Single-electron transfer upon formation of 2,2,3,3-tetracyano-1-phenyl-7,8-dithiabicyclo[3.2.1]octane from allyl dithiobenzoate and tetracyanoethylene. Electrochemical investigations*

K. P. Butin,[a]* **A. A. Moiseeva,**[a] **R. D. Rakhimov,**[a] **and I. V. Magedov**[b]

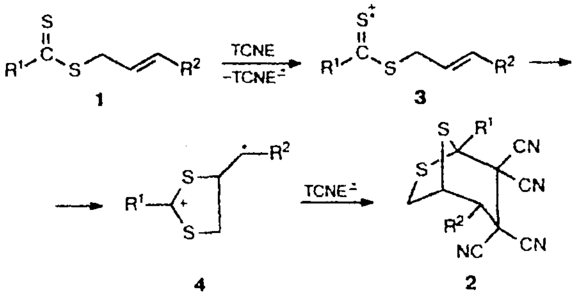
[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 5546. E-mail: butin@org.chem.msu.su
[b]*K. A. Timiryazev Moscow Agricultural Academy,*
49 ul. Timiryazevskaya, 127550 Moscow, Russian Federation.
Fax: +7 (095) 128 8093

Studies by the method of cyclic potential scanning from 0.2 to 1.9 V provided electroanalytical evidence that the reaction of allyl dithiobenzoate with tetracyanoethylene (TCNE) in MeCN proceeds as the reaction of the TCNE$^{\cdot-}$ radical anion with the PhSSAll$^{\cdot+}$ radical cation to form phenyl-substituted 2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octane. When current is not applied, the reaction does not proceed at 20 °C for 3 days. However, this reaction in boiling MeCN occurs without electrochemical activation and, apparently, involves intermediate formation of the above radical ions. It was established by semiempirical PM3 calculations that allyl dithiobenzoate and TCNE form a stable charge-transfer complex that precedes chemical electron transfer.

Key words: allyl dithiobenzoate, tetracyanoethylene, electron-transfer reaction, electrochemical activation; semiempirical quantum-chemical calculations, PM3 method.

Previously,[1] it was demonstrated that the reactions of substituted allyl dithiocarboxylates (**1**) with tetracyanoethylene (TCNE) in a boiling acetonitrile solution afforded substituted 2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octanes (**2**). It was suggested that bicyclooctanes are formed in a three-stage reaction, which involves the transfer of the charge from dithioester to TCNE as the key stage (Scheme 1). Radical cation **3** that forms as a result of single-electron transfer undergoes further rapid cyclization (*via* intramolecular 1,5-addition at the C=C bond) to cyclic radical cation **4**, which adds the radical anion TCNE$^{\cdot-}$ to give the final product **2**.

Scheme 1



It was demonstrated[2] that allyl dithiobenzoate reacts also with atmospheric oxygen according to the *SET* mechanism (single-electron transfer) to form the same radical cations **3** and **4**, which are converted into 1-phenyl-2,6,7-trithiabicyclo[2.2.1]heptane 2,2-dioxide.

In this work, we verified the assumption that the reaction with TCNE proceeds according to the *SET* mechanism by electrochemical methods and semiempirical calculations using allyl dithiobenzoate (**1**: R^1 = Ph and R^2 = H) as an example.

Experimental

Acetonitrile was purified by successive treatment with CaH$_2$, a H$_2$SO$_4$/KNO$_3$ mixture, and P$_2$O$_5$. Electrochemical studies were carried out in MeCN in the presence of Bu$_4$NBF$_4$ (0.05 mol L^{-1}) on a platinum electrode under an atmosphere of argon by cyclic voltammetry and the rotating disk electrode method with the use of a PI-50-1.1 potentiostat. The potentials were measured relative to a silver-chloride electrode. Quantum-chemical calculations were performed by the semiempirical PM3 method.[3]

Results and Discussion

Electrochemical measurements were carried out at room temperature at concentrations of the initial re-

---

* Dedicated to the memory of Professor Viktor Nikolaevich Drozd.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 78—81, January, 1999.

1066-5285/99/4801-0079 $22.00 © 1999 Kluwer Academic/Plenum Publishers

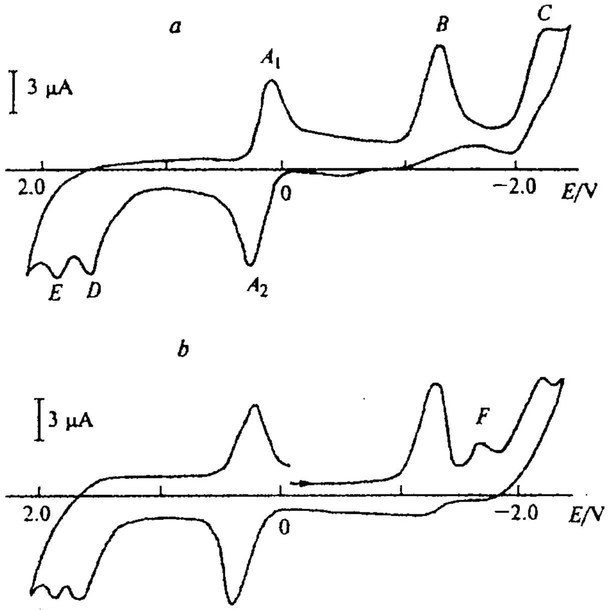


Fig. 1. Cyclic voltammogram of a mixture of TCNE and allyl dithiobenzoate **1** (R^1 = Ph and R^2 = H); *a*, at the beginning of electrolysis; *b*, after scanning of the potential for 2 h between 0.2 and 1.9 V with a rate of 10 V s^{-1}.

agents of 10^{-3} mol L^{-1}. In addition to the cyclic voltammetry and rotating disk electrode techniques, we used electrolysis in the cyclic potential scanning mode. The results are given in Table 1. Under these conditions, TCNE was reversibly reduced (the standard potential E^0 = 0.25 V relative to a silver-chloride electrode) and allyl dithiobenzoate was irreversibly oxidized in two single-electron stages (see Table 1). For the final product **2**, one one-electron reduction peak is observed. The difference between the potential of the first oxidation peak of dithioester **1** and E^0 of TCNE is 1.57 V, *i.e.*, from the thermodynamic standpoint, charge transfer between these molecules is rather hindered. We attempted to carry out alternating generation of radical anions $TCNE^{\cdot-}$ and radical cations formed upon oxidation of dithioester using cyclic scanning of the potential in the region between the reduction potential of TCNE and the potential of the first single-electron stage of oxidation of dithioester. We believed that there are optimum rates of potential scanning at which radical cations do not all discharge when the potential is scanned in the reverse direction and, therefore, the chemical reaction between these particles can proceed.

Electrolysis was carried out by scanning the potential between 0.20 and 1.90 V for 2 h with a scan rate of 10 V s^{-1}. The cyclic voltammogram for a mixture of TCNE and dithioester **1** (R^1 = Ph and R^2 = H) is shown in Fig. 1, *a*. Peaks A_1/A_2 correspond to the reversible pair TCNE/$TCNE^{\cdot-}$, peaks *B* and *C* correspond to reduction of dithioester, and peaks *D* and *E* correspond to oxidation of this compound. After electrolysis, a new peak (*F*, see Fig. 1, *b*), which corresponds in the potential to the reduction peak of reaction product **2** (R^1 = Ph and R^2 = H), appeared in the cyclic voltammogram. The cyclic voltammogram shown in Fig. 1, *b* completely coincides in the number and positions of the peaks with that obtained for a mixture of TCNE (10^{-3} mol L^{-1}), dithioester (10^{-3} mol L^{-1}), and the reaction product ($3 \cdot 10^{-4}$ mol L^{-1}). However, the height of peak *F* at the concentrations of the compounds in the mixture used in the experiment is approximately two times larger. The height of peak *F* increases as the duration of electrolysis carried out in the cyclic potential scan mode increases.

The control experiments were carried out with the electrochemical cell turned off, *i.e.*, without current. A solution of a mixture of TCNE and dithioester (10^{-3} mol L^{-1}) in acetonitrile containing Bu_4NBF_4 (0.05 mol L^{-1}) was kept at 20 °C under an atmosphere of argon for 3 days. An electrochemical analysis of the reaction mixture demonstrated that the mixture did not

Table 1. Potentials of electrochemical reduction and oxidation of the initial compounds (**1** and TCNE) and the reaction product (**2**) in MeCN (10^{-3} mol L^{-1}, Pt electrode, Bu_4NBF_4 (0.05 mol L^{-1}), relative to Ag/AgCl/KCl(sat.), 20 °C)

Compound	Reduction		Oxidation	
	$E_{1/2}^{red}$ (*n*)	E_p^{red}	$E_{1/2}^{ox}$ (*n*)	E_p^{ox}
1 (R^1 = Ph, R^2 = H)	−1.30 (1 e), −2.43 (1 e)	−1.32, −2.32	1.81 (1 e), 2.51 (1 e)	1.82, 2.13
TCNE	0.24 (1 e)	0.22, 0.28[a]		
2 (R^1 = Ph, R^2 = H)	−1.95 (1 e)	−1.97		

Note. $E_{1/2}$/V is the half-wave potential measured on a rotating disk electrode (v = 20 mV s^{-1}); E_p/V is the peak potential in the cyclic voltammogram (v = 200 mV s^{-1}); *n* is the number of electrons involved in the redox process.

[a] The potential of the reverse peak.

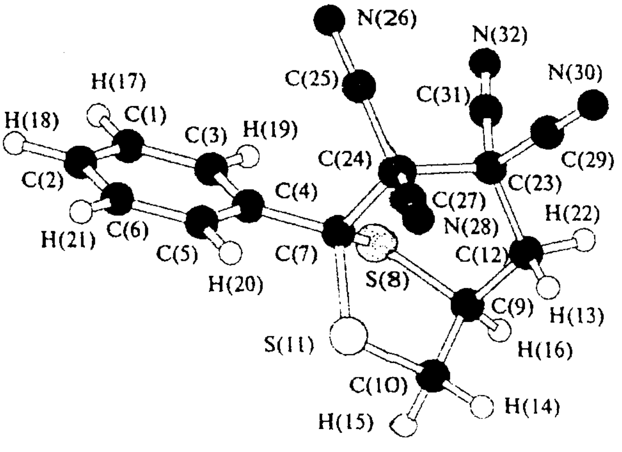


Fig. 2. Geometry of molecule **2** calculated by the PM3 method.

Table 2. Comparison of the experimental bond lengths (*d*) and bond angles (ω) with those calculated by the PM3 method for compound **2**

Bond	*d*/Å	
	experiment	calculation
C(7)—S(11)	1.826	1.872
S(11)—C(10)	1.832	1.828
S(8)—C(7)	1.813	1.856
S(8)—C(9)	1.819	1.832
N(26)—C(25)	1.134	1.158
N(30)—C(29)	1.133	1.158
C(7)—C(24)	1.607	1.584
C(7)—C(4)	1.516	1.501
C(23)—C(24)	1.603	1.596
C(12)—C(23)	1.557	1.551
C(12)—C(9)	1.531	1.533
C(9)—C(10)	1.515	1.525

Angle	ω/deg	
	experiment	calculation
C(7)—S(11)—C(10)	96.3	97
C(7)—S(8)—C(9)	90.2	90
S(11)—C(7)—S(8)	106.6	104
S(11)—C(7)—C(24)	107.7	111
S(8)—C(7)—C(24)	109.0	109
C(7)—C(24)—C(23)	113.7	113
C(24)—C(23)—C(12)	112.9	114
S(8)—C(9)—C(12)	109.9	112
S(8)—C(9)—C(10)	106.7	106
S(11)—C(10)—C(9)	109.3	109

contain the reaction product at a noticeable concentration. Therefore, electrochemical activation promotes the reaction shown in Scheme 1 and is, apparently, indicative of the participation of radical anions and radical cations of the reagents in this reaction.

For the electron transfer between ethyl dithiobenzoate and TCNE to occur, the charge-transfer complex of these molecules must be initially formed. To examine the possibility of formation of the charge-transfer complex, we carried out quantum-chemical calculations with the use of the semiempirical PM3 method.[3] The geometries of the allyl dithiobenzoate radical cation, TCNE, and the complex formed by these molecules were calculated. To test the suitability of the PM3 method to calculations of the systems under study, we first carried out calculations of the final product, dithiabicyclooctane **2** (Fig. 2), for which the X-ray diffraction data are available.[4] The calculated values of selected bond lengths and bond angles are given in Table 2.

It can be seen that the experimental data agree well with the results of PM3 calculations. The largest discrepancies between the experimental and calculated bond lengths are observed for the S(11)—C(7) and C(8)—C(7) bond lengths (0.046 and 0.043 Å, respectively) and the largest differences in the values of the bond angles (~3°) are observed for the S(11)—C(7)—S(8) and S(11)—C(7)—C(24) angles. These results suggest that the calculated geometry of the charge-transfer complex is sufficiently accurate.

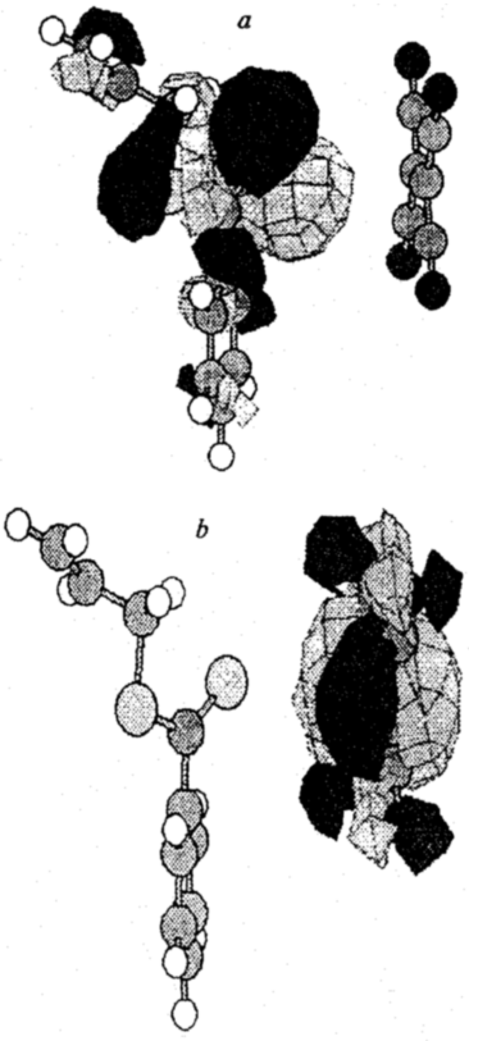


Fig. 3. Geometry and the frontier orbitals of the complex of dithioester **1** with TCNE calculated by the PM3 method: *a*, HOMO; *b*, LUMO.

The calculations of the geometry of the initial dithioester **1** demonstrated that the molecule is planar. All atoms of the $S{=}C{-}S{-}CH_2{-}CH{=}CH_2$ fragment are in a single plane. All atoms of the phenyl ring are also located in this plane. In going to radical cation **3**, the planarity is distorted. However, the $S{=}C{-}S{-}CH_2$ fragment remains planar, while the vinyl group and the Ph ring deviate from this plane by 44° and 28°, respectively.

The geometry of the complex of dithioester with TCNE was calculated as follows. First, the TCNE molecule was placed over the planar dithioester molecule so that the intermolecular C—C and C—S distances were equal to 3 Å. Then the geometry of the molecule was optimized by the PM3 method. As a result of this optimization, the following changes are observed:

(1) the dithioester molecule in the complex becomes nonplanar, while the TCNE molecule remains planar and (2) the molecules are rotated with respect to each other so that the sulfur atom of the C=S group is directed toward the C=C bond of TCNE. In this case, the distance between the sulfur atom of the C=S group and the carbon atoms of the C=C bond of TCNE is 3.75 Å. This value is very close to the sum of the covalent radii of the S atom (1.80 Å) and the C atom involved in the double bond (1.77 Å).[5] Therefore, the charge-transfer complex of molecule **1** with TCNE is actually formed and the charge transfer from dithioester to TCNE can occur.

The ball-and-stick model of the complex of allyl dithiobenzoate with TCNE is shown in Fig. 3. Figure 3 displays also HOMO of dithioester and LUMO of TCNE. It is seen that HOMO of dithioester is primarily located on the sulfur atom of the C=S group and LUMO of TCNE is an antibonding π-orbital. It should be noted that HOMO of dithioester and LUMO of TCNE have identical symmetry, *i.e.*, donor-acceptor interaction is possible, which results in stabilization of the complex and allows charge transfer upon thermal activation.

Therefore, the data of electrochemical studies and theoretical calculations confirmed that the reaction can proceed *via* single-electron transfer.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32095a).

References

1. I. V. Magedov, V. N. Drozd, S. Yu. Shapakin, D. S. Yufit, and Yu. T. Struchkov, *Sulfur Lett.*, 1994, **17**, 119.
2. V. N. Drozd, S. Yu. Shapakin, I. V. Magedov, D. S. Yufit, and Yu. T. Struchkov, *Sulfur Lett.*, 1995, **18**, 67.
3. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
4. I. V. Magedov, S. Yu. Shapakin, V. N. Drozd, A. S. Batsanov, D. S. Yufit, and Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1994, 770 [*Chem. Heterocycl. Compd.*, 1994 (Engl. Transl.)].
5. J. Hine, in *Structural Effects on Equilibria in Organic Chemistry*, Wiley, New York, 1975, 47.

Received May 13, 1998