of West Florida for a Faculty Development Award.

Supplementary Material Available: IR and ^{1}H NMR (300 MHz) spectra and tables of fractional coordinates, equivalent isotropic thermal parameters, bond distances, bond angles, torsional angles, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

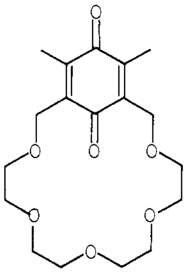
Redox-Active Crown Ethers: Molecules Designed to Couple Ion Binding with a Redox Reaction

Robert E. Wolf, Jr., and Stephen R. Cooper*†

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received March 19, 1984

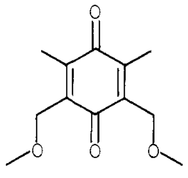
Coupled reactions, i.e., reactions that mutually influence each other, play a fundamental role in biological processes such as ion transport and oxidative phosphorylation.[1] To gain insight into coupled reactions we have begun exploration of the behavior of redox-active crown ethers[2] such as


I

a class of molecules in which the proximity of the electroactive quinone group to the ion-binding crown moiety results in coupling of redox reactions of the quinone with ion bonding by the crown.[7]

Cyclic voltammetric studies of I in DMF provide strong evidence for the desired coupling between complexation and redox reactions of this molecule: the presence of alkali metal salts makes the quinone easier to reduce.[3] Replacement of 0.1 M $Et_4N^+ClO_4^-$ as supporting electrolyte with 0.1 M $M^+ClO_4^-$ (M = Li, Na) $M^+BF_4^-$ (M = K) changes the Q/SQ$^-$ formal potential (E_f) from −0.60 V vs. SCE to −0.55, −0.48, and −0.47 V vs. SCE, respectively, shifts of +50, +120, and +130 mV. These shifts reflect metal ion binding by the crown group (with I-SQ binding Na^+ and K^+ 100 times more strongly than I[4]) and indicate that redox reactions of the quinone and ion binding by the crown influence each other, i.e., these reactions are now coupled.

Both the magnitude and cation dependence of the potential shifts establish that they arise from complex formation, and not from simple ion pairing. For example, E_f of I shifts anodically by 120 mV upon replacement of 0.1 M $Et_4N^+ClO_4^-$ with 0.1 M $NaClO_4$ as supporting electrolyte; that of benzoquinone changes by only 10 mV under the same conditions, and that of II


II

undergoes only a 20-mV shift. Clearly ion pairing between Na^+ or K^+ and the semiquinones cannot account quantiatively for the observed shifts. Moreover, anodic shifts from ion pairing should decrease with the charge/radius ratio of the cation, and therefore decline in the order $Li^+ > Na^+ > K^+$ (as observed for, e.g., benzoquinone); the shifts observed for I, however, decrease in the order $K^+ > Na^+ > Li^+$ and are more consistent with progressively worse "fit" between metal ion and crown. Thus the shifts in E_f caused by alkali metal cations *neither qualitatively nor quantitatively obey those expected for simple ion pairing*; they are, however, consistent with complexation of the metal cations, and as such they indicate coupling between complexation and redox reactions.

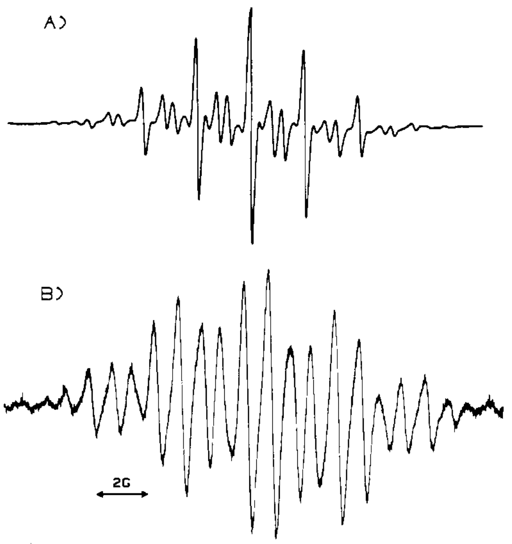


Figure 1. EPR spectra of I-SQ (a) in the absence of $NaClO_4$ and (b) in the presence of 0.2 M $NaClO_4$. Quinone crown concentration 1 mM in DMF containing 0.1 M $Et_4N^+ClO_4^-$. Modulation amplitude 0.05 G; microwave power 0.8 mW.

Parallel EPR studies of the corresponding crown semiquinone I-SQ [(I-SQ$^-$] = 2.5 mM, generated in DMF by reduction of the quinone crown at −0.8 V vs. SCE) provide further evidence supporting complex formation with alkali metal ions, and also yield insight into the structure of the complex formed. In the presence of 0.1 M $Et_4N^+ClO_4^-$ the EPR spectrum of I-SQ has $a(CH_3)$ = 2.05 G and $a(CH_2)$ = 0.83 G (Figure 1a). Introduction of 0.1 M $NaClO_4$ changes the spectrum strikingly to one with $a(CH_3)$ = 2.5 G and $a(CH_2) < 0.2$ G, as well as ^{23}Na superhyperfine splitting of 0.9 G (Figure 1b); that of II-SQ is unaffected. The appearance of ^{23}Na shfs reflects the strength of complexation, while the changes in the CH_3 and CH_2 hfs for I-SQ indicate that complexation perturbs that $1b_{2u}$ (in D_{2h}) HOMO of the semiquinone, causing greater localization of electron density at the methylene end and concomitantly greater localization of spin density at the methyl end. We tentatively suggest that the semiquinone partially cants toward the plane of the complexed crown ring[5] such that the oxygen atom in the 1-position of the

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† Address correspondence to this author at the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR England.

(1) Racker, E. *Acc. Chem. Res.* **1979**, *12*, 338-44.

(2) Synthesis and characterization of I will be described subsequently. Wolf, R. E., Jr.; Cooper, S. R., manuscript in preparation.

(3) Only one cathodic and one anodic wave are observed for the Q/SQ$^-$ couple (with ΔE_{pp} = 60–70 mV), consistent with complexation/decomplexation of the alkali metal ion that is rapid on the cyclic voltammetric time scale. The SQ$^-$/HQ^{2-} potential also shifts, but no more than does benzoquinone itself. These shifts probably derive largely from simple ion pairing and hence are uninteresting.

(4) This difference in stability constants is calculated from $E_f^{complex} - E_f^{free} = -RT/nF\{\ln (K_Q/K_{SQ})\}$.

(5) Seiler, P.; Dobler, M.; Dunitz, J. D., *Acta Crystallogr., Sect. A* **1974**, *B30*, 2744-5.

semiquinone (i.e., that at the methylene end) interacts strongly with the metal ion and that this interaction causes the observed coupling of redox and complexation reactions.

The present experiments show that physical proximity of suitably situated redox-active and ion-binding groups results in coupling of redox and complexation reactions. For redox-active crown ethers reduction/oxidation of the electroactive group affords a means to "turn on" and "turn off" ion binding and offers the possibility of driving ion transport against a chemical concentration gradient by coupling the formation of a chemical concentration gradient with the discharge of an electrochemical potential gradient. In principle this coupling could be used to convert electrochemical energy into chemical concentration gradients, just as, e.g., nerve cells do. Moreover, in a biological context it suggests a means by which electrochemical and chemical energy can be interconverted in an efficient fashion—the essence of the chemiosmotic hypothesis.[6]

Acknowledgment. We are grateful to Professor E. J. Corey of this department for his advice and encouragement and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(6) Mitchell, P. *Nature* (*London*) **1961**, *191*, 144–8.

(7) Several reports of conceptually related compounds have appeared recently: Kaifer, A.; Echegoyen, L.; Gustowski, D. A.; Goli, D. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 7168–9. Gustowski, D. A.; Echegoyen, L.; Goli, D. M.; Kaifer, A.; Schultz, R. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 1633–5. Bock, H.; Hierholzer, B.; Vögtle, F.; Hollman, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 57–8.

(8) **Note Added in Proof**: A prior report on this class of compounds has come to our attention: Sugihara, K.; Kamiya, H.; Yamaguchi, M.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 1619–22.

Effects of Highly Dissociated Salts in Stoichiometric and Catalytic Reactions on Ruthenium Cluster Complexes

Guy Lavigne and Herbert D. Kaesz*

Department of Chemistry and Biochemistry
University of California
Los Angeles, California, 90024

Received April 23, 1984

In attempts to trace the stepwise transformation of $Ru_3(CO)_{12}$ into hydridohalogen derivatives,[1] we observed the stoichiometric transformation shown in eq 1.[2] This parallels the known reactions

$$Ru_3(CO)_{12}/THF + [PPN][Cl]/CH_2Cl_2 \xrightarrow[25\ ^{\circ}C]{5\ min/N_2\ stream} [PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}] + 2CO \tag{1}$$

of $Ru_3(CO)_{12}$ with $[PPN][NO_2]$[3] or [PPN][acetate],[4a] yielding the $[PPN^+]$ salts of anions of general formula $[Ru_3(\mu\text{-}Nu)(CO)_{10}^-]$. The mild conditions for these transformations[4b] suggest labilization of CO in some intermediate such as $[Ru_3(\eta^1\text{-}C(O)Nu)(CO)_{11}^-]$[5a,b] which we have not been able to detect by IR at 25 °C for $Nu^- = Cl^-$. By contrast, such an intermediate with $Nu^- = CH_3O^-$, has recently been isolated under a CO atmosphere and shown to undergo rapid substitution by phosphites.[5c,d]

In attempting to intercept intermediate(s), we examined reaction 1 with a variety of $[PPN^+]$ salts and in the presence of various ligands. We report first that [PPN][acetate] is an excellent catalyst for the *mono*substitution of triphenylphosphine on $Ru_3(CO)_{12}$, eq 2. The yields and the rates match those observed

$$Ru_3(CO)_{12} + PPh_3 \xrightarrow[2\ min/25\ ^{\circ}C/THF]{[PPN][acetate]} Ru_3(CO)_{11}PPh_3 \tag{2}$$

with radical ion initiators.[6] Typically[7a] a solution of $Ru_3(CO)_{12}$ in tetrahydrofuran (THF) containing a stoichiometric amount of PPh_3 is treated with a catalytic amount of $[PPN][CH_3CO_2]$.[7b] Upon addition of the catalyst, the color changes instantaneously from pale to dark orange. IR spectra show 100%[8a] conversion of starting material to $Ru_3(CO)_{11}PPh_3$ within 2 min.[8b] With excess triphenylphosphine, the higher substituted derivatives $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$ are obtained at 25 °C.[9] Starting with the mono-or disubstituted derivatives, we were able to show that the rates of these subsequent reactions[10] are not accelerated by catalytic amounts[7a] of [PPN][acetate].

By contrast, [PPN][CN] promotes instantaneous disubstitution of $Ru_3(CO)_{12}$ in the presence of excess PPh_3 to give $Ru_3(CO)_{10}(PPh_3)_2$.[7a,c] Substitution of $Ru_3(CO)_{12}$ by ligands of lower nucleophilicity, such as $AsPh_3$ and trialkyl or triaryl phosphites, is also promoted by catalytic amounts of [PPN][CN] or by [PPN][acetate] in larger quantities (in both cases giving disubstitution products).[7c,11]

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(1) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390–1397.

(2) (a) $[PPN^+]$ = *bis*(triphenylphosphine)iminium. (b) For the stoichiometric reaction, $Ru_3(CO)_{12}$ (192 mg, 0.300 mmol) is dissolved in 100 mL of freshly distilled THF. A stoichiometric amount of [PPN][Cl] (172 mg) (or a slight excess) disssolved in 1–3 mL of Ch_2Cl_2 is added by syringe. Under bubbling N_2, the reaction is complete within 5 min (IR) proceeding with a change in color from light to dark orange. Spectroscopic yield of the anion $[Ru_3(\mu\text{-}Cl)(CO)_{10}^-]$ is 100%; IR in THF (carbonyl region) (cm^{-1}) 2069 w, 2038 w, 2025 s, 1993 vs, 1981 sh, 1971 sh, 1952 s, 1906 w, 1800 m, 1772 sh. If the [PPN][Cl] is added as a powder, the reaction requires 25 min. By contrast, LiCl shows no effect. Titration of the solution with HBF_4/Et_2O (Aldrich) gives $Ru_3(\mu\text{-}H,\mu\text{-}Cl)(CO)_{10}$ in about 70–75% yield, better than what is obtained in the route using Me_3NO.[1] Acidification is also accompanied by formation of traces of starting material. (c) By contrast, reaction 1 in refluxing THF gives $[PPN][Ru_4(\mu\text{-}Cl)(CO)_{13}]$: Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985–2990.

(3) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034–2042.

(4) (a) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285–1291. (b) The reported reaction of [PPN][acetate] with $Ru_3(CO)_{12}$ was carried out in refluxing THF for 90 min. We find the reaction is complete within 5 min at 25 °C, under the conditions described in ref 2b. A reaction of [PPN][formate] with $Ru_3(CO)_{12}$ was earlier found to proceed at room temperature.[4a]

(5) (a) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704–1706. (b) A triosmium analogue $Nu^- = CH_3^-$ has recently been characterized through ^{13}C NMR: Jensen, C.; Knobler, C. M.; Kaesz, H. D. *J. Am. Chem. Soc.*, submitted for publication. (c) Anstock, M.; Taube, D.; Ford, P. C., personal communication. (d) Working under an atmosphere of CO, intermediate species for $Nu^- = Cl^-, Br^-, I^-$, and $CH_3CO_2^-$ are observed by IR; their characterization by ^{13}C NMR is in progress (C. E. Kampe and authors).

(6) (a) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321–343. (b) Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893–1903.

(7) (a) Experimental conditions for the substitution ractions using an equivalent or excess amount of phosphine are as follows: $Ru_3(CO)_{12}$ (192 mg, 0.3 mmol) and the desired amount of phosphine are dissolved in 100 mL of freshly distilled THF. The reaction is started by the addition of $[PPN^+]$ salt (0.015 mmol) as a powder. This serves to saturate the solution, most of the solid remaining as a suspension. Half-life is determined by the disappearance of the 2060-cm^{-1} absorption of $Ru_3(CO)_{12}$, plotting in absorbance. IR spectra also indicate the degree of substitution. (b) For the preparation of [PPN] salts, see: Martinsen, A.; Songstadt, J. *Acta Chem. Scand. Ser. A* **1977**, *A31*, 645–650. (c) With active salts such as [PPN][acetate] or [PPN][CN], catalytic amounts may be added as CH_2Cl_2 or acetone solutions (1 mL containing 0.015 mmol of salt).

(8) (a) Standard solutions containing 3 mmol of substituted complexes per L of THF are used to determine spectroscopic yields from absorbance data obtained on the FT IR. (b) Experimental details are given in a supplement to this ref (supplementary material).

(9) Details for the syntheses of $Ru_3(CO)_{10}(PPH_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$ are given in a supplement to this ref (supplementary material).

(10) (a) Kinetics for substitution of PPh_3 on $Ru_3(CO)_{12-n}(PPh_3)_n$, $n = 1$ and 2, in decalin in the range 26–50 °C have been reported: Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484–1488. (b) Our observations in THF solution are given here for comparison. Substitution of $Ru_3(CO)_{11}PPh_3$(262 mg, 0.300 mmol) by additional PPh_3 (79 mg, 0.300 mmol) in 100 mL of THF at 25 °C under argon is monitored by disappearance of the 2045-cm^{-1} absorption: $t_{1/2}$ = 35–40 min. Substitution of $Ru_3(CO)_{10}(PPh_3)_2$ (332 mg, 0.300 mmol) by additional PPh_3 (79 mg) is followed by disappearance of the 2018-cm^{-1} band: $t_{1/2}$ = 90 min. Disappearance of $Ru_3(CO)_{11}PPh_3$ after its rapid formation in the presence of 2 mol equiv of PPh_3 and [PPN][acetate] (as catalyst) is identical with disappearance of $Ru_3(CO)_{11}PPh_3$ in its noncatalyzed reaction with PPh_3, supplementary material, Figure 1.

0002-7863/84/1506-4647$01.50/0