Spectroelectrochemical Detection of an Intermediate in the Alcohol Oxidation Process with a Nitroxyl Radical

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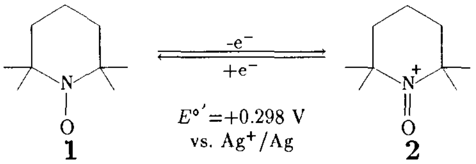
A spectroelectrochemical study revealed the formation of an adduct of nitrosonium ion with 4-methoxybenzyl alcohol as an intermediate in the alcohol oxidation process.

Nitrosonium cations (**2**) formed by one-electron oxidation of nitroxyl radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) (**1**) can oxidize alcohols to their corresponding carbonyl compounds.[1]



Osa and coworkers developed TEMPO modified graphite felt electrodes and showed that nerol and 4-methoxybenzyl alcohol were oxidized to the carbonyl compounds with current efficiencies of more than 90%.[2,3] Though Semmelhack et al.[4] and later de Nooy et al.[5] studied the reaction mechanism, it has not been clarified, yet. Therefore, we have studied the electrode processes of the catalytic oxidation of the alcohol at a glassy carbon disk electrode modified with 4-amino-TEMPO via poly(acrylic acid) layer using cyclic voltammetry and hydrodynamic voltammetry with a rotating disk electrode (RDE). Based on the results of RDE voltammetry, we proposed the reaction mechanism shown in Figure 1, in which an adduct made up of the alcohol and **2** is attacked by a Lewis base to form the second intermediate leading to the products.[6] However, no direct evidence for such an intermediate has been reported.

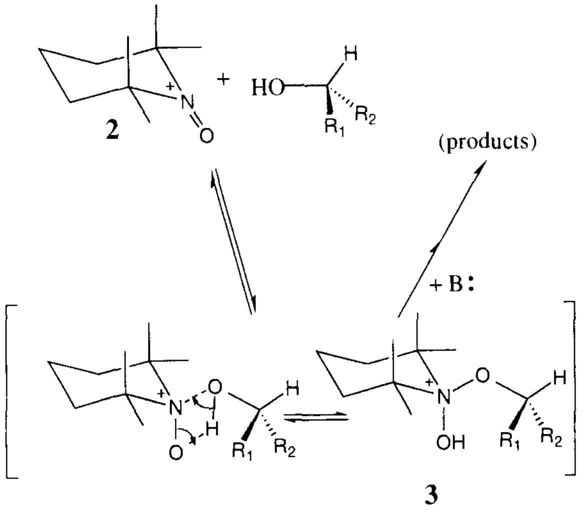


Figure 1. Schematic diagram of the reaction mechanism.

In the present communication, we will report the formation of the adduct (**3** in Figure 1) which has been detected by in situ UV-visible thin-layer spectroelectrochamical measurements.

TEMPO (Aldrich) and 4-methoxybenzyl alcohol (MBA) (Kanto Chemical) as a substrate were used without further purification. Electrolytic solution was prepared with purified acetonitrile (Kanto Chemical) containing 0.2 mol dm^{-3} sodium perchlorate (Kanto Chemical) as a supporting electrolyte. The solution was deaerated with N_2 gas before the measurements. A platinum wire and a silver wire were used as the auxiliary and the quasi-reference electrodes. A home-made optically transparent thin-layer electrode (OTTLE) cell, which was fabricated by sandwiching a piece of gold minigrid (100 mesh) between the wall of a quartz cell and a quartz slide, was used. Spectrolectrochemical measurements were performed using a three-electrode potentiostat (Huso Electrochemical System, HECS 318) and a Hitachi U-3300 spectrophotometer. A series of potentials was applied to the OTTLE, and each spectrum was measured after the equilibrium was attained.

Curve a in Figure 2 is an electronic absorption spectrum in the UV range for 10 mmol dm^{-3} TEMPO measured at 0.0 V and it shows an absorption peak at λ_{max} = 242 nm (ϵ = 1850) ascribed to the $\pi \rightarrow \pi^*$ transition, allowed by symmetry.[7] As the applied potential, E, became more positive than +0.2 V

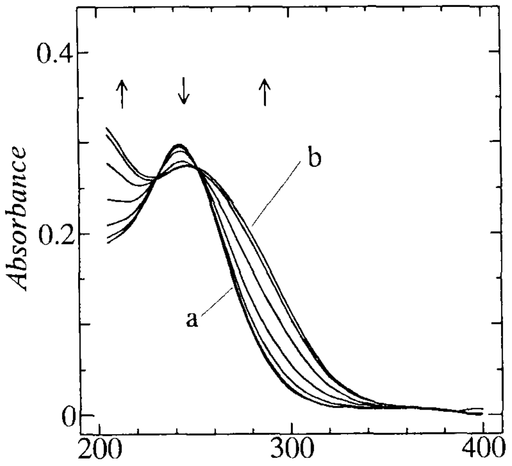


Figure 2. Electronic absorption spectra of 10 mmol dm^{-3} TEMPO in acetonitrile recorded with an OTTLE cell at various potentials (mV *vs.* Ag wire): 0 (curve a), 200, 340, 360, 380, 420, 440, 460 and 500 (curve b). Arrows indicate the direction of more positive potential.

and oxidation proceeded, this band decreased slightly, and a broad shoulder in the more long wavelength region appeared and increased. When E exceeded +0.46 V, the spectrum became unchanged (curve b), indicating that **1** was completely oxidized to **2**, which showed an absorption peak at λ_{max} = 246.5 nm (ϵ = 1720). Isosbestic points occurred at λ = 231 and 253 nm. The thickness of the thin-layer cell was estimated to be 1.62×10^{-2} cm from molar absorptivity at λ_{max} = 242 nm. Then, concentration ratio of **2** to **1** (c_2/c_1) at each potential was evaluated from the absorbance at λ = 265 nm and it was confirmed that the plot of E against $\log(c_2/c_1)$ gave a straight line whose slope was almost 60 mV. This result shows the chemically reversible interconversion between **1** and **2**. Further, no detectable changes in the spectrum recorded at +0.5 V were observed for several hours, indicating that the nitrosonium ion was stable under the experimental conditions employed.

Figure 3 shows the variation of spectra with E for solution of 10 mmol dm^{-3} TEMPO and 0.1 mmol dm^{-3} MBA. Though the spectra were very similar to those in Figure 2, the absorbance intensities were different. As E became more positive, the band at λ_{max} = 242 nm decreased, and a broad shoulder in the longer wavelength region appeared and showed a peak at λ_{max} = 265 nm, when E > +0.46 V (curve d). When the solution fully electrolyzed at +0.5 V was reduced again at 0.0 V, the original spectrum of **1** with MBA was obtained. Further, we confirmed that the spectrum was also reproducible at each potential.

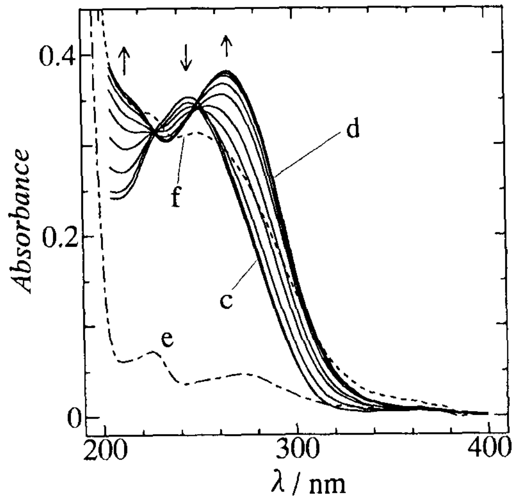


Figure 3. Absorption spectra of 10 mmol dm^{-3} TEMPO and 0.1 mmol dm^{-3} 4-methoxybenzyl alcohol at various potentials: (c) 0 mV, (d) 500 mV. Curve e is a spectrum of 0.1 mmol dm^{-3} 4-methoxybenzyl alcohol. Curve f shows graphical sum of curve e and curve d in Figure 2.

For comparison, the absorption spectrum of 0.1 mmol dm^{-3} MBA is also shown in Figure 3 (curve e), which exhibits two bands at λ_{max} = 226.0 nm (ϵ = 16400) and at λ_{max} = 275.5 nm (ϵ = 2800) ascribed to the $\pi \rightarrow \pi^*$ transition due to aromatic ring. It was found that the graphical sum of curve a and curve e almost agreed with curve c. This indicates that there is no appreciable interaction between **1** and MBA. However, pronounced difference in the spectra can be seen when we compared curve d with curve f, the latter being the graphical sum of curve b and curve e. Appreciable increase in the absorbance around 265 nm indicates formation of a new species, which we consider as the adduct of **2** and MBA (**3** in Figure 1). The disappearance of the isosbestic points in the spectra should result from the presence of equilibrium

$$\mathbf{1} \rightleftharpoons \mathbf{2} + e^-, \qquad \mathbf{2} + \text{MBA} \rightleftharpoons \mathbf{3}$$

Though we tried to determine the formation constant of adduct **3**, we found it difficult because of the high absorbance of MBA. In conclusion, the band at λ_{max} = 265 nm in Figure 3 corroborates the formation process of the adduct in the reaction mechanism we proposed and it would be the first example to demonstrate the formation of the adduct between **2** and alcohol.

References and Notes

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