CHEMISTRY LETTERS, pp. 793-796, 1977. Published by the Chemical Society of Japan

OXIDATION OF NITROALKYLBENZENE WITH ELECTRO-GENERATED SUPEROXIDE ION

Hiromitsu SAGAE*, Masamichi FUJIHIRA*, Tetsuo OSA*, and Henning LUND**
* Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
**Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

THe oxidation of nitroalkylbenzene with electro-generated superoxide ion was studied by cyclic voltammetry and controlled potential macro-electrolysis. The electrochemical reduction of oxygen in the presence of nitrotoluenes (o- and p-) and p-nitroethylbenzene yielded under mild conditions the corresponding nitrobenzoic acids from the former and p-nitroacetophenone plus 1-(p-nitrophenyl)ethanol from the latter.

Recently the reactivity of superoxide ion has attracted a great deal of attention to investigators of organic and biological chemistry.[1,2] Superoxide ion is usually available from the alkali metal salts, such as potassium and sodium superoxides or from the electrochemical reduction of oxygen dissolved in non-aqueous solvents. However, the use of alkali metal superoxides in organic reactions is not practical owing to the low solubility of these salts in many organic solutions. The electrochemical method is experimentally more convenient because continuous generation of superoxide ion is possible in the vicinity of electrode and the solubility of the salts with tetraalkyl-ammonium cations of supporting electrolyte is sufficiently high.

There have been many reports[3-6] on the oxidation of nitrotoluenes to nitrobenzoic acids. However, the oxidation with the electro-generated superoxide ion has not been published. We wish to report here the electrochemical reduction of oxygen dissolved in dimethylformamide (DMF) in the presence of nitrotoluenes or p-nitroethylbenzene. The oxidation with the superoxide ion can be characterized by two advantages, that is, the oxidation proceeds under mild conditions compared with other catalytic oxidations and does not require any oxidizing chemicals. The elucidation of oxidation mechanism of nitrotoluenes with the electro-generated superoxide ion will be also usefull in understanding the metabolism of these compounds in some insects.[7]

EXPERIMENTAL

Cyclic voltammetry. Cyclic voltammetry was carried out in DMF solution containing tetraethylammonium perchlorate (TEAP) as a supporting electrolyte on a hanging mercury drop electrode (HMDE) of 0.046 cm^2. Potentials are referred to a silver-silver chloride electrode (Ag/AgCl-1 N KCl).

Controlled potential macro-electrolysis. For controlled potential macro-electrolysis, an H-type cell was employed in which cathodic and anodic chambers were separated by two porous glass disks and a reference electrode with a Luggin capillary was put near the cathode. A mercury pool of 16 cm^2 was used as a cathode. The electrolytic solution

of 60 ml containing 0.1 M TEAP was placed in the cathodic chamber and 40 ml of the electrolytic solution in the anodic chamber, and oxygen was bubbled through the catholyte. The cathode potential was controlled with a Yanagimoto Type VE-8 controlled potential electrolizer. The catholyte was first poured into 10% aqueous $NaHCO_3$ solution and the starting material in this solution was removed by the extraction with CH_2Cl_2. Since p-nitrobenzoic acid was not obtained as a precipitate by the acidification of the aqueous layer due to the presence of DMF in water, the aqueous layer was evaporated to dryness in vacuo to remove DMF. Then the resulting solid was dissolved in water and acidified with 5% aqueous HCl to give nitrobenzoic acid as a precipitate.

Materials. DMF was dried over anhydrous $CuSO_4$ for 24 hr, then distilled under reduced pressure and further purified through a column of activated alumina. TEAP was synthesized and purified by the ordinary method.[8)]

RESULTS AND DISCUSSION

Some results of the macro-electrolysis of nitrotoluenes are collected in Table 1. The reduction potentials of the predicted reaction intermediates of the oxidation together with nitrotoluenes, nitroethylbenzene and oxygen are shown in Table 2. The controlled potential macro-electrolysis of oxygen in the presence of 1 g of p-nitrotoluene was carried out at -0.9 V for 12 hr. About 600 mg of p-nitrobenzoic acid was obtained and no other products were detected.

Table 1. Controlled potential macro-electrolysis of nitrotoluenes[a)]

starting materials	produced amount of nitrobenzoic acids (g)	yield(%)	selectivity(%)	current[b)] efficiency (%)
o-nitrotoluene	0.52	50	96	59.7
m-nitrotoluene	undetected	—	—	——
p-nitrotoluene	0.60	57	95	51.4

a) Amount of starting material is 1 g; potential of controlled electrolysis is -0.9 V (V vs. Ag/AgCl-1 N KCl). b) This current efficiency is calculated as the electrons of 4 Faradays are necessary to obtain 1 mole of the corresponding acid.

Table 2. Reduction potentials of nitrobenzene derivatives (V vs. Ag/AgCl-1 N KCl)

compounds	E_p^1	E_p^2
o-nitrotoluene	-1.23	-1.92
m-nitrotoluene	-1.14	-1.75
p-nitrotoluene	-1.10	-1.85
p-nitroethylbenzene	-1.13	-1.83
oxygen	-0.85	
c.f.		
p-nitrobenzaldehyde	-0.82	-1.35
p-nitroacetophenone	-0.78	-1.37

electrolyte: DMF/0.1 M TEAP; electrode: HMDE

Cyclic voltammetry of p-nitrobenzaldehyde, which was expected to be an intermediate of this oxidation, was carried out in order to investigate the reaction mechanism (Fig. 1). Two pairs of reversible waves were observed under nitrogen atmosphere with reduction peaks at -0.82 and -1.35 V. In the presence of oxygen a new reduction wave which corresponded to the reduction wave of p-nitrobenzoic acid appeared at -1.1 V. The controlled potential macro-electrolysis of oxygen in the presence of p-nitrobenzaldehyde at -0.9 V yielded only p-nitrobenzoic acid. p-Nitrobenzaldehyde was not isolated when p-nitrotoluene was used as a starting material, because it reacts with electro-generated superoxide ion immediately or is reduced at the electrode directly owing to its lower reduction potential (-0.82 V) than the controlled one. The increasing concentration of p-nitrotoluene did not cause any increase of the reduction peak height of oxygen at -0.85 V in the cyclic voltammograms. Therefore the result shows that the electron transfer reaction[9] from the electro-generated superoxide ion to p-nitrotoluene does not occur or is slow.

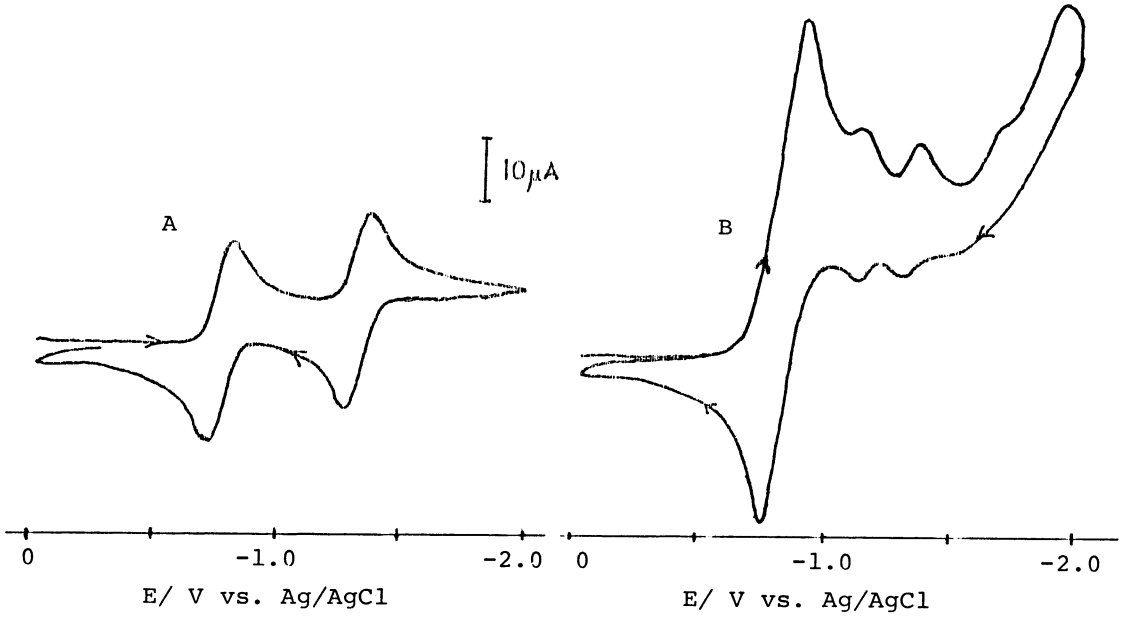

Fig. 1. Cyclic voltammograms of p-nitrobenzaldehyde.
electrolyte: DMF/0.1 M TEAP; electrode: HMDE; sweep rate: 0.1 Vs^{-1}
A: under nitrogen atmosphere; B: under oxygen atmosphere.

A controlled potential macro-electrolysis of oxygen in the presence of o- or m-nitrotoluene was carried out (Table 1). From o-nitrotoluene only o-nitrobenzoic acid was obtained as the final product but from m-nitrotoluene the corresponding m-nitrobenzoic acid was not obtained. These results indicate that the superoxide ion reacted only with a methyl group activated by the nitro group attached to benzene nucleus.

Electrochemical reduction of oxygen in the presence of p-nitroethylbenzene in DMF at -0.9 V yielded p-nitroacetophenone, 1-(p-nitrophenyl)ethanol and an unidentified product. The cyclic voltammograms of oxygen dissolved in DMF with p-nitroethylbenzene (Fig. 2) are remarkble. An increasing concentration of p-nitroethylbenzene did not result in a corresponding increase in the reduction peak height of oxygen, but in a diminution of the re-oxidation peak height of the superoxide ion. In the second sweep the peak heights of both the reduction and re-oxidation were remarkably diminished. These results show that the electro-generated superoxide ion reacts easily with

p-nitroethylbenzene and that the resulting species from p-nitroethylbenzene reacts with oxygen in the vicinity of the electrode to yield p-nitroacetophenone etc.

The reaction scheme for the oxidations of p-,o-nitrotoluene and p-nitroethylbenzene can be suggested as follows: one of hydrogen atoms of the methyl group or α-carbon of the ethyl group activated by the nitro group is abstracted by the electro-generated superoxide ion in DMF under mild conditions, and the resulting species reacts with superoxide ion and/or oxygen to the carboxylic acid or ketone through the aldehyde or alcohol group, respectively.

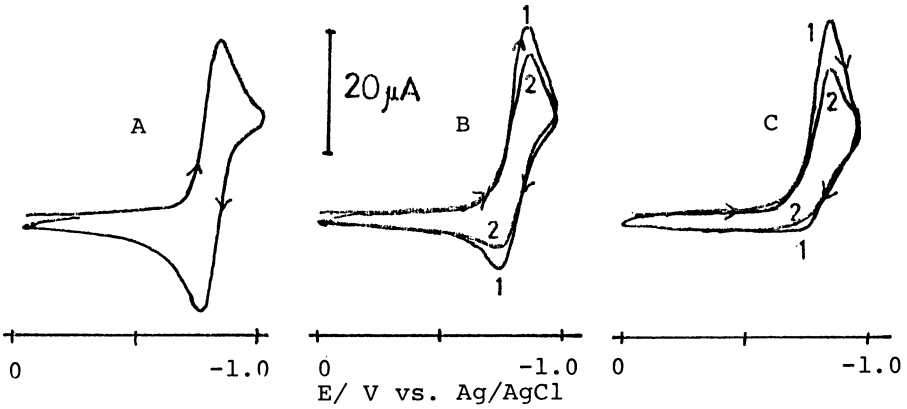

Fig. 2. Cyclic voltammograms of oxygen in the presence of different concentration of p-nitroethylbenzene.
electrolyte: DMF/0.1 M TEAP; electrode: HMDE; sweep rate: 0.1 Vs^{-1}; concentration of p-nitroethylbenzene: A: 0 ; B: 7.9 mM; C: 19.7 mM. 1: the first sweep; 2: the second sweep.

REFERENCES

1) R.Dietz, M.E.Peover, and P.Rothbaum, Chem. Ing. Techn., 42, 185 (1970).

2) T.Osa and M.Tezuka, Denki Kagaku, 44, 2 (1976).

3) G.A.Russell, A.J.Moye, E.G.Janzen, S.Mak, and E.R.Talaty, J. Org. Chem., 32, 137 (1976); T.A.Cooper and W.A.Waters, J. Chem. Soc. (B), 1967, 687; R.S.Barker and A.Saffer, U. S. Patent 3,030,414 (1962); K.A.Chervinskii, Khim Tekhnol., 1968, 60.

4) W.S.Trahanovsky and L.B.Young, J. Org. Chem., 31, 2033 (1966); B.Srinivasan and S.B.Chanadalia, Indian J. Technol., 1971, 274; L.A.Bigelow, J. Am. Chem. Soc., 41, 1559 (1919).

5) R.F.Dunbrook and A.Lowy, Trans. Am. Electrochem. 45, (pre-print) (1924): Chem. Abstr., 18, 1088 (1924); V.S.Kolevatova and S.A.Kolsova, Sb. Nauchn. Tr. Permsk. Politekhn. Inst., 1963, 54: Chem. Abstr., 62, 8670h (1965).

6) T.J.Wallace, J.E.Hofmann, and H.Pobiner, Nature, 204, 376 (1964).

7) J.Chakraborty and J.N.Smith, Biochem. J., 93, 389 (1964).

8) T.Fujinaga, K.Izutsu, and K.Takaoka, J.Electroanal. Chem., 12, 203 (1966).

9) H.Lund, M.-A.Michel, and J.Simonet, Acta Chem. Scand. B, 28, 900 (1974); H.Lund M.-A.Michel, and J.Simonet, ibid., 29, 217 (1975); J.Simonet, M.-A.Michel, and H.Lund, ibid., 29, 489 (1975).

(Received March 22, 1977)