

inhibition of such reactions by hexachloroiridate(IV) has been attributed to rapid oxidation of platinum(III), but the evidence favoring the interpretations in question, while reasonable, has been for the most part indirect and qualitative. We now wish to report quantitative evidence for the intermediate formation of platinum(III) in the chemical oxidation of certain platinum(II) complexes and to describe some features of the chemistry of the intermediate platinum(III) species as revealed by observation of their competitive reactions including oxidation by hexachloroiridate(IV).

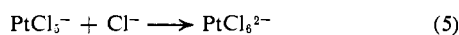
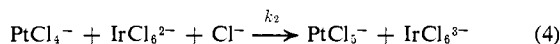
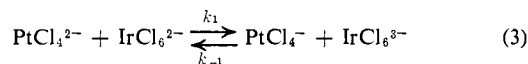
Our principal observations relate to the oxidation of tetrachloroplatinate(II) by hexachloroiridate(IV), according to eq 1, in aqueous sodium chloride–hydrochloric



acid solution. The stoichiometry of the reaction was established spectrophotometrically and the kinetics were determined, also spectrophotometrically, over the following initial concentration ranges of reactants and products: 4.0×10^{-5} to $2.5 \times 10^{-3} M$ PtCl_4^{2-} , 1.3×10^{-4} to $8.0 \times 10^{-4} M$ IrCl_6^{2-} , 0 to $8.0 \times 10^{-2} M$ IrCl_6^{3-} , 0.05 to $1.0 M$ Cl^- , 10^{-5} to $1.0 M$ H^+ . Throughout this combination of concentration ranges the kinetics of the reaction were accurately represented by the rate law, expressed by eq 2, which is derived,

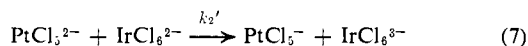
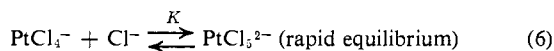
$$\frac{-d[\text{IrCl}_6^{2-}]}{dt} = \frac{-2d[\text{PtCl}_4^{2-}]}{dt} = \frac{2k_1 k_2 [\text{PtCl}_4^{2-}] [\text{IrCl}_6^{2-}]^2 [\text{Cl}^-]}{k_{-1} [\text{IrCl}_6^{3-}] + k_2 [\text{IrCl}_6^{2-}] [\text{Cl}^-]} \quad (2)$$

employing the steady-state approximation for PtCl_4^- , on the basis of the mechanism depicted by eq 3–5.



Our kinetic measurements at 25° , and an ionic strength of $1.0 M$, maintained with NaClO_4 , yield the values $k_1 = 0.62 \pm 0.03 M^{-1} \text{sec}^{-1}$ and $k_{-1}/k_2 = 9.0 \times 10^{-3} M$. The rate was unaffected by variation of the concentration of H^+ between 10^{-5} and $1 M$ and by the addition of up to $10^{-3} M$ PtCl_6^{2-} .

An obvious variant of this mechanism, which is kinetically indistinguishable from that depicted above, is one in which the termolecular step 4 is replaced by a sequence of bimolecular steps (eq 6 and 7). This



variant leads to a rate law identical in form with eq 2, in which k_2 is replaced by $k_2'K$. The observed value of $9.0 \times 10^{-3} M$ then refers to $k_{-1}/k_2'K$, instead of to k_{-1}/k_2 . Favoring this formulation is the recent direct observation⁴ of the formation of PtCl_5^{2-} in aqueous solution by dissociation of PtCl_6^{3-} following electron capture by PtCl_6^{2-} .⁴

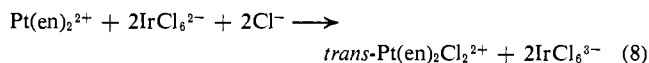
(1) R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).

(2) A. W. Adamson and A. H. Sporer, *ibid.*, **80**, 3865 (1958).

(3) A. J. Pöc and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).

(4) G. E. Adams, R. B. Broszkiewicz, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 1256 (1968).

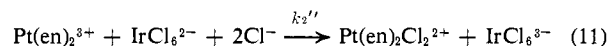
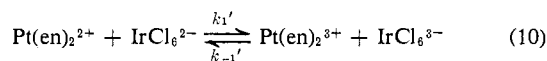
Using the stopped-flow method, we have also investigated the kinetics of the oxidation of $\text{Pt}(\text{en})_2^{2+}$ (en = ethylenediamine) by IrCl_6^{2-} (eq 8) and, in this case also,



found evidence for a stepwise mechanism involving an intermediate platinum(III) species, $\text{Pt}(\text{en})_2^{3+}$ (or, alternatively, $\text{Pt}(\text{en})_2\text{Cl}^{2+}$ or $\text{Pt}(\text{en})_2\text{Cl}_2^+$). Over the initial concentration ranges, 6.2×10^{-5} to $2.5 \times 10^{-4} M$ $\text{Pt}(\text{en})_2^{2+}$, 1.3×10^{-5} to $2.5 \times 10^{-5} M$ IrCl_6^{2-} , 0 to $1.0 \times 10^{-3} M$ IrCl_6^{3-} , 10^{-5} to $0.5 M$ H^+ , and 0.1 to $1.0 M$ Cl^- , the kinetics of this reaction accurately obeyed the rate law described by eq 9, which is derived,

$$\frac{-d[\text{IrCl}_6^{2-}]}{dt} = \frac{-2d[\text{Pt}(\text{en})_2^{2+}]}{dt} = \frac{2k_1' k_2' [\text{Pt}(\text{en})_2^{2+}] [\text{IrCl}_6^{2-}]^2 [\text{Cl}^-]^2}{k_{-1}' [\text{IrCl}_6^{3-}] + k_2' [\text{IrCl}_6^{2-}] [\text{Cl}^-]} \quad (9)$$

employing the steady-state approximation for $\text{Pt}(\text{en})_2^{3+}$, for the mechanism depicted by eq 10 and 11. Our kinetic



measurements (also at 25° and $1.0 M$ ionic strength, maintained with NaClO_4) yield the values $k_1' = (1.40 \pm 0.05) \times 10^5 M^{-1} \text{sec}^{-1}$ and $k_{-1}'/k_2' = 2.0 \times 10^{-2} M^2$. The $\sim 10^5$ -fold difference between the value of k_1 for PtCl_4^{2-} and k_1' for $\text{Pt}(\text{en})_2^{2+}$ is in the direction expected from the difference between the charges of the two reactants.

Preliminary kinetic observations also point to similar mechanisms for the oxidations of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ and $\text{PtCl}_2(\text{OH})_2(\text{C}_2\text{H}_4)$ by IrCl_6^{2-} . The reactivities of these complexes are lower than those of PtCl_4^{2-} and $\text{Pt}(\text{en})_2^{2+}$, presumably reflecting stabilization of the +2 oxidation state of platinum by the coordinated ethylene. The oxidation of these complexes is accompanied by release of the ethylene which does not itself undergo oxidation.⁵

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(5) P. B. Chock and J. Halpern, unpublished results.

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Photosensitized Decomposition of Some Cobalt Amines

Sir:

We wish to report the finding that the redox decomposition of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ in various aqueous and organic solvents is photosensitized by organic compounds known to have relatively stable triplet excited states. This effect, while foreshadowed

Table I. Systems Showing Sensitized Redox Decomposition of Co(III) Amines^a

Sensitizer	Solvent	Complex	Wavelength, $m\mu$
Benzil	80% ethanol-water	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{ClO}_4]_3$	350-370
<i>trans</i> -Stilbene-4-carboxylic acid	80% ethanol-water	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{ClO}_4]_3$	350-370
	3 M aqueous NaOH	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	350-370
Benzophenone	50% ethanol-water	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	
	Dimethylacetamide	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{ClO}_4]_3$	350-370
Biacetyl	50% ethanol-water	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	405-415
	Water	$\text{Co}(\text{NH}_3)_6\text{Cl}_3^b$	405-415

^a Ca. 0.01 M sensitizer and complex. ^b In very low efficiency.

by previous observations that coordination compounds can quench organic triplet state species,¹⁻³ does not seem to have been reported before.

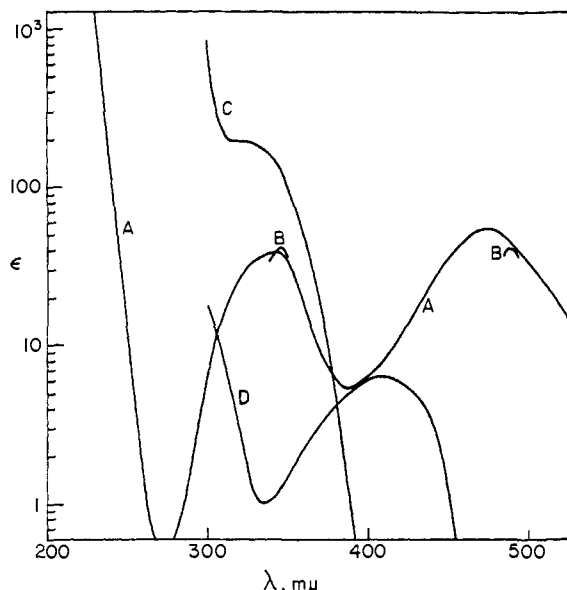


Figure 1. Absorption spectra: (A) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, (B) corresponding maxima for $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{ClO}_4]_3$, (C) benzophenone, (D) biacetyl. The latter two spectra are for 50% ethanol-water solutions.

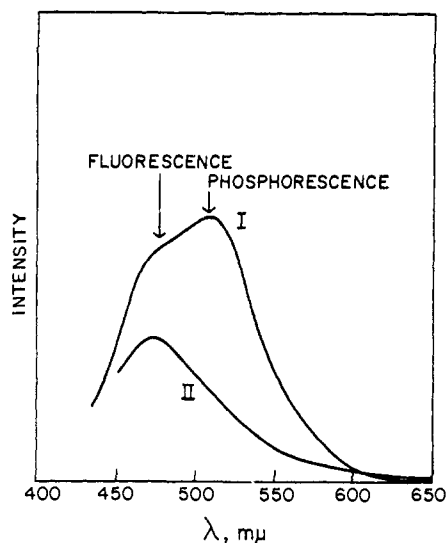


Figure 2. Emission spectra for 0.15 M biacetyl in 50% ethanol-water solution: (I) biacetyl alone; (II) with added 0.005 M $\text{Co}(\text{NH}_3)_6\text{Cl}_3$.

- (1) A. J. Fry, R. S. H. Liux, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966).
- (2) L. Lindquist, *Acta Chem. Scand.*, **20**, 2067 (1966).
- (3) See H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, **82**, 2411 (1960).

The above two complex ions are photosensitive in their own right. With 254- $m\mu$ light, both undergo photoredox decomposition to Co(II) and oxidized ammonia,⁴ the first with a quantum yield of about 0.9 and the second with one of about 0.07. The absorption band irradiated is the first charge-transfer (CT) one in both cases, as indicated in Figure 1. Irradiation of either the first or the second ligand field band gives only a trace of decomposition, the reported quantum yields being about 10^{-3} ⁵ and 5×10^{-4} ,⁶ respectively. The photosensitivity of these two complexes is thus confined to the CT band.

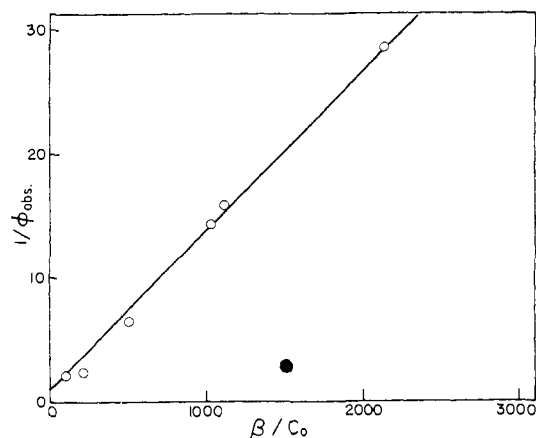


Figure 3. Data for the benzophenone-sensitized decomposition of $\text{Co}(\text{NH}_3)_6^{3+}$ plotted according to eq 4: \circ , nondeaired solutions; \bullet , deaired solution.

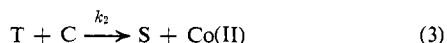
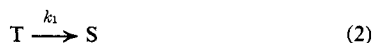
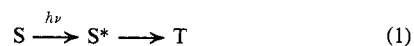
Our general observations are summarized in Table I. In each case, irradiation produced Co(II) with a qualitatively high efficiency in the presence of the sensitizer, and not at all in its absence. The Co(II) determinations were made by means of a colorimetric method involving complexation with thiocyanate;⁷ Reineckate actinometry⁸ was used.

Some quantitative measurements were made with biacetyl and with benzophenone as sensitizers. With 0.15 M biacetyl and 0.005 M $\text{Co}(\text{NH}_3)_6^{3+}$ in 50% ethanol-water solution, the quantum yield for Co(II) production was 0.056 at room temperature, based on the total absorbed intensity of 410- $m\mu$ irradiating light. This wavelength corresponds to the first singlet-singlet transition of biacetyl, as shown in Figure 1. Biacetyl is unusual in showing both fluorescent and phosphorescent emission at room temperature, and the combined emis-

- (4) J. F. Endicott and M. Z. Hoffman, *ibid.*, **87**, 3348 (1965).
- (5) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960).
- (6) D. Klein and C. W. Moeller, *Inorg. Chem.*, **4**, 394 (1965).
- (7) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
- (8) E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

sion spectrum is shown in Figure 2 (as determined with 400-m μ stimulating light, using an Aminco emission spectrometer). In the presence of the complex, however, the phosphorescent or triplet-state emission is quenched, but not that of the first singlet state. The implication is that it is the triplet state that is active in the sensitization.

In addition, a series of measurements was carried out using benzophenone as sensitizer and various concentrations of complex. An oxygen effect is present at least in this particular system, since the yield for Co(II) production rose from 0.064 to 0.36 on thorough degassing of the solution. Further, the quantum yield of the nonde-aerated solutions decreases with decreasing complex concentration, presumably as a result of competition between deactivation of the sensitizer by the complex and by other processes. The following reaction scheme is thus suggested



where S denotes sensitizer and T its triplet state, produced *via* an excited singlet state S*, T being produced in over-all quantum yield ϕ . It is assumed that the complex, C, may reactively deactivate T. In the present case C diminishes with time; assuming $d[T]/dt = 0$, *i.e.*, stationary-state kinetics, one obtains

$$1/\phi_{\text{obsd}} = 1/\phi + (k_1/k_2\phi)(\beta/C_0) \quad (4)$$

where ϕ_{obsd} is the observed quantum yield for Co(II) formation, C_0 is the initial complex concentration, and β is given by

$$\beta = [C_0/(C_0 - C)] \ln(C_0/C) \quad (5)$$

with C now denoting the final complex concentration.

The results are plotted according to eq 4 in Figure 3, and the intercept and slope give about unity and 0.013 for ϕ and k_1/k_2 , respectively. If reaction 3 is diffusion controlled, k_2 should be about $6 \times 10^9 M^{-1} \text{sec}^{-1}$,⁹ which would then make k_1 about $8 \times 10^7 \text{sec}^{-1}$. This last value is similar to those reported for other systems involving benzophenone.¹⁰

Our investigations are continuing, but some preliminary discussion is appropriate here. The wavelengths of the stimulating light used, as well as those corresponding to the triplet-state energies of the various sensitizers, are much longer than the threshold wavelengths for direct photodecomposition of these complexes. This situation plus the lack of any appreciable photosensitivity of the d-d bands themselves make it seem unlikely that energy transfer has occurred into the d-d or ligand field system. On the other hand, the first CT bands of these complexes lie at much higher energies than available here. The remaining possibility seems to be that the sensitizers are interacting with CT triplet states of the complexes. Such triplet states must exist in principle, and their theoretical description has been discussed to some extent.¹¹ The actual

(9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

(10) H. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(11) C. K. Jørgensen, "Absorption Spectra and Bonding in Complexes," Pergamon Press, London, 1962.

singlet-triplet CT transitions are not evident in the absorption spectra of Co(III) complexes, presumably because of being hidden by more intense d-d ones. Our suggestion is then that the sensitized decompositions reported here are those of low-lying CT triplet states which happen not to be easily populated by direct absorption of light.

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Studies of Free Radicals. II. Chemical Properties of Nitronylnitroxides. A Unique Radical Anion

Sir:

In an earlier communication the preparation of the highly stable aromatic nitronylnitroxide radicals III (R = Ar) was described.¹ We now report on some unusual chemical properties of the nitronylnitroxide grouping.

The alkylnitronylnitroxides III (R = alkyl) are prepared like their aromatic analogs by treatment of the bishydroxylamine I with aldehydes to give tetrahydroimidazoles II, which are subsequently oxidized with aqueous sodium periodate or lead dioxide. The resulting radicals are deep red solids which display esr spectra in solution having basic five-line patterns caused by coupling with two equivalent nitrogen nuclei. Further splitting of each line by the α -alkyl hydrogens usually is also observed together with occasionally resolved very weak coupling with the twelve methyl hydrogens (Table I).

Table I. Coupling Constants (in gauss)^a of Nitronylnitroxides III in Benzene

R	a_N	$a_{\alpha-H}$	$a_{4,5-CH_3}$
CH ₃	7.42	3.3	0.21
CH ₂ CH ₃	7.42	2.0	
(CH ₂) ₂ CH ₃	7.45	2.1	
CH ₂ OH	7.48	2.2	0.2
CH(CH ₃) ₂	7.5	~0.9	
CH(OC ₂ H ₅) ₂	7.25	<0.5	0.24

^a ± 0.03 gauss.

Although many of these radicals can be stored at room temperature for several weeks without decomposition, the radicals bearing α hydrogens are somewhat less stable than their aromatic analogs. By comparison, however, the hydroxymethylnitronylnitroxide III (R = CH₂OH)² was exceptionally labile and was found to undergo a gradual change on standing that could be greatly accelerated in alcoholic sodium hydroxide. The almost exclusive product of this reaction was a new red water-soluble radical, identified as III, R = H,² from its esr pattern of five doublets [$a_N = 7.26$,

(1) J. H. Osiecki and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 1078 (1968).

(2) Mass spectral and analytical data were in accord with the assigned structure.