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The Rates and Mechanism of Substitution Reactions of Nickel(II) Acetylacetonato Complexes[1a]

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Rates of some substitution reactions of nickel(II) acetylacetonato complexes in aqueous solution at 25° have been measured using a stopped-flow technique. Hydrolysis of the bis complex occurs in two steps, the second about 200 times slower than the first. Rates of hydrolysis depend on (H^+), suggesting that hydrogen ion traps a half-bonded chelate, causing the reaction to go to completion. When nucleophilic reagents are added, rates of hydrolysis are increased. This effect is attributed to rapid replacement of a water molecule in the first coordination sphere of the nickel by the anion prior to hydrolysis, and not to a direct nucleophilic attack on the metal. The results are rather similar to those found earlier for Pd(acac)$_2$, with which they are compared.

Introduction

Orders of nucleophilic reactivity toward various electrophilic centers are of considerable interest in several connections including that of the concept of hard and soft acids and bases.[2,3] In the case of d^8 metal ions only Pt(II) has been well characterized.[4] Studies of other d^8 systems, such as Au(III)[5] and Pd(II),[6] indicate that their behavior is similar to that of Pt(II). That is, they undergo direct nucleophilic attack, the rates of reaction being strongly dependent on the nature of the entering ligand, and orders of nucleophilic reactivity can be obtained.

The complexes of Ni(II) are labile and thus their reactions have been studied to a lesser extent. One exception to this is the well-studied formation of monosubstituted species in aqueous solution.[7] It is found that the octahedral $Ni(H_2O)_6^{2+}$ reacts *via* an S_N1 mechanism to form $Ni(H_2O)_5L^+$. This agrees with the rule that octahedral complexes tend to react by a dissociative mechanism. This tendency seems to be dictated by steric factors which discourage an increased coordination number in the transition state.[8]

With these facts in mind a study of the substitution reactions of Ni(acac)$_2$ was undertaken. We wished to compare the behavior of this complex with that of other d^8 compounds, in particular the previously studied[6] Pd(acac)$_2$, and possibly to obtain an order of nucleophilic reactivity toward Ni(II).

Experimental Section

Preparation of Materials.—Bis(2,4-pentanedionato)nickel(II),[9] Ni(acac)$_2$, was prepared as described in the literature. The solid compound was characterized by ultraviolet and visible spectra, melting points, and carbon and hydrogen analysis.

Flow Apparatus.—The apparatus used to make the kinetic measurements consisted of a rapid mixing device based on a design by Professor J. M. Sturtevant of Yale University,[10] a Beckman Model DU spectrophotometer modified to give a time resolution of 1.3 msec, and a Tektronix Type 535 oscilloscope with camera. Tests of the apparatus showed that mixing was complete before solutions reached the observation point, a time of less than 5 msec. A study of the decomposition of carbonic acid in water using Dalziel's method[11] gave a rate constant of 11.5 sec^{-1} at 18° and an activation energy of 15.9 kcal/mole, in good agreement with previous results.[11,12]

Treatment of Data.—The data for each kinetic run were obtained in the form of a time-exposure photograph of the oscilloscope screen. Six or more points on the reaction curve were selected, their coordinates were read from the photograph, and the data were punched onto IBM cards. The best least-squares fit to a plot of $-\ln(A - A_\infty)$ *vs.* time, where A_∞ represents absorbancy upon completion of the reaction, was calculated at the Northwestern University Computing Center on an IBM 709 computer. The slope and standard deviation in the slope[13] were printed as output.

All reactions were run under pseudo-first-order conditions in order to simplify the treatment of the data. In this way the problem of having to determine accurately the zero of time and the absorbancy at zero time was avoided. The reported rate constants represent average values of at least two and often three or more kinetic runs. In general the standard deviations in the slopes of kinetic plots were between 1 and 2% of the rate constant. Data were usually rejected when the standard deviation exceeded 5% of the rate constant. Errors are reported as ±2 standard deviations.

Results

Bis(2,4-pentanedionato)nickel(II).—In solutions of low pH Ni(acac)$_2$ is completely decomposed to nickel ion and acetylacetone according to the equations

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[3] R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[4] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 4; (b) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960); (c) F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960); (d) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 418 (1962).

[5] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954); F. Basolo and W. H. Baddley, *Inorg. Chem.*, **3**, 1087 (1964).

[6] (a) R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, **86**, 3983 (1964); (b) D. A. Johnson, Ph.D. Thesis, Northwestern University, 1963.

[7] G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964), and references therein.

[8] F. Basolo and W. H. Baddley, *J. Am. Chem. Soc.*, **86**, 2075 (1964); (see ref 4a, Chapter 3, also).

[9] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

[10] J. M. Sturtevant, private communication.

[11] K. Dalziel, *Biochem. J.*, **55**, 79 (1953).

[12] Q. H. Gibson and F. J. W. Roughton, *Proc. Roy. Soc.* (London), **B143**, 310 (1955); P. Scheurer, R. Brownell, and J. LuValle, *J. Phys. Chem.*, **62**, 809 (1958); J. A. Sirs, *Trans. Faraday Soc.*, **54**, 207 (1958); R. Brinkman, R. Margaria, and F. J. W. Roughton, *Phil. Trans. Roy. Soc.* (London), **A232**, 65 (1933).

[13] Y. Beers, "Introduction to the Theory of Error," Addison Wesley, Reading, Mass., 1957, p 67.

$$Ni(acac)_2(H_2O)_2 + H^+ + 2H_2O \rightleftharpoons Ni(acac)(H_2O)_4^+ + Hacac \quad (1)$$

$$Ni(acac)(H_2O)_4^+ \text{ at } H^+ + 2H_2O \rightleftharpoons Ni^{2+}(aq) + Hacac \quad (2)$$

The two steps occur at quite different rates, reaction 1 being extremely rapid at 25° while reaction 2 is about 200 times slower. The reactions were carried out under pseudo-first-order conditions and gave good first-order plots in all cases. The complex is written as $Ni(acac)_2(H_2O)_2$ because it has been found to be paramagnetic in aqueous solution[14] and presumably has coordinated water molecules above and below the plane of the two acetylacetone rings.

The kinetic data were obtained by observing the change in optical density of the reacting solutions at wavelengths between 305 and 310 mμ. The initial spectrum of $Ni(acac)_2(H_2O)_2$ with a peak at 294 mμ was converted to the spectrum of aqueous acetylacetone at 273 mμ. By running the reaction at several other wavelengths between 250 and 310 mμ, the spectra of two intermediates were obtained. First, the spectrum of $Ni(acac)(H_2O)_4^+$ was produced, due to the rapid decomposition of $Ni(acac)_2(H_2O)_2$. After the slower-reacting $Ni(acac)(H_2O)_4^+$ had also disappeared, the spectrum of enol acetylacetone was observed. This then decreased in intensity until the spectrum of the equilibrium enol–keto mixture was finally reached. In aqueous solution at 25° there is 16 to 20% enol present at equilibrium,[15] and so the enol peak decreases to about one-fifth of its former intensity.

The reason for the choice of 310 mμ for the kinetic experiments is shown in Figure 1. At this wavelength the enol and the keto forms of acetylacetone have nearly the same optical density. This made it possible to obtain a good determination of the optical density after completion of reactions 1 and 2 without the interfering effect of the ketonization of the enol acetylacetone which is the initial product of the hydrolysis. The rate of this third, slower reaction was also measured and found to correspond to the change that occurred when acid was added to a basic solution of acetylacetone.

Reaction 1 was so extremely rapid that it was complete in less than 10 msec in solutions of pH lower than 3. For this reason it was necessary to make studies in a series of phthalate buffer solutions in order to maintain pseudo-first-order conditions. The data which were obtained are shown in Table I. The reproducibility of these experiments was not good, but it appears that the observed pseudo-first-order rate constant increases linearly with increasing hydrogen ion concentration up to $(H^+) = 1.4 \times 10^{-4}$ *M*. The intercept at zero hydrogen ion concentration is very close to zero. A second-order rate constant $k_H' = (8 \pm 2) \times 10^5 M^{-1} sec^{-1}$ was obtained from the slope.

Reaction 2 is slow enough to be followed on the stopped-flow apparatus up to about 0.05 *M* hydrogen ion concentration at 25°. Table II shows the data which were obtained. The increase in rate produced by increasing the ionic strength (due to sodium perchlorate) is also shown in Table II. There appears to be a slight curvature in the plot of the observed rate constant *vs.* hydrogen ion concentration, but this may be due to the inaccuracy of rate constants greater than about 60 sec^{-1}. For the lower portion of the plot, however, we have

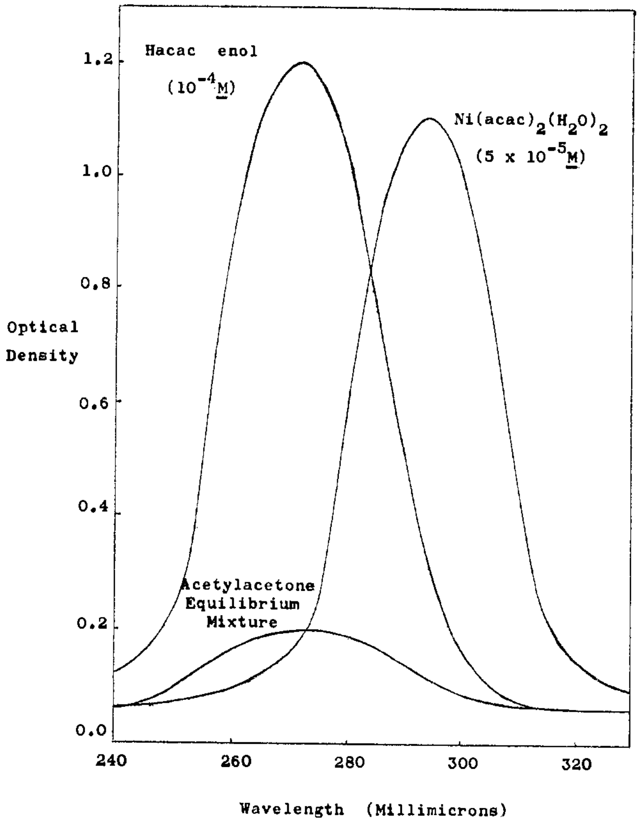

Figure 1.—Spectra of $Ni(acac)_2$, enol form of acetylacetone, and equilibrium mixture of enol and keto forms in water at 25°.

Table I

Observed Rate Constants for the Acid Hydrolysis of $Ni(acac)_2$ at 25.0° (λ 3050 A)

$Ni(acac)_2(H_2O)_2 + H^+ + 2H_2O \rightarrow Ni(acac)(H_2O)_4^+ + Hacac$

$H^+, M \times 10^4$	k_{obsd}, sec^{-1}	$H^+, M \times 10^4$	k_{obsd}, sec^{-1}
0.006	2.5 ± 0.2	0.093	11.1 ± 1.2
0.010	3.8 ± 0.2	0.16	24 ± 2.0
0.021	4.9 ± 0.4	0.29	19 ± 2.0
0.033	7.8 ± 0.8	0.44	27 ± 2.4
0.048	12.2 ± 0.8	0.74	95 ± 10.
0.074	14.2 ± 1.2	1.40	116 ± 14.

$$k_{obsd} = k_H''(H^+) \quad (3)$$

and we obtain $k_H'' = (3.5 \pm 0.5) \times 10^3 M^{-1} sec^{-1}$ from the slope.

This type of behavior is expected if the role of the hydrogen ion is to trap a half-opened chelate ring. It is the same as that found for the acid hydrolysis of $Pd(acac)_2$.[6] In this case a definite leveling off of the observed rate constant is found at high (H^+). An attempt was made to see if Cu^{2+} could take the place of H^+ in trapping the half-open chelate. Little, if any, catalysis was observed up to 0.045 *M* Cu^{2+}. The ef-

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[14] R. S. Nyholm, *Quart. Rev.* (London), **7**, 404 (1953).

[15] A. S. N. Murthy, A. Balasubramanian, C. N. R. Rao, and T. R. Kasturi, *Can. J. Chem.*, **40**, 2267 (1962).

TABLE II

OBSERVED RATE CONSTANTS FOR THE ACID HYDROLYSIS OF Ni(acac)$^+$ AT 25.0° (λ 3050 A)

$Ni(acac)(H_2O)_4^+ + H^+ \rightarrow Ni^{2+}(aq) + Hacac$

H^+, M	k_{obsd}, sec^{-1}	Ionic strength[a]
0.004	15.9 ± 0.32	0.25
0.010	37.1 ± 0.50	0.25
0.020	64 ± 2.0	0.25
0.040	120 ± 7.1	0.25
0.010	19.1 ± 0.26	0.01
0.010	25 ± 1.6	0.05
0.010	30 ± 1.2	0.11
0.010	33 ± 1.8	0.21
0.010	38 ± 2.2	0.31
0.010	41 ± 2.2	0.41
0.010	28 ± 1.4	0.055[b]
0.010	32 ± 1.8	0.100[c]
0.010	21 ± 1.8	0.21[d]

[a] Constant ionic strength achieved by adding sodium perchlorate. [b] Containing also 0.030 M $Cu(NO_3)_2$. [c] Containing also 0.045 M $Cu(NO_3)_2$. [d] Containing also 0.20 M $AgClO_4$.

fect of Ag^+ was also tested, following a report of a complex between silver ion and $Ni(acac)_2$ in the solid state.[16] If anything, Ag^+ had a decelerating effect. The difference between Cu^{2+} and Ag^+ might be due to the fact that silver was used as the perchlorate salt and copper as the nitrate. The data obtained when these ions were present are shown in Table II.

The second step in the hydrolysis, reaction 2, was also carried out in the presence of various nucleophilic reagents. Increasing concentrations of thiocyanate, sulfate, pyridine, hydroxylamine, fluoride, acetate, chloride, and perchlorate ions produced increases in rate. Variations in the concentrations of thiourea had no effect on the rate of reaction. Table III gives the rate constants except for perchlorate ion which is in Table II. The values of k_{cor} in Table III are obtained by subtracting from k_{obsd} the rate constant predicted by eq 3 for hydrogen ion catalysis alone. A small correction for differences in ionic strength was also made. The k_{cor} values give a better comparison in cases where the hydrogen ion concentration or ionic strength were not held constant. The increase in the rate of hydrolysis with increasing perchlorate ion concentration (Table II) was originally attributed to a medium effect, but recent reports[17] of perchlorate complexes indicate that this ion may not be as innocuous as was heretofore assumed.

In the case of thiocyanate, sulfate, acetate, pyridine, hydroxylamine, and fluoride, a plot of k_{obsd} *vs.* concentration of reagent, at constant hydrogen ion concentration, is linear and has an intercept equal to k_{obsd} for hydrogen ion alone. This indicates a k_{obsd} of the form

$$k_{obsd} = k_H''(H^+) + k_X''(X) \tag{4}$$

where (X) represents the concentration of added nucleophile. The slope of such a plot also depends on hydrogen ion concentration and so k_X'' must be a function of (H^+). Figure 2 gives the plots obtained for thiocyanate ion.

TABLE III

OBSERVED RATE CONSTANTS FOR HYDROLYSIS OF Ni(acac)$^+$ IN THE PRESENCE OF ADDED NUCLEOPHILES AT 25° (λ 3100 A)

H^+, M	X, M		k_{obsd}, sec^{-1}		k_{cor}, sec^{-1}	Ionic strength
0.005	0.00	SCN^-	16.7[a]	± 0.20	...	0.25
0.005	0.01		18.4	± 0.07	1.7	0.25
0.005	0.02		21.3	± 0.90	4.3	0.25
0.005	0.04		24.5	± 1.0	7.3	0.25
0.005	0.08		31.	± 1.3	14.3	0.25
0.005	0.16		46.	± 1.5	29.3	0.25
0.010	0.00	SCN^-	33.5[a]	± 0.5	...	0.25
0.010	0.01		40.	± 2.0	6.5	0.25
0.010	0.02		46.	± 2.0	12.5	0.25
0.010	0.04		55.	± 3.0	21.5	0.25
0.010	0.08		88.	± 4.0	54.5	0.25
0.010	0.00	Cl^-	19.1	± 0.26	...	0.01
0.010	0.01		17.0	± 0.13	...	0.01
0.010	0.03		17.9	± 0.26	...	0.03
0.010	0.06		21.7	± 0.24	...	0.06
0.010	0.10		25.6	± 0.48	...	0.10
0.010	0.20		28.8	± 0.42	...	0.20
4.9×10^{-5}	0.004	OAc^-	0.29	± 0.006	0.21	0.01
5.2×10^{-5}	0.020		0.92	± 0.012	0.79	0.07
6.2×10^{-5}	0.000	OAc^-	0.27[a]	± 0.006	...	0.25
6.2×10^{-5}	0.051		2.41	± 0.028	2.20	0.23
6.2×10^{-5}	0.066		3.04	± 0.05	2.81	0.31
6.4×10^{-5}	0.079		3.94	± 0.06	3.71	0.39
6.5×10^{-5}	0.097		4.72	± 0.12	4.45	0.48
2.0×10^{-4}	0.0000	OAc^-	0.60[a]	± 0.02	...	0.25
2.0×10^{-4}	0.0021		0.84	± 0.02	0.14	0.25
2.1×10^{-4}	0.0041		1.24	± 0.04	0.50	0.25
2.0×10^{-4}	0.0206		2.92	± 0.05	2.22	0.25
0.010	0.00	tu[b]	19.1	± 0.26	...	0.01
0.010	0.01		18.1	± 0.2	...	0.01
0.010	0.04		17.0	± 0.3	...	0.01
0.010	0.10		19.8	± 0.5	...	0.01
0.010	0.20		18.1	± 0.6	...	0.01
5.6×10^{-5}	0.000	py[b]	0.12[a]	± 0.003	...	0.04
5.6×10^{-5}	0.005		0.25	± 0.003	0.12	0.04
5.6×10^{-5}	0.012		0.33	± 0.003	0.17	0.09
5.6×10^{-5}	0.021		0.57	± 0.009	0.40	0.17
5.6×10^{-5}	0.026		0.66	± 0.008	0.48	0.21
0.0068	0.000	SO_4^{2-}	20.[a]	± 0.5	...	0.14
0.0068	0.038		56.	± 3.2	36.	0.14
0.0072	0.053		80.	± 2.4	57.	0.18
0.0068	0.077		96.	± 2.9	73.	0.25
0.0068	0.095		119.	± 5.8	94.	0.31
0.0030	0.026	SO_4^{2-}	18.6	± 0.4	10.7	0.07
0.0042	0.043	SO_4^{2-}	41.5	± 1.8	29.3	0.12
1.1×10^{-4}	0.0000	hx[b]	0.38[a]	± 0.01	...	2.0
1.1×10^{-4}	0.0013		0.47	± 0.03	0.10	2.0
1.1×10^{-4}	0.0025		0.55	± 0.03	0.17	2.0
1.1×10^{-4}	0.0042		0.65	± 0.04	0.28	2.0
2.8×10^{-4}	0.00	F^-	0.95	± 0.03	...	0.25
2.7×10^{-4}	0.03		1.18	± 0.05	0.25	0.25
3.0×10^{-4}	0.13		1.66	± 0.07	0.64	0.25
2.8×10^{-4}	0.18		2.14	± 0.11	1.19	0.25

[a] Extrapolated from previous data. [b] Abbreviations used: tu, thiourea; py, pyridine; hx, hydroxylamine.

Discussion

The acid dependence of the hydrolysis of $Ni(acac)_2$ suggests that the usual mechanism for the acid hydroly-

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(16) D. N. Busch and R. A. Krause, *Nature*, **181**, 1529 (1958).

(17) (a) F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965); (b) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

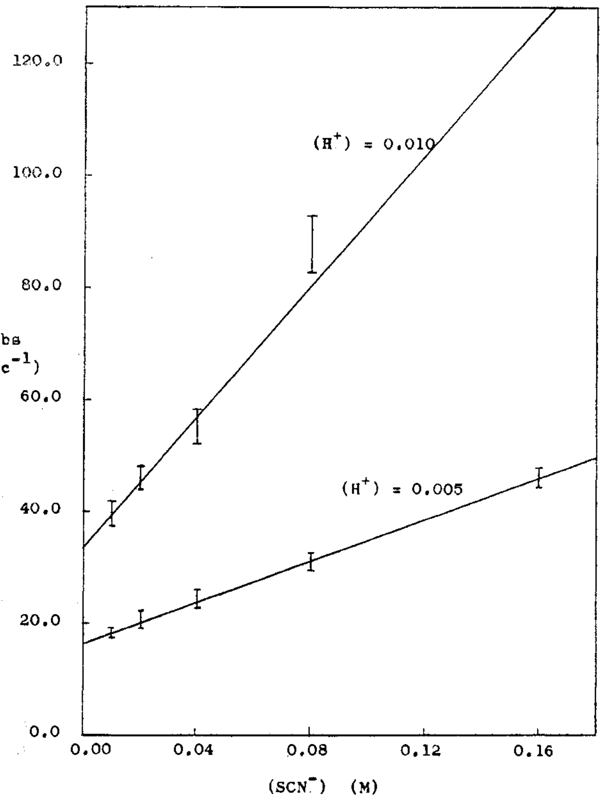

Figure 2.—Plot of k_{obsd} *vs.* thiocyanate ion concentration for acid hydrolysis of $\mathrm{Ni(acac)^+}$ at 25°.

sis of flexible chelates[18] is operating here. In this mechanism protonation of a dangling chelate ligand prevents reclosing of the ring. An example of this type of mechanism for $\mathrm{Ni(acac)(H_2O)_4{}^+}$, where O–O⁻ represents acetylacetonate ion, is given on the left side of Figure 3. This mechanism was found to be the most reasonable one for hydrolysis of $\mathrm{Pd(acac)_2}$,[6] and a half-bonded intermediate has been reported by other workers[19] in the isomerization of substituted acetylacetonates.

If the assumption is made that intermediates (2) and (3) are present in small, constant concentrations throughout the reaction, then the following rate law may be derived for the mechanism shown on the left side of Figure 3.

$$\text{rate} = k_{\mathrm{obsd}}(\text{complex}) \tag{5}$$

$$k_{\mathrm{obsd}} = \frac{k_1(\mathrm{H^+})}{\dfrac{k_{-1}}{k_2K_1} + (\mathrm{H^+})} \tag{6}$$

If $(k_{-1}/k_2K_1) \gg (\mathrm{H^+})$, k_{obsd} will be of the form observed in eq 3, where

$$k_{\mathrm{H}}'' = (k_1k_2K_1/k_{-1}) \tag{7}$$

but if $(\mathrm{H^+}) \gg (k_{-1}/k_2K_1)$, a leveling effect with increasing $(\mathrm{H^+})$ will be observed and the rate will finally become independent of $(\mathrm{H^+})$ with $k_{\mathrm{obsd}} = k_1$. Such a leveling effect was observed for $\mathrm{Pd(acac)_2}$ when the hydrogen ion concentration exceeded about 0.2 *M*.[6a]

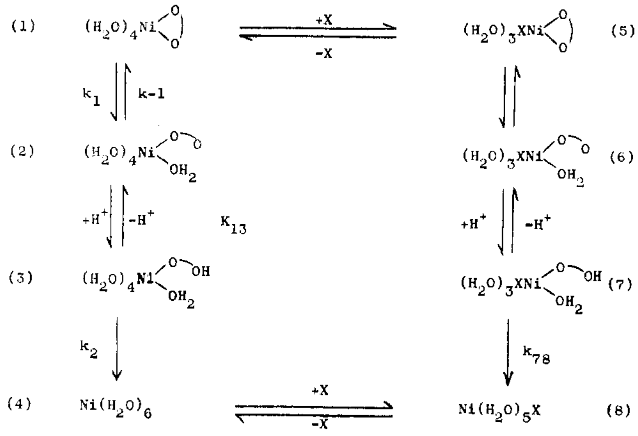

Figure 3.—Probable mechanism for acid-catalyzed hydrolysis and substitution of $\mathrm{Ni(acac)(H_2O)_4{}^+}$.

A slight curvature in the plot of k_{obsd} *vs.* $(\mathrm{H^+})$ for $\mathrm{Ni(acac)^+}$ was observed and might be taken as evidence for this type of mechanism. However, the deviation from linearity was small and, especially in the case of runs at larger $(\mathrm{H^+})$, might also be attributed to experimental errors.

A consideration of the various factors which appear in eq 6 suggests that the ratio k_{-1}/k_2K_1 for nickel would be similar to that for palladium. This would predict that a leveling of the rate would not occur until about 0.2 *M* $(\mathrm{H^+})$ for both metal ions. This would be impossible to detect for nickel ion since the rate would be outside the accessible range. This is true both for $\mathrm{Ni(acac)_2}$ and $\mathrm{Ni(acac)^+}$.

The increased rate of reaction when various nucleophiles are added is again quite similar to what was found in the acid cleavage of $\mathrm{Pd(acac)_2}$.[6] The chief difference in the two systems is that the reactions of $\mathrm{Ni(acac)_2}$ and of $\mathrm{Ni(acac)^+}$ are some 10^6 and 10^4 times faster, respectively, than the reactions of $\mathrm{Pd(acac)_2}$. Also the reagents which are most effective for palladium(II) are not the same as those for nickel(II).

The rate law for that part of the reaction due to added nucleophiles in the case of $\mathrm{Pd(acac)_2}$ was found to be[6]

$$k_{\mathrm{oor}} = \frac{k_x(\mathrm{H^+})(\mathrm{X})}{K_x + (\mathrm{H^+})} \tag{8}$$

where k_x and K_x are constants whose interpretation depends on the mechanism assigned. The data in Table III also fit eq 8, as far as they go, though in no case is there evidence for the $(\mathrm{H^+})$ term in the denominator. This is not unexpected in view of the previous discussion.

On the assumption that eq 9 is valid, values of k_x/K_x

$$k_{\mathrm{cor}} = \frac{k_x}{K_x}(\mathrm{H^+})(\mathrm{X}) \tag{9}$$

have been extracted from the results of Table III to give a set of numbers which are a measure of the reactivity of various nucleophiles X. These are listed in

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[18] (a) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 152–157.

[19] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

TABLE IV

RATE CONSTANTS FOR SUBSTITUTION OF VARIOUS LIGANDS IN $Ni(acac)(H_2O)_4^+$ AT 25°

X	H^+, *M*	$k_x(H^+)/K_x$, sec^{-1} M^{-2}	k_x/K_x, sec^{-1} M^{-2}	K_{f1}, M^{-1}
SO_4^{2-}	0.0068	1000 ± 100	$(1.5 \pm 0.2) \times 10^5$	10–250[a]
	0.0042	680 ± 50	$(1.6 \pm 0.1) \times 10^5$	
	0.0030	410 ± 30	$(1.4 \pm 0.1) \times 10^5$	
py	5.6×10^{-5}	18 ± 3	$(3.2 \pm 0.5) \times 10^5$	15–83[a]
hx	1.1×10^{-4}	66 ± 5	$(6.0 \pm 0.5) \times 10^5$	32[b]
SCN^-	0.010	580 ± 80	$(5.8 \pm 0.8) \times 10^4$	15–57[a]
	0.005	180 ± 16	$(3.6 \pm 0.4) \times 10^4$	
OAc^-	0.6×10^{-4}	44 ± 5	$(7.3 \pm 0.9) \times 10^5$	2.5 to 63[a]
	2.0×10^{-4}	111 ± 15	$(5.6 \pm 0.8) \times 10^5$	
F^-	2.8×10^{-4}	6.1 ± 1.5	$(2.2 \pm 0.5) \times 10^4$	4.6[a]
Cl^-	0.010	75 ± 25	$(7.5 \pm 2.5) \times 10^3$	0.2–7.8[a]
ClO_4^-	0.010	66 ± 30	$(6.6 \pm 3.0) \times 10^3$	Small[c]
tu	0.010	0	0	Not reported
H_2O	...	...	$(3.5 \pm 0.5) \times 10^3$	0.018

[a] Ref 20. [b] I. Szilard, *Acta Chem. Scand.*, **17,** 2674 (1963). [c] Ref 17.

Table IV. These numbers may now be compared with the corresponding number for water as a nucleophile, which is just k''. For a more valid comparison k'' should be divided by 55.5 *M*, the concentration of water.

The corresponding numbers for the case of $Pd(acac)_2$ may also be calculated. These correspond to $k_3k_4K_n/k_{-3}$ for various nucleophiles, using the terminology of ref 6. Dividing the constant for water by 55.5 gives the relative reactivities for $Pd(acac)_2$ as approximately

H_2O	Cl^-	Br^-	I^-	SCN^-	OAc^-
1	1500	5000	5×10^4	2×10^5	100

Where the same nucleophiles are involved, the data of Table IV give relative reactivities

H_2O	Cl^-	SCN^-	OAc^-
1	100	1000	10^4

The same ordering is not found. This is not unexpected since Pd(II) is a typical soft electrophile, whereas Ni(II) is a borderline case, intermediate between hard and soft.[3] Thus the rather low reactivity of SCN^- and the high reactivity of acetate ion are not unexpected for nickel complexes. Also the high reactivity of SO_4^{2-} and F^- shown in Table IV is reasonable. The table shows the formation equilibrium constants, K_{f1}, for the various nucleophiles which are available in the literature.[20] There is a strong correlation between the stability constants and the rate parameter, k_x/K_x.

The rate increases produced by added nucleophiles are somewhat surprising for $Ni(acac)^+$ in view of the expectation that octahedral complexes react by a dissociation mechanism.[8] The assumption is that the species present is $Ni(acac)(H_2O)_4^+$. However this is a rather special case in that the water ligands are probably considerably more labile than is acetylacetone anion. Thus for both $Ni(acac)_2(H_2O)_2$ and $Ni(acac)(H_2O)_4^+$ it is likely that a nucleophile simply adds on as a ligand in place of one of the coordinated water molecules in a rapid, preequilibrium step. This new complex could then be the reactive species for ring opening. The right-hand side of Figure 3 shows a possible detailed mechanism.

Confirmation that this type of preequilibrium is indeed a possibility is found in the work of Horrocks, Taylor, and LaMar[21a] and Happe and Ward.[21b] They report, on the basis of proton magnetic resonance measurements, that rate constants for exchange of ligands in the apical positions on Ni(acac) are in excess of 10^3 sec^{-1}. Eigen[22] gives a constant slightly larger than 10^4 sec^{-1} for replacement of a water molecule in the first coordination shell of Ni^{2+}. These rates are well in excess of the over-all rates of cleavage observed in this work.

In order to rationalize the relative efficiencies of various nucleophiles, it is unnecessary to consider the several intermediate steps of the mechanism. One need go only to the transition state for the rate-determining step, which is labeled k_{78} in Figure 3. This transition state is identical in composition with the transition state for the corresponding slow step in the hydrolysis of $Pd(acac)_2$. In the latter case solvent molecules above and below the plane of the complex are assumed to give effective six-coordination.[23] In both cases the nucleophile X is firmly bound in the transition state and the half-open chelate is in the act of opening completely.

Since the effect of X in the $Pd(acac)_2$ case could be explained in terms of the expected nucleophilic reactivity series for a soft electrophile, it appears logical to say that the effect of X in $Ni(acac)^+$ is related to a nucleophilic reactivity series for a somewhat harder electrophile. Thus in this special case X plays a similar role to a nucleophile in stabilizing the transition state even though an SN2 mechanism is not operating. The steric factor which usually prevents a nucleophile from acting on an octahedral complex can be circumvented if one or more very labile ligands are present in the complex.

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It has been shown for certain cationic tropolone and diketone complexes that hydroxide ion can attack the carbonyl function of the ligand.[24] The great sensitivity of $Si(acac)_3^+$ to a variety of basic reagents may be due to attack on the carbonyl group, rather than to an SN2 attack on metal as was originally supposed.[25]

For $Pd(acac)_2$ there is no detectable attack on the carbonyl group by hydroxide ion.[6] In the case of $Ni(acac)^+$ it cannot be excluded that some of the more basic reagents of Table III are not attaching themselves to the carbonyl group. However, the fact that thiocyanate ion, which is ineffective as a nucleophile toward the carbonyl function,[25] shows such a large rate effect suggests that this is a minor mode of reaction in all cases. It should be mentioned that there is a rapid reaction of $Ni(acac)_2$ with hydroxide ion. However, the kinetic results are complex and not easy to interpret.[26]

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The Rates and Mechanism of Hydrolysis Reactions of Some Metal Acetylacetonates[1a]

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Rates of hydrolysis of acetylacetone complexes of oxovanadium(IV) and beryllium(II) have been measured using a stopped-flow technique. In aqueous solution at 25° $VO(acac)_2$ decomposes in two steps with the second ring being removed 150 times slower than the first. Both rings were removed from $Be(acac)_2$ at the same rate. The hydrogen ion dependence of the rates indicates that the special chelate mechanism, in which H^+ traps a half-bonded intermediate, is a general one for hydrolysis of acetylacetonates. The behavior of hydrolysis rates upon addition of nucleophilic reagents is consistent with the interpretation that direct nucleophilic attack on the metal ion does not occur. The vanadyl complex, however, can add a sixth group which influences the rate of dissociation.

Introduction

In recent kinetic studies of inorganic reactions there has arisen a clear correlation of structure of a metal complex and its mechanism of reaction. The SN1 (dissociative) mechanism is usually characteristic of octahedrally coordinated complexes such as those of Co(III),[2] while the SN2 (nucleophilic displacement) mechanism is found to occur in square-planar complexes such as those of Pt(II).[2] One might expect this type of correlation to extend to other coordination arrangements than the square plane and octahedron, but little is known of the mechanisms of reaction of, for example, tetrahedral complexes because they usually react rapidly.[3] The situation is even less clear in other cases, though recently a detailed study was made of five-coordinated trigonal-bipyramidal complexes of Pt(II).[4]

Complexes of 2,4-pentanedione (acetylacetone, acacH) are formed by a wide variety of metal ions and also have a number of different coordination numbers and geometries. These include tetrahedral,[5] square-planar,[6] square-pyramidal,[7] square-antiprismatic, and octahedral[8] complexes. In addition, several previous studies of acetylacetone complexes have been reported in an attempt to determine orders of nucleophilic reactivity toward metal ions.[9] Thus this study of two other metal acetylacetonates was undertaken in order to extend our knowledge of the reactions of less commonly studied coordination geometries, the tetrahedral and square-pyramidal.

Experimental Section

Materials.—Bis(2,4-pentanedionato)oxovanadium(IV),[10a] $VO(acac)_2$, and bis(2,4-pentanedionato)beryllium(II),[10b] $Be(acac)_2$, were prepared as described in the literature. The solid compounds were characterized by ultraviolet and visible spectra and

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