to expect that it is in light of the F^{19} shift. Thus the compound is probably formed as the result of association of the protons with the fluoride of the CsF.

The solid remaining after reaction of the adduct with an acyl fluoride has been found to be thermally stable. Severe etching took place when a sample of gas, formed by thermally decomposing this solid, was introduced into an infrared cell with NaCl windows. It is likely that this solid could be $CsF\cdot 2HF$[14] but a mixture of other CsF–HF adducts cannot be excluded.

However, on the basis of the observation that a maximum of 2 moles of $(CF_3)_2NOH$ combines with 1 mole of CsF, we are led to believe that the reactions reported occur in two steps

$$n(CF_3)_2NOH + CsF \rightleftarrows ((CF_3)_2NOH)_n\cdot CsF \quad (n \leq 2) \qquad (1)$$

$$((CF_3)_2NOH)_n\cdot CsF + nR_fC(O)X \longrightarrow n(CF_3)_2NOC(O)R_f + CsF\cdot nHX \qquad (2)$$

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CONTRIBUTION FROM THE ISTITUTO CHIMICO DELL'UNIVERSITÀ, CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO-ORGANICI DEL C.N.R., FERRARA, ITALY, AND THE ISTITUTO CHIMICO "G. CIAMICIAN" DELL'UNIVERSITÀ, CENTRO NAZIONALE DI CHIMICA DELLE RADIAZIONI E DEI RADIOELEMENTI DEL C.N.R., SEZIONE III, BOLOGNA, ITALY

Photochemistry of Coordination Compounds. XVI. Hexabromoplatinate(IV) and Hexaiodoplatinate(IV) Ions[1]

BY VINCENZO BALZANI, FRANCESCA MANFRIN, AND LUCA MOGGI

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The photochemical behavior of $PtBr_6^{2-}$ was investigated with radiation of 313, 365, 433, and 530 mμ, corresponding to electron-transfer and d–d bands of the complex. Spectrophotometric and pH measurements were used to establish the nature and the kinetics of the photoreaction. The results show that both d–d and electron-transfer excitations cause a photoaquation reaction. The quantum yield was found to be about 0.4, independent of the wavelengths of irradiation. The mechanism of the photoreaction is discussed, and it is proposed that the primary photochemical act is the heterolytic fission of a Pt–Br bond. On the basis of the constant value of the quantum yield, it is also suggested that the photoreaction originates from the same chemically active electronic state, independent of the wavelength of irradiation. The photochemical behavior of PtI_6^{2-} was investigated by irradiating at 254, 313, 365, and 530 mμ, which correspond to electron-transfer bands. The study was made difficult by the rapid thermal decomposition of the complex; however, it was proved that, also in this case, electron-transfer excitations cause a photoaquation reaction.

The photosensitivity of aqueous solutions of the hexahalo complexes of Pt(IV) has long been known.[2–6] Recently, studies have been reported on the photoexchange PtX_6^{2-}–X^- reactions[7–15] and on the behavior of flashed solutions of $PtBr_6^{2-}$ and PtI_6^{2-},[16] but no systematic investigations about the photochemical reactions of these complexes have been done. We wish to report the results obtained by irradiating $PtBr_6^{2-}$ and PtI_6^{2-} with radiation corresponding to their various absorption bands, in order to elucidate the mechanism of their photoreactions.

Experimental Section

Preparation of Complexes.—K_2PtBr_6 was prepared following the method of Gutbier and Bauriedel.[17] K_2PtI_6 was obtained according to Datta.[18] The complexes were recrystallized from dilute solutions of HBr and KI, respectively. The electronic absorption spectra of the complexes were found to agree well with the literature reports.[19] We tried also to prepare $PtBr_4$ following the method of Meyer and Züblin;[20] however, elemental analysis of the products obtained from different preparations showed Br:Pt ratios slightly higher than 4 and water contents between 20 and 30%.[21,22]

Apparatus.—Radiation of 254, 313, and 365 mμ was obtained using the irradiation equipment previously reported.[23] Narrow

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[1] Paper XV: L. Moggi, F. Bolletta, V. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

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[19] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956); *Mol. Phys.*, **2**, 309 (1959).

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[21] The impossibility to obtain pure samples of platinum tetrabromide was recently pointed out by other authors.[22]

[22] C. M. Davidson and R. F. Jameson, *Trans. Faraday Soc.*, **61**, 2462 (1965).

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spectral bands centered at 433 and 530 mμ were isolated from a Philips Attralux Spot 150-w incandescent lamp by means of Schott and Gen. interference double filters (T_{max}, 50 and 45%; half-width, 20 and 11 mμ, respectively). To reduce heating in the filters 5 ml of $CuSO_4$ (4%, w/v) in 0.1 *N* H_2SO_4 solution was situated facing the lamp. The reaction cells were standard spectrophotometric cells (thickness 1 or 4 cm) housed in thermostated cell holders. The homogeneity of the solutions was maintained during irradiation by bubbling with a stream of purified N_2.

The light intensity, measured by means of the ferric oxalate actinometer, was of the order of 0.5×10^{-6} einstein/min at each wavelength used. As regards the wavelengths 254, 313, 365, and 433 mμ, the quantum yield values we assumed for the decomposition of the ferric oxalate were the ones recommended by Hatchard and Parker.[24] No values are available for the quantum yield at 530 mμ. Thus, we measured the light output of the Philips incandescent lamp at 546 mμ, assuming the quantum yield 0.15 reported by Hatchard and Parker; then, on the hypothesis of equal light outputs at 530 and 546 mμ, we determined the value 0.2 for the quantum yield of the ferric oxalate actinometer at 530 mμ.

Spectrophotometric measurements were performed with an Optica C.F.4 NI spectrophotometer, which makes possible both manual measurements and automatic recording. pH measurements were carried out by means of a Knick Type 350 pH meter.

Procedure.—The complexes were dissolved in the selected medium as quickly as possible in red light. All of the experiments were carried out at 25°. The concentration was 1.6×10^{-4} *F* for $PtBr_6^{2-}$ and 1.0×10^{-4} *F* for PtI_6^{2-}. pH measurements were accomplished directly in the reaction cell during irradiation by means of a glass-reference combined microelectrode. In order to obtain reliable values, pH measurements were always made in a slightly buffered medium (0.5×10^{-3} *F* Na_2HPO_4 and KH_2PO_4). Because some experiments had to be carried out in solutions containing different amounts of neutral salts, the ionic strength was always adjusted to 1 by adding Na_2SO_4. The buffer solution had pH 6.45 and it proved to give, in the pH range 6.9–6.0, linear variation of pH *vs.* the concentration of added acid or base, provided these were so strong ($pK_i < 5$) as to produce stoichiometric displacements of the buffer equilibrium. As we had to measure the rate of formation of acidic species (see below), the buffer solution used as solvent was brought to pH 6.9 with dilute NaOH in order to make complete use of the range of linear pH variation. The changes in absorbance for the photochemical experiments were measured by the differential spectrophotometric method in order to take into account only the photochemical effects.

Results

Thermal Reactions.—It was reported that $PtBr_6^{2-}$ [6,22] and PtI_6^{2-} [10] undergo thermal aquation reactions. Before beginning the photochemical studies, we carried out some investigations in order to extend the information about this topic. The results obtained on aqueous, buffer, and acid (0.01–1.0 *N* H_2SO_4) solutions of $PtBr_6^{2-}$ were qualitatively the same and may be summarized as follows:[25] (a) The absorbance decreased around the absorption maxima (226, 315, and 365 mμ) and it increased in the region 250–290 mμ; no isosbestic points were present. The spectrum of solutions at thermal equilibrium depended on the pH of the reaction medium. (b) The pH slowly decreased (for example, from 6.45 to 6.27 in 1 hr), and after a long period of time it tended to reach a constant value. (c) The presence of Br^- ions in the solution decreased the rate of variation of the pH and of the spectrum. Solutions containing more than 0.1 *F* Br^- were quite stable. (d) When solid NaBr was added to an aged solution of $PtBr_6^{2-}$ so as to give a 0.1 *F* Br^- concentration, the spectrum (see, for example, Figure 3) and the pH rapidly came back to the "zero-time" values.[26] (e) In acid solutions both the direct and the reverse reactions were much more rapid than in neutral solutions. (f) The presence of 1.6×10^{-4} *M* H_2O_2 did not influence the thermal reaction. (g) When 1.6×10^{-4} *M* hydroquinone was present, a new absorption maximum slowly arose at 244 mμ; moreover, the presence or the addition of Br^- ions was not able to stop or to reverse the reaction, respectively.

Regarding PtI_6^{2-}, we verified that aqueous and acid solutions of this compound rapidly gave rise to a black precipitate which after some time prevented the spectrophotometric study of the reaction. Elemental analysis and chemical properties[27] showed that the black precipitate was PtI_4. During the reaction the pH slowly decreased. The presence of I^- ions in the solution slowed down the thermal decomposition of PtI_6^{2-}. Solutions containing more than 0.01 *F* I^- were quite stable. When solid NaI was added to a decomposed solution so as to give a 0.1 *F* concentration of I^- ions, the black precipitate dissolved completely and the absorbance resumed the "zero-time" values.

These results confirm that solutions of $PtBr_6^{2-}$ and PtI_6^{2-} thermally undergo reversible aquation reactions. The lack of isosbestic points, in the case of $PtBr_6^{2-}$, and the rapid formation of PtI_4, in the case of PtI_6^{2-}, indicate that in both cases more than one aquation product rapidly forms, according to the reactions

$$PtX_6^{2-} \underset{X^-}{\overset{H_2O}{\rightleftarrows}} PtX_5H_2O^- \underset{X^-}{\overset{H_2O}{\rightleftarrows}} PtX_4(H_2O)_2 \underset{X^-}{\overset{H_2O}{\rightleftarrows}} \ldots$$

Photochemical Reactions.—Aqueous, buffer, and acid (0.01 *N* H_2SO_4) solutions of $PtBr_6^{2-}$ were irradiated with 313-, 365-, 433-, and 530-mμ radiations, corresponding to electron transfer and d–d bands[19] (Figure 1). The experimental results were independent of the wavelength of excitation. During irradiation, the pH rapidly decreased (Figure 2, a) and the spectrum changed in the same way as it did in the case of the thermal reaction, but much more rapidly. The rate of the pH and spectrum variations decreased with increasing concentration of Br^- ions contained in the irradiated solutions (Figure 2, a and b). When solid NaBr was added to irradiated solutions so as to give a 0.1 *F* concentration of Br^- ions, the pH and the spectrum (see, for example, Figure 3) came back to the "zero-time" dark values. In acid solutions the photochemical reaction and the reverse dark reaction were more rapid than in neutral solutions.

These results show that at all of the wavelengths of

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[24] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[25] Similar results were also obtained at 50°.

[26] "Zero-time" values mean the pH and absorbance values of a portion of the same solution to which the same amount of NaBr was added immediately after the dissolution of the complex.

[27] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p 1615.

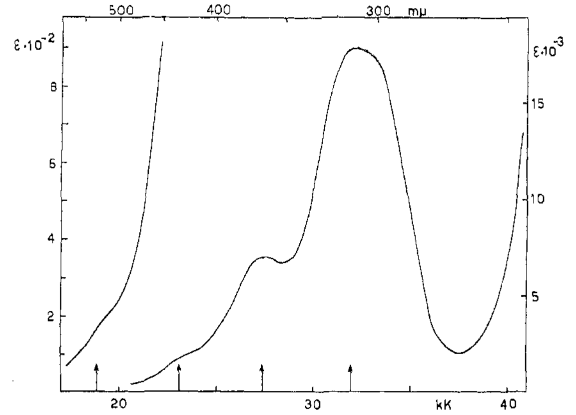

Figure 1.—Electronic absorption spectrum of $PtBr_6^{2-}$. The arrows indicate the radiations used for the photoexcitations.

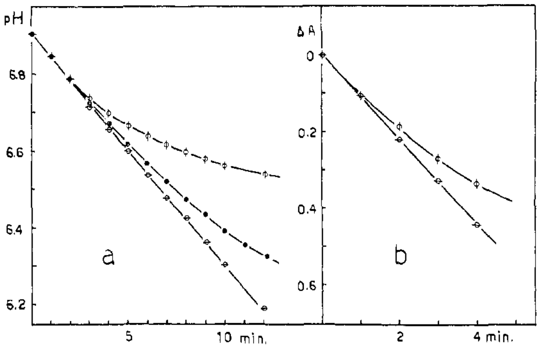

Figure 2.—Photochemistry at 313 mμ of $PtBr_6^{2-}$ solutions containing 0 (⊖), 0.01 (●), and 1 *M* (ϕ) NaBr: a, pH variation; b, decrease of the absorbance at 313 mμ.

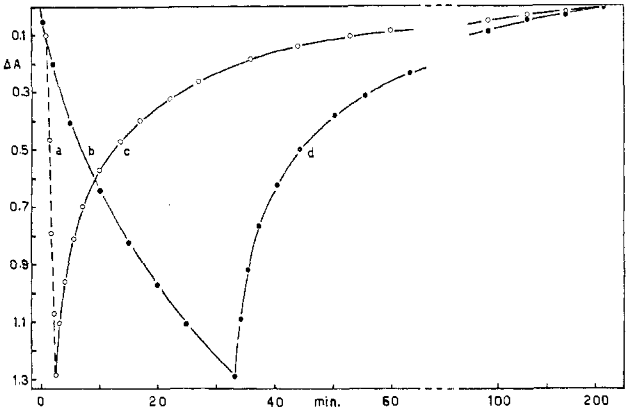

Figure 3.—Differential measurements of the variation of the absorbance at 313 mμ for a $PtBr_6^{2-}$ solution in 0.01 *N* H_2SO_4: a, photochemical reaction (irradiation at 313 mμ); b, thermal reaction; c and d, reverse thermal reactions caused by the addition of solid NaBr so as to give 0.1 *M* Br^- concentration.

irradiation the photochemical reaction of $PtBr_6^{2-}$ is a reversible aquation reaction like the thermal one. Because in our experimental conditions only the reagent (that had both concentration and absorptivity much higher than those of the reaction products) absorbed the light, the lack of isosbestic points indicates that secondary thermal reactions rapidly follow the photochemical process.

Quantum yield values for the photoaquation of $PtBr_6^{2-}$ could be obtained from the initial pH *vs.* irradiation time plots for the buffer solution of the complex (see Figure 2, a). In fact, $PtBr_5H_2O^-$ formed by irradiation is acid enough ($pK_a = 4.4$[22]) to produce linear changes in the pH of the buffer solution, whereas the thermal secondary aquation reactions (which convert $PtBr_5H_2O^-$ in stronger acid species) cannot cause any further pH variations.[28] Therefore, by using a calibration plot of the pH of the buffer solution *vs.* the amount of acid added (see Procedure), it was possible to calculate the over-all amount of aquation products formed, which obviously was equal to the amount of $PtBr_6^{2-}$ decomposed. Such a calculation leads to the value 0.50 ± 0.10, *independently of the wavelength of irradiation.*

Quantum yield values for the photoaquation of $PtBr_6^{2-}$ could also be obtained from spectrophotometric measurements. In fact, for the buffer solution the variation of absorbance with the irradiation time was constant at 313 mμ, whereas it increased at the wavelengths lower than 313 mμ and it decreased at the wavelengths higher than 313 mμ (see, for example, Figure 4).

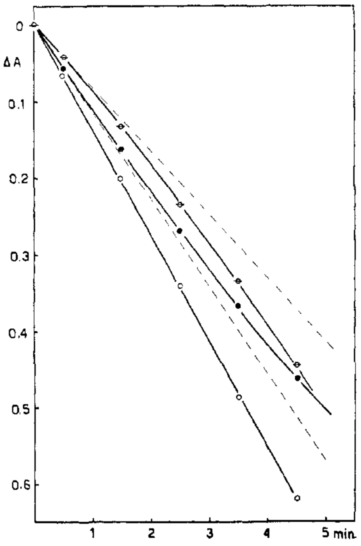

Figure 4.—Decrease of the absorbance at 300 (⊖), 313 (○), and 330 mμ (●) of a $PtBr_6^{2-}$ solution irradiated with 313-mμ radiations.

This means that at 313 mμ the products that originate as a direct or indirect consequence of irradiation have the same absorptivity. Therefore, the value of the quantum yield for the photoaquation of $PtBr_6^{2-}$ may be obtained by using the absorptivity (ϵ_{313} ~7000) we found for aqueous $PtBr_4$, which corresponds to the second aquation product. The quantum yield calculated in such a way was again independent of the wavelength of irradiation, and its value (0.35 ± 0.10) agreed well with the one obtained by means of pH measurements.[29]

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(28) Moreover, the thermal reactions should be negligible for short irradiation periods.

(29) According to Davidson and Jameson[22] the hydrolysis products of $PtBr_6^{2-}$ do not appreciably absorb at 313 mμ; in this hypothesis the quantum yield 0.2 should result.

We also carried out some investigations irradiating, at all of the wavelengths previously indicated, $PtBr_6^{2-}$ solutions containing H_2O_2 or hydroquinone. We found that 1.6×10^{-4} M H_2O_2 did not affect the photochemical reaction. On the contrary, 1.6×10^{-4} M hydroquinone remarkably influenced the photochemical behavior of the complex. In fact, when hydroquinone was present, an absorption maximum at 244 mμ arose as the one observed in flashed[16] or thermally decomposed solutions of $PtBr_6^{2-}$ containing hydroquinone; moreover, the presence or the addition of Br^- ions was not able to stop or to reverse, respectively, the changes in absorbance caused by irradiation.

PtI_6^{2-} was excited with 254-, 313-, 365-, and 530-mμ radiations, corresponding to electron-transfer bands.[19] The rapid thermal reaction made the photochemical studies difficult. Nevertheless, we observed that irradiation accelerated the precipitation of PtI_4 and the lowering of pH. Moreover, the presence of I^- ions in the irradiated solutions decreased the above-mentioned irradiation effects; if the solution contained more than 0.1 F I^-, the irradiation had no effect at all. Finally, if the same excess of I^- ions was added both to an irradiated and to a nonirradiated sample of the same solution, the black precipitate dissolved and both of the samples showed the same spectrum, which strictly corresponded to the spectrum of the original PtI_6^{2-} solution.

Discussion

Thermal Reactions.—The reversible thermal aquation reactions of $PtBr_6^{2-}$ and PtI_6^{2-} in aqueous solutions are best described in terms of a simple heterolytic mechanism, the first step of which may be represented as[30]

$$PtX_6^{2-} \xrightarrow[\text{S}_\text{N}1 \text{ or } \text{S}_\text{N}2]{H_2O} PtX_5H_2O^- + X^- \quad (1)$$

In particular, the absence of inhibition by substances such as K_2IrCl_6[14] and H_2O_2 (our observation f) rules out the catalytic mechanisms, involving species containing Pt in lower oxidation states, postulated for other replacement reactions of Pt(IV) complexes.[31] Our results also show that, when hydroquinone is present, an irreversible thermal reaction different in nature from the aquation reaction occurs.

Photochemical Reactions.—The results obtained demonstrate that the photochemical reactions of PtX_6^{2-} ($X = Br, I$) have the same nature as the corresponding thermal reactions, *i.e.*, that they are reversible aquation reactions; the verified complete reversibility of the irradiation effects by the addition of X^- ions rules out photochemical reactions other than photoaquation, unless they have very small quantum yields. It must be pointed out that, as far as we know, $PtBr_6^{2-}$ and PtI_6^{2-} appear to be the first example of complexes that give rise to aquation reactions when irradiated in electron-transfer bands.

Some suggestions have already been reported about the mechanism of the photochemical reactions of $PtBr_6^{2-}$. In order to interpret the extremely high quantum yield found for the $PtBr_6^{2-}$–Br^- photoexchange at 360 and 450 mμ, Adamson and Sporer[9] suggested that light causes the homolytic fission of a Pt–Br bond

$$PtBr_6^{2-} \xrightarrow{h\nu} PtBr_5^{2-} + Br \quad (2)$$

However, in a recent paper Penkett and Adamson[16] report that after flashing aqueous solutions of $PtBr_6^{2-}$ and PtI_6^{2-}, they did not find any indication of the presence of halogen atom transients and, therefore, they rejected the photolytic mechanism (2). In the same paper they report that hydroquinone was oxidized during the flash of solutions of $PtBr_6^{2-}$ containing hydroquinone. Taking this observation as the proof that an oxidizing species was produced by flashing $PtBr_6^{2-}$, these authors conclude that the primary photochemical act of $PtBr_6^{2-}$ is in nature an oxidation–reduction reaction, and they suggest the photochemical mechanism

$$PtBr_6^{2-} \xrightarrow{h\nu} PtBr_4^{2-} + Br_2 \quad (3)$$

This mechanism, however, does not seem to fit our experimental results, according to which the aquation is the sole observable reaction caused by irradiation of aqueous $PtBr_6^{2-}$. On the other hand, it must be pointed out that the results obtained by flash experiments on $PtBr_6^{2-}$ solutions containing hydroquinone cannot be useful in order to elucidate the mechanism of the photoreaction of aqueous $PtBr_6^{2-}$; in fact, we have found that the nature of the photochemical reaction is changed when the easily oxidizable substrate hydroquinone is present.

Therefore, on the basis of our experimental results and of the lack of any evidence of oxidation–reduction mechanisms, it is reasonable to accept the simple mechanism

$$PtBr_6^{2-} \xrightarrow[H_2O]{h\nu} PtBr_5H_2O^- + Br^- \quad (4)$$

involving a heterolytic fission of a Pt–Br bond.

As regards the strong photocatalytic effect observed for the $PtBr_6^{2-}$–Br^- exchange system, it must be noted that both the thermal and the photochemical exchanges are extremely complicated and scarcely reproducible processes[9,14] affected by the presence of oxidative species.[14] On the contrary, thermal and photochemical aquations are reproducible reactions not influenced at all by oxidative species such as K_2IrCl_6[14] or H_2O_2. Thus it appears that no relation exists between hydrolysis and exchange processes. The photocatalysis of the exchange process could involve a photochemical mechanism (such as (2) or (3)) different in nature from the one involved in the photoaquation but occurring with quantum yield too small to give rise to detectable amounts of products.

Regarding $PtBr_6^{2-}$, the results obtained enable us to make some speculations about the role played by the various excited states in determining the photochemical

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[30] According to Pöe and Vaidya[10-12] a simple S_N1 or S_N2 mechanism is involved also in the PtI_6^{2-}–I^- and $PtBr_6^{2-}$–I^- reactions.

[31] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

behavior of the complex. The wavelengths used for irradiation correspond (Figure 1) to ligand→metal electron-transfer bands (313 and 365 mμ), to a singlet d–d band (443 mμ), and to a triplet d–d band (530 mμ).[19] *In spite of the difference in energy and also in nature among the various excited states reached by irradiation, the same type of photochemical reaction occurs, and, moreover, it has the same quantum yield.* This result strongly suggests that the photoreaction does not take place directly in the various excited states, but it originates from the same chemically active state, independently of the wavelength of irradiation. Therefore, it appears that radiationless transitions having nearly unitary efficiency should lead the higher excited states to the lowest one (*i.e.*, to the triplet d–d state). Then, the following alternative possibilities could occur: (a) The triplet state has a lifetime long enough to react. (b) An intersystem crossing process between the triplet d–d state and the electronic ground state leads to "hot" (*i.e.*, vibrationally excited) $PtBr_6^{2-}$ ions which can react during their relaxation periods. Both of these reaction paths agree with the proposed heterolytic mechanism (4). In fact, both the triplet d–d state (which has the same electronic distribution between the central ion and the ligands as the ground state) and the vibrationally excited levels of the ground state react with a heterolytic mechanism as $PtBr_6^{2-}$ ions do when they thermally decompose.

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Influence of Temperature on Some Octahedral–Tetrahedral Equilibria in Solution

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The effect of temperature on the equilibria

$$X^- + [MX_2\cdot 4\text{solvent}]_{\text{octahedral}} \rightleftharpoons [MX_3\cdot\text{solvent}]^-_{\text{tetrahedral}}$$

has been studied for some cobalt and nickel halides in water and alcohols. High temperatures and high halide ion concentrations favor the tetrahedral species, and heats of reaction between 11.7 and 17.1 kcal/mole have been found. Considerations of these heats of reaction and the ligand field stabilization energies suggest that the curves of the negative heats of formation in solution (corrected for ligand field stabilization) of the octahedral and tetrahedral species intersect between Co and Ni, the slope of the curve for the tetrahedral species being greater. An equilibrium

$$[NiBr_2\cdot 4(n\text{-}C_4H_9OH)]_{\text{octahedral}} \rightleftharpoons [NiBr_2\cdot 2(n\text{-}C_4H_9OH)]_{\text{tetrahedral}}$$

with a heat of reaction of 17.0 kcal/mole is also reported.

Solution equilibria involving tetrahedrally coordinated complex halide species of the first-row transition series have been studied by many workers, but there has been little work on the influence of temperature on these equilibria. Furlani and co-workers have observed marked changes in spectra with temperature for nickel halides[1] and copper halides[2] in various solvents with added halide ion, while Katzin[3] obtained ΔH values for the reaction

$$[CoCl_2\cdot 4py]_{\text{octahedral}} = [CoCl_2\cdot 2py]_{\text{tetrahedral}} + 2py$$

by observing changes in spectra with temperature. This paper reports work on the temperature effect for some nickel and cobalt halides in water and alcohols in the presence of large concentrations of added halide ion.

Experimental Section

For the studies in nonaqueous solvents, anhydrous salts of the type $[(C_2H_5)_4N]_2MX_4$ and $[(C_6H_5)_4As]_2MX_4$, prepared by the methods of Gill and Nyholm,[4] were used as sources of the appropriate metal halide. The dissociation of these salts in the solvents gave solution species the same as those obtained from the anhydrous halides themselves. For the $CoCl_2$–H_2O system, $CoCl_2\cdot 6H_2O$ was used. In each case, the halide salt was dissolved in a solution of lithium halide in the required solvent of sufficient concentration to give the intense blue color of a tetrahedral species on heating. Under these conditions in the systems studied, the room-temperature spectra were generally of an octahedral species, with occasionally a small intensity of tetrahedral species also present. On heating, a progressively intensifying spectrum of a tetrahedral species became present, as shown in Figures 1–3.

A Beckman DK2A recording spectrophotometer was used to follow the spectra, with 1-cm stoppered cells. The temperatures were controlled by a Beckman temperature-regulated cell holder, calibrated by thermocouples and calibrated thermometers.

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(1) C. Furlani and G. Morpurgo, *Z. Physik. Chim.*, **28**, 93 (1961).

(2) C. Furlani and G. Morpurgo, *Theoret. Chim. Acta* (Berlin), **1**, 102 (1963).

(3) L. I. Katzin *J. Chem. Phys.*, **35**, 467 (1961).

(4) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).