Near-UV photolysis of μ-dibromotetrabromo- dipalladate(II) in chloroform

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Broadband ($\lambda > 320$ nm) irradiation of $(Bu_4N)_2Pd_2Br_6$ in chloroform causes the conversion of $Pd_2Br_6^{2-}$ to $Pd_2Cl_6^{2-}$. During the conversion, chloroform is decomposed photocatalytically at a rate that accelerates then decelerates as coordinated bromines are replaced by chlorines. The primary bromine-containing product is CCl_3Br. The observations are consistent with a mechanism in which $Pd_2Br_6^{2-}$ and the intermediate $Pd_2Br_{6-n}Cl_n^{2-}$ complexes undergo homolytic photodissociation of a bromine or chlorine atom, which terminates with a trichloromethyl radical or abstracts a hydrogen from chloroform, respectively.

Keywords: Photolysis; Photosubstitution; μ-Dibromotetrabromodipalladate(II); Photodecomposition; Chloroform

1. Introduction

Ligand substitution generally refers to a substitution on a metal center without change of oxidation state in which bond breakage and new bond formation occur heterolytically. It is relatively uncommon for metal complexes, especially those not normally designated as organometallic, to undergo substitution through homolytic bond breakage and bond formation without oxidation or reduction of the metal. Two examples are the photoconversion in chloroform of $[Ru(bpy)_2(N_3)_2]$ (bpy = 2,2′-bipyridine) to $[Ru(bpy)_2Cl_2]$ [1] and the photoconversion, likewise in chloroform, of $[Fe(Et_2dtc)_3]$ (Et_2dtc = diethyldithiocarbamate) to $[Fe(Et_2dtc)_2Cl]$ [2]. The photolysis of transition metal complexes in chloroform and other chloroalkane solvents is more typically characterized by redox processes [3–14].

In the cases noted above, radicals were formed through irradiation at 254 nm, under which circumstances $CHCl_3$ undergoes C–Cl bond homolysis [15]. Under 254 nm excitation, chloroform forms trichloromethyl radicals through hydrogen abstraction by the primary radicals [16, 17].

$$CHCl_3 \xrightarrow{\text{h}\nu} \cdot CHCl_2 + Cl\cdot \qquad (1)$$

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$$\cdot CHCl_2 + CHCl_3 \rightarrow CH_2Cl_2 + \cdot CCl_3 \tag{2}$$

$$Cl\cdot + CHCl_3 \rightarrow HCl + \cdot CCl_3 \tag{3}$$
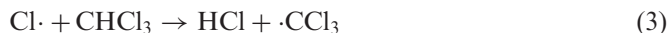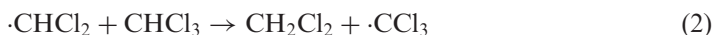
Photochemical ligand replacement through direct photolysis of chloroform could take place by a radical substitution by either chlorine atoms, competing with hydrogen abstraction, or trichloromethyl radicals [18, 19].

$$ML + Cl\cdot \rightarrow MCl + L\cdot \tag{4}$$

$$ML + \cdot CCl_3 \rightarrow MCl + L\cdot + CCl_2 \tag{5}$$

Photochemical chlorine substitution on $[Ru(bpy)_2(N_3)_2]$ and $[Fe(Et_2dtc)_3]$ was, in both cases, presumed to take place as in equation (5) [1, 2]. However, the availability of photochemically accessible oxidation states, here Ru(III) and Fe(II), renders mechanistic conclusions less certain by allowing the participation of redox steps and, for example, thermal substitution on the metal in an oxidation state different from the initial (and final) state.

Halogen radicals may also be formed through photodissociation of a halometallate complex, which frequently may be achieved with near-UV or visible light [20, 21]. Chlorine atoms photodissociated from a chlorometallate may cause the same kinds of reactions promoted by the direct photolysis of chloroform, and in addition, may catalyze the photodecomposition of chloroform by means of longer wavelength light than that required for direct photodegradation [20–22].

In the work reported here, we have sought to reduce the possibility that a photochemical radical substitution could occur through the intermediacy of a photoredox process. We present results from the near-UV photolysis of a bromopalladate(II) complex, $Pd_2Br_6^{2-}$, in chloroform. The only other common oxidation state for halopalladate complexes is Pd(IV), which would require a two-electron transfer. Halopalladate(IV) complexes generally lie at relatively high potentials, relative to the $+2$ state [23], and there appear to be no examples of stable palladium(IV) complexes being formed photochemically. This contrasts with platinum, for which photooxidation to Pt(IV) has been reported [13, 14, 22].

$Pd_2Br_6^{2-}$ was employed for this study rather than the commercially available $PdBr_4^{2-}$. Solutions of PdX_4^{2-} are in equilibrium with $Pd_2X_6^{2-}$ [24, 25]:

$$2PdX_4^{2-} \rightleftharpoons Pd_2X_6^{2-} + 2X^- \tag{6}$$
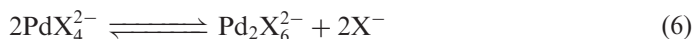
In organic solvents, the right-hand side is strongly favored [24]. Furthermore, in water the common tetraalkylammonium salts of $Pd_2Br_6^{2-}$ are less soluble than those of $PdBr_4^{2-}$ and in the presence of tetraalkylammonium cations, $(R_4N)_2Pd_2Br_6$ precipitates from aqueous solutions of $PdBr_4^{2-}$ [26]. Consequently, this study was undertaken on $(Bu_4N)_2Pd_2Br_6$.

2. Experimental

Chloroform (Aldrich, HPLC grade, stabilized with ethanol) was washed five times with water to remove the ethanol, then dried over molecular sieves. The absence of ethanol was verified by GC–MS.

$(Bu_4N)_2Pd_2Br_6$ was made by mixing aqueous solutions of Na_2PdBr_4 (Aldrich) and Bu_4NBr, filtering the precipitate and air drying. Anal. Calcd for $C_{32}H_{72}Br_6N_2Pd_2$(%): C, 32.7; H, 6.2; N, 2.4; Pd, 18.1. Found(%): C, 33.7; H, 6.0; N, 2.5; Pd, 17.7. The UV spectrum in methanol exhibited peaks at 238 and 283 nm, in agreement with literature results [26–28]. $(Bu_4N)_2Pd_2Cl_6$ was made in an analogous manner.

Photolyses were carried out on solutions in 1 cm rectangular fused silica cuvettes. Broadband irradiation was carried out with an Oriel 350 or 100 W mercury lamp passed through a Schott WG320 long pass filter, which can be characterized approximately as passing $\lambda > 320$ nm. Absorption spectra were recorded on a Cary 50 spectrophotometer.

The concentration of HCl in irradiated solutions was determined by adding a 25 or $50\,\mu L$ aliquot to a 3.0 mL solution of tetraphenylporphyrin (H_2TPP) in chloroform. The equilibrium constant for the formation of H_4TPP^{2+} from HCl and H_2TPP is large in $CHCl_3$ [29], from which it may be assumed that the double protonation is virtually quantitative. The concentrations of H_4TPP^{2+} were determined by use of literature extinction coefficients at 446 or 660 nm [30, 31].

The total concentration of oxidants in irradiated solutions was determined by mixing an aliquot with a solution of Bu_4NI in chloroform and calculating the resulting I_3^- concentration from the extinction coefficient (2.50×10^4) at 365 nm [32].

The initial concentrations of $(Bu_4N)_2Pd_2Br_6$ in chloroform were determined from absorption spectra by use of the extinction coefficient at 289 nm, $2.2 \times 10^4\,M^{-1}\,cm^{-1}$, from a Beer's Law plot.

3. Results

The addition of Bu_4NBr to a chloroform solution of $Pd_2Br_6^{2-}$ led to the disappearance of the intense peak at 289 nm and a smaller peak at 420 nm, which were replaced by a peak at 346 nm, characteristic of the $PdBr_4^{2-}$ species [33]. The conversion to $PdBr_4^{2-}$ is illustrated in figure 1 in which approximate isosbestic points are apparent at 276 and 328 nm.

The addition of Bu_4NCl to a chloroform solution of $Pd_2Br_6^{2-}$ caused a blue-shift to a very similar spectrum with peaks at 248 and 346 nm, matching the spectrum of $Pd_2Cl_6^{2-}$ [26]. With a sufficient excess of chloride ion, this spectrum was slowly replaced by one with λ_{max} at 290 nm, characteristic of $PdCl_4^{2-}$ [33].

When anhydrous HCl was bubbled into a solution of $(Bu_4N)_2Pd_2Br_6$ in chloroform, the $Pd_2Br_6^{2-}$ peaks were replaced by one peak at 283 nm. From the similarity to the spectrum of $PdCl_4^{2-}$, this may represent a protonated form of tetrachloropalladate, H_2PdCl_4.

Broadband ($\lambda > 320$ nm) irradiation of solutions of $(Bu_4N)_2Pd_2Br_6$ in chloroform exposed to air caused a blue-shift from the 289 nm absorption maximum, as illustrated in figure 2. Spectral changes were initially very slow, but accelerated considerably toward the end. The final spectrum showed a maximum at 248 nm (not visible in figure 2) and was readily identifiable as $Pd_2Cl_6^{2-}$.

During irradiation, acid, presumed to be HCl (*vide infra*), was produced in greater than stoichiometric quantities, as seen in figure 3. Initially, HCl was produced only
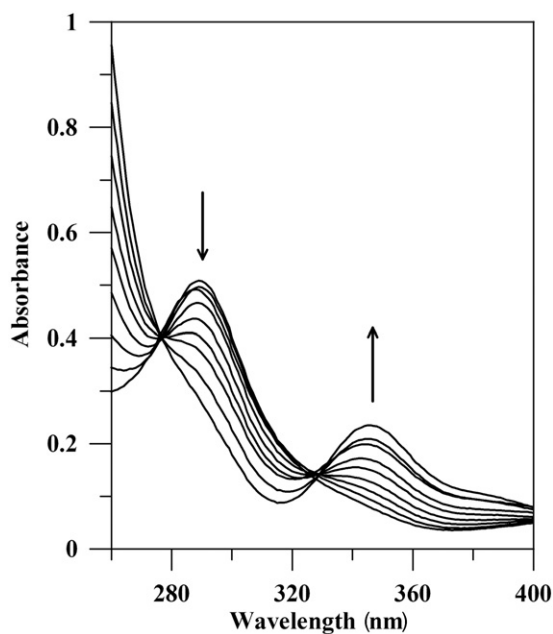
Figure 1. Spectral changes accompanying the addition of Br^- to $Pd_2Br_6^{2-}$. Each successive spectrum represents the addition of approximately two equivalents of Bu_4NBr to a 2×10^{-5} M solution of $(Bu_4N)_2Pd_2Br_6$ in $CHCl_3$.

Figure 2. Sequential spectra during the $\lambda > 320$ nm irradiation of $(Bu_4N)_2Pd_2Br_6$ in chloroform showing the conversion of $Pd_2Br_6^{2-}$ to $Pd_2Cl_6^{2-}$. Spectra recorded every 4 min for a total of 44 min. Group A spectra represent mainly $Pd_2Br_6^{2-}$ and Group C mainly $Pd_2Cl_6^{2-}$. Spectrum B was taken after 24 min irradiation.

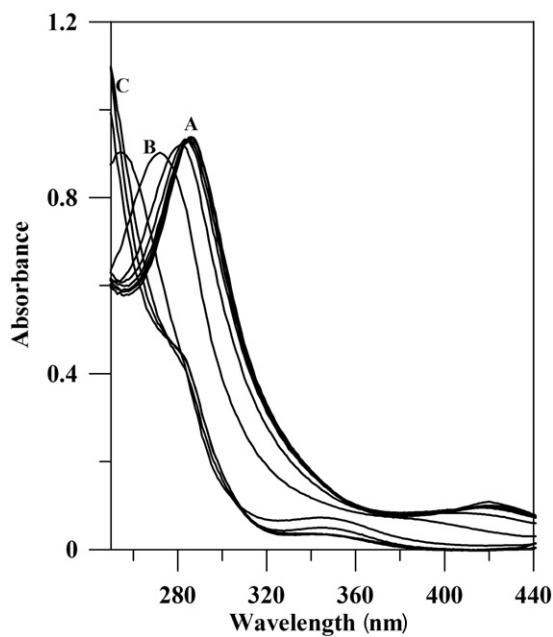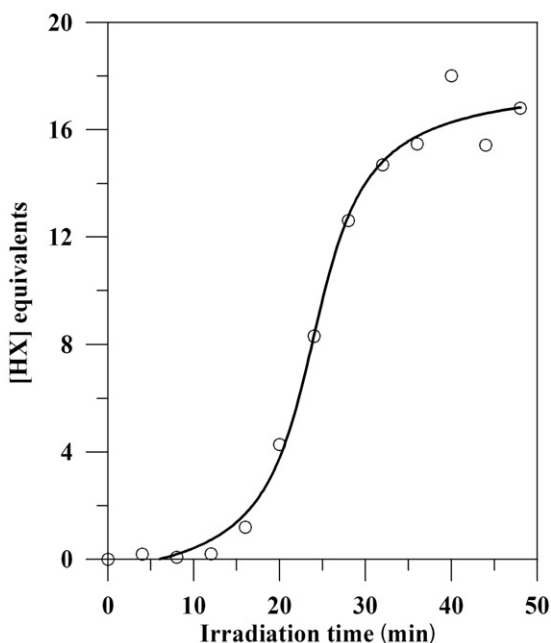Figure 3. Acid generated during the broadband ($\lambda > 320$ nm) irradiation of 3.7×10^{-5} M $(Bu_4N)_2Pd_2Br_6$ in chloroform, relative to $[Pd_2Br_6^{2-}]$. Data fitted arbitrarily to an arc tangent function.

slowly. In parallel with the acceleration of the spectral changes, the rate of HCl production increased, but as the palladium spectrum converged on that of $Pd_2Cl_6^{2-}$, the rate slowed considerably.

Acid, again presumably HCl, was also generated during the broadband ($\lambda > 320$ nm) irradiation of deoxygenated solutions of $(Bu_4N)_2Pd_2Br_6$ in $CHCl_3$; however, the amount formed was less than in aerated solutions–more than ten times less at long irradiation times.

GC–MS analysis of photolysates showed only one bromine-containing peak, that for CCl_3Br. In particular, no HBr was detectable. The other haloalkane product peaks were identifiable as C_2HCl_5 and C_2Cl_6. HCl was detectable by GC–MS, eluting with the air peak.

Several photolysates were tested with I^- for the presence of oxidizing species. Deoxygenated samples converted no I^- to I_3^-, while aerated samples were found to produce as much as 10 equivalents of triiodide ion.

The irradiation of $(Bu_4N)_2Pd_2Br_6$ in $CHCl_3$ with the unfiltered output of a mercury lamp led to a considerably more rapid production of HCl and conversion of $Pd_2Br_6^{2-}$ to $Pd_2Cl_6^{2-}$. However, this appears to take place primarily via a solvent-initiated mechanism [34], since the initial rates were found to vary linearly with the fraction of light absorbed by the chloroform while exhibiting a negative correlation with the fraction absorbed by the palladium complex. Presumably this mechanism involves direct substitution of coordinated bromine by atomic chlorine. In contrast, when a 320 nm cutoff filter was used, although initial rates were not well defined, because the reaction accelerated with time, rates were clearly seen to increase with the fraction of light absorbed by the metal complex.

4. Discussion

The observation that the rate of chloroform decomposition, as measured by the accumulation of HX in the photolysate, is initially low, then accelerates points toward the conclusion that it is not an excited state of $Pd_2Br_6^{2-}$ that leads to acid production, but rather several or all of the intermediate halide complexes on the path toward $Pd_2Cl_6^{2-}$. A viable mechanism for the photochemical conversion of $Pd_2Br_6^{2-}$ to $Pd_2Cl_6^{2-}$ in chloroform must be in agreement with the following experimental observations:
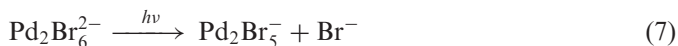
(1) The only detectable bromine-containing product is CCl_3Br.
(2) The reaction occurs in deoxygenated solutions, but much more rapidly in aerated solutions.
(3) The rate of HX production is initially slow, then accelerates, but eventually slows down again.
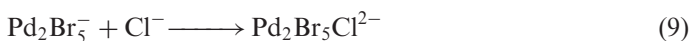
In general terms, the excited state palladium complex might cause a chemical reaction through (a) homolytic dissociation of a Pd–Br bond, (b) heterolytic dissociation of a Pd–Br bond, (c) electron transfer to or from a substrate, (d) bromine atom transfer to a substrate, (e) atom transfer from a substrate, or (f) energy transfer to a substrate. Photodissociation, (a) or (b), is taken to include the dissociation of one end of a bridging bromine atom.

Initially, chloroform is the only possible substrate. Given that its excited states lie at higher energy than the lowest charge transfer and d–d excited states of the palladium complex, energy transfer can be ruled out. It can also be excluded based on the acceleration of the rate of HCl production, since homolytic cleavage of a C–Cl bond following energy transfer would produce HCl through hydrogen abstraction at a rate that should decrease with time as bromines were replaced by chlorines and the palladium complex thereby absorbed a smaller fraction of the incident radiation. Electron transfer to palladium from $CHCl_3$ is unlikely due to the general instability of Pd(I) and the difficulty in oxidizing chloroform. Atom transfer in either direction can only occur with displacement of an atom on the substrate or fission of a bridging Pd–Br bond, thus requiring the breakage of two bonds to form one. While electron transfer from excited $Pd_2Br_6^{2-}$ to $CHCl_3$ is possible, and is considered below, it seems most likely that photodissociation is the photochemical pathway for excited $Pd_2Br_6^{2-}$.

As a general rule, excitation into ligand field bands promotes heterolytic dissociation from a metal complex [35], while excitation into ligand-to-metal charge transfer (LMCT) bands promotes homolytic dissociation [36–39]. Most of the light absorbed by the complex from the broadband illumination is absorbed through strong LMCT bands in the near-UV, while the visible portion of the spectrum comprises lower intensity ligand field bands [26].

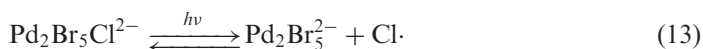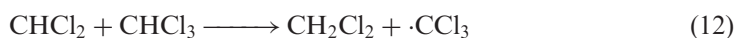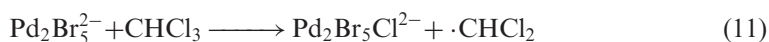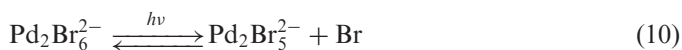If heterolytic dissociation were to take place, halide exchange with chloroform could provide a mechanism by which the photodissociated bromide could be replaced by chloride:

$$Pd_2Br_6^{2-} \xrightarrow{h\nu} Pd_2Br_5^- + Br^- \qquad (7)$$

$$Br^- + CHCl_3 \rightleftharpoons Cl^- + CHCl_2Br \qquad (8)$$

$$Pd_2Br_5^- + Cl^- \longrightarrow Pd_2Br_5Cl^{2-} \tag{9}$$

Halide exchange with chloroform is known to occur [40] and photodissociation of bromide could continue until $Pd_2Cl_6^{2-}$ was reached. Heterolytic dissociation would be expected to occur from d–d excited states, arising either through direct excitation by visible irradiation or internal conversion from LMCT excited states. However, a significant photolytic pathway for the photosubstitution of bromine by chlorine by heterolytic dissociation can be ruled out because the expected bromine-containing product, $CHCl_2Br$, was not detected in any of the photolysates subjected to GC–MS analysis.

A homolytic dissociation pathway for the replacement of bromine by chlorine, driven by absorption into the LMCT bands, would not be able to proceed analogously to the heterolytic pathway outlined above, because halogen exchange is energetically unfeasible, since the C–Cl bond energy is significantly greater than the C–Br bond energy. However, chlorine abstraction by the $Pd_2X_5^{2-}$ fragment would allow the photosubstitution to proceed.

$$Pd_2Br_6^{2-} \underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}} Pd_2Br_5^{2-} + Br \tag{10}$$

$$Pd_2Br_5^{2-} + CHCl_3 \longrightarrow Pd_2Br_5Cl^{2-} + \cdot CHCl_2 \tag{11}$$

$$CHCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \cdot CCl_3 \tag{12}$$

$$Pd_2Br_5Cl^{2-} \underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}} Pd_2Br_5^{2-} + Cl\cdot \tag{13}$$

$$Cl\cdot + CHCl_3 \longrightarrow HCl + \cdot CCl_3 \tag{14}$$

$$Pd_2Br_5Cl^{2-} \underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}} Pd_2Br_4Cl^{2-} + Br\cdot \tag{15}$$

$$Br\cdot + \cdot CCl_3 \longrightarrow CCl_3Br \tag{16}$$
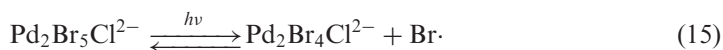
In this mechanism, the photoactive species are $[Pd_2Br_nCl_{6-n}]^{2-}$ complexes. If a Pd–Br bond is broken, the net effect is to substitute Cl for Br. If a Pd–Cl bond is broken, the complex is reconstituted, but a molecule of HCl is formed during the subsequent hydrogen abstraction. This will continue until $Pd_2Cl_6^{2-}$ is reached, whereupon the rate of HCl production would be predicted to stay constant.

This mechanism is consistent with the acceleration then deceleration of the rate of HCl formation shown in figure 3. The rate is initially very slow because HCl can only be formed once chlorine has begun to replace bromine in the complex so that chlorine atoms can be photodissociated, as in equation (13). The rate increases as the average number of chlorines in the $Pd_2X_6^{2-}$ complex increases, but at the same time the blue-shift of the charge-transfer bands reduces the fraction of $\lambda > 320\,nm$ light absorbed by the palladium complex, as can be seen in figure 2. Eventually this causes the rate of HCl formation to decline to a slower rate that can be attributed to catalysis by $Pd_2Cl_6^{2-}$.

Hydrogen abstraction from $CHCl_3$ by Cl and $CHCl_2$ radicals (equations (12) and (14)) is favorable, but as the H–Br bond energy [41] is $35\,kJ\,mol^{-1}$ smaller than the C–H bond energy in chloroform [42], bromine atoms cannot abstract hydrogen and must terminate with another radical. Trichloromethyl radicals being, according to the proposed mechanism, the most numerous it would be predicted that the bromine will terminate as in equation (16) to form CCl_3Br, as observed.

The $CHCl_2$ and CCl_3 radicals would be expected to terminate to form C_2Cl_6, C_2HCl_5 and $C_2H_2Cl_4$, which is what was observed, with, however, only a small amount of $C_2H_2Cl_4$, as would be expected because of rapid hydrogen abstraction by $CHCl_2$ radicals [43].
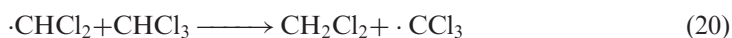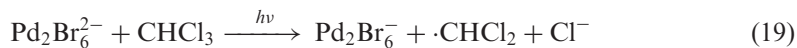
The proposed mechanism is also consistent with the much greater rate of HCl production in aerated solutions. Trichloromethyl radicals combine readily with oxygen to form trichloromethylperoxy radicals [16, 44, 45]. These may abstract hydrogen to form CCl_3OOH, which accumulates gradually in irradiated chloroform [46].

$$CCl_3 + O_2 \rightarrow CCl_3OO\cdot \qquad (17)$$

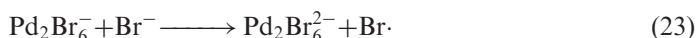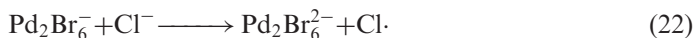$$CCl_3OO\cdot + CHCl_3 \rightarrow CCl_3OOH + \cdot CCl_3 \qquad (18)$$

Trichloromethylhydroperoxide decomposes by breaking the O–O bond in the presence of a substrate to which the OH fragment, as hydroxide [47] or as hydroxyl [48], can bond (the $Pd_2X_5^{2-}$ intermediates could potentially serve this function), yielding eventually HCl and CO_2. CCl_3OO radicals themselves also undergo a first-order decomposition of uncertain mechanism to produce HCl and CO_2 [47]. The oxidant found in irradiated aerated solutions of $Pd_2Br_6^{2-}$ in $CHCl_3$ is presumed to be CCl_3OOH.

The key step in the mechanism is equation (11) in which chlorine atom transfer from chloroform restores coordinative saturation to the palladium, producing dichloromethyl radicals. Chlorine abstraction from chloroalkanes by metal complexes has been seen in other systems [49, 50], but the feasibility of chlorine atom transfer in this case clearly depends on the relative bond strengths for homolytic cleavage of the Pd–Cl and C–Cl bonds. In chloroform, the latter is $339\,kJ\,M^{-1}$ [51], while the Pd–Cl bond energy in $PdCl_4^{2-}$ has been estimated to lie between 339 and $351\,kJ\,M^{-1}$ [52]. Thus chlorine atom transfer appears to be feasible.

Finally, we return to the possibility that substitution occurs through electron transfer from $Pd_2Br_6^{2-}$ to chloroform, the very possibility we were hoping to avoid by choosing a palladium(II) bromo complex to photolyze. The substitution process could occur through the substitution of chloride ion for bromide on $Pd_2Br_6^{2-}$, which was shown to take place experimentally when Bu_4NCl was mixed with $(Bu_4N)_2Pd_2Br_6$ in chloroform.

$$Pd_2Br_6^{2-} + CHCl_3 \xrightarrow{h\nu} Pd_2Br_6^{-} + \cdot CHCl_2 + Cl^- \qquad (19)$$

$$\cdot CHCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \cdot CCl_3 \qquad (20)$$

$$Cl^- + Pd_2Br_6^{2-} \rightleftharpoons Pd_2Br_5Cl^- + Br^- \qquad (21)$$

HCl could potentially be generated upon the rereduction of the $Pd_2Br_6^-$ intermediate, by direct oxidation of Cl^- to chlorine atoms, followed by hydrogen abstraction from chloroform. The reduction of $Pd_2Br_6^-$, or a mixed $Pd_2Br_{6-n}Cl_n^-$, could also generate bromine atoms which would terminate as CCl_3Br.

$$Pd_2Br_6^- + Cl^- \longrightarrow Pd_2Br_6^{2-} + Cl\cdot \qquad (22)$$

$$Pd_2Br_6^- + Br^- \longrightarrow Pd_2Br_6^{2-} + Br\cdot \qquad (23)$$

Though this mechanism reproduces most of the observable aspects of the photodissociation mechanism, there are several arguments against it. One is that LMCT bands are not well suited to cause photooxidation of the metal. There are other examples of halometallates that undergo photooxidation, but it appears that a charge-transfer-to-solvent excited state, in the midst of LMCT states, is responsible [53]. Another point is that the time development of the rate of HCl production does not fit well. Chloride would be predicted to begin forming immediately from the photoreduction of chloroform, and would be available for oxidation by the $Pd_2X_6^-$ intermediate to chlorine radicals and subsequent hydrogen abstraction to yield HCl. Because $Pd_2X_6^-$ ought to be highly reactive, it should rapidly reach a steady state concentration, which means that by charge balance the concentration of halide ions could not increase steadily, which is one way a steadily increasing rate of HCl production might have occurred.

5. Conclusions

The photochemical conversion of $Pd_2Br_6^{2-}$ to $Pd_2Cl_6^{2-}$ in chloroform under broadband, $\lambda > 320\,nm$, irradiation causes chloroform decomposition at an accelerating, then decelerating rate. In the process, the bromine atoms are incorporated into CCl_3Br. The observations appear to be best explained by a mechanism involving homolytic photodissociation of bromine and chlorine atoms from $Pd_2Br_nCl_{6-n}^{2-}$ complexes together with chlorine abstraction from $CHCl_3$ by the $Pd_2X_5^{2-}$ intermediates.

Acknowledgement

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