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Photochemistry of Complex Ions. X. $Pt(C_2H_4)Cl_3^-$

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Abstract: The photochemistry of Zeise's salt exhibits several unusual features. Zeise's salt, $Pt(C_2H_4)Cl_3^-$, is the first Pt(II) square-planar complex to exhibit an *antithermal* photoreaction, photoaquation of ethylene in the present case. The dominant thermal reaction is, by contrast, aquation of the trans chloride. In addition, cis chloride aquation occurs, both thermally and photochemically. The wavelength dependence of the quantum yields indicates that the first absorption features, presumably due to transitions to excited triplet states, are *not* photoactive; this is again rather unusual behavior. The photoaquation of ethylene is sensitized by acetone and acetophenone, but not that of cis chloride. It appears, consequently, that the ethylene aquation derives from the first excited singlet state and that of a cis chloride from a hot ground-state reaction. Alternatively, it is possible that a nonspectroscopic triplet excited state is responsible for the ethylene aquation, and the first excited singlet state for that of cis chloride. The first explanation is preferred, but further theoretical study of the excited-state system is needed.

The substitutional photochemistry of square-planar Pt(II) complexes has appeared so far to consist largely of photoaccelerations of thermal reactions. This is true for the series $Pt(NH_3)_{4-x}Cl_x^{2-x}$ for which only photoaquation of chloride is observed;[1-4] quantum yields are a few tenths and are relatively independent of which low-intensity ligand-field band is irradiated, although in the case of $Pt(NH_3)Cl_3^-$ the proportion of cis to trans chloride photoaquation is somewhat different from that for the thermal reaction.[4] In addition, photoisomerization has been reported to occur with $Pt(NH_3)_2(H_2O)_2^{2+}$,[1] $Pt(P(C_2H_5)_3)_2Cl_2$,[5] Pt(glycine)$_2$,[2,6] and Pt(pyridine)$_2$Cl$_2$.[7]

It has been proposed, especially in connection with the last set of examples, that the photoreaction proceeds through a highly distorted and perhaps tetrahedral excited state.[5-7] The conclusion has been drawn partly on the grounds that the isomerizations appear not only to be intramolecular and, in the case of Pt(glycine)$_2$, to occur without even partial detachment of a ligand. Also, however, theoretical support has come from an interpretation of the absorption spectrum of $PtCl_4^{2-}$ which assigned the equilibrium configuration of certain excited states as tetrahedral,[8] and of the spectrum of another d^8 system, $Ni(CN)_4^{2-}$, for which case it was concluded that certain transitions terminate on a potential surface of D_{2d} equilibrium symmetry.[9]

If the distorted excited-state mechanism is a general one, then the photochemistry of Pt(II) complexes is essentially a study of the reaction chemistry of tetrahedral or near-tetrahedral rather than of square-planar forms. The present investigation was undertaken to determine whether the photochemistry of a complex having at least one strongly π-bonded ligand shows peculiarities that strengthen (or weaken) the evidence for such a general mechanism. The relative strengths of σ and π bonding should be considerably altered with

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(2) V. Balzani and V. Carassiti, *ibid.*, 72, 383 (1968).

(3) J. R. Perumareddi, Ph.D. Dissertation, University of Southern California, 1962, p 83.

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(9) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *ibid.*, 4, 514 (1965).

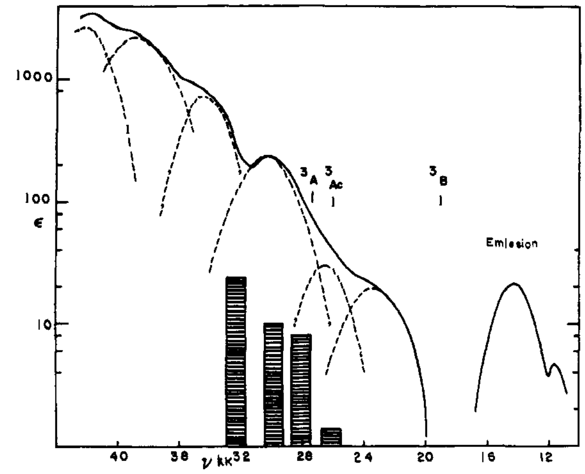

Figure 1. Absorption and emission spectra for Zeise's salt. Emission intensity, in arbitrary units, is plotted on a logarithmic scale. The superimposed bar diagram shows the quantum yields for ethylene aquation over the indicated width of wavelengths; the bars are linearly proportional to the quantum yields. The ties marked ^{3}A, ^{3}Ac, and ^{3}B locate the wavelengths for the lowest triplet states of acetone, acetophenone, and biacetyl, respectively.

any major change in molecular symmetry and therefore possibly also the reaction chemistry of the molecule.

Zeise's salt, $KPt(C_2H_4)Cl_3$, is a well-established compound which appears to meet the above specifications. The ethylene is known to be oriented at a right angle to the plane containing the Pt–Cl bonds.[10] Moreover, the bonding of the ethylene has been viewed as σ bonding to the platinum with strong back π bonding into the ethylene π^* orbital,[11] and this qualitative picture is supported by a semiempirical molecular orbital calculation.[12]

Zeise's salt is interesting from the point of view of reaction kinetics in that it exhibits a very marked trans effect, that is, the chloride trans to the ethylene is especially labile, and in aqueous solution the equilibrium

$$Pt(C_2H_4)Cl_3^- + H_2O \overset{K_1}{\rightleftharpoons} trans\text{-}Pt(C_2H_4)(H_2O)Cl_2 + Cl^- \quad (1)$$

is established within the time of dissolving of the salt. The reported value for K_1 is 3.0×10^{-3} M.[13] (See ref 14 for a discussion of the trans effect.) Thermal aquation of the ethylene is not observed, but slow aquation of a cis chloride has been reported[13,15]

$$Pt(C_2H_4)Cl_3^- + H_2O \underset{k_{-2}}{\overset{k_2,\ K_2,\ \phi_2}{\rightleftharpoons}} cis\text{-}Pt(C_2H_4)(H_2O)Cl_2 + Cl^- \quad (2)$$

with $k_2 = 2.9 \times 10^{-6}$ sec^{-1} and $K_2 \leq 4.5 \times 10^{-4}$ M. The aquation of $trans$-$Pt(C_2H_4)(H_2O)Cl_2$ to give $Pt(C_2H_4)(H_2O)_2Cl^+$ is slow, the rate constant being reported to be 2.8×10^{-5} sec^{-1}.[15] (All of the above data are for 25°.) The above reactions are best studied in acid solution; in neutral or alkaline media redox decomposition of Zeise's salt occurs.[11,16]

The "normal" photochemical reactions of Zeise's salt should thus be reaction 1, unobservable with ordinary photolysis techniques because of the speed of the back anation reaction, and reaction 2. As will be seen, we find an important component of the photochemistry to be the *antithermal* reaction

$$H_2O + Pt(C_2H_4)Cl_3^- \xrightarrow{h\nu} Pt(H_2O)Cl_3^- + C_2H_4 \quad (3)$$

Experimental Section

Preparation of Zeise's Salt. The method of preparation of Zeise's salt was based on modifications suggested by Cramer.[17] A 4.15-g amount of K_2PtCl_4 (Alfa Chemicals, New York) was dissolved in a mixture of 20 ml of water and 2.5 ml of concentrated hydrochloric acid. Ethylene gas (CP from Matheson) was passed through the solution in such a manner as to sweep air from the reaction vessel. A 0.1-g amount of reagent grade stannous chloride was added and the bubbling of ethylene through the solution was continued for 12 hr. On cooling to 4°, a crop of bright yellow crystals appeared; the supernatant was decanted under a nitrogen atmosphere (and the decanted solution used as the solvent in subsequent preparations), and the crystals were washed in cold 1% methanolic hydrochloric acid and recrystallized from this same solvent. They were then dried over magnesium perchlorate.

Absorption and Emission Spectra. Sensitization Experiments. The absorption spectrum of the above preparation was obtained by means of a Cary Model 14A spectrophotometer, and is shown in Figure 1. The extinction coefficients at 330 and 240 nm are 240 and 3500 cm^{-1} M^{-1}, respectively; these are 10% higher than the values reported by Lokken and Martin,[15] but the entire spectrum closely matches theirs if corrected by the 10% factor.

The solid shows a broad emission when irradiated with a Hg lamp using filters (aqueous $NiSO_4$ plus a Corning CS 7-54 filter) which pass 250–350-nm light.[18] Also shown in Figure 1, this emission peaks at 700 nm; the wing at around 875 nm is reproducible and is probably not instrumental. Emission yields were not obtained, but are low, and none could be detected in room-temperature aqueous solution.

Emission spectra of acetone and of biacetyl were obtained by means of an Aminco spectrofluorimeter. The acetone and acetophenone used were analytical reagent quality and the biacetyl was purified by distillation (87.5–88.0°). Sensitization experiments were carried out under the same solvent conditions as the compared direct photolyses, but with sufficient sensitizer present to absorb at least 99% of the incident radiation.

Irradiation Procedures. The light sources used for irradiations in the near-ultraviolet were a G.E. AH6 mercury lamp with Pyrex optics, a Hanovia medium-pressure No. 673A mercury lamp with quartz optics, or a PEK lamp with quartz optics. Irradiations at 254 nm were made with the latter lamp or with a pen ray lamp (Ultra-violet Products, Inc.); this last was used unfiltered as 90% of its output is at 254 nm. The general irradiation train was similar to that previously described.[19]

The filter combinations used for monochromatization are listed in Table I; these gave a band pass of about ±10 nm around the indicated wavelength. Ferrioxalate actinometry[20] was employed for the light intensity determinations, correcting where necessary for any difference in the degree of light absorption between the actinometric and the Zeise's salt solutions. Most irradiations were carried out in a 5-cm-path-length cylindrical spectrophotometer cell equipped with a jacket which allowed thermostating to ±0.5°.

Ethylene Analysis. Direct analysis for photoproduced free ethylene was made by means of a modification of the method of Miller and Pearman.[21] Water-saturated helium gas was bubbled through the irradiated solution and thence through a liquid nitrogen cooled trap containing 1 ml of a solution consisting of 5 g of potassium bromide, 1 ml of bromine, and 300 ml of acetic acid. After 20 min the helium flow was stopped and the trap was closed off from the irradiated solution and evacuated. The system was then allowed to warm to room temperature, the ethylene now reacting with the bromine. After 15 min of shaking (in the dark), an excess

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[12] J. W. Moore, *Acta Chem. Scand.*, 20, 1154 (1966).

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Table I. Ethylene Photoaquation of Zeise's Salt

Irradiation wavelength, nm	Filter combination[a]	Concentration, M Complex	HCl	Temp, °C	% reaction[b]	ϕ_3[c]
420	CS-3-73 + BL 410	0.01	0.75	25	0	$<10^{-4}$
		2.5×10^{-3}	0.065	5	0	$<10^{-4}$
410	CS-4-67 + BL-410	0.01	0.75	25	0	$<10^{-4}$
385	CS-4-96 + BL-380	2.5×10^{-3}	0.75	25	0.93	0.008
345	CS-4-96 + BL-520	2.5×10^{-3}	0.75	25	3.5	0.066
340	BL-520 + BL-670	2.5×10^{-3}	0.75	25	3.72	0.078
		2.5×10^{-3}	0.50	20	8.6	0.057
		2.5×10^{-3}	0.50	28	9.0	0.060
		2.5×10^{-3}	0.50	36	9.0	0.090
305	OT-305	2.5×10^{-3}	0.75	25	5.1	0.100

[a] CS, Corning glass filter; BL, Bausch and Lomb interference filter; OT, Optics Technology interference filter. [b] Per cent of ethylene aquation. [c] Quantum yield for ethylene aquation.

of 10% aqueous potassium iodide was added to the contents of the trap and the liberated iodine was titrated with standard thiosulfate solution to a starch end point. The amount of ethylene present was calculated from the loss of bromine titer.

To test the procedure, a dose of ethylene was measured in a gas buret and then swept with helium through the trap as described above; the amount was determined by the titration procedure. Four determinations were made, using millimolar amounts of ethylene; the titration gave results 8% low on the average, perhaps due to incomplete trapping of the ethylene.

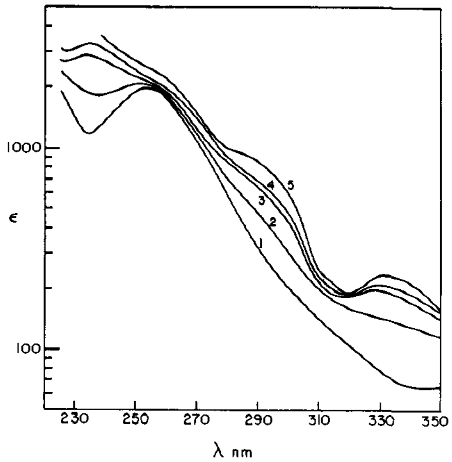

Figure 2. Spectral changes on anation of *cis*-$Pt(C_2H_4)(H_2O)Cl_2$; 1, initial; 2–4, after 4, 20, and 40 hr; 5, Zeise's salt.

Separation of *cis*-$Pt(C_2H_4)(H_2O)Cl_2$. The following procedure was used to identify qualitatively the presence of *cis*-$Pt(C_2H_4)(H_2O)Cl_2$ in irradiated solutions of Zeise's salt. A 5×10^{-3} M solution of the latter in 0.1 M hydrochloric acid was irradiated with light of wavelength greater than 320 nm, to about 20% reaction; the solution was then added to an anion-exchange column (Biorad AG1-X4, 100–200 mesh, perchlorate form). The column had previously been washed until the effluent showed no absorption at wavelengths longer than 220 nm.

The first portion of the irradiated solution to pass through the column yielded the absorption spectrum shown in Figure 2. Zeise's salt is absorbed under the conditions of the experiment and the initial effluent should contain only the monoaquo product. On making the effluent 1 M in chloride ion, the spectrum changed with time and in 40 hr became identical with that of Zeise's salt, as also shown in the figure. The ordinate gives apparent molar extinction coefficients, based on a determination of the Pt(II) content of the solution by a colorimetric method.[22] The solution was too dilute for isolation and confirmatory elemental analysis of the product as a solid, but we feel that curve 1 does represent the absorption spectrum of essentially pure *cis*-$Pt(C_2H_4)(H_2O)Cl_2$.

Preliminary Experiments. Our solutions were always about 0.1 M (or more) in hydrochloric acid, under which conditions Zeise's salt is indefinitely stable. The acidity inhibits the redox decomposition mentioned earlier and the excess chloride ion drives equilibrium 1 to the left.

Two types of preliminary experiments were made. In the first, a solution 2.5×10^{-3} M in complex and 0.75 M in hydrochloric acid was irradiated using light of wavelength greater than 320 nm, for various periods of time. The irradiated solutions were then allowed to stand in the dark for 2–3 hr for chloride anation of aquo products to be complete (this was more than adequate, as the optical density did not change appreciably after 15 min). The sequence of absorption spectra that resulted is shown in Figure 3, along with the spectrum of Zeise's salt and of $PtCl_4^{2-}$. Both the presence of isosbestic points and the detailed shapes indicate that the solutions consisted of mixtures of the last two complexes only. (The presence of $PtCl_4^{2-}$ was also confirmed qualitatively by precipitating it as the green Magnus' salt, $[Pt(NH_3)_4][PtCl_4]$. We interpret the appearance of $PtCl_4^{2-}$ to mean that photoreaction 3 occurs, the product $Pt(H_2O)Cl_3^-$ being rapidly anated under our conditions.

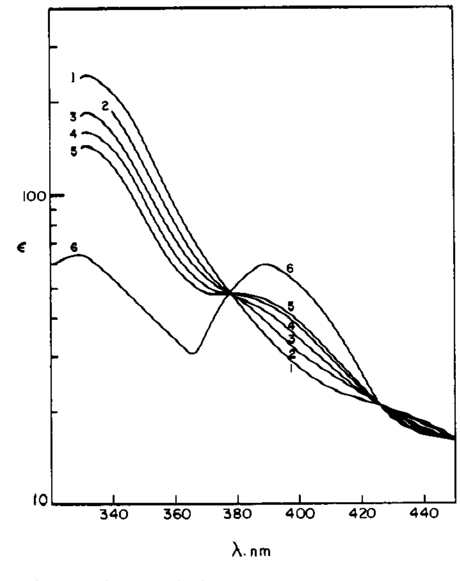

Figure 3. Photolysis of Zeise's salt at 320–350 nm; 2.5×10^{-3} M complex, 0.75 M HCl: 1, initial spectrum; 2–5, spectra following successively longer irradiations; 6, spectrum of $PtCl_4^{2-}$.

Direct confirmation of the above conclusion was desirable, however, and the presence of released ethylene was first established qualitatively as follows. About 100 ml of a solution 5×10^{-3} M in complex and 0.75 M in hydrochloric acid was irradiated as before, but in a flask closed off by means of a stopcock. The flask was then connected to a vacuum line through a liquid nitrogen trap, and the dissolved gases were discharged by repeated freeze–thaw cycles under vacuum. The trap was then warmed to Dry Ice temperature and the evolved gas, which contained nothing less

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[22] E. B. Sandell, "Colorimetric Metal Analysis," 3rd ed, Interscience, New York, N. Y., 1959.

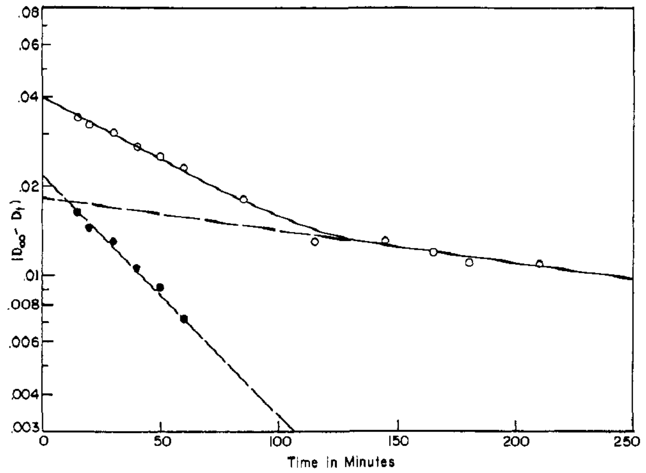

Figure 4. Photoaquation of Zeise's salt; 2.5×10^{-3} *M* complex, 0.065 *M* HCl, 305 nm, 5°: ○, optical density of irradiated solution at 235 nm and 25°; ●, $PtCl_3(H_2O)^- + Cl^- \rightarrow PtCl_4^{2-}$; —, *cis*-$Pt(C_2H_4)(H_2O)Cl_2 + Cl^- \rightarrow Pt(C_2H_4)Cl_3^-$.

volatile than ethylene, was collected in a second liquid nitrogen trap and then transferred to an infrared spectrophotometer cell. The observed spectrum was identical with that of a sample of pure ethylene.

As a more quantitative check on the use of spectral changes to follow ethylene aquation, two runs were made in which the irradiated solution was analyzed for ethylene by the titration procedure, giving 2.72×10^{-4} *M* and 4.03×10^{-4} *M* produced ethylene. The optical densities of the same irradiated solutions were then measured at 330 nm and gave 3.08×10^{-4} *M* and 4.05×10^{-4} *M* as the respective concentrations of $PtCl_4^{2-}$ and hence of photoproduced $Pt(H_2O)Cl_3^-$. The results established that our interpretation of the photochemistry is correct and the indirect spectrophotometric procedure, being more precise, was used in all further measurements of ethylene photoaquation.

Results

Wavelength and Temperature Dependence of Ethylene Photoaquation. The runs summarized in Table I were made with the indicated filter combinations and using the AH6 lamp, except for the one at 305 nm, for which the Hanovia source was employed. The optical density at 330 nm (after standing) allowed determination of the amount of $PtCl_4^{2-}$ present and hence of the degree of ethylene photoaquation (as described in the Experimental Section).

The quantum yield, ϕ_3, is essentially zero over the long-wavelength feature of the absorption spectrum, but rises sharply at around 360 nm or as the first absorption maximum (at 330 nm) is approached. The trend is shown in Figure 1. The results of irradiations at wavelengths below 305 nm are described further below. The data of Table I also show that ϕ_3 is essentially temperature independent; nor was it affected by deaeration of the solution.

Chloride Aquation. Direct photolysis procedures did not allow the determination of whether any photoaquation of trans chloride occurs, because of the need to use high chloride ion concentrations in repressing reaction 1. Under this condition complete anation of any *trans*-$Pt(C_2H_4)(H_2O)Cl_2$ occurs on a time scale very short compared to that of the irradiation. An attempt to measure this rate by a stopped-flow experiment in which a low-chloride Zeise's salt solution was mixed with a high-chloride one showed the anation to be fast on a millisecond time scale (the apparatus of ref 23 was used).

We could observe photoaquation of cis chloride, however. The procedure followed was to irradiate solutions 2.5×10^{-3} *M* in complex and 0.065 *M* in HCl, the latter concentration being such as to give the maximum equilibrium concentration of *trans*-$Pt(C_2H_4)(H_2O)Cl_2$ which we felt to be tolerable, about 5%. To further reduce the rate of back anation of *cis*-$Pt(C_2H_4)(H_2O)Cl_2$, the irradiations were conducted at 5° and were limited to 10-min duration.

After each irradiation, the solution was brought rapidly to 25° and made 0.25 *M* in HCl. The thermal anation reactions were then followed spectrophotometrically, using the optical density change at 235 nm, this being the wavelength of maximum difference in extinction coefficient between *cis*-$Pt(C_3H_4)(H_2O)Cl_2$ and Zeise's salt (note Figure 2). The cells were thermostated at 25 ± 0.1°. A typical semilogarithmic plot of the $(D_\infty - D_t)$ values as obtained *vs.* time is shown in Figure 4. The plot analyzes into two straight-line portions, the steeper of which corresponds to anation of $Pt(H_2O)Cl_3^-$ (A) and the other to that of *cis*-$Pt(C_2H_4)(H_2O)Cl_2$ (B). The actual rate expression is

$$D_\infty - D_t = (\epsilon_Z - \epsilon_A)C_A{}^0e^{-k_{-5}t} + (\epsilon_Z - \epsilon_B)C_B{}^0e^{-k_{-2}t} \quad (4)$$

where Z denotes Zeise's salt and superscript zero indicates the concentration of indicated species at the end of the irradiation. Each experiment then yielded a value of k_{-2} and of k_{-5}

$$Pt(H_2O)Cl_3^- + Cl^- \xrightarrow{k_{-5}} PtCl_4^{2-} + H_2O \quad (5)$$

Our average values from several runs are $k_{-5} = (4.8 \pm 0.7) \times 10^{-3}$ sec^{-1} M^{-1} and $k_{-2} = (3.5 \pm 0.5) \times 10^{-4}$ sec^{-1} M^{-1}. The latter value agrees with the estimate of *ca.* 10^{-3} sec^{-1} M^{-1} from the data of Lokken and Martin,[15] and the former compares well with the range of values in the literature,[24] 1.2×10^{-3}–2.8×10^{-3} sec^{-1} M^{-1}.

The intercepts of the straight-line components are proportional to the concentrations of A and of B present immediately after photolysis, and the actual concentrations were obtained using the extinction coefficients at 235 nm of 3160, 7120,[2] 1620,[24d] and 1190 cm^{-1} M^{-1} for Zeise's salt, $PtCl_4^{2-}$, A, and B, respectively. The analysis is somewhat approximate—the absolute concentrations of A differed from those determined by spectrophotometry on the completely anated solutions (as described in connection with Table I) by about 20%. The procedure does serve to give reproducible concentrations and quantum yields, however.

We find ϕ_2/ϕ_3 to be 1.8 ± 0.1 at 340 nm and 1.4 ± 0.1 at 305 nm, from three experiments at each wavelength. In combination with the results given in Table I, the sum $\phi_2 + \phi_3$ is then 0.22 and 0.24 at the two wavelengths, respectively, at 25°, and assuming the ratios not to be appreciably temperature dependent. No cis

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(23) P. H. Tewari, R. H. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, 6, 611 (1967).

(24) (a) L. F. Grantham, T. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, 77, 2965 (1955); (b) A. A. Grinberg, G. A. Shagisultanova, and M. I. Gelfman, *Sv. Kem. Tidskr.*, 73, 18 (1961); (c) A. A. Grinberg and Y. N. Kukushkin, *Zh. Neorg. Khim.*, 6, 306 (1961); (d) L. I. Elding, *Acta Chem. Scand.*, 20, 2559 (1966).

aquation could be detected in an irradiation at 410 nm, ϕ_2 being less than 10^{-4}.

Photolysis at 254 nm. Irradiation of a solution 2.5 $\times 10^{-3}$ *M* in Zeise's salt and 0.75 *M* in HCl with the pen ray lamp, or essentially with 254-nm radiation, led to an entirely different sequence of spectral changes than did the longer wavelength irradiations. For example, the absorption at 360 and below 320 nm increased, in contrast to the behavior when >320-nm irradiation was used. Anation or other postphotolysis reactions were complete within a few minutes after stopping the irradiation, and these spectra were stable for at least 10 hr.

A possibility is that 254-nm radiation leads to some redox decomposition. To test this, the irradiated solution was evaporated at 40° to a small volume and then saturated with CsCl, as a likely precipitant for any Pt(IV) species present. Some precipitate formed which was centrifuged out and dissolved in water; the spectrum of this last solution corresponded closely to that of $PtCl_6^{2-}$. The separation procedure was not quantitative, and the quantum yield for the redox process can only be estimated as about 10^{-3}. The stoichiometry of the process was not determined.

Sensitization Experiments. Biacetyl phosphorescence (stimulated by 410-nm light) is efficiently quenched by Zeise's salt; 5×10^{-5} *M* complex in 0.5 *M* HCl and 0.2 *M* biacetyl reduces the emission intensity by two-thirds. The fluorescence is not affected, however. No detectable sensitized reaction of the complex occurred, the yield for either process 2 or 3 being $<10^{-4}$.

Acetone shows only fluorescence in room-temperature aqueous solution, and its emission is unaffected by up to 10^{-3} *M* complex, using 310-nm exciting radiation. Acetone does, however, sensitize reactions of Zeise's salt. Irradiation at 305 nm of solutions 0.05 *M* in HCl, 5×10^{-4} *M* in complex, and 0.40 *M* in acetone led to spectral changes resembling those following direct 254-nm irradiation of the complex and suggestive of the production of Pt(IV) species as well as of ethylene aquation. A similar observation was made using acetophenone as sensitizer.

Acetone is subject to photodecomposition, the products including methyl radical,[25] and it is possible that the complicating presence of Pt(IV) is due to a chemical mechanism. A second series of experiments was therefore carried out with 0.1 *M* methyl methacrylate also present as a radical scavenger. The spectrum of the photolyzed solutions (above 325 nm) now corresponded to those of mixtures of Zeise's salt and $PtCl_4^{2-}$ only, which allowed spectrophotometric determination of the degree of ethylene aquation.

The Stern-Volmer plot (see Discussion) of the resulting yields is shown in Figure 5; there was no appreciable effect of acetone concentration. The slope and intercept are 1.9×10^{-3} M^{-1} and unity, respectively.

Discussion

Excited-State Assignments. The absorption spectrum of Zeise's salt consists of a series of overlapping bands ascending in intensity toward the ultraviolet, and the positions of the true band maxima were estimated by formulating a best set of gaussian components (using a Du Pont curve analyzer), as shown in Figure 1. The long-wavelength shoulder could be represented by one instead of two components, although less credibly. The maxima presumably correspond to transitions terminating on high vibrational levels of one or another excited state and hence to Franck-Condon rather than to pure electronic excited states. Symbol designations for the latter will carry a right superscript zero.

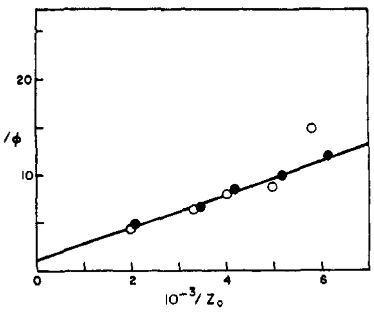

Figure 5. Quantum yields for the acetone-photosensitized ethylene aquation of Zeise's salt as a function of concentration, at 25°: ○, 1.6 *M* acetone; ●, 1.33 *M* acetone.

A ligand-field treatment for Zeise's salt has been made by Moore.[12] While the Franck-Gordon excited-state energies calculated by him differ considerably from the observed values, we assume, *faute de mieux*, that the theoretical ordering is correct for the purpose of making assignments. These are summarized in Table II. As a less specific terminology than Moore's and one not tied to representations of an assumed point group, we denote spin-allowed d-d (or ligand field) absorption bands as L_1, L_2, etc., in order of increasing energy of the band maxima, and, similarly, charge-transfer absorptions as CT_1, CT_2, etc. Following a practice that has been useful in the case of Cr(III) complexes,[26] spin-forbidden ligand-field transitions are designated in terms

Table II. Excited States of Zeise's Salt

Absorption spectrum components State[a]	Energy, kcal mol^{-1}	Description in C_{2v}[b] Term[c]	Single-electron[c] MO	Quantum yield for aquation ϕ_3[d]
$^3T_1{}^0$	56			$<10^{-4}$
$^3T_1$	67	$^1A_1 \rightarrow {}^3A_2$	$2a_2 \rightarrow 8a_1$	$<10^{-4}$
$^3T_2{}^0$	67			$<10^{-4}$
$^3T_2$	76	$^1A_1 \rightarrow {}^3A_2$	$5b_1 \rightarrow 4b_2$	0.02
$^1L_1{}^0$	75			0.02
$^1L_1$	86	$^1A_1 \rightarrow {}^1A_2$	$2a_2 \rightarrow 8a_1$	0.09
$^1L_2{}^0$	90			0.095
$^1L_2$	99	$^1A_1 \rightarrow {}^1A_2$	$5b_1 \rightarrow 4b_2$	0.11
$^1CT_1{}^0$	98			(0.11)
$^1CT_1$	111			(Redox)
$^1CT_2{}^0$	111			(Redox)
$^1CT_2$	120			(Redox)

[a] States without superscript zero refer to band maxima (Franck–Condon states); those with superscript are true electronic states with energy estimated as that at an extinction coefficient which is 5% of the value of the band maximum. [b] See ref 28. [c] Presumed transitions corresponding to band maxima. [d] Interpolated from values in Table I and merely corresponding to the wavelength of the indicated energy.

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(25) R. D. Doepker and G. J. Mains, *J. Amer. Chem. Soc.*, **83**, 294 (1961).

(26) J. E. Martin and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).

of the spin multiplicity of the excited state, T for triplet in the present case. Finally, if a symbol refers to the excited state rather than to the transition to it from the ground state, the excited-state multiplicity is given as a left superscript. The above nomenclature is included in Table II.

Since there is no appreciable emission in room-temperature solution (and since quantum yields are relatively low), all of these excited states must degrade primarily by radiationless deactivation processes. The low-temperature emission of the solid (Figure 1) lies so far to the red that it seems reasonable to regard it as emanating from the $^3T_1{}^0$ state. Even so, the large Stokes' shift indicates that there is considerable excited-state distortion.[27] Thus, half the difference between $^3T_1$ and the energy of maximum emission gives 13 kcal mol^{-1}. In the absence of emission, experience with Cr(III) complexes suggests that a useful measure of such distortion is the energy difference between the band maximum and the point at which the extinction coefficient is 5% of that at the maximum.[28] Application of this rule gives $(^3T_1 - {}^3T_0{}^0) = 11$, $(^3T_2 - {}^3T_2{}^0) = 9$, $(^1L_1 - {}^1L_1{}^0) = 12$, $(^1L_2 - {}^1L_2{}^0) = 9$, and $(^1CT_1 - {}^1CT_1{}^0) = 13$ kcal mol^{-1}. On this basis all of the excited states show similar distortion energies.

Photochemical Assignments. An interesting problem arises in considering what states can be assigned as immediate precursors to chemical reaction. The direct irradiation results indicate that neither the $^3T_1$ nor $^3T_2$ state is chemically active with respect to either ethylene or cis chloride aquation. Both modes of reaction could, however, be assigned to the $^1L_1$ and $^1L_2$ or $^1L_1{}^0$ and $^1L_2{}^0$ states; if these last are taken to be near-tetrahedral in geometry, considerable bond weakening, especially of the Pt–C_2H_4 bond, should occur.

The bonding of ground-state Zeise's salt has been the object of considerable discussion, most recently by Wheelock and coworkers.[29] The platinum d_{xz} and d_{yz} orbitals are regarded as strongly π bonding with the $p\pi$ orbitals of the ethylene. In tetrahedral geometry, however, the platinum d_{xy}, d_{xz}, and d_{yz} orbitals as a group form a basis for the main σ-bonding framework of the molecule, and there are no σ-nonbonding d orbitals of suitable geometry for π bonding with ethylene. It is thus reasonable that the Pt–C_2H_4 bond would be weak in a tetrahedral excited state and that ethylene aquation should be observed. One could, in fact, suppose that the Pt–C_2H_4 and the Pt–Cl σ bonds are comparable in strength and that bond breaking in the excited state is roughly statistical, thus accounting for the 1.4 to 1.8 ratio of cis chloride to ethylene aquation.

The sensitization results require an important modification of the above suppositions. First, the lack of any acetone fluorescence quenching by the complex implies that the sensitized ethylene aquation involves the first triplet state of acetone. The same is presumably true for acetophenone. The lack of any sensitization by biacetyl implies that the phosphorescence quenching does not involve excitation energy transfer to the complex. The energies of these three sensitizer triplet states are located on Figure 1, and it appears that either acetone or acetophenone could populate the $^1L_1{}^0$ (or the $^3T_2$) state of the complex, but that biacetyl could at best populate the $^3T_1{}^0$ state. The lack of any sensitized reaction in this last case is consistent with the lack of any direct photochemistry for the T_1 band. Further, the absence of any observable photochemistry on irradiating the T_2 band suggests that it is not the $^3T_2$ (or $^3T_2{}^0$) state that is populated by acetone and acetophenone, but only the $^1L_1{}^0$ one.

A problem develops on considering the detailed acetone sensitization results, however. We assume the scheme

$$S_0 \xrightarrow{h\nu} S_1 \xrightarrow{\phi_T} T_1$$

$$T_1 \xrightarrow{k_d} S_0 \text{ (deactivation by medium)}$$

$$T_1 + Z \xrightarrow{k_q} S_0 + Z^*$$

$$Z^* \xrightarrow{\phi_Z} \text{ethylene aquation}$$

where S and T denote sensitizer singlet and triplet states, respectively. Stationary-state analysis yields the relationship

$$1/\phi = 1/\phi_T\phi_Z + (k_d/k_q\phi_T\phi_Z)\beta(1/Z^0) \qquad (6)$$

where ϕ is the observed sensitization yield and ϕ_Z is the fraction of encounters of Zeise's salt with triplet-state acetone which leads to ethylene aquation. Z_0 is the initial complex concentration and β is a term close to unity which allows for consumption of complex during photolysis.[30]

The sensitization data are plotted according to eq 6 in Figure 5, and the near-unity intercept implies that ϕ_Z and ϕ_T are separately close to unity. The intersystem-crossing yield for acetone has indeed been reported as very high.[31] The lifetime of the acetone triplet state, τ, is given as 4×10^{-7} sec,[31] and from the slope of the plot, 1.77×10^{-3} *M*, we find $k_q = 1.4 \times 10^9$ sec^{-1} M^{-1}. This value is only somewhat below the diffusion-controlled rate as estimated in the usual way[32] (subject to the uncertainty that τ is for *n*-hexane rather than water as solvent).

The situation is thus that the only state of Zeise's salt which appears to be populated by the acetone triplet is the $^1L_1{}^0$ state, and the sensitization data indicate that this state proceeds to ethylene aquation with high efficiency. While this is indeed reasonable in terms of the bonding analysis made earlier, there remains the matter of the cis chloride aquation found on direct photolysis. While it was not possible to apply our analytical procedure to determine *cis*-Pt(C_2H_4)(H_2O)Cl_2 under sensitization conditions (the scavenger absorbs too strongly at 235 nm), the fact that ϕ_Z is essentially unity precludes the presence of any appreciable sensitized cis chloride aquation.[33] We thus have the situation in which direct population of the $^1L_1$ state produces both reaction modes, while energy-transfer population of $^1L_1{}^0$ produces only ethylene aquation; nor does cis chloride

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[27] We assume the emission to be molecular in origin. Essentially the same emission peak is observed in a 50% aqueous ethylene glycol glass at 77°K using 450-nm stimulating radiation, although the detector was not sufficiently red sensitive to report in the region of the satellite shoulder, so the presence of the latter is not confirmed (private communication from J. Martin).

[28] P. D. Fleischauer and A. W. Adamson, unpublished work.

[29] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **92**, 5110 (1970).

[30] A. Vogler and A. W. Adamson, *ibid.*, **90**, 5943 (1968).

[31] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

[32] J. C. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1964.

[33] While the extrapolation in Figure 5 is fairly long, neither a least-squares nor any other reasonable fitting of a straight line allows an intercept appreciably greater than unity.

aquation proceed from any state seen in direct absorption.

As mentioned earlier above, there is enough latitude in the fitting of gaussian components to the absorption spectrum to allow the long-wavelength tail to be interpreted as due to a single, albeit rather broad, absorption band, T_1. It would then be possible that a *very weak* second absorption feature, $^3T_2$, is present between L_1 and T_1. A possible interpretation of our results is therefore that the ethylene aquation proceeds from the $^3T_2$ (or $^3T_2^0$) state, populatable either by intersystem crossing from $^1L_1$ state or by excitation energy transfer, but not by direct irradiation. In this latter case, the $^3T_1$ state dominates the absorption and is chemically inert. Cis chloride aquation would then be assigned to the $^1L_1$ (or $^1L_1^0$) state.

The above explanation, while entirely possible, seems forced. In particular, we see no reason why the extinction coefficient for the T_2 band should be about 10^{-3} of that of the T_1 band, as would be required to explain the quantum yield data. We prefer, therefore, to keep the more reasonable appearing gaussian analysis shown in Figure 1, and therefore to return to the conclusion that both the $^3T_1$ and $^3T_2$ are chemically inactive, and that it is the $^1L_1^0$ state which undergoes ethylene aquation. The sensitization results then imply that this state undergoes *only* such aquation, and we are driven to conclude that cis chloride aquation may be a hot ground-state reaction.

In summary, it appears that sensitization populates $^1L_1^0$, which undergoes only ethylene aquation, and direct irradiation either of the L_1 or L_2 bands leads in part to $^1L_1^0$ and in part to vibrationally excited ground-state Zeise's salt, which then undergoes chloride aquation. Since the L_1 band absorption represents an orbitally forbidden process and hence also radiationless deactivation from $^1L_1$, it is possible that in the latter asymmetric vibrational modes of the ground state are preferentially excited and that these are similar to those excited in the thermal activation process for chloride aquation.

The finding of redox decomposition on irradiation of the more intense and presumably CT_1 band is interesting in that oxidation of the central metal ion occurs, suggesting that the excitation is of the charge transfer to ligand type. The primary photolysis products could be Pt(III) and $C_2H_4^-$ (or $C_2H_5\cdot$ and OH^-) or Pt(IV) and $C_2H_4^{2-}$ (or C_2H_6 and 2 OH^-). We were unable, however, to determine the chemical state of the species reduced.

It remains to consider why the T_1 and T_2 states are neither chemically active nor populated by sensitizers. This evidence indicates that the states are not simply the spin-free equivalents of $^1L_1^0$ and $^1L_2^0$, as the assignments of Table II would suggest. Some further theoretical analysis is certainly indicated.

Excited *vs.* Chemical States. The above discussion has been couched in terms of excited states of square-planar Zeise's salt. In view of the extensive geometry change postulated, the $^1L_1^0$ state is really a different molecule from the ground-state complex and can alternatively be regarded as the very reactive *ground state* of *tetrahedral* Zeise's salt. The spectroscopic language that describes the radiationless deactivation process $^1L_1^0 \rightarrow {}^1A_1$ may now be rephrased as a thermal rate process whereby the tetrahedral form isomerizes to the square-planar one. In this second terminology, the $^1L_2^0$ state may represent the first excited state of the tetrahedral isomer. The chemical as opposed to the spectroscopic description of these states has perhaps the advantage of directing attention to the expected reaction chemistry. Another point is that the transition state of chemical kinetics may not always represent a very different chemical concept from that of the excited state of photochemistry. This is especially true of reactions showing chemiluminescence.

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