

Studies in Nickel(IV) Chemistry. Part 2.† Kinetics of Proton-assisted Decomposition of Tris(dimethylglyoximato)nickelate(IV) with Concomitant Intramolecular Electron Transfer in Aqueous Media ‡

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The kinetics of proton-assisted decomposition of tris(dimethylglyoximato)nickelate(IV), $[\text{Ni}(\text{dmg})_3]^{2-}$, with concomitant intramolecular electron transfer forming bis(dimethylglyoximato)nickel(II) and/or hexa-aquanickel(II) have been studied. The values of pseudo-first-order rate constants (k_{ad}) corresponding to the solvent-assisted and proton-assisted decompositions satisfy the expression (1)

$$k_{ad} = \frac{k_{0d} + k_{1d}K_{1H}[\text{H}^+] + k_{2d}K_{1H}K_{2H}[\text{H}^+]^2}{1 + K_{1H}[\text{H}^+] + K_{1H}K_{2H}[\text{H}^+]^2} \quad (1)$$

at $I = 0.57$ and 0.25 mol dm^{-3} , where k_{0d} , k_{1d} , and k_{2d} , respectively, refer to the pseudo-first-order rate constants for the solvent-assisted, first protonation-assisted, and second protonation-assisted decomposition paths, and K_{1H} and K_{2H} are the first and second protonation equilibrium constants of $[\text{Ni}(\text{dmg})_3]^{2-}$. Results are interpreted in terms of a mechanism involving formation of protonated nickel(IV) species prior to axial ring-opening and concomitant intramolecular electron transfer.

Recently reports have appeared on the decomposition of some octahedral complexes of Co^{III} , involving ligand dissociation and intramolecular electron transfer.¹ Even though many data are available on proton-assisted dissociation kinetics of metal complexes,²⁻⁸ such reports appear to be scanty for complexes with the central metal atom in an unusual higher oxidation state. We have made a brief mention of the stability of tris(dimethylglyoximato)nickelate(IV), $[\text{Ni}(\text{dmg})_3]^{2-}$ ($\text{dmg}^{2-} =$ dimethylglyoximate dianion), in an earlier paper.⁹ Apart from a qualitative report¹⁰ on the decomposition of this complex in solutions at various pH values, no data are available regarding the nature and extent of decomposition of this complex. An investigation of the proton-assisted decomposition of $[\text{Ni}(\text{dmg})_3]^{2-}$ with concomitant intramolecular electron transfer is now reported.

Experimental

Materials.—The preparation and characterisation of the complex $\text{K}_2[\text{Ni}(\text{dmg})_3]$ and its aqueous solutions have been reported;⁹ freshly prepared aqueous solutions of the complex were employed. Analytical grade reagents were used for preparing buffers or acid solutions; doubly distilled water was used exclusively. The pH values of the solutions were recorded with a Systronics 335 digital pH meter (equipped with glass and saturated calomel electrodes) both before and after the reactions, and the average (which did not differ by more than ± 0.01 unit from the measured values) was taken; the H^+ concentrations were calculated after due correction for the ionic strength effect.¹¹ The ionic strength (I) was maintained with the help of KCl as supporting electrolyte.

Potentiometric Titrations.—Potentiometric pH titrations of an alkaline solution of the Ni^{IV} complex against H^+ were

performed under nitrogen. The pH meter was standardised before use. The protonation constants (which are reciprocals of the acid-dissociation constants of the corresponding conjugate acids) were calculated by earlier reported procedures.¹² The average values of K_{1H} and K_{2H} in aqueous medium at 35°C were respectively 8.07×10^{10} and $2.24 \text{ dm}^3 \text{ mol}^{-1}$ ($I = 0.57 \text{ mol dm}^{-3}$), and 7.08×10^{10} and $4.46 \text{ dm}^3 \text{ mol}^{-1}$ ($I = 0.25 \text{ mol dm}^{-3}$).

Spectrophotometric Titrations.—Spectrophotometric pH titrations were carried out in the 210–380 and 380–600 nm regions by mixing equal volumes of the Ni^{IV} and the buffer or acid solution at 35°C and $I = 0.57 \text{ mol dm}^{-3}$.

Kinetics.—U.v.-visible spectra and kinetic data were recorded with a Pye Unicam SP 1800 or a Zeiss VSU 2-P spectrophotometer, or in an Aminco stopped-flow assembly. In a typical kinetic run, a freshly prepared aqueous solution of the complex was rapidly mixed with an equal volume of acid (or buffer) solution at the desired pH, temperature ($\pm 0.1^\circ\text{C}$) and ionic strength in the cell of the spectrophotometer or the stopped-flow assembly. The decrease in absorbance was recorded continuously as a function of time at 460 nm ($\epsilon_{460} = 9.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Almost no change in rate of absorbance decrease was observed when the monitoring wavelength was other than 460 nm (440–480 nm range), nor was there any appreciable change in rate observed when the reactions (in representative runs) were conducted under nitrogen. The pseudo-first-order rate constant (k_{ad}) was obtained by a linear least-squares analysis of the absorbance and time data in accordance with the expression (i) (which was

$$-\ln[(A_t - A_\infty)/(A_0 - A_\infty)] = k_{ad} t \quad (i)$$

valid for well over three half-lives of disappearance of Ni^{IV} , where A_t , A_0 , and A_∞ , respectively, represent the absorbance at time t , the initial absorbance, and the absorbance at effective infinite time. $[\text{Ni}(\text{Hdmg})_2]$, a product of the reaction, has negligible absorbance at 460 nm. For the major part of the Ni^{IV} disappearance, the reaction medium was homogeneous; slow precipitation of $[\text{Ni}(\text{Hdmg})_2]$ towards the later stages

† Part I is ref. 9.

‡ Presented in part at the All India Symposium on Recent Developments in Chemical Kinetics, Waltair, India, 1981.

Non-S.I. unit employed: $1 \text{ mmHg} = (101.325/760) \text{ Pa}$.

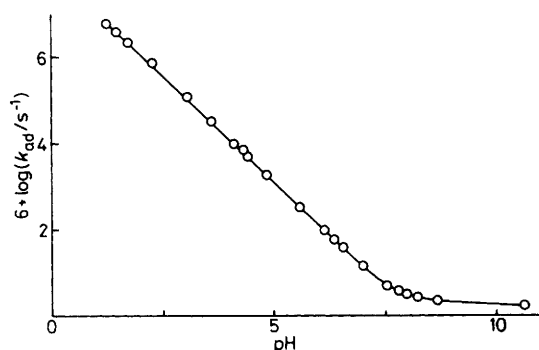


Figure 1. Plot of $\log k_{ad}$ vs. pH; $I = 0.57 \text{ mol dm}^{-3}$, 35°C ; the solid line refers to calculated values

(after three half-lives), particularly at higher pH, did not significantly influence the kinetics at least for three half-lives. The rate constants in replicates (two to seven) were reproducible to within $\pm 5\%$. Computations were carried out with a DCM Data Products minicomputer, Microsystem 1121.

Products.—The acid decomposition of $[\text{Ni}(\text{dmg})_3]^{2-}$ was found to yield $[\text{Ni}(\text{Hdmg})_2]$ as the major product at $\text{pH} \geq 4.5$, and $\text{Ni}^{2+}(\text{aq})$ at $\text{pH} < 3$. The products were identified as follows. A strong solution of Ni^{IV} ($2.5 \times 10^{-2} \text{ mol dm}^{-3}$) containing alkali was treated with a calculated amount of acid so that a pH of *ca.* 6.5 was attained in the final solution. After the decomposition was complete, the red flakes were filtered off. The residue was washed well with water, then with dilute ethanol, air-dried for several hours, and finally dried at *ca.* 110°C . An i.r. spectrum of the dried product matched well that of an authentic sample of $[\text{Ni}(\text{Hdmg})_2]$. In another set of experiments, a strong solution of Ni^{IV} was treated with aqueous acid ($\text{pH} < 1$). The resulting solution was shaken repeatedly with diethyl ether and the aqueous layer was separated, neutralised to pH *ca.* 7 and tested for Ni^{II} with ethanolic H_2dmg or by dropwise addition of aqueous potassium cyanide. The diethyl ether layer was subjected to g.l.c. analysis on a Packard 377 instrument and compared with a diethyl ether extract of an incompletely oxidised mixture of H_2dmg and $[\text{Fe}(\text{CN})_6]^{3-}$. The chromatogram of the acid-decomposed product of $[\text{Ni}(\text{dmg})_3]^{2-}$ showed two bands corresponding to H_2dmg and 3,4-dimethylfuran 5-oxide. The latter product (yellow oil) was separated (b.p. 108°C at 5 mmHg); it is reported to be the product of oxidation of H_2dmg by various other oxidants.¹³

Results and Discussion

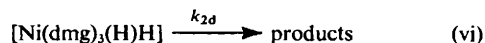
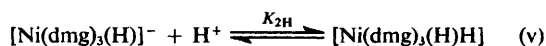
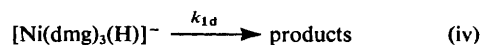
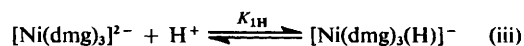
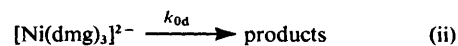
In order to elucidate pathways for acid decomposition of $[\text{Ni}(\text{dmg})_3]^{2-}$, a series of experiments was performed. The reaction was found to exhibit a pseudo-first-order pattern. The first-order disappearance of the Ni^{IV} was maintained for varying $[\text{Ni}^{\text{IV}}]_0$, as seen from constancy of the k_{ad} values over a 25-fold range (8×10^{-6} to $2.1 \times 10^{-4} \text{ mol dm}^{-3}$) at pH 4.3, 4.68, and 5.6, and over a four-fold range (2×10^{-5} to $8 \times 10^{-5} \text{ mol dm}^{-3}$) at pH 9.2; at higher pH, higher $[\text{Ni}^{\text{IV}}]_0$ values could not be used because of earlier precipitation of $[\text{Ni}(\text{Hdmg})_2]$.

The k_{ad} values in aqueous medium were determined in two sets of experiments (pH 1.23–12.3, $I = 0.57 \text{ mol dm}^{-3}$; pH 1.38–10.4, $I = 0.25 \text{ mol dm}^{-3}$). The observations showed a complex dependence of k_{ad} on $[\text{H}^+]$. At pH *ca.* 1.23 to *ca.* 7.6, the k_{ad} values decreased consistently with increasing pH; beyond pH 7.6 (*ca.* 8.3 to *ca.* 10.6) the decrease became marginal (Table 1). A plot of $\log k_{ad}$ vs. pH was almost linear, with a unit negative slope in the pH range *ca.* 1.23–7.6, but became

non-linear beyond pH *ca.* 7.6 (Figure 1); this indicated probable participation of different orders of $[\text{H}^+]$. Use of different buffers at the same pH did not markedly alter the k_{ad} value.

A scheme proposed to account for the observed $[\text{H}^+]$ dependence is presented in equations (ii)–(vi).

The observed k_{ad} can be expressed by equation (vii).



$$k_{ad} = \frac{k_{0d} + k_{1d}K_{1H}[\text{H}^+] + k_{2d}K_{1H}K_{2H}[\text{H}^+]^2}{1 + K_{1H}[\text{H}^+] + K_{1H}K_{2H}[\text{H}^+]^2} \quad (\text{vii})$$

The solvent-assisted decomposition rate constant of $[\text{Ni}(\text{dmg})_3]^{2-}$ (k_{0d}) was evaluated by an approximation. With the assumption that at high pH the protonated complex species are virtually non-existent, so that $k_{ad} \approx k_{0d}$, pseudo-first-order rate constants with respect to the disappearance of Ni^{IV} were obtained at pH 11.6–12.3 ($I = 0.57 \text{ mol dm}^{-3}$; 35°C) by monitoring (initial percentages in nine runs) the decrease in absorbance at 460 nm over 20 days. The average k_{ad} value, $(2.6 \pm 0.5) \times 10^{-7} \text{ s}^{-1}$, was taken as the solvent-assisted decomposition constant (k_{0d}) of the complex for both sets of experiments. The value of k_{0d} was independent of the ionic strength of the medium.

On rearrangement, equation (vii) becomes (viii). From a

$$\frac{k_{ad}(1 + K_{1H}[\text{H}^+] + K_{1H}K_{2H}[\text{H}^+]^2) - k_{0d}}{K_{1H}[\text{H}^+]} = Z$$

$$= k_{1d} + k_{2d}K_{2H}[\text{H}^+] \quad (\text{viii})$$

least-squares analysis of Z and $[\text{H}^+]$ data, the values of k_{1d} and k_{2d} can be obtained. The $k_{ad}(\text{calc.})$ values, estimated from (vii) by employing the computed values of k_{1d} and k_{2d} and the experimentally determined k_{0d} , K_{1H} , and K_{2H} values (at both ionic strengths), match well the observed k_{ad} values (Table 1). Table 2 provides a comparison of the values of various constants.

The complex $[\text{Ni}(\text{dmg})_3]^{2-}$ contains several potential protonation sites, but in the pH range investigated the influence of only two protonations has been detected kinetically. The subsequent protonations are not noticeable either because they do not constitute kinetically significant steps or because their occurrence is outside the investigable range of rate constants at low pH. Of the two kinetically detectable and effective protonations, the constant for the first one is $> 10^{10} \text{ dm}^3 \text{ mol}^{-1}$, and that of the second $< 10 \text{ dm}^3 \text{ mol}^{-1}$. Such a wide divergence in the values of two successive protonation constants is normally not encountered. However, the high value of K_{1H} may be attributed to the formation of an (outside) protonated species by intramolecular hydrogen bonding between dioximate oxygens of two dmg^{2-} ligands. The high values of protonation constants of Ni^{II} ⁸ and Cu^{II} ¹⁴ peptide complexes have been rationalised in terms of intramolecular hydrogen bonding.

In devising the reaction scheme it has been assumed that the first (outside) protonation occurs at dioximate oxygens of two ligands and that rupture of a metal–nitrogen (ligand) bond is not involved. In other words, the low-spin $[\text{Ni}(\text{dmg})_3]^{2-}$, in

Table 1. Pseudo-first-order rate constants ^a for proton-assisted decomposition of [Ni(dmg)₃]²⁻ (aqueous medium, 35 °C)

pH ^b	10 ³ k _{ad} /s ⁻¹	10 ³ k _{ad} (calc.)/s ⁻¹ ^c	pH ^b	10 ³ k _{ad} /s ⁻¹	10 ³ k _{ad} (calc.)/s ⁻¹ ^c
At I = 0.57 mol dm ⁻³					
1.23	5 990 ± 190	5 990	4.85	1.95 ± 0.07	1.9
1.43	4 160 ± 140	4 160	5.60	(3.5 ± 0.13) × 10 ⁻¹	0.35
1.68	2 210 ± 70	2 220	6.15	(1.0 ± 0.04) × 10 ⁻¹	0.1
1.68 ^d	2 100 ± 66	2 220	6.35	(6.4 ± 0.25) × 10 ⁻²	0.064
2.26	736 ± 23	734	6.55	(4.1 ± 0.15) × 10 ⁻²	0.041
3.04	121 ± 5	125	7.01	(1.6 ± 0.06) × 10 ⁻²	0.016
3.60 ^e	34.7 ± 0.7	34.7	7.55	(6.0 ± 0.22) × 10 ⁻³	0.006
3.60 ^f	33.0 ± 1.1	34.7	7.80	(4.0 ± 0.18) × 10 ⁻³	0.004
3.60 ^g	33.9 ± 1.2	34.7	8.01	(3.5 ± 0.15) × 10 ⁻³	0.0036
4.10	11.0 ± 0.4	10.9	8.23	(3.0 ± 0.12) × 10 ⁻³	0.0030
4.30	6.9 ± 0.2	6.9	8.70	(2.5 ± 0.11) × 10 ⁻³	0.0025
4.40	5.5 ± 0.2	5.5	10.66	(1.8 ± 0.08) × 10 ⁻³	0.0021
4.60	3.5 ± 0.1	3.5	11.6—12.3	(2.6 ± 0.5) × 10 ⁻⁴ ^h	
At I = 0.25 mol dm ⁻³					
1.38	7 500 ± 270		4.59	5.0 ± 0.12	
1.52	5 620 ± 200		4.66	4.3 ± 0.15	
1.76	3 310 ± 130		4.85	2.8 ± 0.09	
1.92	2 290 ± 80		4.95	2.2 ± 0.07	
1.92 ^d	2 340 ± 78		5.09	1.6 ± 0.03	
2.18	1 260 ± 50		5.26	1.0 ± 0.02	
2.34	891 ± 29		5.42	(8.0 ± 0.28) × 10 ⁻¹	
2.54	560 ± 21		5.46	(7.0 ± 0.29) × 10 ⁻¹	
2.70	390 ± 14		5.72 ⁱ	(4.0 ± 0.14) × 10 ⁻¹	
3.02	189 ± 7		5.75 ^j	(3.5 ± 0.07) × 10 ⁻¹	
3.16	141 ± 6		6.05	(1.7 ± 0.07) × 10 ⁻¹	
3.40	81 ± 3		6.16	(1.4 ± 0.03) × 10 ⁻¹	
3.62	50 ± 2		6.27	(1.0 ± 0.03) × 10 ⁻¹	
3.77	33.2 ± 1.3		6.40	(1.0 ± 0.02) × 10 ⁻¹	
3.77 ^e	33.2 ± 1		6.75	(4.0 ± 0.1) × 10 ⁻²	
3.78 ^f	33.5 ± 1.2		7.12	(2.3 ± 0.06) × 10 ⁻²	
3.77 ^g	33.8 ± 1.4		7.62 ^k	(1.5 ± 0.04) × 10 ⁻²	
4.03	18.3 ± 0.7		7.65	(1.6 ± 0.05) × 10 ⁻²	
4.08	16.2 ± 0.7		8.30	(1.3 ± 0.04) × 10 ⁻²	
4.24	11.0 ± 0.3		8.64	(1.2 ± 0.03) × 10 ⁻²	
4.35	8.8 ± 0.3		9.42	(1.1 ± 0.04) × 10 ⁻²	
4.35 ^e	8.8 ± 0.3		9.73 ^l	(1.0 ± 0.02) × 10 ⁻²	
4.41	7.6 ± 0.2		10.4	(9.0 ± 0.35) × 10 ⁻³	
4.51	6.0 ± 0.2				

^a Standard deviations calculated from two to seven replicates. ^b From corrected [H⁺]. Key to buffers (unless otherwise mentioned), buffer (pH range): HCl-KCl (1.23—2.26), hydrogen phthalate-H⁺/OH⁻ (2.34—5.72), H₂PO₄⁻-OH⁻ (5.75—7.80), BO₃³⁻-H⁺/OH⁻ (8.01—10.4), HPO₄²⁻-OH⁻ (10.66, 11.6—12.3). ^c Calculated from a least-squares fit of data to equation (vii) (representative). ^d Cl₃CCO₂H-KCl. ^e Acetate-acetic acid. ^f Citric acid-OH⁻. ^g Glycine-OH⁻. ^h Solvent-assisted decomposition (k_{ad}). ⁱ Hydrogenphthalate-OH⁻. ^j H₂PO₄⁻-OH⁻. ^k Tris(hydroxymethyl)aminomethane-HCl. ^l HCO₃⁻-OH⁻.

Table 2. Average values of various constants for proton-assisted decomposition of [Ni(dmg)₃]²⁻ (aqueous medium, 35 °C)

Constant	I = 0.25 mol dm ⁻³	I = 0.57 mol dm ⁻³
k _{ad} /s ⁻¹ ^a	2.6 × 10 ⁻⁷	2.6 × 10 ⁻⁷
K _{1H} /dm ³ mol ⁻¹ ^b	7.08 × 10 ¹⁰	8.07 × 10 ¹⁰
		(8.33 × 10 ¹⁰) ^c
k _{1a} /s ⁻¹	1.16 × 10 ⁻⁵	2.2 × 10 ⁻⁶
k _{1a} K _{1H} /dm ³ mol ⁻¹ s ⁻¹	8.24 × 10 ⁵	1.8 × 10 ⁵
K _{2H} /dm ³ mol ⁻¹ ^b	4.46	2.24
k _{2a} /s ⁻¹	44.3	22.7
k _{2a} K _{2H} /dm ³ mol ⁻¹ s ⁻¹	197.6	50.8

^a Solvent-assisted decomposition in the pH range 11.6—12.3.

^b Values obtained from potentiometric titrations. ^c Value obtained from spectrophotometric pH titrations.

which the dioximate units are co-ordinated symmetrically through nitrogen donors only,⁹ remains octahedral during the formation of the first (outside) protonated species. The cleavage of a Ni-N bond is envisaged as the rate-determining

step, which may lead to ring-opening with a concomitant intramolecular, or a subsequent, very rapid, electron transfer from the ligand to the central Ni^{IV} and dissociation.

The results of spectrophotometric pH titration showed that the characteristics of the visible absorption spectrum did not undergo much noticeable change when the pH of an aqueous solution of the Ni^{IV} was lowered (pH < 9); the 460 nm band retained its original pattern except that it gradually decreased in intensity with time and finally disappeared as the pH was lowered. However, the u.v. spectrum of the complex was significantly affected in solutions of lower pH (Figure 2). The original 265 nm band, displayed by an alkaline solution of the complex (pH ≥ 11.5),⁹ was assigned^{9,15,16} to π-π* transitions of co-ordinated dmg²⁻ and the new band at 225 nm in solutions of lower pH could be assigned to the protonated forms of the dimethylglyoxime ligand.^{15,16} The broad band appearing at 278 nm might be due to the oxidised ligand or an N-protonated species.¹⁷ The titration results indicate that in the pH range 11.68—10.17, the Ni^{IV} complex remains in equilibrium with the first protonated species.

The protonation constant (K_{1H}) and ε_{app} of the first proton-

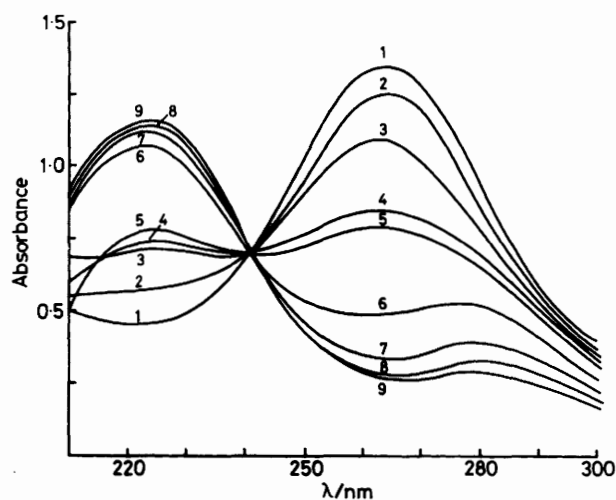


Figure 2. Spectrophotometric pH titrations; $[\text{Ni}(\text{dmg})_3]^{2-}]_0 = 8 \times 10^{-6} \text{ mol dm}^{-3}$; at pH 11.24 (1), 10.93 (2), 10.59 (3), 10.43 (4), 10.17 (5), 9.49 (6), 8.44 (7), 6.88 (8), and 6.05 (9); $I = 0.57 \text{ mol dm}^{-3}$; 35°C

ated species have been calculated from equation (ix), where A_u , A_H , and A_m , respectively, represent the absorbance at 225 nm of the unprotonated $[\text{Ni}(\text{dmg})_3]^{2-}$, the protonated species,

$$(A_m - A_u)^{-1} = (A_H - A_u)^{-1}(K_{nH})^{-1}([\text{H}^+])^{-n} + (A_H - A_u)^{-1} \quad (\text{ix})$$

and an equilibrium mixture. If it is assumed that in the pH range concerned (11.68–10.17) only first protonation occurs (as indicated by kinetics observations as well), then $n = 1$. From a least-squares treatment of absorbance and $[\text{H}^+]$ data (at 225 nm, for solutions of varying pH) in accordance with (ix), the average values of K_{1H} and $\epsilon_{1H(\text{app})}$ computed at 35°C and $I = 0.57 \text{ mol dm}^{-3}$ are $8.33 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1}$ and $1.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. A close agreement of the K_{1H} values obtained from potentiometric and spectrophotometric pH titrations is observed (Table 2).

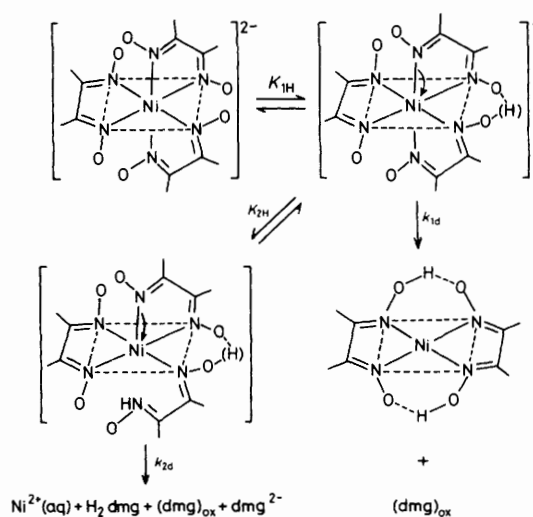
It can be seen from Table 2 that $k_{0d} < k_{1d} \ll k_{2d}$, and the first protonation step enhances the decomposition by a factor (k_{1d}/k_{0d}) of ca. 10; the corresponding increase in the factor (k_{2d}/k_{1d}) caused by the second protonation is ca. 10^7 . In contrast, the magnitudes of the net decomposition rate constant ($k_{nd}K_{nH}$) are in the reverse order; the net decomposition rate due to the second protonation ($k_{2d}K_{2H}$) is actually smaller than that due to the first ($k_{1d}K_{1H}$) by a factor of ca. 3×10^3 . The second protonation, therefore, appears to have only a limited additional effect as far as the total decomposition rate is concerned.

Several explanations can be considered regarding the sites of protonation.

(1) As mentioned earlier, the first protonation is an outside one since K_{1H} is high and k_{0d} and k_{1d} are similar.

(2) The second protonation may be envisaged to occur at another ligand oxygen. That both protonations occur at ligand oxygens does not appear acceptable (at least qualitatively) because of the divergent values of K_{1H} and K_{2H} ; the difference in magnitude would have been less (differing by 10^3 or 10^4) if the two protonation processes were essentially of a similar nature. In fact, the observation that $K_{2H} \ll K_{1H}$ may be taken to indicate only that the second protonation is distinctly different in type from the first.

(3) The other alternative is that the second proton reacts via a direct proton transfer to a ligand nitrogen. This implies that the net decomposition rate due to second protonation



Scheme.

(which is a product of the second protonation constant and the second decomposition rate constant, $K_{2H}k_{2d}$) is actually a single-step second-order rate constant for the direct proton transfer to a ligand nitrogen.

If the first and third explanations were to work in conjunction, the implication is that the second proton is directly added to a weakened or free ligand nitrogen (resulting from assistance by the first protonation). This cumulative effect can explain the observations $K_{1H} \gg K_{2H}$, $k_{2d} \gg k_{1d}$, $(k_{2d}/k_{1d}) \gg (k_{1d}/k_{0d})$, and $(k_{1d}K_{1H}) \gg (k_{2d}K_{2H})$. These suggestions are depicted in the Scheme.

Indirect evidence in support of this suggestion was found when solutions of the Ni^{IV} were mixed (at $I = 0.57 \text{ mol dm}^{-3}$ and 35°C) with acid solutions (so as to obtain a final pH of 1.23, 1.43, 1.68, 2.0, or 2.26 in the reaction mixture) in the stopped-flow apparatus. A sudden deep purple colouration was observed ($\lambda_{\text{max}} = 572 \pm 20 \text{ nm}$) which faded abruptly. However, under the conditions employed, the reaction was too rapid to allow a precise measurement of the initial absorbance.

In summary, (a) $[\text{Ni}(\text{dmg})_3]^{2-}$ decomposes with dissociation and a concomitant intramolecular, or a subsequent very rapid, electron transfer to yield $[\text{Ni}(\text{Hdmg})_2]$ and/or $\text{Ni}^{2+}(\text{aq})$; (b) the decomposition proceeds through a rate-determining cleavage of an Ni-N(ligand) bond in which participation of two protonated species of the Ni^{IV} complex has been detected kinetically; (c) the high value of the first (outside) protonation constant (K_{1H}) and its significant contribution to the overall decomposition rate ($k_{nd}K_{nH}$) suggest that it occurs at dioximate oxygens forming an intramolecular hydrogen bond; (d) the second protonation presumably takes place by direct proton transfer to a ligand nitrogen site; and (e) the subsequent protonations are kinetically unidentifiable.

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