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THE ELECTROCHEMISTRY OF ORGANIC SULFUR COMPOUNDS. PART II. CATHODIC REDUCTION OF 1,2-DITHIOLYLIUM IONS, REDOX ANALOGY TO THE TROPYLIUM-BITROPENYL SYSTEM.

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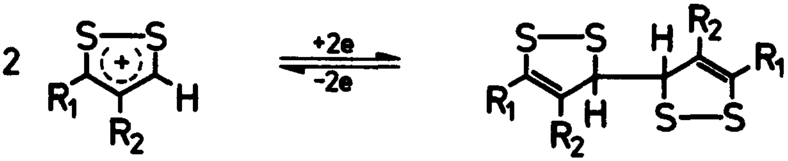
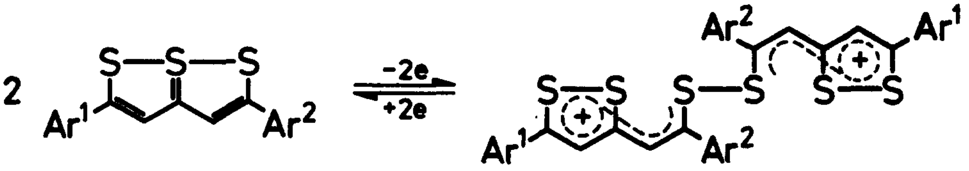
We have observed that cathodic reduction of several 1,2-dithiolylium ions (I) in acetonitrile at a platinum electrode is accompanied by the formation of the dimers (II). This reaction is remarkably efficient with coulometric n values of 1.0 being observed. Furthermore, the 1,2-dithiolylium ions (I) can be regenerated efficiently by anodic oxidation in the same solvent. We have recently observed reversible electrochemical interconversion of the 1.6.6a^{IV}S-trithiapentalene (III) and the disulfide linked dimer (IV) (2). The latter redox system is unusual in that chemical oxidation of III results either in total destruction or in partial desulfuration and formation of 1,2-dithiolylidene aldehydes or ketones and formation of the trithiapentalene ring system



I II



III IV

by reductive reactions had not been reported previously. The reactions described in this communication are opposite to the previous case in that the dimer is formed by reduction in the former and by oxidation in the latter case. The reductive cleavage of the disulfide linkage in going from IV to III is perhaps less surprising than the oxidative cleavage of the carbon - carbon bond during conversion of II to I.

The electrochemical interconversion of Ia and IIa ($R_1 = R_2 = Ph$) is clearly illustrated by the cyclic voltammograms of the two compounds in acetonitrile. For a solution of Ia (1.0 mM) in acetonitrile containing sodium perchlorate (0.1 M), an anodic sweep to +1.0 V. (3) failed to reveal any oxidizable species (Figure a). On the cathodic cycle a reduction peak was observed at -0.46 V. and on the second cycle an anodic peak was observed at +0.59 V. The cyclic voltammogram of IIa (0.5 mM) in the same solvent system showed no reduction peaks on the initial cathodic sweep to -0.8 V. and an oxidation peak was observed at +0.59 V. on the first anodic sweep while the second cathodic sweep showed the reduction peak at -0.45 V. expected for the dithiolylium ion (Figure b).

Constant current coulometric (4) reduction of Ia resulted in the consumption of precisely 1.0 Faradays per mole. Preparative reduction of Ia (2.5 mmol) in acetonitrile (50 ml) resulted in the precipitation of essentially pure IIa (5) which is only slightly soluble in acetonitrile.

Peak potentials for the reduction of several 1,2-dithiolylium ions and oxidation of the corresponding dimers are listed in the Table. It is of interest that the magnitudes of the peak potentials are insensitive to the nature of the substituents, R_1 and R_2. For example 4,4'-dimethoxystilbene, which has a structural feature in common with IIe, is oxidized considerably easier than stilbene (analogous to IIa), a result which can be attributed to the electron donating ability of the *p*-methoxy group (6). Yet IIa is oxidized about 0.1 V. less anodic than IIe which must be indicative that the positive charge in the 1,2-dithiolylium ions resides in the ring almost exclusively irregardless of the substitution. The latter is understandable when we consider the fact that 1,2-dithiolylium ions are isoelectronic with tropylium ions and any structures which take the charge out of the five membered ring are less aromatic.

Thus, the foregoing considerations suggest that an analogy exists in the redox behavior of 1,2-dithiolylium ions and tropylium ion. In fact, the redox behavior of the two systems is almost identical. Tropylium ion is reduced cathodically in acetonitrile to bitropenyl which undergoes anodic cleavage to regenerate tropylium ion (7). Under the conditions of our experiments, tropylium ion is reduced at -0.33 V. and bitropenyl is oxidized with a peak potential of +1.35V.

The stability of the dimeric products (II) is dependent on the nature of R_1 and R_2. For example, complete recovery of Ia, Ic and Id was observed when the dithiolylium salt were first reduced and the resulting products then oxidized.

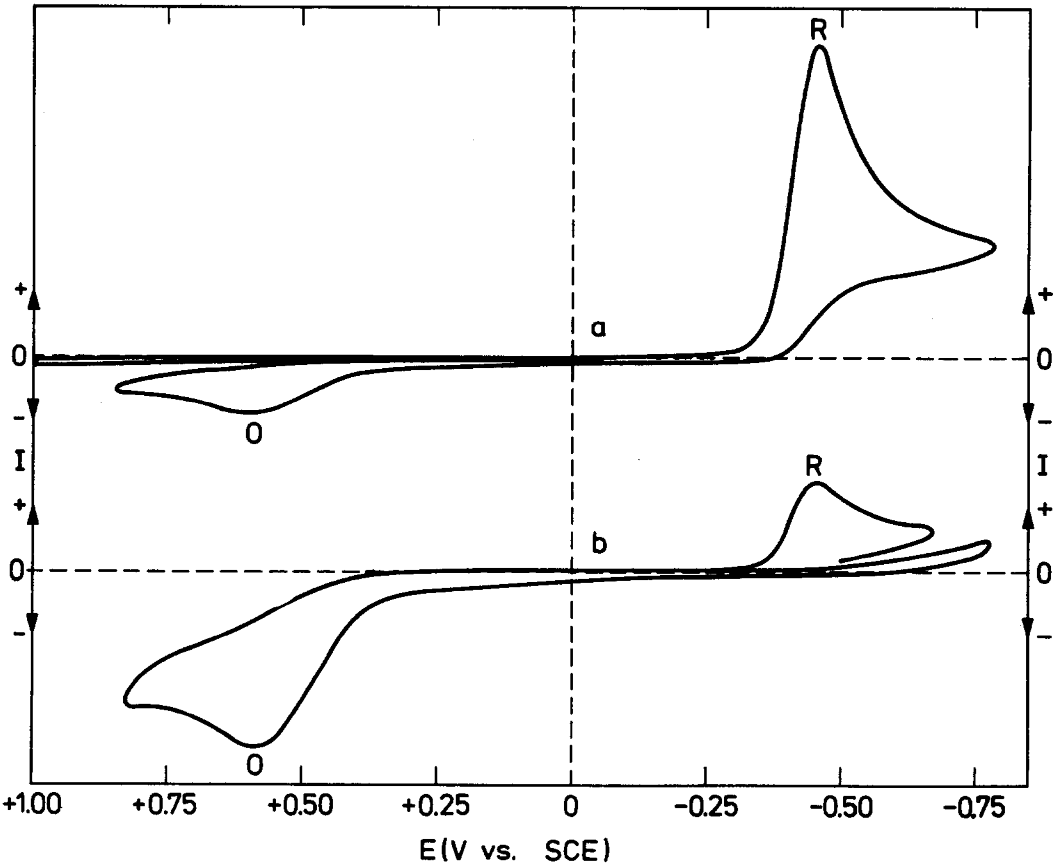


Figure. Cyclic voltammograms of (a) reduction of Ia and (b) oxidation of IIa in acetonitrile. Voltage Sweep rate = 150 mV per second.

The same procedure carried out on Ib and tropylium ion resulted in considerable loss of substrate.

TABLE

Peak Potentials for the Electrochemical Interconversion:

2 Dithiolylium Ion + 2e $\rightleftharpoons$ Bis (1,2-dithiole-3-yl)

I II

	R_1	R_2	E_R[a]	E_O[b]
a	Ph	Ph	-0.46	+0.59
b	Ph	H	-0.45	+0.70
c	An[c]	H	-0.46	+0.72
d	An[c]	An[c]	-0.33	+0.70

a. Peak potential for reduction of I.

b. Peak potential for oxidation of II.

c. *p*-Anisyl group.

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3. All voltages are for oxidation or reduction at a platinum electrode versus the saturated calomel electrode.
4. V. D. Parker, *Acta Chem. Scand.*, **24**, 2768 (1970).
5. Mass spectral fragments were observed at m/e 444 (100%, M-H_2S_2), 414 (12%, M-S_3), 325 (8.5%), 223 (9.1%), 221 (7.4%), 121 (10.8%). ^{1}H nmr (pyridine d_6, 80°) δ 5.74 (s) δ 6.93-7.10 (m) ratio 1:10.
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