Reductive cleavage of dichalcogenide bonds

3.* Selectivity of electron exchange in diaryldichalcogenide—bispyridinium systems

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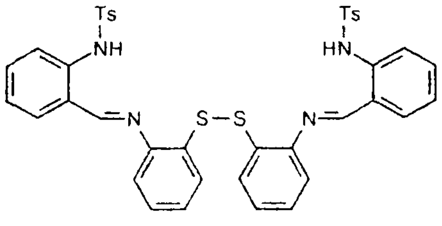
The kinetics of reductive cleavage of the dichalcogenide bond in dimeric Schiff's bases ArEEAr (E = S, Te) induced by indirect electron transfer by *in situ* generated bridged bispyridinium radical cations and biradicals was studied by cyclic voltammetry. It was shown that the dependence between the apparent rate constants of intermolecular electron transfer and the electron-withdrawing properties of diaryldichalcogenides is violated. The mechanisms of homogeneous (chemical) and heterogeneous (electrochemical) reductive cleavage of diaryldichalcogenides were discussed.

Key words: bispyridinium, mediator, electrochemical catalysis; dichalcogenide bond cleavage; cyclic voltammetry.

Control of processes occurring in a living cell, such as signal translation, gene expression, and proliferative regulation, involves redox reactions of sulfide residues of proteins.[2] Disulfide groups can "catch" excessive electrons primarily localized on other protein fragments.[3] These intermediate one- and two-electron redox processes are described by the known mechanism of thiol-disulfide exchange.[4–7]

Electron transfer reactions in proteins of a living cell are quantitatively simulated by synthetic electron transport systems.[8,9] Activation of the disulfide bonds in diorganyl disulfides RSSR is possible, for example, in electrochemical experiments, by reduced centers of bispyridinium dications formed similar to the redox system of coenzyme NAD^+.[10] The process formally proceeds against the potential difference of electrochemical reduction of a mediator to biradical $^\cdot M^\cdot$ (E_{p1}) and of a "trap" to the primary radical anion $RSSR^{\cdot -}$ (E_{p3}). In this work, we studied the mechanism of reductive cleavage of the S—S and Te—Te bonds in Schiff's bases **1**—**4** in analogous electron transfer systems **5**—**9**.[1]



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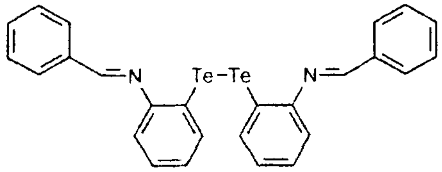

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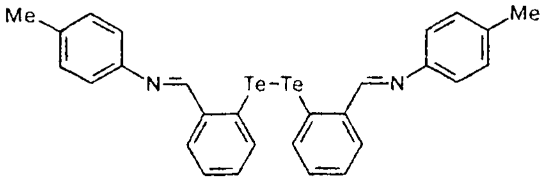

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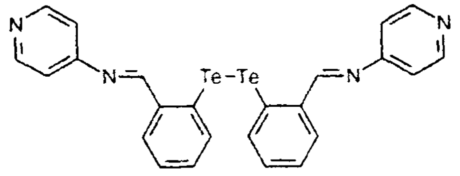

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Experimental

Disulfide **1**,[10] ditellurides **2**,[11] **3**,[12] and **4**,[12] and perchlorates of 1,2-di(2,4,6-triphenylpyridinium-1)ethane (**5**),[1] 1,4-di-(2,4,6-triphenylpyridinium-1)butane (**6**),[1] 1,6-di(2,4,6-triphenylpyridinium-1)hexane (**7**),[1] 1,4-di(*N*-methyl-4,6-diphenylpyridinium-2)benzene (**8**),[10] and 2,7-di(*N*-methyl-

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* For Part 2, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1522—1526, August, 1999.

4,6-diphenylpyridinium-2)fluorene (**9**)[1] were synthesized by the previously described procedures.

The procedure of electrochemical experiment has previously been described.[10] The studies were carried out in a dry argon atmosphere in DMF containing 0.1 mol L^{-1} Et_4NClO_4 purified by multiple recrystallization from isopropyl alcohol (special purity grade) followed by vacuum drying at 80 °C.

A Pt disk electrode (diameter 2 mm) was used. The potentials were measured against the aqueous saturated calomel electrode (SCE) with a waterproof membrane.

Results and Discussion

In the studied potential region (from 0 to −1.2 V), bridged dications **5**—**9** are reversibly transformed into stable (i_{pc}/i_{pa} = 1) paramagnetic intermediates: radical cations and biradicals by diffusion-limited successive one-electron electrochemical reactions. In the case of **5**, separated redox centers are electrochemically nonequivalent: the formation of biradicals occurs at a more negative (~0.1 V) potential than that in the case of radical cations. According to CVA study, the electrophoric centers of dications **6**—**9** are equivalent: radical cations and biradicals are statistically formed[1,13] at the potential of a two-electron peak in the region from −0.93 to −1.01 V. Typical voltammograms of electron transfer (ET) reactions involving dications **6** and **9** are shown in Figs. 1 and 2. These are two-electron electrochemically reversible reactions ($i_d{}^0$, see Figs. 1, *a* and 2, *a*, curves *1*), which are complicated by subsequent electron exchange with the introduced "electron trap," organic dichalcogenide (i_p, see Figs. 1, *b* and 2, *b*).

In all mediator systems ($i_p/i_d{}^0$), the introduction of the "electron trap," disulfide **1**, results in a relative increase in the height of the peak corresponding to electrochemical generation of radical species. The cathodic current increases as the content of disulfide increases (at least, at moderate concentrations). The peaks of maximum currents (i_p) in the "carrier—electron acceptor **1**" systems are only insignificantly (by 6—15 mV) shifted to the cathodic region relative to the distinct peaks of the mediator reduction in the absence of the oxidant ($i_d{}^0$).

In the presence of a multiple excess of disulfide **1**, the sharp maximum in the voltammograms disappears, and they gain a characteristic smoothed shape (see Fig. 1, *b*). For a 5—10-fold excess of the electron acceptor, the profiles for the relative increase in the reduction current ($i_p/i_d{}^0$), the content of the M^{2+} mediator in the bulk solution (C_M), and also the square root of the concentration of the activated substrate

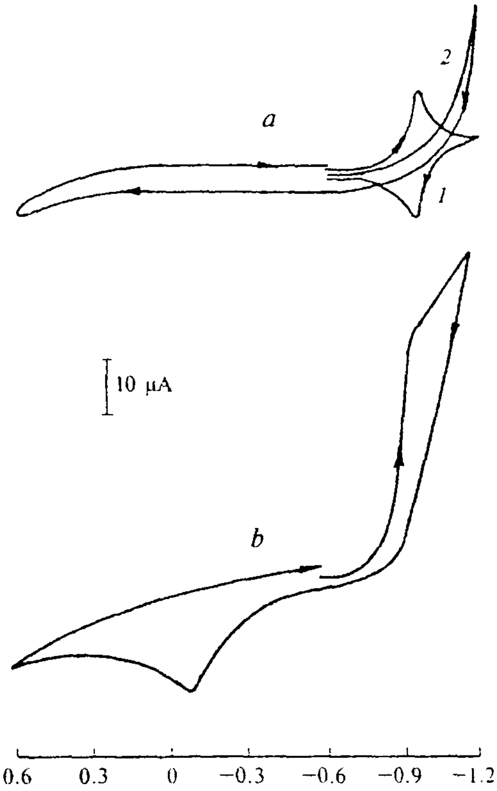


Fig. 1. Cyclic voltammograms of reduction of carrier **6** ($1 \cdot 10^{-3}$ mol L^{-1}; *a*, curve *1*), disulfide **1** ($1 \cdot 10^{-2}$ mol L^{-1}; *a*, curve *2*), and carrier **6** ($1 \cdot 10^{-3}$ mol L^{-1}) in the presence of disulfide **1** ($1 \cdot 10^{-2}$ mol L^{-1}) (*b*) in DMF on a Pt disk electrode (potential sweep 0.1 V s^{-1}).

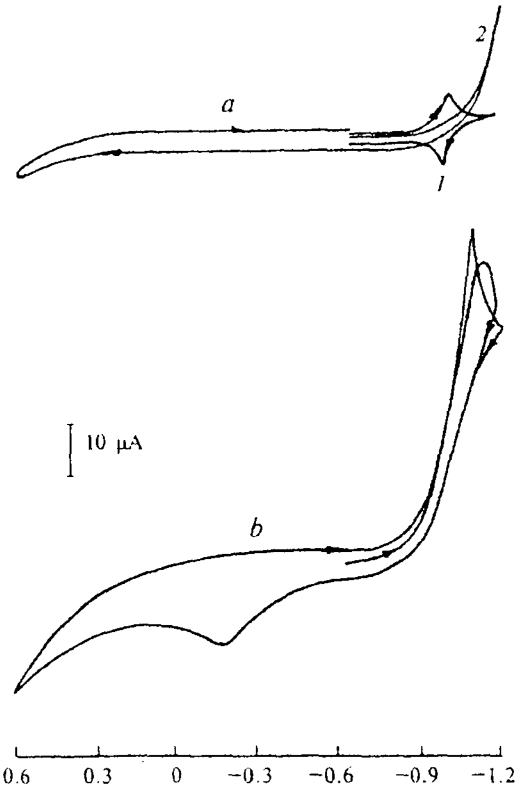
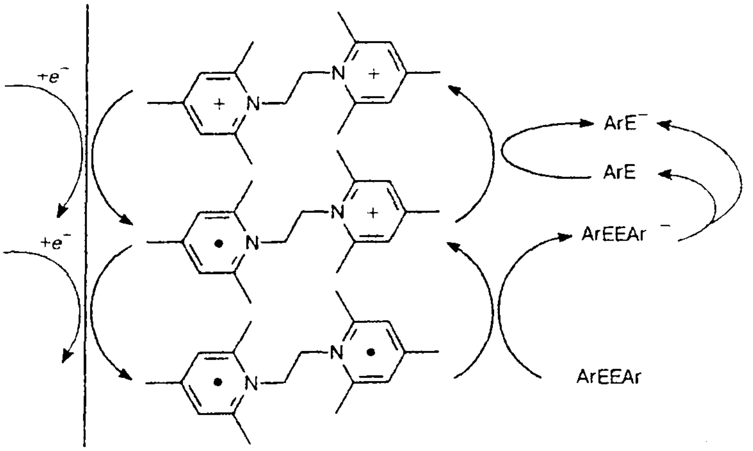


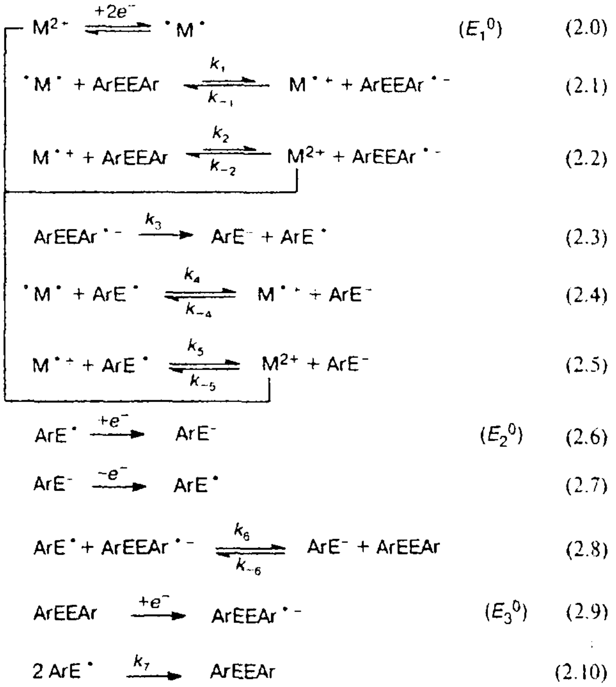
Fig. 2. Cyclic voltammograms of reduction of carrier **9** ($5 \cdot 10^{-4}$ mol L^{-1}; *a*, curve *1*), ditelluride **4** ($5 \cdot 10^{-3}$ mol L^{-1}; *a*, curve *2*), and carrier **9** ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of ditelluride **4** ($5 \cdot 10^{-3}$ mol L^{-1}) (*b*) in DMF on a Pt disk electrode (potential sweep 0.1 V s^{-1}).

Scheme 1



ArEEAr (E = S, Te) are linear. It was found that the i_p values are equal for close-in-potential one-electron stages of reduction of the dication and radical cation with the short ethylene bridge **5**, which agrees with the concept on two-electron transfer within a total cycle of electrocatalysis (Schemes 1 and 2).

Scheme 2



$$M^{2+} \underset{}{\overset{+2e^-}{\rightleftharpoons}} {}^{\bullet}M^{\bullet} \qquad (E_1^0) \qquad (2.0)$$

$${}^{\bullet}M^{\bullet} + ArEEAr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{\bullet +} + ArEEAr^{\bullet -} \qquad (2.1)$$

$$M^{\bullet +} + ArEEAr \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{2+} + ArEEAr^{\bullet -} \qquad (2.2)$$

$$ArEEAr^{\bullet -} \xrightarrow{k_3} ArE^- + ArE^{\bullet} \qquad (2.3)$$

$${}^{\bullet}M^{\bullet} + ArE^{\bullet} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M^{\bullet +} + ArE^- \qquad (2.4)$$

$$M^{\bullet +} + ArE^{\bullet} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} M^{2+} + ArE^- \qquad (2.5)$$

$$ArE^{\bullet} \xrightarrow{+e^-} ArE^- \qquad (E_2^0) \qquad (2.6)$$

$$ArE^- \xrightarrow{-e^-} ArE^{\bullet} \qquad (2.7)$$

$$ArE^{\bullet} + ArEEAr^{\bullet -} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} ArE^- + ArEEAr \qquad (2.8)$$

$$ArEEAr \xrightarrow{+e^-} ArEEAr^{\bullet -} \qquad (E_3^0) \qquad (2.9)$$

$$2\,ArE^{\bullet} \xrightarrow{k_7} ArEEAr \qquad (2.10)$$

In the bimolecular electron transport systems under study, the relative increase in the catalytic component of the reduction current of the mediator (i_p/i_d^0) is the highest in the "carrier **9**—acceptor **4**" system (see Fig. 2, *b*), which agrees with the value of the bimolecular ET constant (Table 1).

For inverse scanning, the voltammograms exhibit the peak of oxidation of the secondary products of reduction, ArE^- anions, in the potential regions of 0 to −0.13 V (E = S) and −0.2 to −0.3 V (E = Te). The diffusion character of the kinetics of reaction (2.7) characterizes the relatively high rate of the preceding decomposition of the primary products, $ArEEAr^{\bullet -}$ radical anions (2.3).

For thermodynamically allowed processes ($E_3^0 - E_1^0 > 0$), the recombination of a substrate with an electron donor can proceed *via* an outer-sphere coordination mechanism involving functional groups of the substrate.[14] Intermediate kinetically unstable complexes between the $1e^-$- or $2e^-$-carrier and the acceptor can be formed at the stage of regeneration of dications and radical cations:

$${}^{\bullet}M^{\bullet} + ArEEAr \rightleftharpoons {}^{\bullet}M^{\bullet}...ArEEAr \longrightarrow$$
$$\longrightarrow {}^{\bullet}M^{\bullet}ArEEAr \longrightarrow M^{\bullet +} + ArEEAr^{\bullet -},$$

Table 1. Bimolecular electron transfer constants in reactions of induced cleavage of diaryldichalcogenides (20 °C; DMF)

Electrocatalytic system		ΔE_p/V	log(k'/L mol^{-1} s^{-1})
Carrier[a]	Acceptor[b]		
5	**1**	0.51[c]	6.70
6	**1**	0.38	7.15
7	**1**	0.37	7.20
8	**1**	0.36	6.93
9	**1**	0.33	7.58
7	**2**	0.43	—[d]
9	**2**	0.40	—
7	**3**	0.43	—
9	**3**	0.40	7.22
7	**4**	0.42	6.48
9	**4**	0.39	8.35

[a] $C = 5 \cdot 10^{-4}$ mol L^{-1}.

[b] $C = 5 \cdot 10^{-3}$ mol L^{-1}.

[c] Referred to the potential of the first one-electron transfer E_{pc1}.[1]

[d] Bimolecular ET is not detected.

where $^{\cdot}M^{\cdot}$...ArEEAr is the outer-sphere molecular complex, and $^{\cdot}M^{\cdot}$ArEEAr is the electroactive complex.

It cannot be ruled out that at the charge transfer stage, the reaction center has a structure for which almost simultaneous transfer of two electrons is preferable.

Based on the experimental data obtained (see Fig. 2, curves *1*, *2*; Table 1) and taking into account the chemical irreversibility of two-electron reduction of diaryldichalcogenides *via* the ECE mechanism,[10] we can propose the scheme of induced reductive cleavage of diaryldichalcogenides (see Scheme 2).

Along with the main reactions (2.0)—(2.5), the scheme contains side reactions (2.6)—(2.10), including the direct (cathodic) reduction of ArE$^{\cdot}$ (2.6) and ArEEAr (2.9). Since k_1 and k_2 should be relatively low, in the absence of specific adsorption of the carrier and substrate ArEEAr on the electrode (which is confirmed by the unchanged character of the electrode process during multiple scanning), the electron transfer occurs outside the double layer (a great thickness of the reaction layer) and can be considered as a homogeneous process. The k_4, k_5, and k_6 constants can be calculated by the equation of diffusion kinetics due to a substantial difference between the oxidative properties of the ArE$^{\cdot}$ radicals and $^{\cdot}M^{\cdot}$, $M^{\cdot +}$, and ArEEAr$^{\cdot -}$ species.

Two particles participate in the homogeneous redox process. In an excess of the ArEEAr oxidant, the stage of reductive activation of the E—E bond can be considered as a *pseudo-first*-order reaction. The following catalytic current corresponds to this condition[15]:

$$i_p = \frac{2FA\sqrt{D_0 k_{app} C_M^0}\left(C^0_{ArEEAr}\right)^{1/2}}{1 + \exp\left[2F(E - E_{1/2})/(RT)\right]},$$

where F is Faraday's number, A is the disk electrode surface, D_0 is the diffusion coefficient of the carrier, k_{app} is the effective rate constant of dication regeneration, and $C_M{}^0$ is the concentration of the dication, the oxidized form of the ET system; $C^0{}_{ArEEAr}$ is the concentration of the ArEEAr acceptor, and R is the universal gas constant.

When the potentials of the half-peak and half-wave of currents of carrier generation are equal ($E_{p/2} = E_{1/2}$), the ratio of the catalytic (i_p) to diffusion (i_d) currents is transformed into the form[15]

$$i_p/i^0{}_d = (k_{app}C^0{}_{ArEEAr})^{1/2}/(0.446a^{1/2}).$$

The second-order rate constants of intermolecular electron transfer ($k' = k_{app}/C_M{}^0$) were determined in this approximation (see Table 1).

Electrocatalytic systems are characterized by a distorted inverse logarithmic dependence between the difference in the electrochemical potentials of carrier formation and "trap" reduction (ΔE_p) and the rate of homogeneous ET (if the kinetic cycle (reactions (2.0)—(2.10)) can occur). Structurally nonrigid molecules **5**—**7** and rigid molecules **8** and **9** (bridged electron carriers) reduce the disulfide bond. At the same time, the electron-donor activity of reduced forms **5**—**8** with respect to ditellurides **2**—**4** is low or absent (see Table 1). The intermolecular ET constants for the five electron carriers under study increase in the series **5** < **8** < **6** < **7** ≪ **9** with an insignificant decrease in the activation parameter ΔE_p. The experimental results suggest that for many or all diaryldichalcogenides **1**—**4**, the azomethine group and other substituents participate in binding of the carrier in the transition state. This confirms the thesis of "structural conformity" for participants in the electron exchange.

The authors thank I. D. Sadekov, A. A. Maksimenko, A. S. Burlov, and A. M. Bochkin for kindly presented dichalcogenides and valuable recommendations in discussion.

The work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32026a).

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Received June 24, 1998;
in revised form February 16, 1999