

## ***Electrochemistry***

### **Reactivity of some Acetylenic Derivatives in Electroinitiated Polymerization**

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#### SUMMARY

The charge distribution in phenylacetylene, methyl propiolate, diphenyldiacetylene as well as in their anion-radicals was calculated by CNDO/2 and EHT methods. According to the obtained results, the electroinitiated polymerization of these monomers takes place by their direct reduction. A good agreement between theoretical and electroanalytical data was observed.

#### INTRODUCTION

The electrochemical initiated polymerization of acetylenic derivatives allows the obtention of different macromolecular compounds through a much simpler technique as compared to that using organometallic catalysts (FARAFONOV et al., 1977; SUBRAMANIAN et al., 1978; SIMIONESCU et al., 1983a ). This new investigation field has both practical and theoretical importance since the combination of the spectrophotometrical and electroanalytical methods leads to the understanding of the reaction mechanism and to the right choosing of optimum polymerization conditions (SIMIONESCU et al., 1983b ). Some polarographic investigations made evident the reduction capacity of phenylacetylene (PhA), diphenyldiacetylene (DPhDA) and methyl propiolate (MP). By determining the  $E_{1/2}$  and  $n$  values ( $n$  being the number of electrons transferred in the electrode process) information on the reversible process was obtained (SIMIONESCU et al., 1983b ). The half-wave potentials,  $E_{1/2}$ , characterize the monomer electronic affinity and thus they may be correlated to some theoretical data obtained through molecular orbital calculations. Qualitative estimations of the electrochemically initiated reaction were obtained from the MO data by CNDO/2 (POPLE et al., 1966) and EHT (HOFFMANN et al., 1963, 1964) methods.

#### EXPERIMENTAL

The polarographic measurements were performed on a OH - 102 Radelkis polarograph by using a dropping Hg electrode ( $m^{2/3}xt^{1/6} = 3-5$ ) or a platinum stationary microelectrode as

a cathode at  $25 \pm 0.5^\circ\text{C}$ . In Table 1 the half-wave potentials,  $E_{1/2}$ , of the acetylenic monomers determined in 0.1 M dimethylformamide (DMF) solutions of  $(\text{CH}_3)_4\text{NClO}_4$  are listed.

TABLE 1  
Half-wave potentials of some acetylenic monomers  
in  $(\text{CH}_3)_4\text{NClO}_4$  0.1 M DMF solution

Monomer	$-E_{1/2}(\text{I}), \text{V}$		$E_0(\text{I}), \text{V}$	$-E_{1/2}(\text{II}), \text{V}$		$E_0(\text{II}), \text{V}$	$\alpha^x$ deg.
	Hg	SCE		Hg	Hg		
PhA	2.36	2.00	-2.20	-	-	52	
DPhDA	1.88	1.535	-1.78	2.36	2.20	50 53	
MP	1.90	1.550	-1.70	2.85	2.70	35 65	

$\alpha^x$ ) - angle between basic solution line and polarogram step

The polarogram of PhA shows a single well-defined step, while those of DPhDA and MP present two steps. By comparing the first reduction step of DPhDA and MP, the  $E_{1/2}(\text{MP})$  is seen to be somewhat shifted to negative values (with  $0.02-0.05\text{V}$ ) instead of showing positive values due to the pronounced irreversibility of the electrode process expressed by  $\alpha$ .

The polymerization reactions were carried out according to a method previously described by using quaternary ammonium, phosphonium, arsonium and stibonium salts as 0.1 M solutions in DMF, a polar aprotic solvent, with monomer concentrations in the electrolysis cell of 1.5 M (PhA), 0.6 M (DPhDA) and 1.9 M (MP), respectively.

The polymers obtained following the electrochemical synthesis were proved to present a rather narrow polydispersity. The molecular weights determined with a vapor pressure osmometer (Knauer Damfdruck Osmometer) in DMF or benzene were:  $\bar{M}_n = 1000 - 1500$  for poly(PhA),  $\bar{M}_n = 1100 - 2200$  for poly(DPhDA) and  $\bar{M}_n = 2200 - 7000$  for poly(methyl propiolate). The melting ranges of the polymers depend on their molecular weights (SIMIONESCU et al., 1983a).

### THEORETICAL

MO calculations by CNDO/2 and EHT methods were performed by means of a Felix-256 computer based on the following molecular geometry data:

$-\text{C}=\text{C}-$  1.20 Å;  $\text{C}_{\text{te}}-\text{H}$  1.09 Å;  $\text{C}_{\text{di}}-\text{H}$  1.06 Å;  $\text{C}_{\text{tr}}-\text{H}$  1.08 Å;  
 $\text{C}=\text{C}$  (aromatic) 1.397 Å;  $\text{C}_{\text{tr}}-\text{C}_{\text{di}}$  1.43 Å;  $\text{C}_{\text{tr}}=\text{O}$  1.22 Å;  
 $\text{C}_{\text{tr}}-\text{O}_{\text{te}}$  1.34 Å;  $\angle \text{O}=\text{C}-\text{O}$   $120^\circ$ ;  $\angle \text{C}-\text{O}-\text{C}$   $105^\circ$ ;  $\angle \text{H}-\text{C}-\text{H}$   $109^\circ 28'$

(te- tetrahedral; tr- trigonal; di- digonal).

## RESULTS AND DISCUSSION

The charge distributions in phenylacetylene and methyl propiolate as determined by CNDO/2 method are given in Figures 1 and 2. Based on data presented in Figure 1, the PhA radical-anion,  $[\text{C}_6\text{H}_5\text{-C}\equiv\text{CH}]^-$  is supposed to dimerize through the carbon

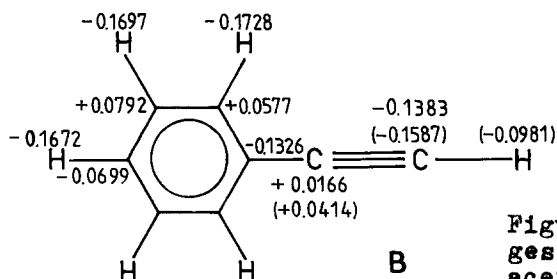
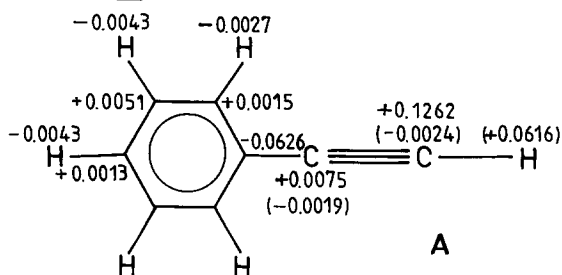


Figure 1. Net atomic charges ( $\pi$  charge) in phenylacetylene (A) and anion-radical (B).

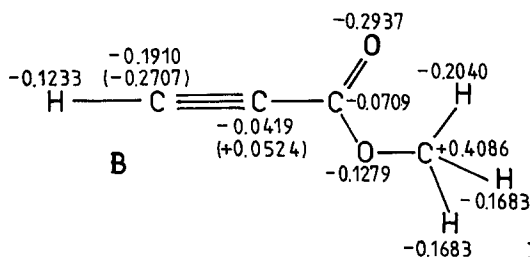
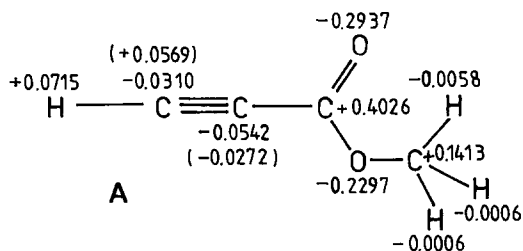
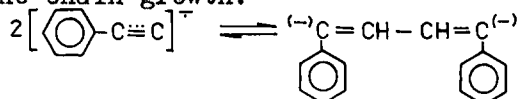


Figure 2. Net atomic charges ( $\pi$  charge) in methyl propiolate (A) and anion-radical (B).

atom having a maximum free valence index ( $\pi$ ) -  $E_{\alpha} = 0.451$ ;  $F_{\beta} = 0.820$ , leading to the following dicarbanion able to determine the chain growth:

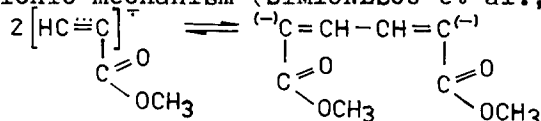


GEIDERICH et al., (1976) studied the polymerization of PhA in the presence of  $n\text{-C}_4\text{H}_9\text{Li}$  or  $\text{C}_6\text{H}_5\text{-C}\equiv\text{CLi}$ , in polar solvents, and established the following solvation capacity order toward  $\text{Li}^+$  cation:  $\text{DMF} < \text{DMSO} < \text{HMPT}$ . It thus appears that in the electroinitiated polymerization the anions do not solvate with solvent, a strong solvation of the cations of the electrolyte taking place. Phenylacetylene behaves as a weak acid- $\equiv\text{C-H}$  group ( $\text{p}k = 18.5$ ) (HENDRICKSON et al., 1976).

During the electroinitiated polymerization of PhA, the monomeric proton may interact with the active center, this determining the interruption of the "living chain" growth. The maintaining of the "living" centers in the reaction medium is proved by the fact that the electrolysis solution is a good initiator for the polymerization of vinylic monomers, while it doesn't initiate the polymerization of PhA (SIMIONESCU et al., 1979).

These arguments suggest a mechanism involving free anions and characterized by chain transfer reactions to monomer for polymerization of PhA.

The direct reduction of the methyl propiolate leads to the corresponding radical-anion,  $\left[ \text{HC}\equiv\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{C} \end{array} \text{OCH}_3 \right]^{-}$  also able to recombine through the carbon atom of the maximum free valence index ( $\pi$ ) -  $F_{\alpha} = 0.428$ ;  $F_{\beta} = 0.785$ . The formed dicarbanion-dimer allows the chain growing at a very high rate through an anionic mechanism (SIMIONESCU et al., 1983b) :

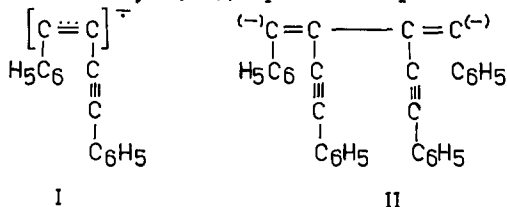


Since the chain growth cannot be interrupted by proton transfer from the solvent to the carbanion, one can suppose that the active center could be also destroyed by chain transfer to the monomer. This phenomenon was evidenced by means of IR and NMR spectral data obtained in cyanoacetylene polymerization by deuterium transfer from the monomer to the carbanion (WALLACH et al., 1969).

The comparison of charge distributions at the triple bond carbon atoms of PhA and MP in neutral molecules and in the corresponding radical-anions confirms the polarographic results on the polymerization initiation by the direct reduction of the monomers. In cathodic polarography of PhA and MP the starting of the reduction ( $E_0$ ) is  $-2.20$  V and  $-1.70$  V, respectively, this indicating the much easy reduction of the acetylenic ester.

The charge distribution obtained for diphenyldiacetylene by EHT method is shown in Figure 3. The initiation process also takes place by the electron attack on the triple bond as

observed in the case of phenylacetylene. The formation of the radical-anion (I) and dianion-dimer (II) can be thus assumed. Since in both electroinitiated polymerization of DPhDA (SIMIONESCU et al., unpublished data) and in the polymerization initiated with  $n\text{-C}_4\text{H}_9\text{Li}$  or Ziegler catalysts (MISSIN et al., 1976; TEYSSIE et al., 1964) quite complex structures are ob-



tained, no other explanation seems possible.

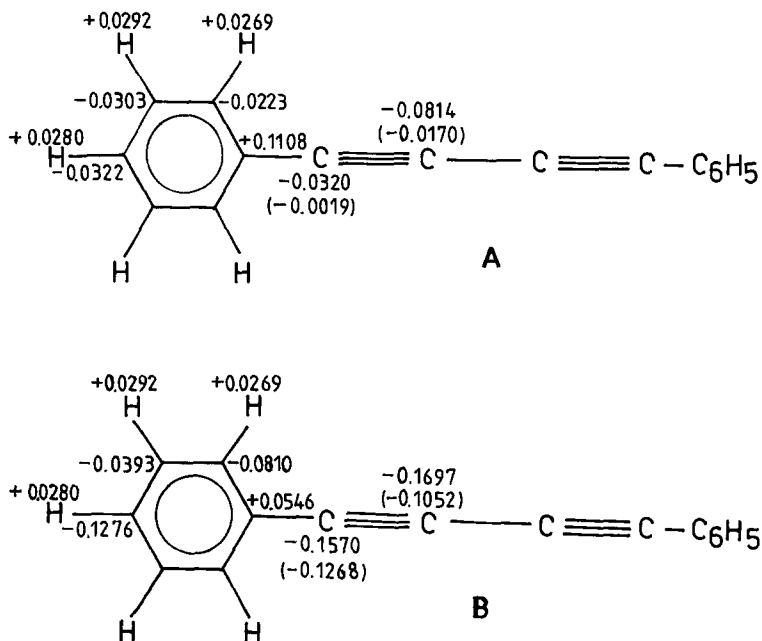


Figure 3. Net atomic charges ( $\pi$  charge) in diphenyldiacetylene (A) and anion-radical (B).

A fairly good agreement of the results is observed through the correlation of the electrolysis conditions and the yields of the reaction products (SIMIONESCU et al., 1983a) with the theoretical data obtained by MO calculations as well as by the polarographic method (SIMIONESCU et al., 1983b). One has to point out that the electroinitiated polymerization of acetylenic monomers under study proceeds by their direct reduction on the cathode and the growing mechanism is anionic.

As regards the reduction capacity, under the mentioned reaction conditions, methyl propiolate was found to be reduced easier and phenylacetylene with the greatest difficulty. One has to mention also that 1,2,4-triphenylbenzene and the ester of 1,3,5-benzene tricarboxylic acid were also separated from the reaction medium; the conditions promoting the formation of cyclic oligomers will be further investigated.

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