

On the Decomposition of the Dinitrogenpentammine-osmium(II) Ion in Aqueous Solutions

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The decomposition of the dinitrogenpentammineosmium(II) ion in aqueous solutions at different pH and temperatures has been studied by infrared spectroscopy. It has been found that the decomposition in both acid and alkaline solutions is more complicated than what corresponds to a pure first order reaction. This has been shown to depend on an autocatalysis effect. In acid solution it is a homogeneous catalysis, while in alkaline solution there probably is a heterogeneous catalysis. The $\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$ also contains a considerable amount of a bisdinitrogen complex, *viz.* $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{Cl}_2$. It has been found that the bisdinitrogen complex is quite stable both in acid and alkaline solutions, and thus can be separated from the monodinitrogen complex. This has been done in acid solution, and the bisdinitrogen complex was obtained in pure form. The fact that the bisdinitrogen complex is more stable in solution than the monodinitrogen complex is discussed.

Although extensive work on the properties of coordinated dinitrogen in osmium dinitrogen complexes has been reported,¹⁻⁴ little information from kinetic measurements on these complexes is available. Thus, only the substitution of dinitrogen by phosphorus ligands in some osmium dinitrogen complexes has been reported.⁵ The purpose of this study was to investigate the kinetics and mechanism when the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion decomposes in aqueous solutions. As has been pointed out before,⁶ the $\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$ also contains a considerable amount of the bisdinitrogen complex $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{Cl}_2$. The frequencies ν_{NN} are different in the two complexes, indicating different perturbations of the dinitrogen group, and therefore it can be expected that the complexes will have different stabilities in solution. It would perhaps be possible to characterize the mono- and the bisdinitrogen complexes through kinetic measurements. The corresponding ruthenium dinitrogen complex was found to decompose rapidly in aqueous solution and consequently it must be difficult to follow the decomposition by infrared spectroscopic measurements. This investigation has therefore been limited to the osmium dinitrogen complex.

EXPERIMENTAL

$\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$, prepared and analyzed as described before,⁶ was used in this investigation. A suitable amount of this complex, which also contains $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{Cl}_2$, was dissolved in an aqueous solution of desired pH. The solution was placed in a thermostat (25°C or 50°C) and samples were withdrawn at time intervals of about half an hour. The spectrum of the sample was recorded within the region 2200–1950 cm^{-1} , where the N–N stretching vibration bands occur. Cells with CaF_2 -windows and 25 μ platinum spacers were used. The infrared spectroscopic measurements were performed on a Perkin Elmer Spectrophotometer Model 521 with 5 \times ordinate expansion. The decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion was followed at pH = 1, 6, 7, 13, and 14, and at 25°C and 50°C. Two series of measurements were performed at each pH and temperature, and good reproducibility was found.

The ultraviolet spectra were recorded on a Hitachi Recording Spectrophotometer Model EPS-3T.

MEASUREMENTS AND RESULTS

1. Acid solution. At pH = 1, $\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$ was dissolved in 0.1 M hydrochloric acid. The absorbance ($\log T_0/T$) of the N–N stretching vibration band at 2035 cm^{-1} was found to decrease with time. The other two bands corresponding to N–N stretching vibrations in the $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ ion were, on the other hand, found not to decrease. If it is supposed that the decomposition of the monodinitrogen complex follows a first order rate law, a plot of $\log T_0/T$ against time should give a straight line. Such a plot is presented in Fig. 1. As can be seen in Fig. 1, the straight line bends downwards at a certain value of time, which thus indicates that the decomposition reaction becomes more rapid than for the first order reaction. The decomposition at 50°C is more rapid than at 25°C. When $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ decomposes, $\text{Os}(\text{NH}_3)_5\text{OH}_2^{2+}$ is probably formed and this product then somehow catalyzes the further decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$.

The measurements at 50°C were performed until the N–N band at 2035 cm^{-1} disappeared and thus the monodinitrogen complex had been destroyed.

The other two N–N bands in the infrared spectrum which are assigned to $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ do not disappear, but have the same absorbance as at the beginning of the measurements. The bisdinitrogen complex is thus not affected in acid solution, but seems to be quite stable. When a saturated solution of sodium iodide was added to the acid solution, which thus only contains one dinitrogen complex, $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$, a small amount of a grey-yellow precipitate was formed. The precipitate was collected on a millipore filter, washed and airdried. It was then dissolved in water and precipitated again with saturated sodium iodide. The infrared spectrum of the solid showed two N–N bands at 2115 cm^{-1} and 2170 cm^{-1} . The UV-spectrum showed a maximum at 221 nm. The solid is thus ³ $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{I}_2$, which has been separated from $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ through its stability in acid solution. This is remarkable since the bisdinitrogen complex is expected to be more unstable than the monodinitrogen complex, depending on the fact that the frequency of the N–N stretching vibration is higher for the bisdinitrogen complex than for the monodinitrogen complex (*cf.* the discussion in Ref. 7). $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{Br}_2$ has also been obtained in a similar way as the corresponding iodide and the complex has been identified through IR- and UV-spectra. The chloride complex on the

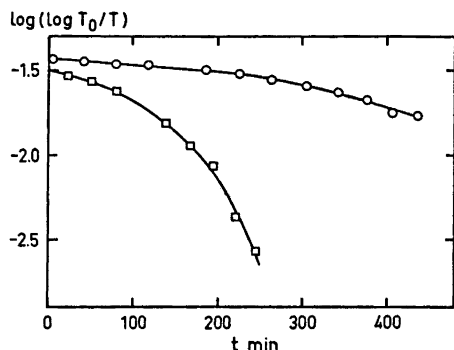


Fig. 1. Decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion according to the first order reaction at pH=1 and 25°C (○) and 50°C (□). Initial concentration of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ at 25°C 1.08×10^{-2} M and at 50°C 1.04×10^{-2} M.

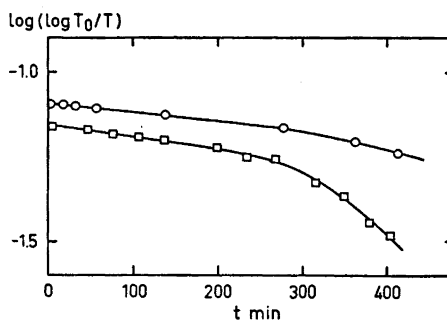


Fig. 2. Decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion according to the first order reaction at pH=13 and 25°C (○) and 50°C (□). Initial concentration of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ at 25°C 2.39×10^{-2} M and at 50°C 1.92×10^{-2} M.

other hand could not be obtained by precipitation owing to its high solubility in water. No precipitation of the rest of the monodinitrogen complex together with the bisdinitrogen complex was detected from the infrared spectrum. The molar absorption coefficient at 221 nm was found to be somewhat smaller than that reported by Taube *et al.*³ It is therefore plausible that the precipitated bisdinitrogen complex is contaminated with a small amount of the rest of the monodinitrogen complex. The absorption intensities of the N–N bands in $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2\text{X}_2$, X = Br, I, were determined. The values agreed well with the intensities calculated from the mixture of the two complexes,⁶ so the contamination must be small. The intensity values A_{NN} for the bisdinitrogen complex have been reported earlier (Table 2, Ref. 6). As was also pointed out in Ref. 6, the complicated infrared spectrum in the region 600–400 cm^{-1} for the monodinitrogen complex could now be resolved. The intensity of the M–N₂ band in the monodinitrogen complex could therefore be determined more accurately. This has also been dealt with in the earlier work.⁶

2. *Neutral solution.* The decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion was also followed in neutral solution. The complex was dissolved in an acetic acid-acetate buffer solution with pH=6.7. A buffer solution was used, as it is of importance to keep a constant pH-value. An aqueous solution of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ has earlier been found to darken within 24 h. This is probably a result of ammonia and also dinitrogen having left the complex. The aqueous solution thus becomes alkaline and after some time a black precipitate of some osmium hydroxide is formed. This fact shows that pH is not constant in an aqueous solution of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and therefore a buffer solution must be used. At 25°C the measurements were performed during 24 h. No decrease in absorbance of the N–N stretching vibration band at 2035 cm^{-1} was observed during this time. At 50°C the measurements were performed during 400 min (*i.e.* the same time as in the measurements at pH=1). No decrease in absorbance of the

N–N band was found during this time. The result is thus that the complex ion $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ is much more stable in neutral solution, at least during that time the measurements have been performed. The absorbance of the two N–N bands in the bisdinitrogen complex did not decrease during the measurements. Therefore, this complex also must be quite stable in neutral solution.

3. *Alkaline solution.* The decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion was also investigated in alkaline solution both at $\text{pH} = 13$ and $\text{pH} = 14$. It was found that there is a decrease in absorbance of the N–N band at 2035 cm^{-1} . The decomposition followed the first order reaction in the beginning but became more rapid after some time, which is demonstrated in Fig. 2. As in the acid solution, the decomposition product probably catalyzes the further decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. The course of the decomposition at $\text{pH} = 13$ and $\text{pH} = 14$ is about the same. The only difference is that the decomposition is more rapid at $\text{pH} = 14$ than at $\text{pH} = 13$. The decomposition in alkaline solution seems to be more complicated than in acid solution. When the reaction has been followed for about 1 h, the yellow solution has become brown-yellow and in the infrared spectrum a small band appears at 1993 cm^{-1} , about 45 cm^{-1} lower than the N–N stretching vibration frequency in $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. The band at 1993 cm^{-1} is probably the N–N stretching vibration in the complex $\text{Os}(\text{NH}_3)_4\text{N}_2(\text{OH})^+$, for exchange of one ammonia against hydroxide ion in the complex $\text{Ru}(\text{NH}_3)_5\text{NO}^{2+}$ lowers the frequency ν_{NO} about 70 cm^{-1} (cf. Ref. 8). The absorbance of the band at 1993 cm^{-1} soon reaches a maximum and then the absorbance of this band decreases simultaneously as the absorbance at 2035 cm^{-1} decreases. The brown-yellow solution becomes darker and soon a black crystalline precipitate is formed. After the precipitate has been formed, the decrease in absorbance of the N–N band at 2035 cm^{-1} became more pronounced and thus the reaction becomes more rapid. At the moment of precipitation in the solution, the small band at 1993 cm^{-1} had disappeared, which might indicate that the solid compound could be $\text{Os}(\text{NH}_3)_4(\text{OH})_2$. This solid compound then probably catalyzes the further decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. The precipitate was filtered off after about 24 h. The IR-spectrum of the compound shows bands, which are assigned ⁹ to hydroxide and ammonia (cf. Table 1). The solid compound can therefore be $\text{Os}(\text{NH}_3)_4(\text{OH})_2$ and perhaps the final product is an osmium hydroxide. It is thus quite reasonable that both the dinitrogen and the ammonia ligands in the complex $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ are replaced by hy-

Table 1. Infrared absorption frequencies of the solid compound obtained after treatment of $\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$ with 1 M NaOH for about 24 h.

Frequency cm^{-1}	Assignment ⁹
3400 (broad)	$\nu(\text{OH})$
3200 (broad)	$\nu(\text{NH})$
1600	$\delta_{\text{as}}(\text{NH}_3)$
1320	$\delta_{\text{s}}(\text{NH}_3)$
1000	$\delta(\text{MOH})$

dioxide ions. Even in alkaline solution the bisdinitrogen complex seems to be quite stable, as no decrease in absorbance of the N—N bands assigned to this complex was found. The bisdinitrogen complex was, however, not separated from the solution because of the black precipitate of the decomposition product from the monodinitrogen complex.

The rate constants of the decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion for the part of the decomposition which follows the first order reaction were calculated from the slopes of the $\log (\log T_0/T)$ versus t lines. The obtained values are collected in Table 2. The rate constants are not given with error limits as the

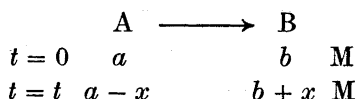
Table 2. Rate constants for the first order decomposition of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion.

pH	$k \times 10^4 \text{ min}^{-1}$		$\frac{k_{50^\circ\text{C}}}{k_{25^\circ\text{C}}}$
	25°C	50°C	
1	9.0	31.0	3.5
6.7	0	0	—
13	6.0	8.3	1.4
14	23.0	30.0	1.3

exact values are of little importance in this investigation. At pH=1 and 50°C, the rate constant is about 3.5 times greater than that at 25°C. Thus, if one wishes to separate the bisdinitrogen complex from the monodinitrogen complex, it is easily done in acid solution and at high temperatures. The slowest decomposition rate was found at pH=13 and 25°C. In the more alkaline solution (pH=14), the rate constants are about 4 times greater than those determined at pH=13. The relationship between the rate constants at 50°C and 25°C is about the same both at pH=13 and pH=14, as can be seen from Table 2.

DISCUSSION

In both acid and alkaline solutions it was found that the decomposition of the complex ion $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ after some time became more rapid than what corresponds to a first order reaction. It is thus reasonable that the reaction product catalyzes the reaction. To check if it really is an autocatalysis the following reaction is considered (*cf.* Ref. 10, p. 19):



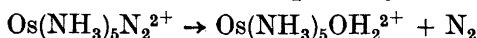
The second order rate law is $dx/dt = k(b+x)(a-x)$. The solution of this differential equation is

$$\log \frac{a-x}{b+x} = -\frac{k(a+b)t}{\ln 10} + \log \frac{a}{b}$$

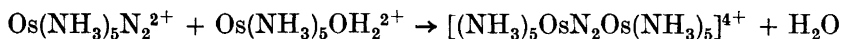
If now b is neglected in relation to x and absorbance is introduced instead of concentration, the left side of the equation above becomes

$$\log \frac{\log T_0/T}{(\log T_0/T)_{t=0} - \log T_0/T}$$

This quantity plotted against time should give a straight line within the time interval where the autocatalysis is effective. This is illustrated in Fig. 3 for the measurements at pH = 1 both at 25°C and 50°C. It has thus been shown that there can be an autocatalysis effect in acid solution. The mechanism of the decomposition in acid solution can thus probably be described as

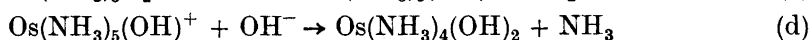
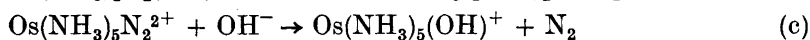
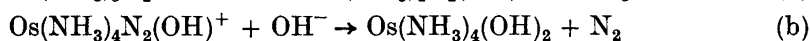
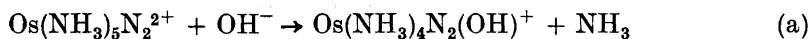


and then, when the decomposition is catalyzed by the product

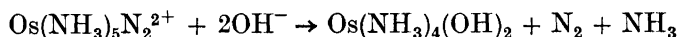


The binuclear ion must be infrared inactive, since it is completely symmetrical. The formation of this ion causes a more rapid decrease in the concentration of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and thereby also in the measured absorbance of the N–N band in $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. The binuclear ion, the formation of which has been suggested to be responsible for the observed autocatalysis effect, is probably not stable for a long time, but decomposes and dinitrogen is lost.

In the alkaline solutions, the decomposition rate of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ was found to increase when a precipitate had been formed in the solutions. It has also been shown in this case that there can be an autocatalysis effect, as for the acid solutions. The difference is, however, that in the alkaline solution it probably is a heterogeneous catalysis, while in acid solution it is a homogeneous catalysis. As mentioned above, the mechanism of the decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in alkaline solution seems to be complicated. The small band at 1993 cm^{-1} indicates that coordinated ammonia is exchanged for hydroxide. The decrease in absorbance of the N–N band at 2035 cm^{-1} indicates that dinitrogen is replaced by hydroxide. Thus



The total reaction of the decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ thus becomes



The $\text{Os}(\text{NH}_3)_4(\text{OH})_2$ then loses ammonia and the final product is probably $\text{Os}(\text{OH})_2$. It is difficult to know exactly the composition of the solid that catalyzes the further decomposition of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and thereby also the mechanism of the autocatalysis. On the other hand, it is quite reasonable that the autocatalysis is only effective on the reactions (b) and (c) and not on reaction (a). This assumption can then possibly explain the increase and the fol-

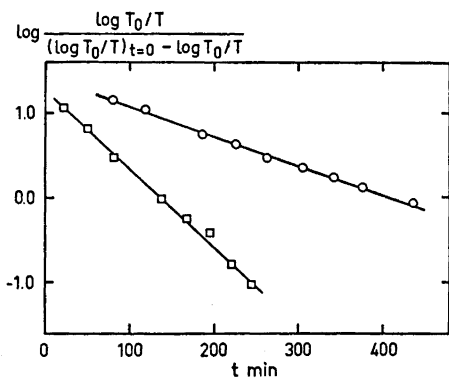


Fig. 3. A representative example of the autocatalysis effect in acid solution (pH = 1) at 25°C (O) and 50°C (□).

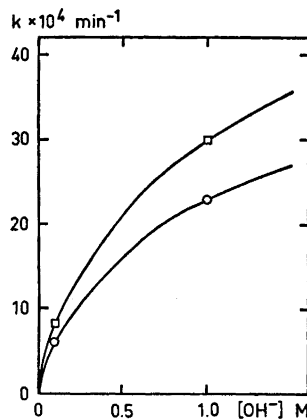
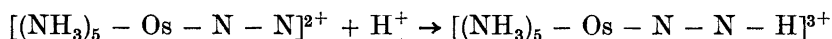


Fig. 4. A rough sketch of the experimental rate constants against the hydroxide ion concentration at 25°C (O) and 50°C (□).

lowing decrease of the absorption band at 1993 cm^{-1} . It was also found that the decomposition became more rapid when the band at 1993 cm^{-1} had disappeared, which suggests that the autocatalysis is effective on reaction (c).

The most important result of the present investigation is, however, that the bisdinitrogen complex has been found to be stable both in acid and alkaline solution and thus could be separated from the monodinitrogen complex. The earlier attempts to prepare a pure compound of the monodinitrogen complex were not successful, since it was always found⁶ that the compound also contained a bisdinitrogen complex. Every attempt to separate the two complexes through various reaction conditions during the preparation procedure failed. To get a reasonable explanation of the stability of the bisdinitrogen complex in solution, the charges on the nitrogen atoms must be considered. It has been found by ESCA measurements^{11,12} on iridium and rhenium dinitrogen complexes that there is a chemical shift in the nitrogen $1s$ binding energies, which indicates¹³ different effective charges on the nitrogen atoms. It has also been found¹¹ that the lower the N–N stretching vibration frequency, the greater is the chemical shift, corresponding to a smaller value of the nitrogen $1s$ binding energy of the terminal nitrogen atom. The lower the binding energy, the more negative is the nitrogen atom. Consequently, the lower the N–N stretching frequency, the greater is the negative charge on the terminal nitrogen atom. If the decomposition of the monodinitrogen complex in acid solution is considered, it is quite plausible that a first step in the decomposition is



and that this trivalent complex then decomposes. As the N–N stretching frequency is higher in the bisdinitrogen complex than in the monodinitrogen

complex, the nitrogen 1s binding energy should be greater and consequently the negative charges on the terminal nitrogen atoms in the bisdinitrogen complex are smaller than the corresponding charge in the monodinitrogen complex. Thus, the bisdinitrogen complex probably shows smaller affinity to protons than the monodinitrogen complex. Consequently, the bisdinitrogen complex can be more stable in acid solution than the monodinitrogen complex, in accordance with the result of the present investigation.

However, it must be pointed out that it seems¹¹ difficult to know which nitrogen atom in the M–N–N unity that is carrying which charge. Both the nitrogen atoms are found to be negatively charged. The lower the N–N stretching frequency, the more negative are both the nitrogen atoms. The explanation given above is thus valid independent of if the inner or the terminal nitrogen atom is the most negative one.

The stability of the bisdinitrogen complex in alkaline solution can be explained if it is suggested that the hydroxide ions attack the central metal atom in the complexes. In Fig. 4, a plot of the experimental rate constants against the hydroxide ion concentration is presented. The curves are described by the following expression:

$$k = k_1 \frac{\beta_1 [\text{OH}^-]}{1 + \beta_1 [\text{OH}^-]}$$

β_1 is the stability constant of the complex MOH^+ , k is the experimental rate constant and k_1 the rate constant for the decomposition of the complex MOH^+ . From the expression above and Fig. 4, it was possible to obtain an approximate value of $\beta_1 \approx 2.5 \text{ M}^{-1}$. However, it must be pointed out that as the ionic strength is not kept constant in the investigated solutions, it is difficult to make any accurate quantitative comparison between the obtained rate constant values. The ionic strength has not been kept constant, because of difficulties of dissolving the osmium dinitrogen complex in suitable concentrations. On the other hand, if there had been a primary salt effect, the rate constant should decrease with increasing ionic strength according to the Brønsted equation.¹⁴ This is not the case here, so the salt effects are probably small. The estimation of the stability constant β_1 above is consequently only approximate. Nevertheless, it is of interest to get an idea of the order of magnitude of the stability constant. It has been found earlier⁶ that a reasonable explanation of the different influence of dimethyl sulfoxide on the osmium monodinitrogen complex and the osmium bisdinitrogen complex can be that the charge on the metal ion is smaller in the bisdinitrogen complex than in the monodinitrogen complex. Thus, if it is a nucleophilic attack in alkaline solution, this is certainly more pronounced for the monodinitrogen complex than for the bisdinitrogen complex. Consequently, the bisdinitrogen complex can be the most stable, which also has been found.

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