ELECTROSYNTHESIS OF ORGANIC COMPOUNDS VIII ELECTROCHEMICAL OXIDATION OF MALONONITRILE AND ITS SODIUM SALT IN NONAQUEOUS MEDIUM

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Anodic oxidation of malononitrile and its sodium salt was carried out on platinum in nonaqueous solvents (acetonitrile, dimethylformamide and methanol) using different electrolytes [$Ba(ClO_4)_2$, KI and NaOMe] at a controlled potential of 1.9 ± 0.03 V vs SCE in divided and undivided cells. The product was found to be mainly the dimer-1,1,2,2-tetracyanoethane. In addition a small amount of polymerised material (5%) was also formed. A suitable mechanism involving the formation of the free radical intermediate $CH(CN)_2$ is suggested.

The electrochemical oxidation of diethyl sodium malonate in different solvents<1-7> has been carried out and dimerized, trimerized and/or polymerised products were obtained. Also, the anodic oxidation of 2-nitrobutane and 2-nitropropane in different conditions was reported<5>.

Previous work in this laboratory is concerned with the oxidation of dimethyl sodium malonate <8> and nitromethane anions <9> in the presence of aromatic hydrocarbons in methanol as solvent at controlled anode potentials.

The present study was aimed to electrosynthesize the tetracyanoethane derivatives in a reasonable yield. This has a wide application in industry.

EXPERIMENTAL

Instrumentation

Two cells were used in the experimental work. The first cell was of two compartments of 65 ml and 35 ml capacities, separated by a diaphragm of sintered glass No. 2. The second cell had a single compartment of 100 ml capacity. The electrodes were of platinum anode 2.0x1.0 cm^2 platinum cathode 1.0 x 1.0 cm^2 and a saturated calomel electrode was the reference electrode with its bridge close to the anode. The temperature of electrolysis was maintained at 20° C using an ultrathermostat and insulation. The electro-oxidation was carried out at an anodic potential of +1.9 ±0.03 V vs SCE using a potentiostat. A Pye Unicem SP 200 G IR spectrophotometer with KBr disc was used for analysis. TLC was used to identify products.

Chemical Used

Barium perchlorate (Fluka) and KI (BDH) were used without further purification as supporting electrolytes. Absolute metanol, N,N-dimethylformamide (Fluka) and acetonitrile (Fluka) were utilized as solvents. DMF and acetonitrile were distilled under vacuum and atmospheric pressure respectively from calcium hydride immediately prior to use. Malononitrile (Merck) was distilled under vacuum before using. 1,1,2,2-tetracyanoethane was prepared using the reported procedure, m.p. 170-5° C with decomposition

General Procedure of Oxidation

In case of using devided cell, a solution of malononitrile (3.3 gm) in 65 ml solvent containing 0.05 M supporting electrolyte was placed in the anode compartment. The cathode compartment was filled with a solution of 25 ml solvent containing 0.05M supporting electrolyte. The solution was electrolyzed at 20° for a period of 24-96 hrs. (see Table 1) under controlled anodic potential value of + 1.9 ± 0.03 V vs SCE using a potentiostat. During electrolysis the colourless solution in the anode compartment became brown, (in exp. 4 a violet colour was observed; no gas evolution was observed). At the end of the electrolysis, solvent in anodic solution was distilled under atmospheric pressure and the residue was extracted with ether, (In case of DMF as solvent, the electrolysate was diluted with 200 ml of water and extracted three times with 150 ml ether). The ether extracts were dried over anhydrous magnesium sulfate and filtered. The filterate was distilled and the residue was crystallized from ethyl acetate. 1,1,2,2-Tetracyanoethane (m.p. 170-5°C) was obtained. TLC and

0013 466 x (35) 40 221-223

TABLE 1

CONDITIONS AND PRODUCTS OF ANODIC OXIDATION OF 0.05 MOLE MALONONITRILE ON PLATINIUM ANODE AT +1.9 V VS SCE AT 20 C

Solvent	Electrolyte	Current (A)	Time (hrs)	Charge F	Conversion (%)	Products	(% Yield)		
CH_3CN	$Ba(ClO_4)_2$	0.035	96	0.125	59	$[CH(CN)_2]_2$	(80),	$[-C(CN)_2-]_n$	(15)
Methanol	"	"	"	"	41	"	(50),	"	(25)
D.M.F.	"	"	"	"	48	"	(70),	"	(18)
Methanol	Na	0.10	24	0.089	68	"	(90),	"	(6)
CH ON	KI	0.15	24	0.134	72	"	(80),	"	(17)
Methanol[a]	$Ba(ClO_4)_2$	1.2	36	1.611	78	"	(90),	"	(8)

(a) This experiment was carried out in undevided cell.

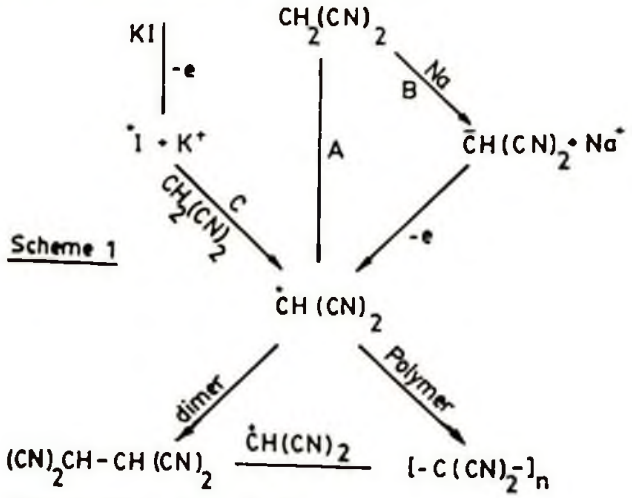
IR analyses were also made for identification of 1,1,2,2-tetracyanoethane and compared with those of authentic sample.

RESULTS AND DISCUSSION

The results of electro synthesis experiment are shown in Table 1.

Anodic Reaction Mechanisms In Devided Cell

Formation of 1,1,2,2-tetracyanoethane and polymerized material can be interpretted in terms of formation of free radical intermediates which are formed via the abstraction of one hydrgen from the malononitrile (exps. 1-3, Scheme 1 A) or one electron from its carbanion (exp.4, Scheme 1 B) by the platinum anode directly. The free radical intermediates are dimerized and polymerized to give the corresponding dimers and polymers respectively. This can be visualized as in Scheme 1.



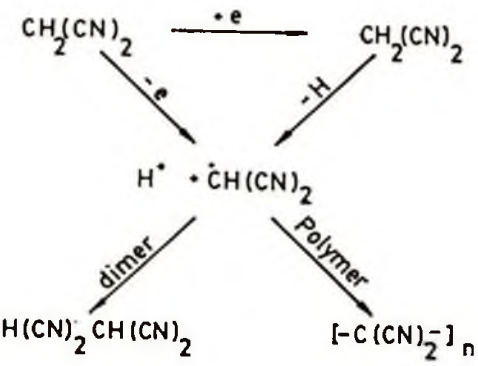
Scheme 1

In experiment 5, iodide ion is discharged directly on the platinum anode to form the iodine radicals , which attack the malononitrile to give the malononitrile radicals which in turn are dimerized or polymerized (Scheme I-C)

In Undivided Cell

The malononitrile radicals can be formed via direct oxidation of malononitrile or its anions (Scheme 1), or by the anodic oxidation of the anion radicals $\dot{C}H(CN)_2^-$ which may be formed by the cathodic reduction of malononitrile compound on the platinum cathode. However the concentration of the malonitrile radicals was increased and consequently the yield of the products is increased. These mechanisms can be seen in Scheme 2.

Scheme 2.



It is clear from Table 1 that the electrolysis of methanolic solution of sodium malononitrile gave the highest yield of the corresponding dimer (exp. 6, 90%). Therefore, this method could be used successfully for the synthesis of 1,2,2,2-tetracyanoethane and its derivatives

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