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Photochemical Reactions of 1,1-Diphenyl-2-picrylhydrazyl with Gold(III) Complexes

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The reactions of 1,1-diphenyl-2-picrylhydrazyl(DPPH) with some metal salts have recently aroused interest. DPPH has been reported to undergo certain types of oxidation-reduction reaction with various metal ions[1,2] as well as chelates,[3,4] or charge transfer (CT) complex formation with CuCl.[5] All these systems, however, were treated under thermal conditions. No photochemical reactions of DPPH with metal salts have so far been reported. In the course of studies on the photo-cationic polymerization of *N*-vinylcarbazole sensitized by $(n\text{-}C_4H_9)_4NAuX_4(X=Cl^-, Br^-)$,[6] we found that under irradiation of a solution containing DPPH and Au(III) complexes the characteristic purple color of the former disappeared. This communication describes the novel reaction in acetophenone as a solvent in connection with the photochemistry of Au(III) complexes, which has not been investigated quantitatively in spite of their extreme photosensitivities. Experimental methods are the same as described elsewhere.[6] All reactions were carried out without eliminating dissolved air.

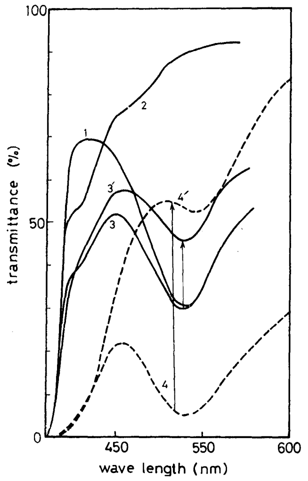

Fig. 1. Photochemical reactions between AuX_4^- and DPPH in acetophenone.
1; [DPPH]$=5\times10^{-5}$M, 2; $[AuBr_4^-]=5\times10^{-5}$M, 3; [DPPH] $=5\times10^{-5}$M, $[AuBr_4^-]=5\times10^{-5}$M, 4; [DPPH]$=5\times10^{-5}$M, $[AuCl_4^-]=2\times10^{-3}$M, 3′ and 4′; after irradiation of 3(30 min) and 4(45 min) irradiation at 436 nm, 30 °C.

When an acetophenone solution containing equimolar amounts (5×10^{-5} M) of DPPH and $AuBr_4^-$ was irradiated by 436 nm light for 30 min at 30 °C, the characteristic purple color (λ_{max} 540 nm) of DPPH faded as shown in the figure. This was also observed under thermal conditions, although the rate of disappearance was negligibly small. No interaction between DPPH and $AuBr_4^-$ species was observed spectroscopically and irradiation of a solution of DPPH alone induced no fading of its color. Irradiation at 546 nm was ineffective. These facts indicate that effective light absorbing species leading to the reaction is not DPPH but $AuBr_4^-$ itself. The quantum yield ($\phi_{-\mathrm{DPPH}}$) for the disappearance of DPPH was calculated from the plots of its absorbance at 540 nm against time to be 0.17 after correcting for the inner filter effect:

$$I_{\mathrm{abs,A}} = \frac{\varepsilon_A[A]}{\varepsilon_A[A]+\varepsilon_D[D]} I_0[1-\exp\{-(\varepsilon_A[A]+\varepsilon_D[D])\}]$$

where A and D denote $AuBr_4^-$ and DPPH, and $I_{\mathrm{abs,A}}$, I_0 and ε denote amounts of light absorbed by $AuBr_4^-$, the intensity of incident light and molar extinction coefficient, respectively. The quantum yield ($\phi_{-AuBr_4^-}$) for the photodecomposition of $AuBr_4^-$ under irradiation at 436 nm at 30 °C has been obtained as 0.20.[6] It is interesting that both $\phi_{-\mathrm{DPPH}}$ and $\phi_{-AuBr_4^-}$ are nearly the same, indicating that the photodecomposition of $AuBr_4^-$ corresponds to the equimolar fading of DPPH.

A similar fading reaction of DPPH was also observed by the use of $AuCl_4^-$ as shown in the figure. In this case, however, thermal reaction should be considered because of the high concentration of $AuCl_4^-$. The value of $\phi_{-AuCl_4^-}$ was calculated to be 0.24 on the assumption of 1: 1 correspondence between $\phi_{-AuCl_4^-}$ and $\phi_{-\mathrm{DPPH}}$.

The characteristic absorption band at 540 nm of DPPH radical has been reported[5] to be probably due to the picryl ring having an appreciably delocalized unpaired spin. Metal ions or chelates have been assumed[2] to react with equimolor proportion of DPPH with production of 1,1-diphenyl-2-picrylhydrazine ($DPPH_2$) *via* hydrogen atom transfer mechanism or election transfer accompanied by proton transfer mechanism. Alternatively, it has been known[5] to form CT complex with metal ion coordinating to the picryl ring. The purple color of DPPH has been reported to disappear in these systems, whereas the absorption maximum attributed to hydrazine or CT complex appears in ultraviolet region. In the present system, the solution became pale yellow by prolonged irradiation although the absorption maximum was not observable due to hindrance of the absorption band of solvent.

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As to the photodecomposition of AuX_4^- under irradiation of its CTTM band, its primary process seems to be intramolecular photoredox reaction as suggested[7] from the flash photolysis studies in which transient spectrum of X_2^- was detected. The mechanism of primary processes is proposed as follows:

$$Au^{III}X_4^- \xrightarrow{h\nu} A^{II}X_3^- + X \xrightarrow{\text{free } X^-} X_2^-$$

The reaction of DPPH with either transient species Au(II) or X (or X_2^-) formed photochemically may be explained from the viewpoint of the electron-transfer reaction in which DPPH acts as an oxidant. The direction of the electron-transfer may be controlled by the relative magnitude of the redox potential (E°) of the reacting species. The E° for the DPPH system[2] and the Au(III)/Au(II) couple[8,9] have been estimated to be -1.1—-1.2 V and -0.5—-0.96 V, respectively. The halogen atom, a strong oxidant, has not been reported to act as a reductant presumably because of difficulty in the formation of X^+ cation from X atom. X_2^- anionradical has been reported to be a stronger oxidant than X_2 molecule.[10] Thus, electron-transfer from these halogen species to DPPH seems to be highly unlikely. This might be supported by the results obtained in the flash photolysis of $AuBr_4^-$, *i.e.* the amount of Br_2^- was less than that of photodecomposed $AuBr_4^-$ by a factor of about ten, which is not in line with the results where both ϕ_{-DPPH} and $\phi_{-AuBr_4^-}$ are of nearly the same value. The electron-transfer reaction between Au(II) and DPPH seems to be energetically more favorable. If Au(II) is reoxidized to Au(III), the dark red color of $AuBr_4^-$ should be restored. However, the presence of hydrazine derivatives as a result of the reduction of DPPH would cause the formation of a colorless complex with Au(III). The Au(III) complexed with amine is colorless as shown for the tetramine-[11] and bisethylenediamine-[12] Au(III) complexes.

Another possibility is that formation of the charge-transfer complex between DPPH radical with the halogen-Au(I) species may result from the spontaneous reduction of Au(II) species. This case is similar to the DPPH/CuCl complex reported by Leh and Wan.[5] It seems most likely that some gold species is responsible for the fading reaction of DPPH.

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