Oxidation Reactions of Aromatic Ethenes in Solution
Exposed to Low-Temperature Oxygen Plasma

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1. Introduction

The plasma generated by a radiofrequency (rf) discharge provides a fascinating reaction media for organic as well as inorganic chemistry. Molecules in plasma can easily be activated to high-energy states never attained by conventional methods, and are often ionized through electron collisions, leading to unique transformations. Many intriguing plasma chemical reactions have been reported.[1] However, such plasma-phase reactions have sometimes been complex and comparatively unselective. Recently, some attention has been focused on reactions induced by the plasma-liquid interaction, with the aim of improving selectivity and material balance.[2-3] In this work, the oxidation reaction of 1,2-bispyridylethlenes in dimethyl glutarate solution exposed to radiofrequency oxygen plasma will be examined and an organic preparation method based on a new chemical concept of plasma-liquid interaction will be discussed.

2. Method

Experiments were carried out using a 50 ml conventional four-necked flask connected to a vacuum line via liquid nitrogen traps. After a fixed amount of the dimethyl glutarate solution containing 1,2-bispyridylethylene as a reactant had been put into the reactor, a pressure gauge, a thermometer and a Pyrex discharge tube (45 mm outer diameter and 80 mm length) were mounted on it. Copper coil tubing, connected to a 13.56 MHz rf generator via an antenna tuner and a watt meter, was wound onto the discharge tube. The reactant liquid was kept below 278 K using a methanol bath in order to adequately deplete the vapor pressure even when evacuated. Pure oxygen was introduced into the discharge tube. The flow rate was controlled by a mass flow controller. Inductively coupled oxygen plasma was generated in the discharge tube, transported to the reactor and allowed to flow over the reactant liquid. Reaction parameters were the concentration of reactant (0.02-0.1 mol dm⁻³), solution temperature (T/K, 243-273), plasma exposure time (t_p/min, 0-50), flow rate of oxygen (r_O₂/cm³ min⁻¹ STP, 5.0-20.0), pressure (p/Pa, 40-75) and rf power (P/W, 0-100).

Chemical analysis of the reaction mixture was carried out by gas-liquid chromatography (GC) using Hitachi G-5000 with a flame ionization detector (FID) and GC-mass spectrometry (GC-MS) using JEOL JMS-SX102. GL Sciences TC-FFAP and J&W Scientific DB-1 capillary columns (0.25-mm internal diam., 0.25-μm thickness, and 30-m length) were used. For detail analysis, products were isolated by thin layer chromatography (TLC) and analyzed by nuclear magnetic resonance spectroscopy (NMR) using...
JEOL JNM-ECP500, and infrared spectroscopy (IR) using JEOL JIR-7000.

The following materials were all commercially available as reagent grade chemicals and were used without further purification: solvent, dimethyl glutarate (DBE-5, supplied by Du Pont Japan Co., Ltd., C₇H₁₂O₄, F.W. 160.17, low vapor pressure of ca. 13 Pa at 293 K, low freezing point of 236 K, low viscosity and high solvency in various organic compounds), which was little lost by evaporation though the reaction system was kept under vacuum for reaction period; reactants, trans-1,2- bis(2-pyridyl)ethylene (2-pyE) and trans-1,2-bis(4-pyridyl)ethylene (4-pyE) (both supplied by Aldrich, C₁₂H₁₀N₂, F.W. 182.22); authentic samples, trans-stilbene (Aldrich, C₁₄H₁₂, F.W. 180.25), trans-stilbene oxide (Aldrich, C₁₄H₁₂O, F.W. 196.25) for g.l.c. quantitative analysis of 2-pyE and 4-pyE oxidation products mentioned in detail later, and dimethyl 3-oxoglutarate and its isomer dimethyl 2-oxoglutarate (Aldrich, C₇H₁₀O₅, F.W. 174.15), dimethyl 3-hydroxyglutarate (Aldrich, C₇H₁₀O₅, F.W. 146.14), and mono-methyl glutarate (Aldrich, C₆H₁₀O₄, F.W. 146.14) for solvent oxidation by-product analysis; internal standard for GC quantitative analysis, dibenzyl (Tokyo Kasei Co., Ltd., C₁₄H₁₄, F.W. 182.26).

3. Results and discussion

After reaction, the reaction mixture was immediately analyzed by GC and GC-MS. PEG-20M terminated with 2-nitrotetraphthalic acid (TC-FFAP) and 100% dimethyl polysiloxane (DB-1) were used as stationary phases for GC. Typical gas chromatograms using TC-FFAP are shown in Fig. 1, where peak 1 is the overlap peak of acetone and methanol used for recovery of chemicals from the reactor vessel, peak 3 is DBE-5 used as a solvent, peaks 2 and 4 are dibasic esters contained originally in DBE-5 as impurities, peak 6 is dibenzyl used as a internal standard, peaks 5 and 7 are dimethyl 2-oxo-glutarate and mono-methyl glutarate, respectively, formed from DBE-5 [3], peaks 8 and 9 are reactants: 2-pyE and 4-pyE, respectively, and peaks 9 and 9' are products from 2-pyE and 4-pyE, respectively.

To identify these products, mass spectra were measured by both electron impact method (E.I.) and chemical ionization method using iso-butane (C.I.). We obtained the following results: for peak 9, E.I. mass spectrum: m/e(%) 199(100), 183(100), 169(100), 168(8), 120(5), 78(7), and C.I. mass spectrum:

![Scheme 1](image)

**Scheme I.** Formation mechanism of the m/e 169 fragment ion from bispyridylacetalddehyde or bispyridylethylene oxide molecule bombarded by an energetic electron.

| m/e(%) | M⁺+1 199(100), 183(100); and for peak 9', E.I. mass spectrum: m/e(%), 198(100), 181(7), 169(21), and C.I. mass spectrum: m/e(%) M⁺+1 199(100), 183(90). Particularly, C.I. mass spectra evidently prove that molecular weights of these products are both 198, which suggest that they came from 2-pyE and 4-pyE, respectively, by the addition of an oxygen atom. On the other hand, we found the m/e-169 mass fragment on E.I mass
Table 1. Reactions of pyEs in DBE-5 solution exposed to radio-frequency oxygen plasma.

<table>
<thead>
<tr>
<th>Run</th>
<th>t/ min</th>
<th>Conversion%</th>
<th>Yields of products%</th>
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<td></td>
<td></td>
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<td>2-pyEO</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>1</td>
<td>13.7</td>
<td>7.5</td>
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<tr>
<td>3</td>
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<td>4</td>
<td>3</td>
<td>36.5</td>
<td>18.8</td>
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<td>8</td>
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<td>40.3</td>
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<tr>
<td>9</td>
<td>20</td>
<td>91.0</td>
<td>44.9</td>
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- \$^{a}\$Solution conditions: concentration of reactant 0.04 mol dm$^{-3}$, temperature -20 °C, stirring 120 rpm; plasma conditions: RF power 50 W, O$_2$ flow rate 10 cm$^3$ min$^{-1}$ (SATP). \$^{b}\$Time exposed to plasma. \$^{c}\$Conversion of reactant: 2pyE. \$^{d}\$Yields of products based on initial moles of reactant.

showed that the molecule had five non-equivalent protons: H$_a$ ($\delta$ 4.24), H$_b$ ($\delta$ 8.65), H$_c$ ($\delta$ 7.30), H$_d$ ($\delta$ 7.77) and H$_e$ ($\delta$ 7.41), and their signals except H$_e$ were splitting into two, three, three and two, respectively. The ratios of integrations of signals, H$_a$: H$_b$: H$_c$: H$_d$: H$_e$ = 1 : 2 : 1 : 1 : 2, were well agreed with the theoretical. H$_a$: H$_b$: H$_c$: H$_d$: H$_e$ = 1 : 1 : 1 : 1 : 1, except H$_e$. The integration ratio of H$_e$ deviated largely because of the influence of impure chloroform contained in chloroform-d. Furthermore, the $^{13}$C-NMR spectrum showed the molecule had six non-equivalent carbon atoms: C$_a$ ($\delta$ 62.2), C$_b$ ($\delta$ 151.5), C$_c$ ($\delta$ 124.0), C$_d$ ($\delta$ 137.8), C$_e$ ($\delta$ 121.1) and C$_f$ ($\delta$ 157.7). These data and GC retention time suggest that the product is trans-1,2-bis(2-pyridyl)ethylene oxide (2-pyE). In the same way, the $^1$H-NMR spectrum of the product from 4-pyE revealed that the product molecule had three non-equivalent protons: H$_a$ ($\delta$ 3.81), H$_b$ ($\delta$ 7.23) and H$_i$ ($\delta$ 8.59), and signals except H$_g$ were splitting into two. The ratios of
integrations of signals, $H_0$: $H_1 = 1:2.95:2.11$, were agreed well except $H_0$ to the calculated ratios, $H_0$: $H_1 = 1:2:2$. The deviation in $H_0$ was because of the influence of chloroform containing in chloroform-d as an impurity. The $^{13}$C-NMR spectrum showed the product molecule had four non-equivalent carbon atoms: $C_8$ ($\delta$ 61.5), $C_2$ ($\delta$ 121.1), $C_4$ ($\delta$ 150.9), $C_7$ ($\delta$ 145.8). These data consistently suggest that the product from 4-pyE is trans-1,2-bis(pyridyl)ethylene oxide (4-pyEO).

Products were quantified by GC based on the assumption that the FID sensitivity of pyEO against pyE was equal to that of stilbene oxide against stilbene which was determined by examining their calibration curves using authentic samples. The results of reactions are shown in Table 1 with reaction conditions in the footnote. Generally, pyE was exponentially decreased as the reaction proceeded and pyEO was produced as a primary product presumably by addition of atomic oxygen dissolved in the solution, which is represented by $O_{solv}$ and we call it solvated oxygen atom, to the double bond of pyE molecule. Interestingly, cis-isomers never formed. The yields of pyEO, however, did not reach the stoichiometric values, and the total yield of unknown products increased with increasing rate. These facts suggest that another primary pathway may exist: for example, pyE molecule may suffer attack of $O_{solv}$ at pyridyl group to be changed into the more polar product; and also primarily-produced pyEO may suffer consecutive attack of $O_{solv}$ to be changed into the higher oxidation product.

The relationship between $t_p$ and the natural logarithm of the recovery of a reactant ($A/A_0$) is plotted in Fig. 3, which includes plots of 2-pyE, 4-pyE, and DBE-5 as a solvent. Each of them has a good linear relationship between $t_p$ and $\ln(A/A_0)$, which proves all reactions are first-order. The apparent consumption rate constant ($k_{wp}$) can be estimated at 2.2x$10^3$ s$^{-1}$ for 2-pyE, 3.2x$10^3$ s$^{-1}$ for 4-pyE, and 1.8x$10^4$ s$^{-1}$ for DBE-5. Actually, the decrease in DBE-5 was almost negligible during the plasma exposure time adopted in this study.

Conclusively, the reaction mechanism in our reaction system discussed above is briefly summarized in Scheme II.

References