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ONE-ELECTRON PHOTOREDUCTION OF N,N'-1,3-PROPANO-BRIDGED INDIGO

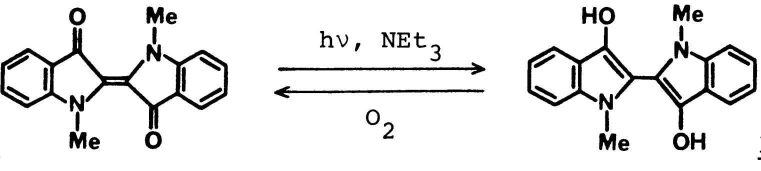
Jun-ichiro SETSUNE,* Toshikazu MATSUURA, Takashi FUJIWARA, and Teijiro KITAO
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

N,N'-1,3-Propano-bridged indigo was reduced by one electron to the semi-reduced radical when irradiated by visible light ($\lambda > 500$ nm) in a deaerated benzene solution containing triethylamine whereas N,N'-dimethylindigo and N,N'-diacetylindigo were reduced by two electrons to their leuco forms under the same reaction conditions.

Photoredox behavior of dyes has attracted much interest related to the development of photo-devices which utilize visible light energy.$^{1,2)}$ As has recently been reported by Whitten$^{3)}$ that photolysis at 546 nm of a degassed solution of thioindigo with tertiary amines led to the two-electron reduction to leucothioindigo, indigo chromophore is regarded as one of the most intriguing photo-responsive molecular systems. Herein, we would like to show that N,N'-disubstituted indigos are reduced photochemically in the presence of triethylamine and that the redox chemistry of indigo chromophore differs according to trans-cis structural change.

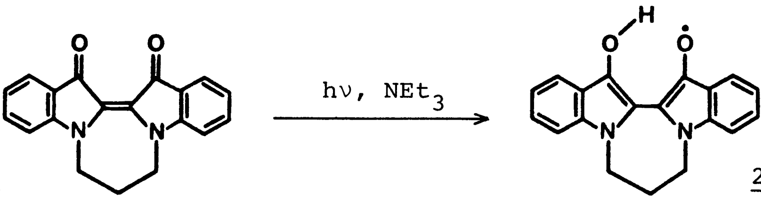
A degassed benzene solution of N,N'-dimethylindigo$^{4)}$ (1) (5×10^{-5} M) and triethylamine (5×10^{-2} M) was irradiated by a 300-W tungsten lamp ($\lambda > 500$ nm) with

1

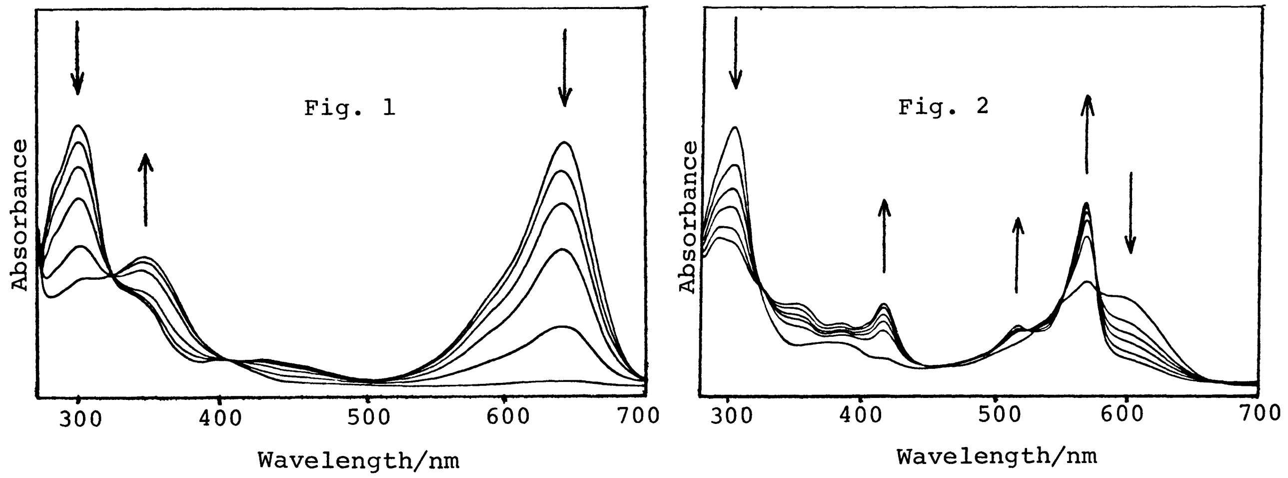


1-H$_2$

2



2-H



Figs. 1 and 2. Spectral changes upon photolysis of benzene solution of 1 and 2 respectively with triethylamine. Spectra were recorded at 15 minutes' intervals for Fig. 1; at 0, 15, 30, 45, 75, 105 min for Fig. 2.

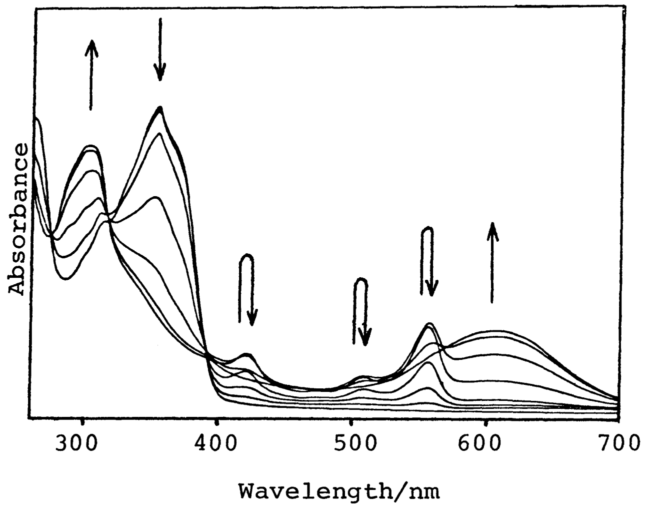


Fig. 3. Spectral change with autoxidation of ethanol solution of $2\text{-}H_2$ recorded at 0, 30, 45, 60, 80, 100, 123, 154 min.

a filter solution, and the reaction was monitored spectrophotometrically as shown in Fig. 1. Intensities of the absorption bands at 643 and 303 nm due to 1 decreased and a 348 nm band developed with showing clean isosbestic points at 403 and 318 nm. This spectral change was reversible when the colorless solution generated after 1 h photolysis was allowed to be in contact with air. Two-electron photoreduction of 1 to the leuco form ($1\text{-}H_2$) in this case is supported by two lines of evidence. In the first place, this spectral change parallels that reported for photoreduction of thioindigo to the leuco form and autoxidation of the latter to the former.[3] Secondly, the UV-vis spectrum of the photogenerated colorless solution is nearly identical with that of the reaction product which is obtained from 1 and zinc in acidic ethanol and is air-oxidized to regenerate 1. In a striking contrast to 1, photolysis of N,N'-1,3-propano-bridged indigo[5] (2) under the same reaction conditions as 1 resulted in the color change from blue to red and a subsequent autoxidation caused an irreversible spectral change. Monitoring visible spectrum change upon photolysis of 2 showed the development of the absorption bands at 568, 517, and 416 nm (see Fig. 2). This same set of the absorption bands are observed transiently when the leuco form ($2\text{-}H_2$) which is prepared by the reduction of 2 with zinc in acidic ethanol is autoxidized in ethanol as shown in Fig. 3. This spectral change upon oxidation of $2\text{-}H_2$ is rationalized in terms of two successive one-electron processes, providing the best evidence in support of the formation of the semi-reduced radical (2-H) in the photolysis of 2 by one-electron transfer. The ESR spectrum of 2-H generated photochemically in a deaerated benzene solution showed a structured signal at $g = 2.004$ with the line width ranging over 15 G.

Photoreduction of N,N'-diacetylindigo$^{6)}$ (3) under the same reaction conditions occurred rapidly to give the leuco form ($3\text{-}H_2$) with showing a similar spectral change to that observed for the photoreduction of 1. The relative quantum yield (0.09 : 1) for the formation of $1\text{-}H_2$ and $3\text{-}H_2$ which was measured under the irradiation of the filtered tungsten lamp ($\lambda > 500$ nm) points to the importance of electronic effect of the N-substituents on the reactivity toward photoreduction of indigo chromophore. The quantum yield ($\Phi = 0.091$) of the photoreduction at 546 nm of 3 was determined relative to ferrioxalate actinometry. Autoxidation of $3\text{-}H_2$, in turn, occurred much slower than $1\text{-}H_2$ with no intermediate species being detected photospectroscopically.

Excited states of dyes "A" are quenched by an electron transfer from reductants "HD:". Whitten showed$^{3)}$ by using laser flash photolysis technique that the radical pair [AH• / •D] which is formed by a photoinduced electron transfer - proton transfer sequence (Eq. 1) is converted to the reduced dye "AH_2" mainly via a second electron transfer within the pair (Eq. 2). An alternative route to the reduced form was also shown$^{3)}$ to involve the electron transfer between the ground state dye "A" and a diffused radical "D•" (Eq. 3) followed by the disproportionation of the semi-reduced radical "AH•" (Eq. 4). The fact that the semi-reduced radical 2-H of the cis-fixed indigo 2 does not undergo disproportionation or reduction is explain-

$$A + HD: \longrightarrow [A^{-\bullet} / HD^{+\bullet}] \longrightarrow [AH\bullet / \bullet D] \qquad (1)$$

$$[AH\bullet / \bullet D] \xrightarrow{H^+} AH_2 + D^+ \qquad (2)$$

$$D\bullet + A \xrightarrow{H^+} AH\bullet + D^+ \qquad (3)$$

$$2AH\bullet \longrightarrow AH_2 + A \qquad (4)$$

able in terms of the energy level relationships between "A", "AH•", and "AH_2". That is, the electrostatic repulsion between the two carbonyl oxygens of indigo nucleus in the cis form would destabilize 2 relative to 1. $2\text{-}H_2$ is also considered to be destabilized relative to $1\text{-}H_2$ since hydrogen bondings involving the nitrogens are impossible for the cis-fixed leucoindigo structure. On the other hand, 2-H would be stabilized relative to a corresponding radical (1-H) due to an effective overlap of the radical center with the OH proton leading to a symmetrical resonance-stabilized π-radical. The energy level profile of 2, 2-H, and $2\text{-}H_2$ in comparison with that of 1, 1-H, and $1\text{-}H_2$, as discussed above, argues for the less favorable reduction and disproportionation of 2-H than 1-H.

References

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5) Indigo was treated with NaH (2-fold mol) and then with 1,3-dibromopropane to give 2 which was characterized by spectroscopic measurements and microanalysis.

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