TRANSFORMATIONS OF 4,4′-DIMETHOXYSTILBENE IN EARLY STAGES OF OXIDATION

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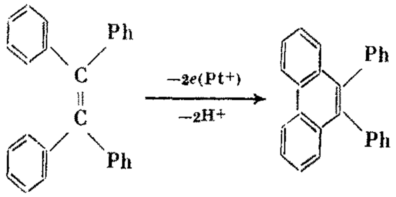
4,4′-Dimethoxystilbene forms a dimer as a result of one-electron anodic oxidation and undergoes cis/trans-*isomerization when bound in a charge-transfer complex (chloranil as acceptor).*

Keywords: *4,4′dimethoxystilbene, chloranil, charge-transfer complex,* cis/trans-*isomerization.*

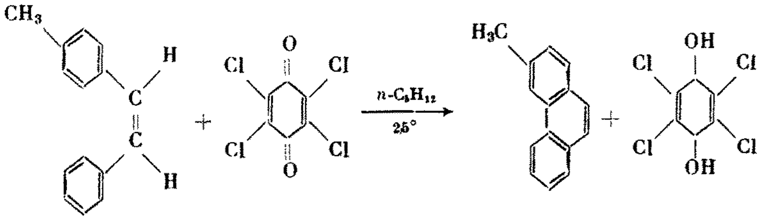
Aromatic, especially polycyclic, hydrocarbons are easily adsorbed on platinum and other metal anodes; it is generally believed that the plane of the hydrocarbon is positioned parallel to the surface of the electrode as a result of π-bonding [1]. This type of binding is formally similar to the formation of a charge-transfer complex (CTC) in the solution. The distance between the hydrocarbon molecule and surface of the electrode has been estimated [1] at 3.5 Å, i.e., it is of the same order as the distance between donor and acceptor in the corresponding CTC [1].

However, the similarity of these two processes probably does not always lead to similar products. One-electron oxidation of tetraphenylethylene on a platinum anode yields 9,10-diphenylphenanthrene as the product of intramolecular cyclization (scheme 1) [2].



(1)

Stilbene and its methyl derivatives (diphenylethylene) does not change in the same conditions [2]. This difference in the anodic behavior of these substances is attributed in [1] to the low stability of the radical cations of stilbene and its methyl derivatives in comparison to the radical cations of tetraphenylethylene. The participation of the radical cations in cyclization of tetraphenylethylene was demonstrated in [3, 4]. However, when p-chloranil (CA) is present in the solution, 4-methylstilbene can be cyclized and converted into 3-methylphenanthrene. The reaction takes place via formation of CTC at a low temperature (under 40°C) and does not require radiation [5] (scheme 2).



(2)

The behavior of 4,4′-dimethoxystilbene (DMOS) on the electrode and with CA was compared in the present communication. We found that the *cis-* and *trans-*isomers of DMOS form different CTC with CA which differ in color and can be converted. We found that conversion to be the *cis* → *trans* direction (scheme 3):

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TABLE 1. Reaction of DMOS and CA (equimolar ratio of reagents)

Solvent (Bp, °C)	25° C		Bp of solvent	
	holding, h	conversion, %	holding, h	conversion, %
Benzene (80)	300	0	15	7
n-Hexane (69) *	300	0	15	50
Methylene chloride (40)	170	30	15	30

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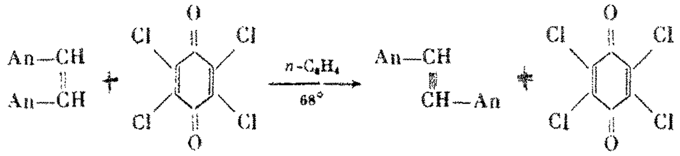
*CA dissolves in hexane only when heated; formation of CTC is observed in homogeneous solution.



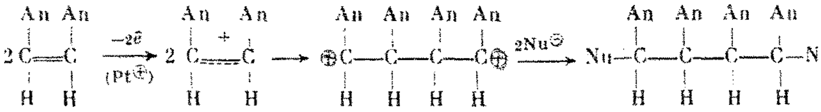
(3)

An=p-$CH_3OC_6H_4$.

Reverse conversion is not observed, and cyclization is also not detected (which takes place in the case of 4-methylstilbene). The degree of *cis/trans*-conversion is a function of the nature of the solvent (Table 1).

As Table 1 shows, conversion is ineffective in the case of benzene. This is perhaps because benzene competes with DMOS in binding with CA in CTC much more successfully than the molecules of the other solvents. This hypothesis is totally logical if we assume that the CA π-acceptor binds in a CTC with DMOS due to the benzene ring and not because of the ethylene bond.

The first stage of anodic oxidation of DMOS yields radical cations which have a sufficient lifetime and are even dimerized in the presence of nucleophiles [6-8] (scheme 4).



$$2\,\underset{H}{\overset{An}{C}}=\underset{H}{\overset{An}{C}} \xrightarrow[(Pt^{\oplus})]{-2\bar{e}} 2\,\underset{H}{\overset{An}{C}}\overset{+}{\cdots}\underset{H}{\overset{An}{C}} \longrightarrow \oplus\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}\oplus \xrightarrow{2Nu^{\ominus}} Nu-\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}-\underset{H}{\overset{An}{C}}-Nu \qquad (4)$$

An=p-$CH_3OC_6H_4$; Nu=OH^-etc.

EXPERIMENTAL

4,4′-Dimethoxystilbene was synthesized by the method in [9]. The PMR spectra were recorded on a Bruker WP-200 SY (200, 13 MHz), TMS internal standard.

Qualitative Determination of CTC between DMOS and CA. A 0.01 *M* solution of a mixture of 4,4′-dimethoxystilbene *cis*- and *trans*-isomers was placed on a Silufol UV-254 plate and eluted with *n*-hexane–ether mixture, 2:1. The plate was removed from the solvent and held in air. After evaporation of the solvent, the plate was sprayed with a 0.025 *M* solution of chloranil (CA) in benzene (this solution was yellow). Two colored regions appeared on the plate: violet (R_f = 0.46) and green (R_f = 0.38), corresponding to a charge-transfer complex (CTC) between *cis*- and *trans*-DMOS, respectively, and CA. It was thus found that *cis*- and *trans*-DMOS yield different colored complexes with chloranil.

Isomerization of DMOS in CTC with CA. A mixture of 0.1186 g of *cis*-4,4′-DMOS (0.5 mmole), 0.138 g (0.5 mmole) of CA, and a solvent (10 ml) was held in an argon current while boiling the solvent. After the CA dissolved, the mixture turned violet, characteristic of CTC between *cis*-DMOS and CA. The PMR spectra of the reaction mixture were recorded every 5 h and the percentage ratio of DMOS *cis*- and *trans*-isomers were calculated from the ratio of the integral intensities of the methoxy group proton signals. In boiling hexane, the degree of conversion of DMOS was 26% after 5 h, 40% after 10 h, and 50% after 15 h; there was no significant increase in the degree of conversion with further holding. Accumulation of DMOS *trans*-isomer caused the color to change from violet to green. The green coloration is characteristic of CTC between CA and *trans*-DMOS.

PMR spectrum of *cis*-4,4'-DMOS (C_6D_6, δ, ppm, J, Hz): 7.3 and 6.7 q (6H, Ar, $^3J = 8.5$), 6.5 s (2H, $-CH=CH-$), 3.25 s (3H, $-OCH_3$). PMR spectrum of *trans*-4,4'-DMOS (C_6D_6, δ, ppm, J, Hz): 7.34 and 6.85 q (6H, Ar, $^3J = 9$), 7 s (2H, $-CH=CH-$), 3.31 s (3H, $-OCH_3$). The character of the spectra and difference in the chemical shifts of signals of $-OCH_3$ groups were the same for both solutions in C_6D_6, as well as in $(CD_3)_2CO$, $CDCl_3$, and CD_2Cl_2.

In a control experiment, *cis*-DMOS was held without CA while boiling the solvent (hexane, CH_2Cl_2). The degree of *cis/trans*-conversion was 5-7% after 10 h, i.e., significantly lower than with CA.

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