would account for the apparent pH independence of $\Delta G°_{4,2}$ at that temperature.

A subsequent manuscript will describe in detail the double-label method for determining $K_{4,2}$ and will correlate the results given here with those of further experiments.

Acknowledgment. This work was supported by NIH Grant HL-16833 and NSF Grant BMS 74-22686.

References and Notes

(1) M. H. Klapper and I. M. Klotz, *Biochemistry*, **7**, 223 (1968).

(2) C. K. Woodward, L. Ellis, and A. Rosenberg, *J. Biol. Chem.*, **250**, 432, 440 (1975).

(3) R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

(4) H. Will and G. J. Damaschun, *J. Theor. Biol.* **30**, 579 (1973).

(5) W. A. Englander and D. Crowe, *Anal. Biochem.*, **19**, 579 (1965).

(6) R. H. Crepeau, C. P. Hensely, Jr., and S. J. Edelstein, *Biochemistry*, **13**, 4860 (1974).

(7) J. O. Thomas and S. J. Edelstein, *J. Biol. Chem.*, **247**, 7870 (1972).

(8) J. O. Thomas and S. J. Edelstein, *J. Biol. Chem.*, **248**, 2901 (1973).

(9) E. Chiancone, L. M. Gilbert, G. A. Gilbert, and G. L. Kellet, *J. Biol. Chem.*, **243**, 1212 (1968).

(10) G. L. Kellet, *J. Mol. Biol.*, **59**, 401 (1971).

(11) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N.Y., 1969, pp 117-118.

(12) R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).

(13) Address correspondence to this author at the Department of Laboratory Medicine and Pathology, Box 198 Mayo Building, University of Minnesota, Minneapolis, Minn. 55455.

G. J. Ide, A. D. Barksdale, A. Rosenberg* [13]

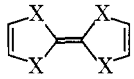
Department of Laboratory Medicine and Pathology
and Laboratory of Biophysical Chemistry
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Received October 23, 1975

Electrochemical Preparation and Control of Stoichiometry for Donor-Halide Salts: TTFX$_n$ and TSeFX$_n$

Sir:

Considerable interest has been shown recently in the charge transfer salts of tetrathiafulvalene[1-3] (I, TTF) and its derivatives.[4] Depending upon the identity of the anion[5] and the stoichiometry[5,6] in these compounds, $(TTF)_xA_y$, a wide range of unique electric,[1b,2,4,7] magnetic,[8] and optical[6a,9] properties have been observed. These salts were previously prepared by direct chemical oxidation of the donor with added acceptor or by metathetical[5] reactions of $TTF_3(BF_4)_2$ with an anion, but these methods do not offer the desired selectivity or control over the multiple product phases often produced for reactions with anions such as halides.[5,6] It appeared to us that reaction of donor cations generated *electrochemically* would afford the most controlled conditions for preparing donor salts of predictable stoichiometry with a wide variety of inorganic and organic acceptors. Therefore, we have studied the electrochemical preparation of some of these salts and wish to report our results here.



I, X = S
II, X = Se

To test the generality of this method, separate CH_3CN solutions containing 100% TTF^+ or $TSeF^+$,[4b] oxidized electrochemically, were treated with Br^-, and the resulting bromide salts were collected.[10] For the reaction of TTF^+, the electrically *insulating* 1:1 bromide salt[6] (III, TTF-Br) was formed. However, in the identical reaction with $TSeF^+$ (Table I), a *conducting*, mixed valence bromide salt (IV, $TSeF\text{-}Br_x$) containing formally neutral TSeF is produced. To understand the reasons for the striking difference in products formed, cyclic voltamograms of I or II in the presence of Br^- were obtained.

Table I. Properties of Electrochemically Prepared Donor Halide Salts

Reactants[a]	Product	$\rho(\Omega\ \text{cm})$[d]	ΔE^0, *eV*[e]
$TTF^+ + Br^-$	(**III**) TTF-Br[b]	$>10^6$	−0.147
$TSeF^+ + Br^-$	(**IV**) $TSeF\text{-}Br_{0.8}$[c]	10^{-1}	+0.017
$TSeF^+ + Cl^-$	(**V**) TSeF-Cl[b]	$>10^6$	−0.246

[a] For experimental conditions cf. ref 10. [b] Correct elemental analysis was obtained. [c] Average stoichiometry determined by elemental analysis. [d] Resistivity determined on compacted samples at room temperature. [e] Formal emf (CH_3CN, 0.1 M Et_4NClO_4) of the reactions, $2TXF^+ + 3Br^- \rightleftarrows 2TXF + Br_3^-$ (X = S or Se) or $2TSeF^+ + 2Cl^- \rightleftarrows 2TSeF + Cl_2$.

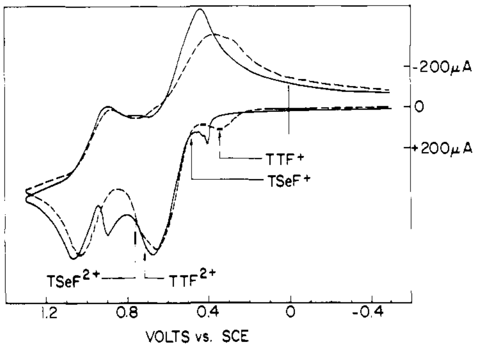


Figure 1. Cyclic voltammograms of donors (6.5×10^{-4} M) I, TTF (- - -), and II, TSeF (—), in CH_3CN (0.1 M Et_4NClO_4) with Br^- added (7.8×10^{-3} M Bu_4NBr) at 340 mV/s on platinum electrode. Arrows indicate E_p for donor cations (+) and dications (2+) in absence of Br^- (cf. ref 11).

Previously we had found[11] that the electrochemistry of I and II was characterized by two simple one-electron couples corresponding to formation of the radical cation and dication. No evidence of any distortion of the current-potential (I-$\mathcal{E}$) curves was observed with potential cycling, indicating these donor redox systems were uncomplicated by any slow coupled chemical reactions, adsorption processes, or electron transfer steps. For TTF there is no change (at these concentrations) in the voltammograms in the presence of Br^- (Figure 1, dotted line) except for the appearance of two reversible bromide[12] couples. However, in the case of TSeF (Figure 1, solid line) addition of Br^- causes sharpening of the oxidation waves, decrease in the peak width, and a shift towards negative potential. Such voltammetric behavior is typical[13] of electrode processes in which species are formed coupled to a follow-up chemical reaction. Formation of IV is the suspected follow-up reaction since this species is formed in bulk reactions of the electrolysis solutions with bromide ion.

These results and the known proximity[11,12] of the Br^-/Br_3^- and $TSeF^+/TSeF$ couples in the cyclic voltammograms suggest that homogeneous electron transfer reactions may occur in the reaction of $TSeF^+$ and Br^-. Specifically, reaction 1

$$2TSeF^+ + 3Br^- \rightleftarrows 2TSeF + Br_3^- \tag{1}$$

has a positive ΔE^0 (Table I, negative ΔG under standard conditions) and could represent the means by which neutral TSeF is produced and thereby made available for incorporation in the mixed valence salt IV. For TTF$^+$, however, with its lower reduction potential than TSeF$^+$,[11] an electron transfer reaction corresponding to eq 1 is not thermodynamically as favorable (Table I). Neutral TTF would not be present in this solution and therefore the stoichiometric 1:1 salt III is formed. Likewise, treatment of the radical cations with Cl$^-$, which has a lower oxidation potential[14] than Br$^-$, leads to the formation of the 1:1 insulating TSeFCl salt V.[15] However, we have found that the mixed valence chloride salts can be prepared from these donors when *both* neutral and cation species are present through partial electrochemical oxidation.[6,16]

These results indicate that the redox chemistry of acceptor anions must be considered when using these species as synthetic reagents in conjunction with donor ion radicals. For example, the multiple TTF-iodide stoichiometries[5,7,9a] that have been found and the inability to form a simple 1:1 iodide salt[16] are undoubtedly related to the multiple, low energy redox states[14,17] (I^-, I_3^-, I_2) for the anions typically used. More importantly, it appears that electrochemical techniques offer unique synthetic and mechanistic tools to this new area of chemistry. As shown here, formation of a single specific product can be achieved via synthetic control over the stoichiometry of the reactants by appropriate choice of specific donor-halide acceptor pairs. In the absence of complicating factors (e.g., nonequilibrium conditions, large differences in solubility products, etc.) the relative redox potentials of organic donor and halide may be useful in predicting product stoichiometries. Furthermore, the electrochemical technique has also enabled us to prepare product mixtures which contain *both* the 1:1 and the structurally[6] dissimilar mixed valence salt.[18] Thus, the tendency to form particular solid-state stacking structures as a function of donor molecular properties can now be evaluated quantitatively.

Acknowledgment. The authors would like to thank R. A. Craven for the conductivity measurements and B. A. Scott for numerous helpful discussions regarding donor-halide mixed valence solids.

References and Notes

(1) (a) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970); (b) F. Wudl, D. Wobschall, and E. J. Hufnagel, *J. Am. Chem. Soc.*, **94**, 671 (1972).
(2) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
(3) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
(4) (a) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973); (b) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974); (c) K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J. Chem. Soc., Chem. Commun.*, 937 (1974); (d) A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Lett.*, **34**, 1561 (1975); (e) E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 671 (1975); (f) R. Schumaker, M. Ebenhahn, G. Castro, and R. L. Greene, *Bull. Am. Phys. Soc.*, **20**, 495 (1975).
(5) F. Wudl, *J. Am. Chem. Soc.* **97**, 1962 (1975).
(6) (a) B. A. Scott, J. B. Torrance, S. J. LaPlaca, P. Corfield, D. C. Green, and S. Etemad, *Bull. Am. Phys. Soc.*, **20** 496 (1975); (b) S. J. LaPlaca, P. W. R. Corfield, R. Thomas, and B. A. Scott, *Solid State Commun.*, **17**, 635 (1975); (c) S. J. Laplaca, J. E. Weidenborner, and D. C. Green, submitted for publication.
(7) G. R. Johnson, D. J. Dahn, M. G. Miles, and J. D. Wilson, *Bull. Am. Phys. Soc.*, **20**, 466 (1975).
(8) (a) Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, *Phys. Rev. Lett.*, **32**, 1363 (1974); (b) J. E. Gulley and J. F. Weiher, *ibid.*, **34**, 1061 (1975); (c) J. C. Scott, A. F. Garito, A. J. Heeger, *Phys. Rev. B*, **10**, 3131 (1974).
(9) (a) R. J. Warmack, T. A. Callcott, C. R. Watson, and C. K. Johnson, *Bull. Am. Phys. Soc.*, **20**, **414** (1975); (b) J. B. Torrance Jr., F. B. Kaufman, and B. A. Scott, submitted for publication.
(10) A solution ca. 5×10^{-4} M of donor in CH_3CN (0.1 M Et_4NClO_4) was coulometrically oxidized at a constant potential equal to the average of the two one-electron donor half-wave potentials (TTF, 0.55 V; TSeF, 0.60 V vs. SCE) to form the cation quantitatively, and Bu_4NBr (two-fold excess) was added to precipitate the bromide salt.
(11) (a) E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, and R. N. Compton, *J. Am. Chem. Soc.*, **97**, 2921 (1975); (b) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).
(12) (a) T. Iwasita and M. C. Giordano, *Electrochim. Acta*, **14**, 1045 (1969); (b) F. Magno, G. Mazzocchin, and G. Bontempelli, *J. Electroanal. Chem. Interfacial Electrochem.*, **47**, 461 (1973).
(13) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); A. J. Fry, "Synthetic Organic Electrochemistry", Harper and Row, New York, N.Y., 1972.
(14) (a) J. C. Marchon, *C.R. Acad. Sci., Ser. C*, **267**, 1123 (1968); (b) L. Sereno, V. A. Macagno, and M. C. Giordano, *Electrochim. Acta*, **17**, 561 (1972).
(15) Multiple phase products are easily formed unless particular care is exercised to ensure 100% oxidation and homogeneous mixing of TSeF$^+$ and excess Cl$^-$.
(16) B. A. Scott, D. C. Green, and R. Thomas, unpublished results.
(17) V. A. Macagno, M. C. Giordano, and A. J. Arvia, *Electrochim. Acta*, **14**, 335 (1969).
(18) F. B. Kaufman, E. M. Engler, D. C. Green, and J. Q. Chambers, submitted for publication.

F. B. Kaufman,* E. M. Engler,* D. C. Green
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

J. Q. Chambers
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Received December 4, 1975

Bidentate and Monodentate Bonding Modes of the 1,3-Diaryltriazenido Ligand in Ruthenium(II) and Platinum(II) Complexes

Sir:

The ligands allyl ($R_2CC(R')CR_2$), carboxylato ($OC(R')O$), amidino ($RNC(R')NR$), and triazenido ($RNNNR$), although isoelectronic, offer a variety of reaction chemistries and bonding arrangements in the presence of transition metals. Each is potentially either a one- or a three-electron donor to the metal. Of this series the latter two, namely amidino and triazenido, appear to have been studied least. Recent interest in these two ligands is apparent.[1-11] A key to understanding the reaction chemistry is the mode of attachment of the ligand to the metal. On the basis of spectroscopic data, structures involving these ligands in monodentate, bidentate, and bridging bonding modes have been proposed. Yet interpretation of these spectroscopic data is not without controversy.[1,2] Surprisingly few x-ray results are available for these metal-ligand systems. In $[Cu(dpt)]_2$ (dpt = 1,3-diphenyltriazenido),[12] $[Ni(dpt)_2]_2$,[13] $[Pd(allyl)(dtt)]_2$ (dtt = 1,3-di-*p*-tolyltriazenido),[3] $[Cu(dmt)]_4$ (dmt = 1,3-dimethyltriazenido),[14] $RhCuCl(CO)(PPh_3)_2(dmt)$,[8] $[Mo(dpb)_2]_2$ (dpb = *N,N'*-diphenylbenzamidinato),[10] and $Re_2(dpb)_2Cl_4$,[11] the ligand bridges metal centers. The bidentate bonding mode for triazenides has been confirmed structurally in $Co(dpt)_3 \cdot C_6H_5CH_3$[15] with the two terminal N atoms of each ligand bonded to Co. Although the monodentate mode of bonding for triazenides has been proposed[1,4,16] and disputed[2] on the basis of ir and NMR data, no structural example had previously been found. Here we report on the x-ray crystal structures of two triazenido complexes, $RuH(CO)(PPh_3)_2(dtt)$ and *cis*-$Pt(PPh_3)_2(dpt)_2$. The former shows the bidentate mode of bonding while the latter provides the first example of the monodentate mode of bonding.

Orange crystals of $RuH(CO)(PPh_3)_2(dtt)$ were obtained by recrystallization of material kindly provided by Dr. S. D. Robinson. The space group is $P\bar{1}$ with $a = 14.074$ (2), $b = 15.264$ (3), $c = 12.195$ (2) Å, $\alpha = 109.78$ (1), $\beta = 111.74$