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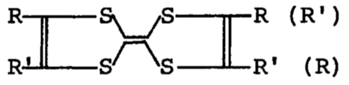
THE REACTION OF TETRATHIOFULVALENES WITH 2,3-DICHLORO-5,6-DICYANO-p-BENZOQUINONE. NEW STABLE CATION- and ANION-RADICAL COMPLEXES

Yoshio UENO and Makoto OKAWARA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayam, Meguro, Tokyo 152

Tetrathiofulvalene derivatives Ia-e reacted with an equimolar amount of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in hot acetonitrile or benzene to give new stable cation-radical and anion-radical complexes IIa-e, which had various mole ratios (1:1, 1:2, 2:1).

A great interest has been recently stimulated in the 1:1 complex of tetrathiofulvalene (TTF) with tetracyanoquinodimethane (TCNQ) by the finding of the high conductive behavior.[1)]

The preliminary results communicated herein demonstrate the new stable complex formation of TTF derivatives Ia-e [2)] with DDQ.



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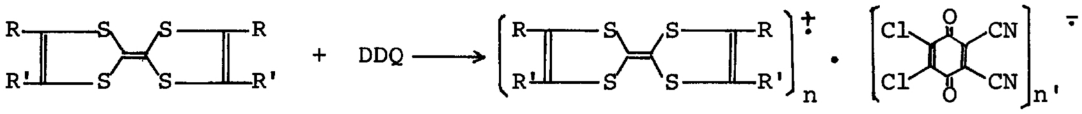
Ia; R,R'= $-(CH_2)_4-$
b; R=Ph, R'=H
c; R=p-MeOC$_6$H$_4$, R'=H
d; R=R'=Ph
e; R=R'=H (TTF)

Complexes with DDQ. TTF derivatives Ia-d react with an equimolar amount of DDQ in hot acetonitrile (MeCN) or benzene to give immediately black or greenish black crystalline products IIa-d, which are essentially insoluble in nonpolar solvents, but can be recrystallized from polar solvents such as MeCN. TTF itself (Ie) can also react with DDQ to give 1:1 adduct IIe (Table 1).

In contrast to the TCNQ complex (1:1), it is quite noticeable that a change in substituents of TTF derivatives can result in significant changes in the mole ratio of each component in the DDQ complexes (1:1, 1:2, 2:1).



Ia-e IIa-e

Table 1. DDQ complexes of TTF derivatives.3)

	Yield (%)	mp (°C)	ratio n/n'	uv λ_{max}(MeCN) (nm)
IIa	82	>235 (d.)	1/2	235, 248(sh), 271, 283(sh), 347, 409(sh), 433 459, 513(sh), 540, 590, 662
IIb	94	190-1 (d.)	2/1	258, 329, 347(sh), 432, 458, 540, 590, 688
IIc	93	201-2 (d.)	1/1	248(sh), 259.5, 273, 292(sh), 334(sh), 347(sh), 407, 460, 542, 590, 767
IId	26	176-8 (d.)	1/1	258(sh), 271(sh), 346, 459, 549, 590, 704
IIe	76	>300 (d.)	1/1	247, 308, 347(sh), 440, 546(broad), 585

The ir spectra of IIa-e are different from those of the components. The carbonyl band of DDQ at 1680 cm^{-1} is absent. The characteristic absorption of phenoxy radical(1562cm^{-1})4)appears at 1560-1565 cm^{-1}. The uv spectrum of IIa in MeCN shows the presence of the both cation-radical and anion-radical of Ia and DDQ, respectively, as summarized in Table 2. Similarly, IIb-e show the characteristic absorptions of DDQ$^{\overline{\cdot}}$ in their spectra.

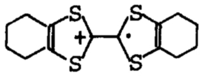
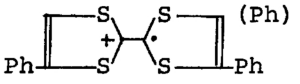
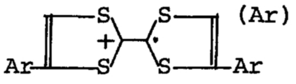
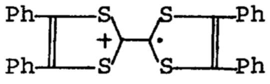
Table 2. Visible spectra in MeCN (nm).

IIa	662, 594, 540, 513(sh), 459, 433, 409(sh), 347
$M^{+}\cdot DDQ^{\overline{\cdot}}$ 5)	590, 545, 457, 345-8
$Ia^{\dot{+}}\cdot ClO_4^{-}$ 6)	662, 508, 459, 433, 409(sh), 343

M^{+}; metallocinium, See Ref. 5.

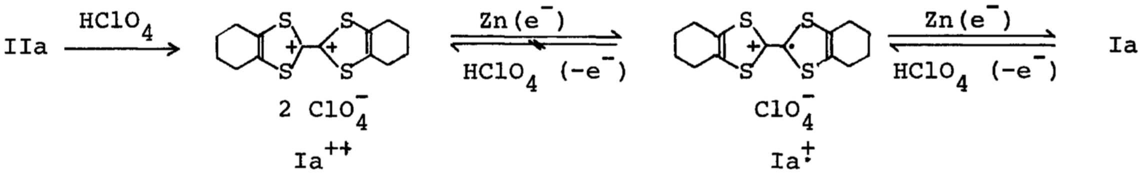
These results suggest that the reaction should proceed as indicated above. Although cation-radicals of Ib-d are not yet known, the uv and visible data may be estimated from the spectra of IIb-d by substracting the absorptions of DDQ$^{\overline{\cdot}}$. The longest wavelength absorption bands of the cation-radicals are summarized in Table 3.

Table 3. The longest wavelength absorptions of the cation-radicals in MeCN (nm).

 Ia$^{+\cdot}$	 Ib$^{+\cdot}$	 Ic$^{+\cdot}$	 Id$^{+\cdot}$
662^{a}	688	767^{b}	704

a; Lit.$^{6)}$ 662 nm b; Ar= p-MeOC$_6$H$_4$

Phenyl groups,especially p-methoxyphenyl group, cause the strong bathochromic shift, which suggests the more developed delocalization of the ion-radical charges. The epr spectrum of IIa in solid state gives broad signals which consist of unresolved fine structures. Treatment of IIa with 70% perchloric acid results in change in color from greenish black into yellow [uv λmax(MeCN): 217, 267.5, 281, 358, 426 nm]. Once again, this yellow compound is converted into deep greenish cation-radical Ia$^{+\cdot}$ by treating with the small amount of zinc powder in MeCN. Treatment of Ia with 70% perchloric acid results in the formation of cation-radical Ia$^{+\cdot}$. Further oxidation to dication Ia^{++}, however, is not observed. These transformations are confirmed by the spectroscopic method. Dication Ia^{++} is stable in MeCN, but unstable in EtOH. In the latter solvent, the characteristic color of Ia^{++} fades rapidly, presumably due to the nucleophilic attack by EtOH.



Complexes with other electron acceptors. In order to know the donor strength of TTF derivatives Ia-d, the reaction of Ia-d with other electron acceptors have been studied. Among the donors Ia-d, only Ia reacts with TCNQ in hot MeCN to give the black 1:1 salt III as lustered fine needle-like crystals (90%)^{3}, mp 200-202°C (d.), uv: λmax (MeCN) 300(sh), 327.5, 374(sh), 395, 460(sh), 681, 746, 840 nm. Other donors Ib-d do not give the isolable crystalline complexes with TCNQ.

Similarly, only Ia reacts with chloranil in MeCN or acetone to give a green solution. The adduct, Ia-chloranil, however,is not deposited out from the reaction mixture. Other donors Ib-d do not bring about any color changes by addition of chloranil.

In conclusion, the mole ratios in the TTF-DDQ complexes and the reactivities of TTF derivatives as electron donors [Ia $\gg$ Ic $>$ Ib $>$ Id] are greatly dependent on the substituents attached to 4- or 5- position. Phenyl groups weaken the donor strength as a result of reducing the electron density of the central sulfur-substituted olefin moiety.

As an acceptor , DDQ molecule is superior to TCNQ or chloranil in combination with the donors of tetrathiofulvalene type.

Studies on the electrical conductivity measurements on the DDQ complexes IIa-e and the TCNQ complex III will be reported elsewhere.

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