Photooxidation of Bis[1,2-diphenylethanedithione]nickel(0)-tetrabutylamine with α-Tocopherol

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(Received October 24, 1988)

Synopsis. The photooxidation of a nickel dithiolate complex by α-tocopherol was found for the development of a recording medium which can be used to read by a laser diode. The mechanism was analyzed. As a result, it was found that α-tocopherol produced oxygen adducts by light; the oxygen adducts oxidized bis[1,2-diphenylethanedithione]-nickel(0)tetrabutylamine.

The development of recording medium for a laser diode is desirable since a laser diode is small in size and conventional. Because of the character of high-density recording and rewritability, photon-mode recording was hopeful and the appearence of a recording dye for the laser diode was desired. A Schrauzer complex was one of the dithiolate complexes; it was synthesized in 1962 by Schrauzer and Mayweg.[1] It was reported by them that some complexes have absorption peaks at 700—900 nm,[2] and that the development of a recording medium which can be read by a laser diode is possible if redox reaction can be induced by light. We obtained the reductant (bis[1,2-diphenylethanedithione]nickel(0)tetrabutylamine=BDNH) of bis[1,2-diphenylethanedithione]nickel(0) (BDN) and investigated its properties, finding that BDNH was oxidized by UV light in the presence of α-tocopherol (αT) and produced the BDN. We thus recognized the possibility for developing a photo-recording medium. We now report on our investigation of the effect of various factors on the photooxidation of BDNH to BDN as well as the mechanism.

Experimental

BDNH was purchased from Midori Chem. Co. and used without purification. α-Tocopherol was purchased from Nakarai Chem. Co., and toluene was purchased from Wako Chem. Co.

The monochromatic light was irradiated by a Ushio-500 type super-high-pressure mercury lamp equipped with a Toshiba KL-28 filter. The light intensity was measured by a method described in the literature.[3] The optical absorption spectra were measured by a Shimadzu MPS-5000.

A Hückel molecular orbital calculation was carried out with Otsuka's program[4] by using a Multi 16 computer.

Results and Discussion

BDNH (5.13×10^{-5} mol dm^{-3}) was dissolved into toluene and α-tocopherol (0.100 mol dm^{-3}) was added. The irradiation of this solution made the peak at 975 nm disappear and new peak appeared at 875 nm (Fig.1). Also, the color changed from brown to green. It was found that BDN was produced. These phenomena were considered by the following mechanism. The oxygen adduct of α-tocopherol was produced by the irradiation of α-tocopherol under aerobic conditions; this adduct substructs a $(C_4H_9)_4N^+$ group from

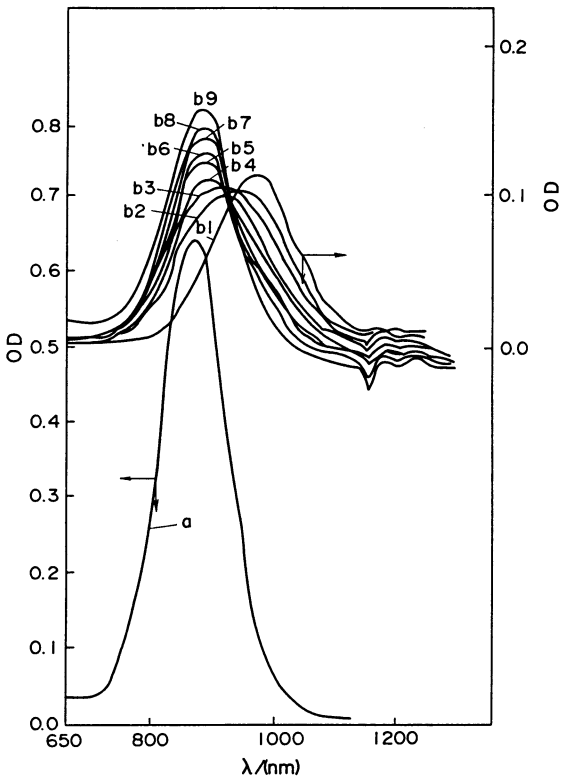


Fig. 1. Change in absorption spectra of BDNH containing α-tocopherol during photo-illumination.
a: BDN, b1: after 0 minutes, b2: 1 min, b3: 2 min, b4 4 min, b5: 9 min, b6: 14 min, b7: 24 min, b8: 34 min, b9: 79 min.
[BDNH]=5.13×10^{-5} mol dm^{-3}, [αT]=0.1 mol dm^{-3}, I=3.24 mol dm^{-3} s^{-1}

BDNH and oxidizes to BDN as the same mechanism as the initiation reaction of the polymerization of methyl methacrylate.[5] The assumed mechanism can be described as in the following equations:

$$\alpha T \xrightarrow{h\nu} \alpha T\cdot, \quad (1)$$

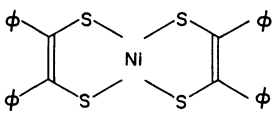
$$\alpha T\cdot + O_2 \xrightarrow{k_i} \alpha TO_2\cdot, \quad (2)$$

$$\alpha TO_2\cdot \xrightarrow{k_q} Q(\alpha T\text{-}O_2\text{-}\alpha T), \quad (3)$$

$$\alpha TO_2\cdot + BDNH \xrightarrow{k_i} \alpha TO_2{=}N(C_4H_9)_4 + BDN \quad (4)$$

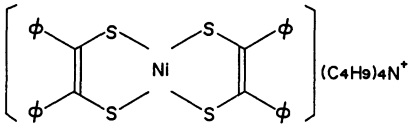
Here, the existence of αT· is assured by the flash-photolysis of an α-tocopherol toluene solution in air.[5] The reaction rate is given by

$$v_i = \frac{k_i C_{BDNH}}{(k_i C_{BDNH}+k_q)} \Phi I[1-10^{-\varepsilon C_{\alpha T} l}]/l, \quad (5)$$



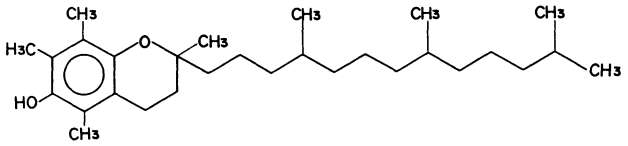
BDN

Scheme 1.



BDNH

Scheme 2.



α-Tocopherol

Scheme 3.

where Φ is the quantum yield for the production of $\alpha T\cdot$, Q is the subproduct, l(cm) is the length of the reaction champer, ε ($1\,mol^{-1}cm^{-1}$) is the molecular extinction constant of α-tocopherol, and I (einstein $cm^{-2}s^{-1}$) is the light intensity. When $\varepsilon C_{\alpha T}l$ is sufficiently small, i.e. light is not completely absorbed, $10^{-\varepsilon C}$ αT^l becomes $1-\varepsilon C_{\alpha T}l$, and Eq. 5 reduces to Eq. 6,

$$v_i=\frac{2.303\,k_iC_{BDNH}}{(k_iC_{BDNH}+k_q)}\Phi I\varepsilon C_{\alpha T}, \quad (6)$$

if $k_iC_{BDNH}\ll k_q$

$$v_i=\frac{2.303k_i}{k_q}C_{BDNH}\,\Phi IC_{\alpha T}. \quad (7)$$

On the contrary, when $\varepsilon C_{\alpha T}$ is sufficiently large, i.e. light is completely absorbed, $10^{-\varepsilon C_{\alpha T}l}$ becomes zero and Eq. 5 can be reduced to Eq. 8.

$$v_i=\frac{2.303\,k_iC_{BDNH}}{(k_iC_{BDNH}+k_q)}\Phi I/l, \quad (8)$$

If $k_iC_{BDNH}\ll k_q$ holds, Eq. 8 can be reduced to Eq. 9 and the reaction rate is proportional to the first order of the BDNH concentration.

$$v_i=\frac{2.303\,k_i}{k_q}C_{BDNH}\Phi I/l. \quad (9)$$

Here, for $\varepsilon_{280}=71$ and $C_{\alpha T}>0.02$ mol dm^{-3} Eq. 9 holds and for $C_{\alpha T}<0.001$ mol dm^{-3} Eq. 7 holds. It was found that $k_i\Phi/k_q=\Phi'=0.373$. A plot of logarithm optical density at 975 nm was proportional to the irradiation time. It was found that the reaction is the mechanism of first order of BDNH i.e. $k_iC_{BDNH}\ll k_q$ holds.

The dependence of the concentration of α-tocopherol on the photooxidation of BDNH is shown in Fig. 2. As can be seen in Fig. 2, v_i becomes constant when $C_{\alpha T}$ is larger than 10^{-3} mol dm^{-3}. Consequently, when $C_{\alpha T}$ is larger than 10^{-3} mol dm^{-3} the condition of the $10^{-\varepsilon}$ $C_{\alpha T}{}^l$ is nearly equal zero holds as well as Eq. 9. The dependence of the light intensity on the photooxidation of BDNH is shown in Fig. 3. As can be seen, since the reaction rate is proportional to the first order of the light intensity, Eq. 5 holds.

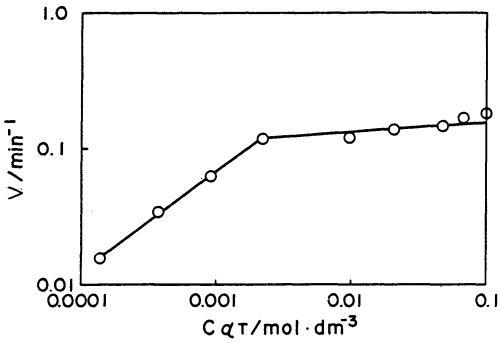


Fig. 2. Dependence of the rate of photooxidation of BDNH on the concentration of α-tocopherol. [BDNH]=5.13×10^{-5} mol dm^{-3}, I=3.24 M s^{-1}

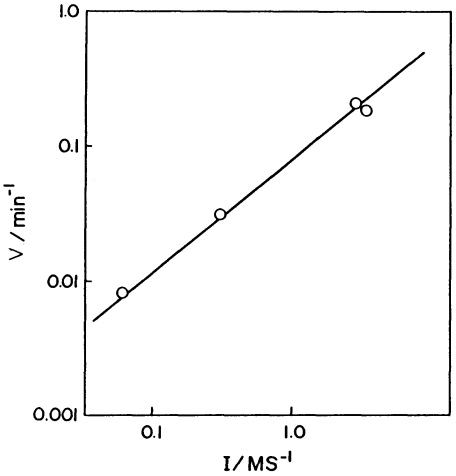


Fig. 3. Dependence of the rate of photooxidation of BDNH on light intensity. [BDNH]=5.13×10^{-5} mol dm^{-3}, [αT]=0.1 mmol dm^{-3}.

Table 1. Effect of Addition of Various Tocopherols on Photo oxidation Rate of BDNH

Tocopherol	v/min^{-1}	$E(E)$ of C_5
α	0.123	3.8985
β	0.146	2.9472
γ	0.351	2.5352
δ	0.904	2.0469

The rates of photooxidation of BDNH are shown in Table 1 under the condition that the concentration of α-tocopherol, β-tocopherol, γ-tocopherol, and δ-tocopherol are 7.74×10^{-3} mol dm^{-3}. As can be seen in Table 1, the photooxidation rate increases according to the order of the action property of vitamine E.[6] Because it was found that tocopherols form a radical at C_5,[7] the delocalization energies of α-tocopherol, β-tocopherol, γ-tocopherol, and δ-

tocopherol to an electrophilic reagent (which are calculated by HMO method) are shown in Table 1. As can be seen, the lower the delocalization energy the larger is the rate of photooxidation of BDNH. The calculation satisfied the experimental results.

The possibility of a photorecording medium was assumed for a BDNH-α-tocopherol system. Increasing the α-tocopherol concentration was not effective for increasing the recording speed, though increasing the light intensity was. In a solid medium this reaction can occur. A device using this reaction will be developed by the present author.

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