(16) Herman, Z. S.; Loew, G. H.; Rohmer, M. M. *Int. J. Quantum Chem.*, submitted for publication.
(17) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.
(18) Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414–2434.

Gilda Loew*
Life Sciences Division, SRI International
Menlo Park, California 94025

Amiram Goldblum
Department of Pharmaceutical Chemistry
School of Pharmacy, Hebrew University of Jerusalem
Jerusalem, Israel

Received October 5, 1979

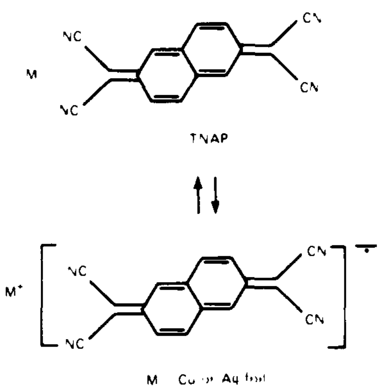
A Reversible Field Induced Phase Transition in Semiconducting Films of Silver and Copper TNAP Radical-Ion Salts

Sir:

The electron-accepting molecule 11,11,12,12-tetracyano-2,6-napthoquinodimethane (TNAP) has been shown to produce electrically conducting solids with aromatic heterocyclics and with alkali and divalent transition metal counterions.[1] In many cases, these charge-transfer complexes have exhibited higher conductivities than the analogous tetracyanoquinodimethane (TCNQ) salts. Several authors[1,2] have noted changes in electrical conductivity due to phase transitions in both TCNQ and TNAP complexes; however, these instabilities have all been induced by varying the temperature of the material.

We report here that we have observed a reversible electric field induced phase transition in polycrystalline aggregates of copper or silver TNAP radical-ion salts. This phase transition is accompanied by an abrupt increase in the electrical conductivity of the organic semiconductor when the applied field surpasses a threshold value. This highly conductive state remains intact as long as the field is present. When the applied field is removed, the system can either return to the high impedance state or, in cases where a voltage significantly higher than the threshold voltage is used to induce the highly conductive state, the material will remain in the low impedance state after the applied field has been removed.

The metal–TNAP films are synthesized by placing a piece of either Cu or Ag metal foil into a boiling solution of dry and degassed acetonitrile which has been saturated with neutral TNAP. Immediately upon dipping the foil into the saturated solution, a direct oxidation–reduction reaction occurs in which the corresponding metal salt of the radical-ion TNAP is formed as a polycrystalline film (eq 1). The reaction can be terminated by simply removing the metal foil from the solution. Using this technique it is possible to grow a film that is in excess of five microns thick in less than one hour. Once the film has been grown to the desired thickness, it is removed from the solution and washed with additional acetonitrile to remove any neutral TNAP. The metal foil containing the charge-transfer salt is then dried under vacuum and an aluminum electrode[3] is evaporated on top of the polycrystalline film. Two electrical connections are then made to the laminated structure, one at the edge of the metal foil, and the other on top of the aluminum pad. Elemental analysis of the bulk of the polycrystalline film reveals that the metal–TNAP ratio is 1:1.[4]



(1)

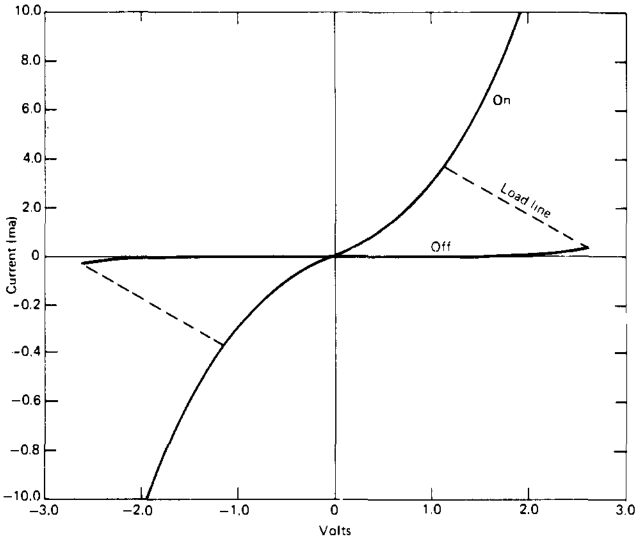


Figure 1. Current-voltage characteristic showing high- and low-impedance states for a 3.75μ Cu–TNAP sample.

Figure 1 shows a dc current voltage characteristic of a 3.75-μ-thick Cu–TNAP film made with a 100-Ω resistor as series load. Initially, at small applied voltages the impedance is $\sim 1.25 \times 10^4$ Ω. When the voltage across the sample surpasses a threshold voltage (V_{th}), the impedance of the sample rapidly drops to a value of 190 Ω. This switching from the high to low impedance state occurred at an applied potential of 2.7 V for this particular sample which corresponds to an applied field strength of $\sim 8.1 \times 10^3$ V/cm. Once the film has been placed in this highly conductive state, it will remain in this state as long as an applied voltage is present. Upon removing the applied voltage, the film will eventually return to its initial low conductivity state. The time required to switch back to the initial state appears to be directly proportional to the film thickness, duration of the applied voltage, and the amount of power dissipated in the sample while in the low impedance state. The electrical characteristics are only slightly dependent upon the direction of current flow and in a few cases a slight hysteresis is observed under conditions of high power dissipation.

Similar results are observed with Ag–TNAP films; however, these films do not exhibit the stability and reproducibility that is observed in the Cu–TNAP films. The impedance of a representative Ag–TNAP film is seen to drop abruptly from 2.4×10^5 to 2.8×10^3 Ω at a field strength of 6.0×10^3 V/cm. The film was ~ 7 μ thick.

Figure 2 is an oscilloscope trace of the voltage and current for a Cu–TNAP sample simultaneously displayed vs. time in response to an applied fast rise-time rectangular voltage pulse. The film originally in its high impedance state is switched to a low impedance state before the peak-applied voltage of the pulse generator was reached. Under these conditions, it is not possible to observe the conventional delay times and switching times as noted in inorganic materials;[5] however, from Figure 2 the combined delay and rise times appear to be less than a total of 4 ns (the limiting time of the pulse generator). In performing this experiment, a minimal overvoltage of 1.0 V was

0002-7863/80/1502-3659$01.00/0

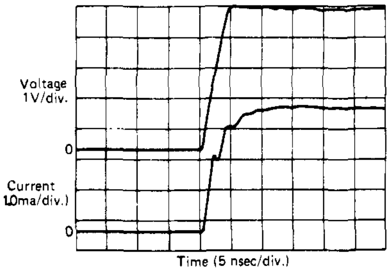


Figure 2. Transient response to a fast rise time rectangular pulse.

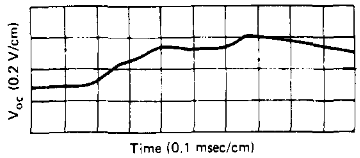


Figure 3. Spontaneous open-circuit potential generated in a Cu/Cu-TNAP/Al sample at room temperature.

applied to the sample to reduce any current oscillations which appear when the applied voltage was set near V_{th}. The fast combined delay and switching time observed in this experiment indicate that the transition between states of different conductivity is not induced by thermal effects.[6]

To obtain information pertaining to the nature of the mechanism of the phase transition, an experiment was designed to determine if the system generates an open-circuit potential or electromotive force (emf) in switching from the high to the low conductivity state since the appearance of a spontaneous emf would indicate that an electrochemical reaction was resonible for switching phenomena.[7] In this experiment, (1) an applied voltage in excess of the threshold voltage was used to place a Cu-TNAP sample into a high conductivity state where this state was such that it would remain intact for a short time after the applied voltage was removed; (2) the sample was then externally short circuited to eliminate any capacitive effects; and finally (3) a high input impedance storage oscilloscope was used to measure open-circuit voltage when the sample spontaneously returned to its original high impedance state. The oscilloscope was set to trigger whenever a voltage exceeding a few millivolts appeared across the sample. The results are shown in Figure 3 where the spontaneous open-circuit voltage measured by the oscilloscope is reproduced and is seen to have a maximum value of ~0.3 V.

The open-circuit voltage of 0.3 V observed in this experiment does show that the mechanism by which the phase transition occurs is due to a field induced solid-state reversible electrochemical redox reaction involving the metal charge-transfer salts. It is postulated that this redox reaction produces mixed-valence species or complex salts. A similar switching phenomena is reported in copper and silver TCNQ.[8] Further work to examine other charge-transfer salts[9] and their possible application to solid-state electronics is in progress.

Acknowledgments. We thank Dr. J. C. Murphy for valuable discussions and comments on this work. We are grateful to Mr. M. Maxfield for supplying neutral TNAP material. We thank Mr. J. W. Leight and Mr. R. A. Murphy for their technical assistance. We gratefully acknowledge support by the National Science Foundation (DMR76-84238) and the Department of the Navy (N00024-78-C-5384).

References and Notes

(1) Johnson, G. R.; Miles, M. G.; Wilson, J. O. *Mol. Cryst. Liq. Cryst.* **1976**, *33*, 67.
(2) (a) Afify, H. H.; Abdel-Kerim, F. M.; Aly, H. F.; Shabaka, A. A. *Z. Naturforsch. A* **1978**, *33*, 344.
(3) The switching phenomena has also been observed with chromium top electrodes.
(4) Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37291.
(5) See, for example, Adler, A.; Henisch, H. K.; Mott, Sir N. *Rev. Mod. Phys.* **1978**, *50*, 209.
(6) Buckley, W. D.; Holmberg, S. H. *Solid-State Electron.* **1975**, *18*, 127.
(7) A spontaneous electrochemical reaction has been reported in magnesium-TCNQ salts. See Gutmann, F., Herman, A. M.; Rembaum, A. *J. Electrochem. Soc.* **1967**, *114*, 323.
(8) Potember, R. S.; Poehler, T. O.; Cowan, D. O. *Appl. Phys. Lett.* **1979**, *34*, 405.
(9) We are currently investigating thin films of the acceptors TCNQ, TCNE, TCNQ-F_4, TCNQ-$(OCH_3)_2$, TCNQ-$(CH_3)_2$, and TCNQ-$(CH_2CH_3)_2$.

Richard S. Potember, Theodore O. Poehler*
Applied Physics Laboratory, Johns Hopkins University
Laurel, Maryland 20810

Angela Rappa, Dwaine O. Cowan,* Aaron N. Bloch
Department of Chemistry, Johns Hopkins University
Baltimore, Maryland 21218

Received October 26, 1979

Competitive Oxidation Processes in the Reaction between (Dicyclopentadienyl)zirconium Bis(phosphine) Complexes and Alkyl Halides

Sir:

Comprehensive kinetic and stereochemical studies of the oxidative addition of alkyl halides to low-valent group 8 complexes have established several mechanisms for these reactions including direct S_N2 attack, radical chain, and nonchain electron-transfer pathways.[1] In contrast, few examples of net carbon-halogen addition to early transition metal complexes are known and, consequently, no systematic investigation involving these species has been reported. We recently found[2] that ligand-induced elimination of alkane from the zirconocene alkyl hydrides provides a straightforward synthesis of Cp_2Zr^{II} bis(phosphine) complexes, species whose ease of preparation and high reactivity toward oxidation make them valuable for elucidation of fundamental processes involving complexes of early transition metals in low-oxidation states. In this context we have investigated the oxidation of Cp_2XrL_2 (L = PPh_2Me or PMe_2Ph) by RX (RX = alkyl halide) and find that both the formal oxidative addition product, Cp_2ZrRX, and the dihalide, Cp_2ZrRX_2, can be formed. Alkyl chlorides, bromides and iodides all react readily with Cp_2ZrL_2 (see Table I). As expected, we find the qualitative ordering of reactivity for alkyl halides to be RI > RBr > RCl. Surprisingly, though, we noted that these halides ranked in order of *selectivity* of reaction with Cp_2ZrL_2 in the *same* way, in opposition to conventional intuition which predicts an inverse relationship between rates and selectivity of reactions. We have set forth a mechanistic scheme to account for these observations (Scheme I) and wish to present our results which are in support of this scheme.

Formation of both Cp_2ZrRX and Cp_2ZrX_2 occurs by multistep processes and involves intermediary organic radicals. These contentions are supported by the following observations. (a) For a given halide primary, secondary and tertiary alkyl halides react with Cp_2ZrL_2 at comparable rates (although product ratios of Cp_2ZrRX:Cp_2ZrX_2 formed from these halides are not the same). (b) The reaction between Cp_2ZrL_2 and *erythro*-1-bromo-3,3-dimethylbutane[3] gives the alkyl zirconium species which has been completely racemized. This was demonstrated unambiguously by ^1H NMR analysis of the corresponding carbonylated product.[3] Excess alkyl bromide recovered at the end of the reaction was unracemized. (c) Reaction between Cp_2ZrL_2 and 6-chloro-1-hexene yielded both acyclic and cyclic products. To a solution of 0.42 mmol of $Cp_2Zr(PPh_2Me)_2$ and 2.4 mmol of PPh_2Me in 7 mL of