

# SPLIT OF THE CARBON-CARBON BOND AT ELECTROREDUCTION OF VICINAL DINITROCOMPOUNDS

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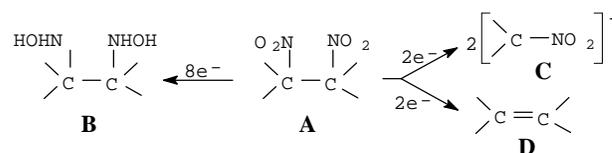
The known examples of the carbon-carbon bond electrochemical split are limited by reduction of biaryls, methylenecyclopropanes and nitriles (split of the cyanide ion). However, when carbon-heteroatom or heteroatom-heteroatom bonds are available in the molecule these very bonds split at electroreduction (ER) but not carbon-carbon ones.

We found out that at ER of vicinal dinitrocompounds in water-alcohol alkaline media salts of mononitrocompounds were generated, i.e. the process is accompanied by a split of the bond between two tertiary carbon atoms (Table 1). The carbon-carbon bond split proceeds quantitatively at ER of 1,1-dinitrobicyclohexyl (I) on a mercury electrode in 0.1 M aqueous NaOH that contains 85% ethanol. In the case of 2,3-dinitro-2,3-dimethylbutane (II), along with 2-nitropropane (yield 80%), about 15% 2,3-dihydroxylamine-2,3-dimethylbutane is generated under similar conditions after catholyte acidification.

The process of the carbon-carbon bond split occurs at the step of the formation of dianions after a sequential transfer of two electrons to the dinitrocompound molecule. It is evidenced by the cyclic voltamperic curves in the alkaline medium of the solution. Fig. 1 shows that the stage of generating relatively stable for these conditions anion radicals (AR) (curve 1) is followed by an irreversible step of the second electron transfer with the formation of a unstable dianion (curve 2).

The carbon-carbon bond split in dianions of dinitrocompounds is also evidenced by a rather rare phenomenon in organic electrochemistry observed in ER of I, II and 3,7-dinitroadamantane (III) - an anomalous change of limiting current with the growth of the absolute value of electrode's negative potential. At pH from 4 to 9 polarographic waves have a curve peaks caused by a change in the ER mechanism as the electrode potential grows (Fig.2). It was shown that the change of the mechanism resulted from the competition of two processes: protonation of AR generated at the first step (with further reduction to dihydroxylamines) and addition of the second electron to AR followed by the carbon-carbon bond split in dianions of nitrocompounds. As absolute values of the electrode potential are growing, the rate of the generation of dianions increases and limiting current of ER waves decreases.

A condition necessary for stabilizing dianions by splitting the carbon-carbon bond is likely to be their solvation and/or formation of ionic pairs. The competing reaction of splitting of nitrate ions to yield 2,3-dimethylbutane from II proceeds notably even in the water-alcohol medium when the metal cation is replaced by the tetraalkylammonium cation (Table 1). In aqueous DMF, in the presence of metal cations the rate of the reaction becomes equal to the rate of 2-nitropropane salt formation. In case  $\text{Bu}_4\text{NClO}_4$  is used as a background catholyte, ER of I is almost solely accompanied by the split of nitrite ions.



Compounds	Solvent	Elektrolyte	Yield,% <sup>1)</sup>		
			B	C <sup>2)</sup>	D
	EtOH, 15% H <sub>2</sub> O	NaOH, 0.1 M	—	100	—
	EtOH, 20% H <sub>2</sub> O	NaOH, 0.1 M	15	85	—
—	EtOH, 20% H <sub>2</sub> O	$\text{Bu}_4\text{NOH}$ , 0.1 M	10	85	5
—	DMF, 20% H <sub>2</sub> O	$\text{NaClO}_4$ , 0.1 M	20	40	40
—	DMF, 5% H <sub>2</sub> O	$\text{Bu}_4\text{NClO}_4$ , 0.05 M	—	3	97

<sup>1)</sup> From chemical analysis data. <sup>2)</sup> Nitroparaffin salts

Table 1. Preparative electroreduction of dinitro compounds on mercury electrode at potentials  $-1.5 \div -1.6$  V (vs SCE) (temperature  $20 \div 30^\circ\text{C}$ ).

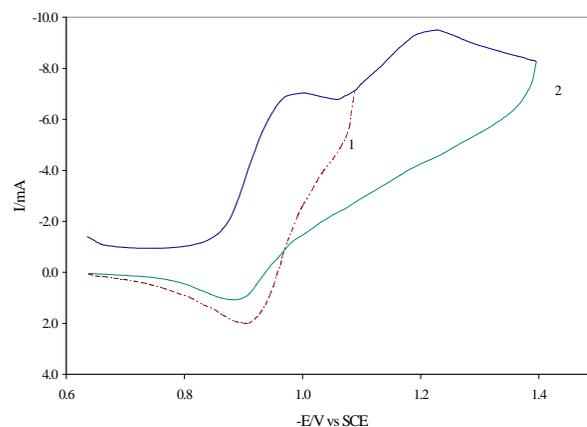


Fig. 1. Cyclic voltamperic curves of reduction of 2,3-dinitro-2,3-dimethylbutane (0.5 mM) on mercury electrode (area - 0.011 cm<sup>2</sup>) in 0.01 M NaOH at potentials of the polarization direction change -1.1 V (1) and -1.4 V (2) (potential overlapping rate 2 V/s).

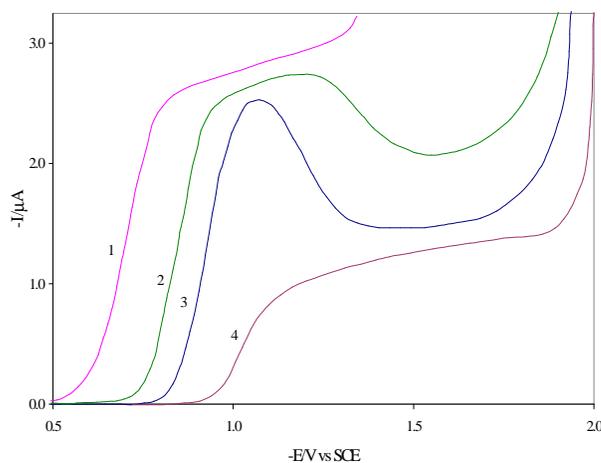


Fig. 2. Polarograms for 2,3-dinitro-2,3-dimethylbutane in water buffer solutions with 10% EtOH and pH: 2.15 (1), 5.91 (2), 7.33 (3), and 10.42 (4) (ionic force of solutions 0.5, concentration of depolarizer 0.5mM, characteristics of mercury dropping electrode  $m = 0.74 \text{ mg s}^{-1}$ ,  $t = 0.43\text{s}$ ).