June, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 1537—1541 (1980) 1537

Oxidation of Nitrotoluenes with Electro-generated Superoxide Ion

Hiromitsu SAGAE, Masamichi FUJIHIRA, Henning LUND,† and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

(Received December 20, 1979)

The oxidation of *o*-, *m*-, and *p*-nitrotoluenes with electro-generated superoxide ion in dimethylformamide was studied using cyclic voltammetry and controlled potential macro-electrolysis. The electrochemical reduction of oxygen in the presence of *o*- and *p*-nitrotoluenes yielded the corresponding carboxylic acids because the methyl groups in these derivatives are activated by the nitro group. An intermediate in these oxidations should be the corresponding nitrobenzaldehyde. The reaction mechanism is discussed.

Recently superoxide ion, $O^{\overline{\cdot}}$, has attracted a great deal of attention of organic and biological chemists, because it is novel activating reagent for organic synthesis and is one of the most important activated forms of molecular oxygen in biological systems.[1–3] Superoxide ion is produced by the electrochemical reduction of oxygen dissolved in non-aqueous solvents, such as pyridine, acetonitrile, and dimethylformamide (DMF) at -0.85 V *vs.* silver-silver chloride (Ag/AgCl)[2,3] as shown in Eq. 1:

$$O_2 + e \rightleftarrows O_2^{\overline{\cdot}}. \qquad (1)$$

Alkali metal superoxides, such as potassium and sodium superoxides, are well known but their insolubility in the usual organic solvents makes them of little preparative use.[4] The electrochemical method is experimentally more convenient because the continuous generation of superoxide ion is possible on the electrode and the solubility of the superoxide ion in the presence of tetraethylammonium cations of the supporting electrolyte is sufficiently high.[5]

We have previously reported preliminary results on the reaction of nitrotoluenes and nitroethylbenzene with electro-generated superoxide ion.[6] In this paper, we describe in detail the reaction of nitrotoluenes with electro-generated superoxide ion in DMF solution, using macro-electrolysis and cyclic voltammetry.

There are many reports[7–10] on the oxidation of nitrotoluenes to nitrobenzoic acids using various oxidizing reagents and conditions, such as cobaltic salts,[7a] nitric acid,[8a] and basic condition.[7b] However, the oxidation with superoxide ion has not previously been reported. Advantageous characteristics of oxidation by electro-generated superoxide ion are two-fold; the oxidation proceeds under mild conditions and does not require any oxidizing chemicals. Elucidation of the reaction mechanism of the oxidation of nitrotoluenes with electro-generated superoxide ion should also prove to be useful in understanding the metabolism of such compounds in certain insects.[11]

Experimental

Materials. DMF was dried over anhydrous $CuSO_4$ for 24 h and then distilled under reduced pressure. Further purification was achieved by passage through a column of molecular sieves (4A 1/16) and activated alumina (both pre-treated by heating at 400 °C). Tetraethylammonium perchlorate (TEAP) was synthesized and purified in the usual manner.[12] Nitrotoluene, *p*-nitrobenzaldehyde, and nitrobenzoic acids of E. P. grade were purchased commercially (Wako Pure Chemical Industries) and were recrystallized before use.

Cyclic Voltammetry. Cyclic voltammetry was carried out in DMF solution containing 0.1 M (1 M = 1 mol dm^{-3}) TEAP as a supporting electrolyte on a hanging mercury drop electrode (HMDE). The cathode potentials were referred to Ag/AgCl, aq 1 M KCl. Cyclic potential sweeps were generated by an NF Circuit Design Block FG-100AD function generator in conjunction with a potentiostat which was self-made according to the literature.[13]

Controlled Potential Macro-electrolysis. For controlled potential macro-electrolysis, a three compartment 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 with a surface area of 16 cm^2 was used as the cathode, and platinum gauze as the anode. The electrolyte solution (0.1 M TEAP) of 60 cm^3 containing 0.06 M substrate was placed in the cathodic chamber, 40 cm^3 of the electrolyte solution in the anodic chamber, and 10 cm^3 of the electrolyte solution in the middle chamber. Oxygen was bubbled through the cathode. The cathode potential was controlled with a Yanagimoto VE-8 controlled potential electrolyzer. The quantity of electricity passed was measured with a copper coulometer.

Separation of Nitrobenzoic Acid. The main products of the electrolyses, nitrobenzoic acids, were separated and identified by the following procedure. The catholyte was poured into 200 cm^3 of 10% aqueous $NaHCO_3$ solution. The starting material and products other than nitrobenzoic acids in this solution were removed by extraction with CH_2Cl_2. Since nitrobenzoic acids could not be precipitated by acidification of the aqueous layer due to the presence of DMF in the water, the aqueous layer was evaporated to dryness *in vacuo* to remove the DMF. The resulting solid was dissolved in water and acidified with 5% aqueous HCl to precipitate the nitrobenzoic acids. The products were purified by recrystallization from alcohol and identified as the expected carboxylic acids by comparing their melting points and infrared spectra (IR) with those of authentic samples. As described later, the peak potentials of the cyclic voltammograms of these products were also found to agree with those of the authentic carboxylic acids.

p-Nitrobenzoic Acid from p-Nitrotoluene. The macro-electrolysis of oxygen in the presence of 0.5 g of *p*-nitrotoluene was carried out at -0.9 V *vs.* Ag/AgCl. The electrolysis time was *ca.* 24 h and the total amount of charge passed was *ca.* 2000 C. About 0.22 g of *p*-nitrobenzoic acid was obtained using the method mentioned above, and about 0.11 g of *p*-nitrotoluene was recovered. The IR spectrum of the product

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[†] On leave from Department of Organic Chemistry, University of Aarhus, DK-8000, Aarhus C, Denmark.

agreed with that of authentic *p*-nitrobenzoic acid. Mp 241—242 °C (lit, 242 °C)[14]

o-*Nitrobenzoic Acid from* o-*Nitrotoluene.* The macro-electrolysis of oxygen in the presence of 0.5 g of *o*-nitrotoluene was carried out at −0.9 V *vs.* Ag/AgCl. The electrolysis time was *ca.* 24 h and the total amount of charge passed was *ca.* 2050 C. About 0.21 g of *o*-nitrobenzoic acid was obtained using the method mentioned above, and about 0.12 g of *o*-nitrotoluene was recovered. The IR spectrum of the product agreed with that of authentic *o*-nitrobenzoic acid. Mp 146—147 °C (lit, 147—148 °C)[14]

p-*Nitrobenzoic Acid from* p-*Nitrobenzaldehyde.* The macro-electrolysis of oxygen in the presence of 0.5 g of *p*-nitrobenzaldehyde was carried out at −0.9 V *vs.* Ag/AgCl. The electrolysis time was *ca.* 24 h and the total amount of charge passed was *ca.* 1100 C. About 0.35 g of *p*-nitrobenzoic acid was obtained using the method mentioned above, and 0.08 g of *p*-nitrobenzaldehyde was recovered. The IR spectrum of the product agreed with that of authentic *p*-nitrobenzoic acid. Mp 241—242 °C (lit, 242 °C)[14]

m-*Nitrobenzoic Acid.* *m*-Nitrobenzoic acid was not obtained from the electrolysis of oxygen in the presence of *m*-nitrotoluene at −0.9 V *vs.* Ag/AgCl.

Results and Discussion

Controlled Potential Macro-electrolysis. The reduction peak potentials of nitrotoluenes, together with those for oxygen, nitrobenzoic acids, and *p*-nitrobenzaldehyde, in cyclic voltammetry are listed in Table 1.

Table 1. Reduction peak potentials of nitrotoluenes, *p*-nitrobenzaldehyde, and nitrobenzoic acids

Compound	E_p^1	E_p^2	E_p^3
o-Nitrotoluene	−1.23	−1.92	
m-Nitrotoluene	−1.14	−1.75	
p-Nitrotoluene	−1.10	−1.85	
p-Nitrobenzaldehyde	−0.82	−1.35	
o-Nitrobenzoic acid	−0.90	−1.20	−1.73
m-Nitrobenzoic acid	−0.92	−1.23	−1.75
p-Nitrobenzoic acid	−0.80	−1.16	−1.70
Cf. oxygen	−0.85	−1.75	

E/V *vs.* Ag/AgCl, solvent: DMF, supporting electrolyte: TEAP, electrode: HMDE.

The controlled potential macro-electrolyses of oxygen in the presence of nitrotoluenes were carried out at −0.9 V *vs.* Ag/AgCl in DMF solution. At −0.9 V *vs.* Ag/AgCl, only oxygen was reduced, to the superoxide ion, while nitrotoluenes were not reduced. The results of the electrolyses are collected in Table 2. *p*-Nitrotoluene reacted with electro-generated superoxide ion to yield *p*-nitrobenzoic acid (Eq. 2). Controlled potential macro-electrolysis of oxygen in the presence of *p*-nitrobenzaldehyde was carried out because *p*-nitrobenzaldehyde is predicted to be an intermediate in the oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid. As expected, the reaction of *p*-nitrobenzaldehyde with superoxide ion yielded *p*-nitrobenzoic acid fairly readily (Eq. 5), although *p*-nitrobenzaldehyde was not isolated when *p*-nitrotoluene was oxidized. These results indicated that the produced *p*-nitrobenzaldehyde reacts with electro-generated superoxide ion immediately, or is reduced at the electrode directly, owing to a more positive reduction potential (−0.82 V *vs.* Ag/AgCl) than that used for the controlled potential electrolysis. *o*-Nitrobenzaldehyde is also considered to be a most probable intermediate in the reaction of *o*-nitrotoluene with superoxide ion.

In order to investigate the positional effect of the nitro group attached to the benzene ring, macro-electrolyses of oxygen in the presence of *o*- and *m*-nitrotoluene were carried out. *o*-Nitrobenzoic acid was obtained from *o*-nitrotoluene, while *m*-nitrobenzoic acid was not obtained from *m*-nitrotoluene (Eqs. 3 and 4). This result indicates that the electro-generated superoxide ion reacts only with a methyl group which is activated by the nitro group attached to the benzene ring, to yield the corresponding carboxylic acid.

Cyclic Voltammetry of Nitrotoluenes. Cyclic voltammetry of nitrotoluenes, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acids in the presence and in the absence of oxygen was carried out in order to investigate the reaction mechanism. Cyclic voltammograms of *p*-nitrotoluene in the presence and in the absence of oxygen, together with that of oxygen, in DMF solution as shown in Fig. 1. In the cyclic voltammogram of oxygen, the first reversible reduction wave at −0.85 V *vs.* Ag/AgCl corresponded to the one-electron reduction of oxygen to the superoxide ion. The second irreversible reduction wave at −1.75 V *vs.* Ag/AgCl corresponded to the further one-electron reduction of superoxide ion to the peroxide ion, O_2^{2-}, followed by protonation. In the cyclic voltammogram of *p*-nitrotoluene under a nitrogen atmosphere, a reversible reduction wave at −1.1 V *vs.* Ag/AgCl and an irreversible reduction wave at −1.8 V *vs.* Ag/AgCl appeared. In the presence of oxygen, the first wave and the second wave are the corresponding first reduction waves of oxygen and *p*-nitrotoluene respectively. The second wave of oxygen

Table 2. Formation of carboxylic acids from nitrotoluenes

Starting material	Amount of nitrobenzoic acid produced/g	Yield/%	Selectivity/%	Current[a] efficiency/%
o-Nitrotoluene	0.21	45 (45—50)[b]	42 (42—96)[b]	52 (40—62)[b]
m-Nitrotoluene	undetected	—	—	—
p-Nitrotoluene	0.22	56 (50—60)	44 (44—95)	55 (45—65)
Cf. *p*-nitrobenzaldehyde	0.35	68 (55—70)	70 (70—90)	49 (49—65)

a) The current efficiency calculated as the electrons of 4 Faradays are necessary to obtain 1 mol of the corresponding acid from nitrotoluene, and 2 Faradays from nitrobenzaldehyde. b) The electrolysis was carried out several times and the range of the values are shown in parentheses.

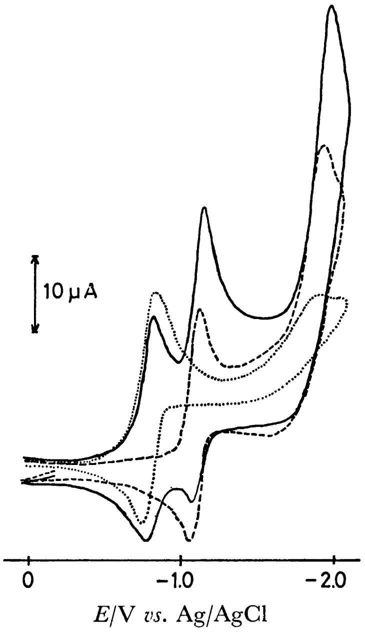


Fig. 1. Cyclic voltammograms of *p*-nitrotoluene. Concentration of *p*-nitrotoluene: *ca.* 10mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ------: in the absence of oxygen, ——: in the presence of oxygen. *Cf.* ······: cyclic voltammogram of oxygen.

overlapped with the second wave of *p*-nitrotoluene at -1.8 V *vs.* Ag/AgCl. In this case no other reduction wave appeared except those for oxygen and *p*-nitrotoluene. Cyclic voltammetry of *o*- and *m*-nitrotoluenes in the presence and in the absence of oxygen gave similar results to those for *p*-nitrotoluene.

Cyclic Voltammetry of Nitrobenzoic Acids. The cyclic voltammogram of *p*-nitrobenzoic acid in DMF solution under a nitrogen atmosphere is shown in Fig. 2. The first and third reduction waves, whose reduction peak potentials are -0.8 V and -1.7 V *vs.* Ag/AgCl respectively, are irreversible. The second reduction wave is reversible with a reduction peak potential of -1.1 V *vs.* Ag/AgCl. Anomaly in shape of the corresponding reoxidation wave at *ca.* -1.1 V of the second reduction wave can be interpreted by the streaming phenonmenon, observed initially by Santhanam and Bard,[15] which occurs during oxidation of radical anion in cyclic voltammetric experiments. The cyclic voltammograms of *o*- and *m*-nitrobenzoic acids under a nitrogen atmosphere are similar to that of *p*-nitrobenzoic acid, and their reduction peak potentials are collected in Table 1.

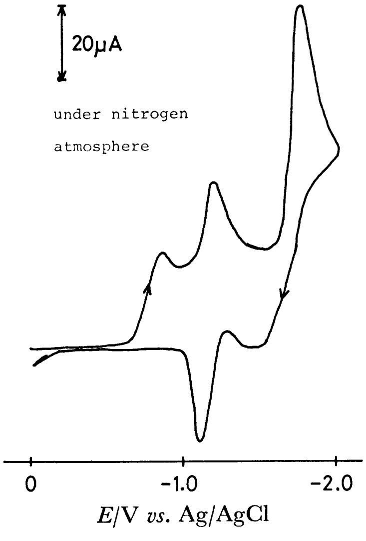


Fig. 2. Cyclic voltammogram of *p*-nitrobenzoic acid. Concentration of *p*-nitrobenzoic acid: *ca.* 10 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}.

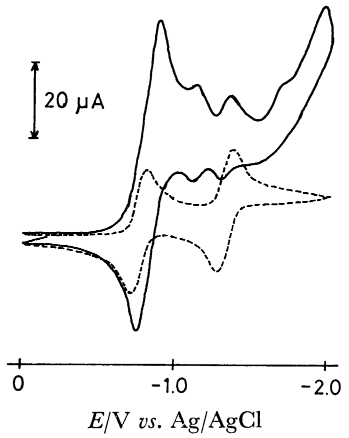


Fig. 3. Cyclic voltammograms of *p*-nitrobenzaldehyde. Concentration of *p*-nitrobenzaldehyde: *ca.* 10 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ------: in the absence of oxygen, ——: in the presence of oxygen.

Cyclic Voltammetry of p-*Nitrobenzaldehyde.* Cyclic voltammetry of *p*-nitrobenzaldehyde, expected to be an intermediate in the oxidation of *p*-nitrotoluene, in the presence and in the absence of oxygen was carried out. The results are shown in Fig. 3. Two reversible reduction waves are observed under a nitrogen atmosphere with reduction peaks at -0.82 V and -1.35 V *vs.* Ag/AgCl. In the presence of oxygen a reversible reduction wave at -1.1 V and an irreversible reduction wave at -1.65 V *vs.* Ag/AgCl appeared as well as those for oxygen and *p*-nitrobenzaldehyde. These new reduction peak potentials corresponded to those of the second and third waves of *p*-nitrobenzoic acid. The first reduction wave of *p*-nitrobenzoic acid overlapped with the first wave of *p*-nitrobenzaldehyde and oxygen. This result indicates that *p*-nitrobenzoic acid was formed during cyclic voltammetry of *p*-nitrobenzaldehyde.

Cyclic Voltammetry of the Catholyte. In the course of macro-electrolysis of oxygen in the presence of *p*-nitrotoluene, cyclic voltammetry of the catholyte was carried out. The result is shown in Fig. 4. Since the *p*-nitrotoluene remained as a major substrate in the solution, two large reduction waves observed at -1.1 V and -1.9 V *vs.* Ag/AgCl should be due to *p*-nitrotoluene. The reduction waves at *ca.* -0.8 V and *ca.* -1.6 V *vs.* Ag/AgCl corresponded to the first and third

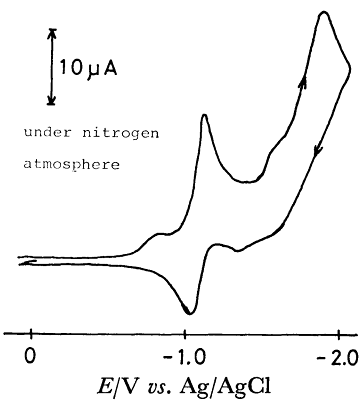
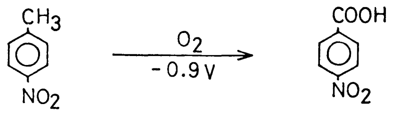


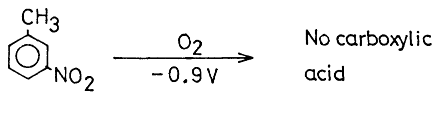
Fig. 4. Cyclic voltammogram of the catholyte in the course of the electrolysis in the presence of *p*-nitrotoluene. Electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}.

reduction waves of *p*-nitrobenzoic acid. The second reduction wave of *p*-nitrobenzoic acid overlapped with the first reduction wave of *p*-nitrotoluene. In the cyclic voltammogram of *p*-nitrotoluene in the presence of oxygen (solid line in Fig. 1), no reduction wave appeared other than those for oxygen and *p*-nitrotoluene. These results indicate that *p*-nitrobenzoic acid was not formed during cyclic voltammetry, and consequently the reaction rate of the superoxide ion with *p*-nitrotoluene is deduced to be slow. Since the reduction wave corresponding to *p*-nitrobenzaldehyde did not appear in the course of macro-electrolysis in the presence of *p*-nitrotoluene as shown in Fig. 4, it is assumed that the produced *p*-nitrobenzaldehyde reacted instantaneously with electro-generated superoxide ion to yield *p*-nitrobenzoic acid. In the cyclic voltammogram of *p*-nitrobenzaldehyde in the presence of oxygen (solid line in Fig. 2), two reduction waves corresponding to those of *p*-nitrobenzoic acid appeared. The reaction rate of superoxide ion with *p*-nitrobenzaldehyde is therefore faster than that of superoxide ion with *p*-nitrotoluene.

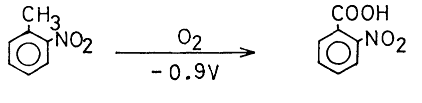
$$O_2 + e \rightleftarrows O_2^{\cdot -} \qquad (1)$$



(2)



(3)



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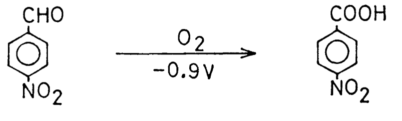


(5)

E/V *vs*. Ag/AgCl

$$RCH_3 + O_2^{\cdot -} \longrightarrow RCH_2\cdot + HO_2^- \qquad (6)$$

$$RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot \qquad (7)$$

$$RCH_2OO\cdot + O_2^{\cdot -} \text{ (or e from electrode)} \longrightarrow RCH_2OO^- + O_2 \qquad (8)$$

$$RCH_2OO^- \longrightarrow RCHO + OH^- \qquad (9)$$

$$RCHO + O_2^{\cdot -} \text{ (or e from electrode)} \longrightarrow [RCHO]^{\cdot -} + O_2 \qquad (10)$$

$$[RCHO]^{\cdot -} + O_2 \longrightarrow [RCOOOH]^{\cdot -} \qquad (11)$$

$$RCHO + O_2^{\cdot -} \longrightarrow [RCOOOH]^{\cdot -} \qquad (12)$$

$$RCHO + O_2^{\cdot -} \longrightarrow RCO\cdot + HO_2^{\cdot -} \qquad (13)$$

$$RCO\cdot + HO_2^- \longrightarrow [RCOOOH]^{\cdot -} \qquad (14)$$

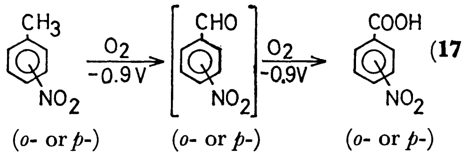
$$[RCOOOH]^{\cdot -} \longrightarrow RCOO\cdot + OH^- \qquad (15)$$

$$RCOO\cdot + O_2^{\cdot -} \text{ (or e from electrode)} \longrightarrow RCOO^- + O_2 \qquad (16)$$

Scheme 1.

Reaction Scheme for the Oxidation. A reaction scheme for the oxidation of *p*- and *o*-nitrotoluenes with electro-generated superoxide ion can be suggested as shown in Scheme 1. One of the hydrogen atoms of the methyl group of the *o*- or *p*-nitrotoluene is abstracted by the electro-generated superoxide ion in DMF solution (Eq. 6). The resulting species reacts with oxygen (Eq. 7) and is further reduced to the peroxy anion by superoxide ion or by an electron from the electrode (Eq. 8). In a basic solvent such as DMF, release of hydroxy anion from this peroxy ion, which yields aldehyde (Eq. 9), occurs predominantly, rather than proton abstraction from the environment by the peroxy anion.[16] This hydrogen abstraction reaction by superoxide ion is similar to the reaction of the superoxide ion with 9,10-dihydroanthracene to yield anthraquinone.[17] The produced nitrobenzaldehyde can be reduced with superoxide ion as well as from the electron uptake at the electrode directly owing to its more positive reduction peak potential (−0.82 V *vs*. Ag/AgCl) (Eq. 10), and the formed anion radical reacts oxygen to produce hydrogen percarboxylic acid anion radical (Eq. 11). As the possible another route, superoxide ion reacts directly carbonyl group to yield addition product,[18] that is, hydrogen percarboxylic acid anion radical (Eq. 12). The nitrobenzaldehyde also reacts with superoxide ion instantly to yield an acyl radical (Eq. 13), which reacts with hydrogen peroxide anion (Eq. 14). The percarboxylic acid anion radical formed by Eqs. 11, 12, and 14 releases hydroxide anion, yielding the carboxyl radical (Eq. 15). This carboxyl radical is finally reduced to carboxyl anion by the superoxide ion or by an electron from the electrode (Eq. 16).

In conclusion, *o*- and *p*-nitrotoluene are considered to react with electro-generated superoxide ion in DMF solution to yield the corresponding nitrobenzoic acid *via* the nitrobenzaldehyde (Eq. 17) as described above.



(17)

(*o*- or *p*-) (*o*- or *p*-) (*o*- or *p*-)

E/V *vs*. Ag/AgCl

We thank the Japan Society for the Promotion of Science for the provision of funds during the period

(Feb.—April 1976) when one of us (H.L.) was a Visiting Professor at Tohoku University. The present work was partially supported by a Grant-in-Aid for Scientific Reseach No. 47017 from the ministry of Education, Science and Culture.

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