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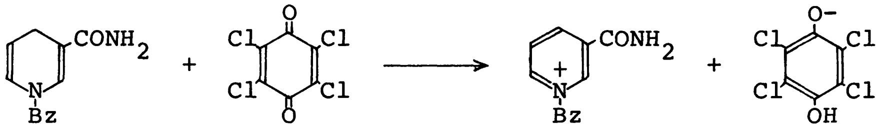
A CHARGE-TRANSFER COMPLEX AS AN INTERMEDIATE IN THE REDUCTION OF CHLORANIL BY A NADH MODEL COMPOUND

Shunichi FUKUZUMI and Toshio TANAKA*

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

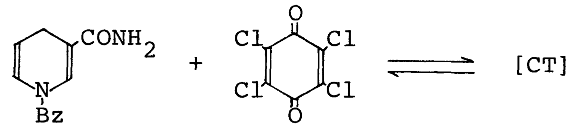
A 1 : 1 charge-transfer (CT) complex between 1-benzyl-1,4-dihydronicotinamide (BzlNH) and chloranil was isolated from a benzene solution of these reactants ($h\nu_{CT}$ = 1.70 eV, λ_{max} = 730 nm). The transient CT band was observed also in the hydride transfer from BzlNH to chloranil in MeCN. The decay of the CT band coincided with the formation of the product, tetrachlorohydroquinone anion.

Many oxidation-reduction reactions of models for dihydronicotinamide coenzymes are considered to involve direct hydride transfer from the dihydronicotinamides to the substrates.1) Although the presence of a charge-transfer (CT) complex as an intermediate has often been suggested for the hydride transfer reactions from various 1-substituted 1,4-dihydronicotinamides based on the kinetic isotope effects,2) there has been reported no direct evidence for the existence of the CT complex as a real intermediate in the reduction by 1,4-dihydronicotinamides.3) We report here the isolation of the CT complex between 1-benzyl-1,4-dihydronicotinamide (BzlNH) and chloranil as well as the direct observation of the transient CT band, the decay of which coincides with the hydride transfer from BzlNH to chloranil (Eq. 1).



(1)

When a benzene solution of BzlNH (0.2 mmol in 15 cm^3) was mixed with that of chloranil (0.2 mmol in 15 cm^3) under nitrogen atmosphere, a green color appeared immediately and a solid slowly separated. Filtration then afforded a green powder which was identified as a 1 : 1 complex between BzlNH and chloranil.4) The KBr pellet IR spectrum indicated that hydrogen is not transferred to chloranil in the complex since the CO streching band of chloranil (ν_{CO} = 1650 cm^{-1}) was still observed in the complex. The isolated complex is sparingly soluble in non-polar and less-polar solvents such as benzene, toluene, chloroform, and dichloromethane. The visible spectrum of the suspension of the complex in benzene showed a broad absorption band at 730 nm, which may be assignable to an intermolecular CT complx (Eq. 2), since neither BzlNH nor chloranil exhibits any absorptions at this wavelength.



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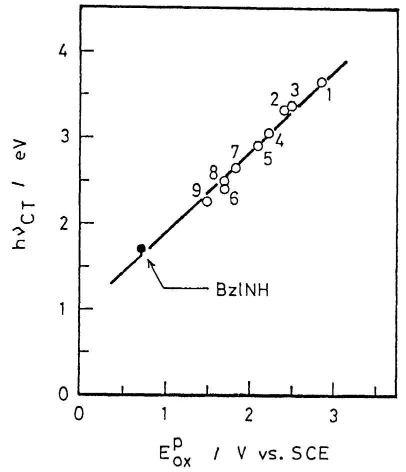


Fig. 1. A correlation between the CT transition energies of chloranil complexes with donor molecules ($h\nu_{CT}$) and the oxidation peak potentials of the donors (E^p_{ox}); (○): benzene derivatives,5) (1) C_6H_6, (2) MeC_6H_5, (3) $t\text{-}BuC_6H_5$, (4) $o\text{-}Me_2C_6H_4$, (5) $1,3,5\text{-}Me_3C_6H_3$, (6) Me_6C_6, (7) Et_6C_6, (8) $m\text{-}(MeO)_2C_6H_4$, (9) $p\text{-}(MeO)_2C_6H_4$; (●): BzlNH.

In order to confirm this assignment, the transition energy of the 730 nm band ($h\nu_{CT}$ = 1.70 eV) is compared with that of known CT complexes between chloranil and other donor molecules as a function of the oxidation peak potentials of the donors. The CT transition energies of chloranil complexes with benzene derivatives ($h\nu_{CT}$) bear a linear relationship with the oxidation peak potentials of the benzene derivatives (E^p_{ox}) as shown by the open circles in Fig. 1.5) The electrochemical oxidation of BzlNH is known to be irreversible6) as the case of the benzene derivatives.5) Since the oxidation peak potentials for such irreversible oxidations measured by the cyclic voltammetry depend on the sweep rates, the cyclic voltammogram of BzlNH in MeCN was measured at the sweep rate (100 mV s^{-1}) as reported for the benzene derivatives.5) The measurement was performed on a Hokuto Denko Model HA-301 potentiostat/galvanostat at 298 K in MeCN containing 0.1 mol dm^{-3} $n\text{-}Bu_4NClO_4$ as the supporting electrolyte, using a platinum microelectrode and a standard NaCl calomel reference electrode (SCE). The oxidation peak potential of BzlNH was obtained as 0.72 ± 0.02 V *vs.* SCE at 100 mV s^{-1}. The transition energy of the BzlNH-chloranil complex plotted against the oxidation peak potential of BzlNH (the closed circle in Fig. 1) is reconciled with the correlation for known CT complexes between chloranil and other donor molecules. Thus, the isolated complex is assigned as the 1 : 1 CT complex between chloranil and BzlNH (Eq. 2).

When the isolated CT complex was dissolved in MeCN, the hydride transfer from BzlNH to chloranil occurred instantly to afford tetrachlorohydroquinone anion (Eq. 1),

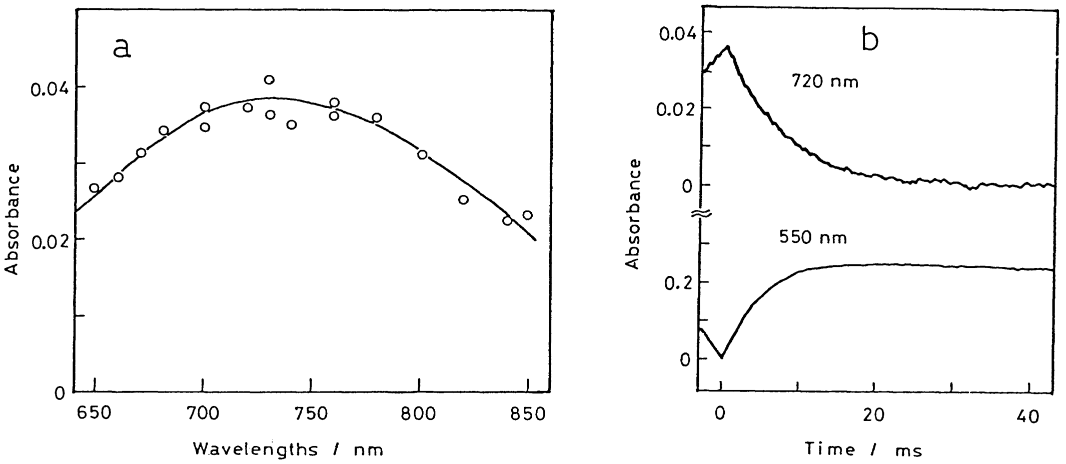
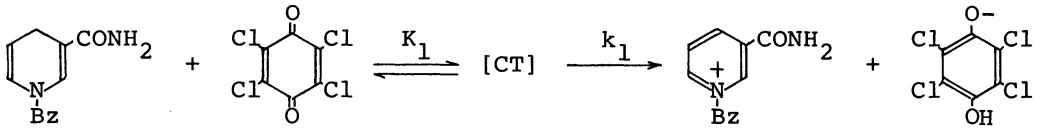


Fig. 2. The transient CT spectrum obtained by plotting the initial absorbances in the kinetic curves against the wavelengths (a), and the decay and the rise of absorbances at 720 nm and 550 nm, respectively (b), in the reaction of BzlNH (7.37×10^{-2} mol dm^{-3}) and chloranil (1.01×10^{-2} mol dm^{-3}) in MeCN at 298 K.

which was characterized by the electronic absorption spectrum (λ_{max} = 448 nm).[7] Thus, the CT complex is indeed an intermediate for the hydride transfer reaction. The reaction rates in MeCN were determined by monitoring the absorption band of the anion at 448 nm, using a Union RA-103 stopped flow spectrophotometer. The second-order rate constant (k_{obsd}) was obtained as $(1.70 \pm 0.04) \times 10^3$ mol^{-1}dm^{3}s^{-1} at 298 K. The activation parameters were determined from the temperature dependence of k_{obsd} measured at 298, 308, and 318 K as $\Delta H^{\ddagger} = 11 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -(126 \pm 10)$ J mol^{-1} K^{-1}.[8] The small activation enthalpy and the largely negative activation entropy are consistent with the presence of the intermediate complex since both the enthalpy and the entropy of the complex formation would have negative values and will decrease the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, respectively.[9]

The transient absorption band which corresponds to the CT band of the isolated complex (λ_{max} = 730 nm) has not been observed for the reaction of BzlNH and chloranil in MeCN under the dilute conditions (both reactants $< 1 \times 10^{-2}$ mol dm^{-3}) as used for the kinetic measurements of the formation of the product anion. However, the reaction in high concentrations of BzlNH (7.37×10^{-2} mol dm^{-3}) and chloranil (1.01×10^{-2} mol dm^{-3}), which are close to the limitation of solubilities, displayed the instant rise of the CT band with λ_{max} = 730 nm (Fig. 2a), which was followed by its decay. The decay rate coincides with the rise of the absorption band due to the product anion (Fig. 2b).[10] Thus, it is concluded that the reduction of chloranil by BzlNH is a two-step process which involves the CT complex between chloranil and BzlNH as a reaction intermediate (Eq. 3).



(3)

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4) Anal. Calcd for $C_{19}H_{14}Cl_4N_2O_3$: C, 49.60; H, 3.07; N, 6.09. Found: C, 50.38, H, 3.11; N, 5.75.

5) The $h\nu_{CT}$ and E^{p}_{ox} values were taken from the literatures; S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 103, 7240 (1981); *J. Org. Chem.*, 46, 4116 (1981).

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8) The activation parameters are calculated from the equation $k_{obsd} = Z \exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R)$, where Z is taken as 1×10^{11} $mol^{-1}dm^{3}s^{-1}$.

9) According to Eq. 3, the observed rate constant is represented as the product of the formation constant K_1 and the rate constant k_1; $k_{obsd} = k_1K_1$. Then, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given by $\Delta H^{\ddagger} = \Delta H_1 + \Delta H_1^{\ddagger}$ and $\Delta S^{\ddagger} = \Delta S_1 + \Delta S_1^{\ddagger}$, respectively.

10) The formation rate of the product anion was determined from the rise of the absorbance at 550 nm since the absorbance at λ_{max} (448 nm) was too large to be measured with a 2 mm cell under the high concentrations of the reactants as shown in Fig. 2. The rate constant obtained under such high concentrations was the same as that determined from the rise of the absorbance at 448 nm under dilute conditions.

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