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FLASH PHOTOLYSIS OF A GOLD(III) COMPLEX

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Flash photolysis of tetra-n-butylammonium tetrabromoaurate (III) was investigated in tetrahydrofuran. Two sorts of transient spectra appeared at 365 nm and 475 nm were analyzed kinetically, the former being assigned to Br_2^- radical-anion. Additive effect of N-vinylcarbazole was examined.

Although the extreme high photosensitivity of gold (III) complexes has been recognized for many years, no quantitative study has been reported on this subject. Dilute aqueous solution of $HAuCl_4$ was reported to undergo a certain type of photoredox decomposition.1) However, the photochemistry of $AuCl_4^-$ in aqueous solution is difficult to be examined, since this anion in aqueous media undergoes thermal hydrolysis leading to the formation of at least five species.2) Recently, we found that the AuX_4^- ($X = Cl^-, Br^-$) acts as a sensitizer for the photopolymerization of N-vinylcarbazole (VCZ), β-propiolactone3) and acrylamide.4) In this connection, we have carried out the flash photolysis of anhydrous $(n\text{-}C_4H_9)_4NAuBr_4$, which was chosen because of its experimental convenience, in tetrahydrofuran. This is the preliminary study of observing the transient species formed during photolysis of Au(III) complex for the first time.

The $AuBr_4^-$ complex was prepared as described by Mason and Gray.5) The electronic spectra of this complex consist of two CTTM bands with their maxima at 256 nm (ε = 27500) and 402 nm (ε = 3200),6) and a shoulder of d-d transition obscured by the CTTM band at 460 nm (ε = 1230, apparently).5) Under continuous irradiation at 436 nm by using a 300 W high-pressure Hg lamp in the air at 30 °C, the dark red color of the solutions of the complex ($5 - 10 \times 10^{-5}$M) disappeared. Any new bands did not appear even after prolonged irradiation. The value of quantum yield ($\Phi_{-Au^{III}}$) for this decomposition reaction was obtained as 0.5 ± 0.02. Furthermore, by the continuous irradiation of $AuBr_4^-$ in the presence of 1,1-diphenyl-2-picrylhydrazyl, the purple color of the latter disappeared with nearly the same quantum yield as $\Phi_{-Au^{III}}$. These facts suggest that $AuBr_4^-$ is photodecomposed via some redox processes.

A solution of $(n\text{-}C_4H_9)_4NAuBr_4$(2 x 10^{-4}M) was flash-photolyzed without deaeration at room temperature. The flash apparatus has been described previously.[7)] When the solution was photolyzed with a Xe spiral flash lamp of about 700 J with a half duration of 180 μsec, two transient absorption maxima are observed at 365 nm (X_{365}) and 475 nm (X_{475}), as shown in Figure. After the single flash, absorption bands due to $AuBr_4^-$ disappeared entirely similar to the results of continuous photolysis.

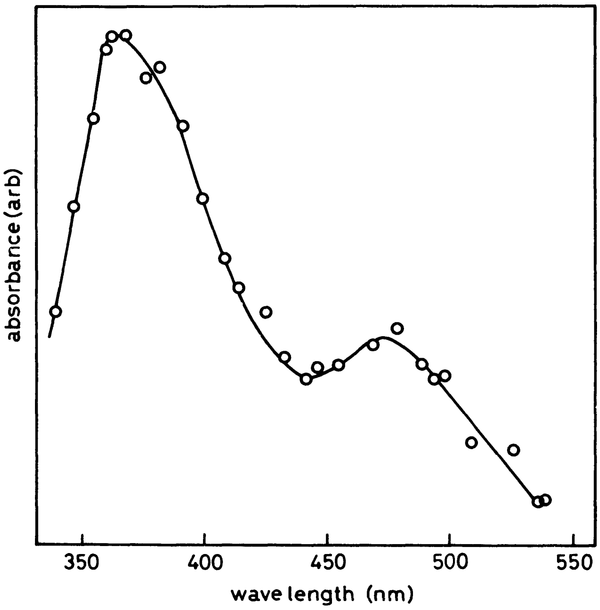

Figure. Transient spectra obtained by flash photolysis of 1 x 10^{-4}M $(n\text{-}C_4H_9)_4NAuBr_4$ in tetrahydrofuran. Spectra taken 200 μsec after the flash.

The decays of these two bands were followed at 360 nm and 470 nm, respectively, and then kinetically analyzed. For this measurement, the linear lamps dissipating about 200 J with the duration of 15 μsec were used, the light of shorter wavelength being eliminated with Toshiba UV-39 glass filters. When the solution of $AuBr_4^-$ (1 x 10^{-4}M) was flashed, X_{365} was produced at the initial absorbance of ca. 0.3 with a life-time of about 10 msec. This absorption decayed by a second-order process and plots of $(\text{absorbance})^{-1}$ against time were linear upto 90 % of disappearance. On the other hand, X_{475} was somewhat difficult to be analyzed kinetically, because its initial absorbance was rather small (ca. 0.1). In addition, the residual $AuBr_4^-$ due to incomplete photodecomposition during the photolysis flash absorbs the light at the monitoring wavelength, which renders gradual decomposition of $AuBr_4^-$. From careful treatment, however, its decay seems to obey the first-order kinetics with the rate constant of about 7×10^2 sec^{-1}.

As described above, the appearance of two transient absorption bands by flash excitation is due to different species. More distinct evidence to distinguish them is obtained, when the nature of the transient species is examined in the presence of VCZ as an additive, light absorption by VCZ being neglected: Addition of VCZ into the $AuBr_4^-$ solution reduced the initial amount of X_{365} by a factor of about one third and enhanced the decay rate. Moreover, the change from second-order into first-order decay was brought about. It is noted that the amount of decomposed $AuBr_4^-$ was not affected by VCZ, suggesting the reaction of VCZ with some sort of precursor of X_{365}. Meanwhile, the behavior of X_{475} was never affected by VCZ.

It is very likely that the filtered light from the flash lamp as well as the continuous irradiation at 436 nm excites almost exclusively the CTTM transition followed by the redox reaction.

$$AuBr_4^- \xrightarrow{\text{CTTM irrad.}} AuBr_3^- + \text{Br atom} \qquad (1)$$

A bromine atom, in turn, may further react with free Br^- ion present in the system to produce Br_2^- radical-anion.

$$\text{Br atom} + Br^- \longrightarrow Br_2^- \qquad (2)$$

The transient Br_2^- in aqueous media has been well known to have its absorption maximum around 360 nm and to decay by a second-order process.[8)] Therefore, the assignment of X_{365} to Br_2^- seems to be most probable. Accordingly, the precursor of Br_2^- reacting with VCZ is presumed to be bromine atom. The production of free bromine ions seems to be triggered by photoirradiation, for instance, via photochemical formation of $AuBr_3^-$ followed by its secondary decomposition. The fact that the order of dependence of the initial amount of Br_2^- on the amount of photodecomposed $AuBr_4^-$ was higher than unity may also support that it was formed not via a monomolecular process like eq. (3)

$$AuBr_4^- \xrightarrow{\text{CTTM irrad.}} AuBr_2 + Br_2^- \qquad (3)$$

but via the successive processes like eq. (1) and (2). As suggested for the reaction,[9)] $SCN\cdot + SCN^- \longrightarrow (SCN)_2^-$, with the rate constant $k > 10^9$ $M^{-1}sec^{-1}$, the reaction (2) seems to be so rapid that the formation of Br_2^- is completed during the flash irradiation. Our further kinetic studies and assignments of the transient spectra are in progress.

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