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 S$_N$2 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]

(24) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **87**, 21 (1965).

(25) R. G. Pearson, D. R. Edgington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

(26) J. W. Moore, Ph.D. Dissertation, Northwestern University, 1964.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

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

BY RALPH G. PEARSON AND JOHN W. MOORE[1b]

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 S$_N$1 (dissociative) mechanism is usually characteristic of octahedrally coordinated complexes such as those of Co(III),[2] while the S$_N$2 (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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(2) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958; (b) F. Basolo and W. H. Baddley, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

(3) Ref. 2a, p 209; F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 56 (1961).

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(7) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

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(10) (a) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 114 (1957); (b) M. M. Jones, *J. Am. Chem. Soc.*, **81**, 3188 (1959).
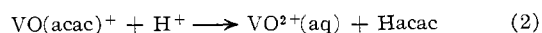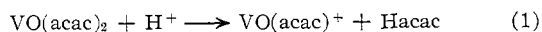
by melting points. Sodium hydroxide solutions were prepared by dilution of a saturated stock and standardized against potassium hydrogen phthalate. A solution of perchloric acid was prepared by dilution of the concentrated reagent and standardized against the sodium hydroxide. Solutions containing various anions were made up by dissolving weighed quantities of reagent grade solids. In the case of strongly basic anions, pH measurements were made before and after reaction, and the average value was used to calculate concentrations of the desired species from their acidity constants. Ionic strength was adjusted using stock solutions of reagent grade sodium perchlorate monohydrate.

Kinetic Measurements.—The flow apparatus described previously[11] was used for all kinetic studies reported here. The mode of operation was the same as that reported in ref 11.

Results

Bis(2,4-pentanedionato)oxovanadium(IV).—This compound was of interest because of its unusual square-pyramidal structure.[6] The reactions of $VO(acac)_2$ were studied at 3150 A, where enol and keto acetylacetone have nearly the same extinction coefficients. The spectra observed for reactants, intermediates, and products were similar to those reported in the case of $Ni(acac)_2$[11] except that λ_{max} for the vanadyl complex is at 3010 A as compared with 2940 A for the nickel compound. Acetylacetone in the enol form was the initial product of reaction. Subsequently about 80% of this isomerized to the keto form.

In aqueous acid $VO(acac)_2$ hydrolyzes stepwise as shown in eq 1 and 2. The rates of the two steps differ

$$VO(acac)_2 + H^+ \longrightarrow VO(acac)^+ + Hacac \quad (1)$$

$$VO(acac)^+ + H^+ \longrightarrow VO^{2+}(aq) + Hacac \quad (2)$$

by a factor of about 150 at 25°, reaction 2 being slower. Good pseudo-first-order plots were obtained for each step by selecting the proper time scale setting on the oscilloscope. When the initial pH of the solution containing $VO(acac)_2$ was adjusted so that 75% of the vanadyl ion present had been converted to $VO(acac)^+$,[12] the rates obtained corresponded to those for the second step of the reaction where the bis chelate was the starting material. Table I gives the data which were obtained. For reaction 1 k_{obsd} is proportional to hydrogen ion concentration over the range $0.005 < (H^+) < 0.200$, and the same is true for reaction 2 over the range $0.005 < (H^+) < 0.7$. In the case of reaction 2 larger hydrogen ion concentrations produced an upward curvature in a plot of k_{obsd} vs. (H^+), indicating some new effect at high acid concentration.

When reactions 1 and 2 were carried out in the presence of added nucleophilic reagents the rates of reaction were increased in some cases. The data in Table II indicate that hx, OAc^-, SCN^-, and F^- have appreciable effects. Plots of k_{obsd} vs. (X) in these cases appear to be linear, but there is a good deal of scatter. In the case of SCN^-, which affects $VO(acac)^+$ more than $VO(acac)_2$, some of the scatter is due to the difficulty of separating the rate constants of the two reactions as they approach one another.
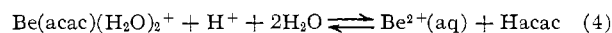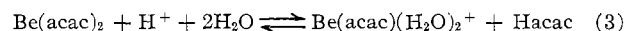
(11) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1523 (1966).
(12) A. E. Martell and L. G. Sillén, Ed., "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

TABLE I

OBSERVED RATE CONSTANTS FOR ACID HYDROLYSIS OF $VO(acac)_2$ AND $VO(acac)^+$ AT 25° (λ 3150 A)

$$VO(acac)_2 + H^+ \rightarrow VO(acac)^+ + Hacac$$
$$VO(acac)^+ + H^+ \rightarrow VO^{2+} + Hacac$$

H^+, M	$VO(acac)_2$	$VO(acac)^+$
	k_{obsd}, sec^{-1} [b]	
0.005	2.5 ± 0.1	0.031 ± 0.001
0.010	5.0 ± 0.3	0.041 ± 0.001
0.012	5.2 ± 0.1	0.038 ± 0.001
0.024	9.6 ± 0.5	0.067 ± 0.002
0.050	15.0 ± 1.6	0.128 ± 0.005
0.100	24.1 ± 2.4	0.251 ± 0.011
0.119	45.7 ± 1.0	0.30 ± 0.01
0.150	51.2 ± 2.9	0.39 ± 0.01
0.200	74.3 ± 5.7	0.45 ± 0.02
0.238	...	0.57 ± 0.02
0.250	...	0.59 ± 0.03
0.712	...	1.64 ± 0.09[c]
1.42	...	5.0 ± 0.3[d]
0.150	...	0.38[a] ± 0.03
0.200	...	0.54[a] ± 0.02

[a] Starting material is $VO(acac)^+$. [b] Ionic strength is 0.25 M except where noted. [c] $I = 0.71 M$. [d] $I = 1.42 M$.

Bis(2,4-pentanedionato)beryllium(II).—The rates of hydrolysis for this tetrahedral complex were considerably slower than for the vanadyl complex, and so a much wider range of hydrogen ion concentrations could be studied. The reaction was assumed to occur stepwise as shown in eq 3 and 4, but it was found that both steps occurred at the same rate.

$$Be(acac)_2 + H^+ + 2H_2O \rightleftharpoons Be(acac)(H_2O)_2^+ + Hacac \quad (3)$$

$$Be(acac)(H_2O)_2^+ + H^+ + 2H_2O \rightleftharpoons Be^{2+}(aq) + Hacac \quad (4)$$

Both reaction 3 and reaction 4 could be studied by preparing solutions of different initial pH. By calculating from the equilibrium constants[12] in the literature, solutions were prepared which contained 90% of the Be as $Be(acac)_2$. When treated with excess acid, these solutions reacted in a single step to form $Be^{2+}(aq)$ and acetylacetone. Good pseudo-first-order plots were obtained. Solutions initially consisting of 65% $Be(acac)(H_2O)_2^+$ also gave pseudo-first-order kinetics, and at a given hydrogen ion concentration the rates were equal to those for $Be(acac)_2$. The data are given in Table III together with results at different temperatures for reaction 3.

These reactions were followed over a range of wavelengths between 2500 and 3100 A, and the presence of enol acetylacetone as the initial product of the reaction was confirmed. Most of the kinetic data were obtained at 3100 A.

A plot of the observed psuedo-first-order rate constant vs. hydrogen ion concentration shows a very interesting dependence of rates on (H^+). Below about 0.1 M (H^+) the rates increase almost linearly with acid concentration. Between 0.1 and 0.5 M (H^+) the plot levels off and then above about 1.0 M (H^+) the rates increase very rapidly again. This behavior is shown in Figure 1.

It was also of interest to see whether $Be(acac)_2$ would undergo nucleophilic attack when various reagents

TABLE II

OBSERVED RATE CONSTANTS FOR ACID HYDROLYSIS OF VO(acac)$_2$ AND VO(acac)$^+$ IN THE PRESENCE OF ADDED NUCLEOPHILES (λ 3150 A)

H$^+$, M	X, M		k_{obsd}, sec^{-1} [b]	
			VO(acac)$_2$	VO(acac)$^+$
0.010	0.000	SCN$^-$	5.0 ± 0.3	0.041 ± 0.001
0.010	0.005		5.2 ± 0.2	0.059 ± 0.003
0.010	0.020		4.8 ± 0.3	0.092 ± 0.005
0.010	0.050		5.3 ± 0.3	0.125 ± 0.009
0.010	0.100		7.2 ± 0.4	0.303 ± 0.009
0.010	0.000	Cl$^-$	5.0 ± 0.3	0.041 ± 0.001
0.010	0.005		4.5 ± 0.2	0.051 ± 0.003
0.010	0.100		4.3 ± 0.2	0.046 ± 0.003
0.010	0.000	Br$^-$	5.0 ± 0.3	0.041 ± 0.001
0.010	0.005		4.4 ± 0.2	0.050 ± 0.003
0.010	0.100		4.6 ± 0.1	0.051 ± 0.003
0.010	0.000	I$^-$	5.0 ± 0.3	0.041 ± 0.001
0.010	0.005		4.2 ± 0.2	0.042 ± 0.002
0.010	0.050		4.4 ± 0.2	0.047 ± 0.001
0.010	0.100		4.1 ± 0.2	0.045 ± 0.001
8.4 × 10^{-5}	0.000	OAc$^-$	0.030[a] ± 0.002	...
8.2 × 10^{-5}	0.005		0.066 ± 0.003	...
8.4 × 10^{-5}	0.010		0.067 ± 0.002	...
8.3 × 10^{-5}	0.020		0.076 ± 0.006	...
8.6 × 10^{-5}	0.030		0.127 ± 0.010	...
2.7 × 10^{-4}	0.00000	hx	...	0.0006[a] ± 0.0001
2.6 × 10^{-4}	0.00057		...	0.0017[c] ± 0.0002
2.7 × 10^{-4}	0.00111		...	0.0012[c] ± 0.0002
2.7 × 10^{-4}	0.00166		...	0.0021[c] ± 0.0005
6.6 × 10^{-5}	0.0006	hx	0.15 ± 0.02	0.00075 ± 0.00002
10.5 × 10^{-5}	0.0018		0.27 ± 0.04	0.00122 ± 0.00005
2.8 × 10^{-4}	0.00	F$^-$	0.10[a] ± 0.01	...
2.7 × 10^{-4}	0.03		0.15 ± 0.01	...
3.0 × 10^{-4}	0.13		0.45 ± 0.02	...
2.8 × 10^{-4}	0.18		0.28 ± 0.02	...

[a] Extrapolated from previous data. [b] Ionic strength is 0.25 M except where noted. [c] Ionic strength is 2.0 M.
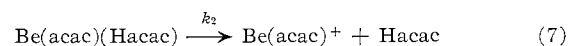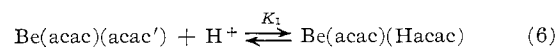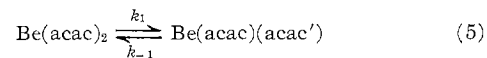
were added to the reaction mixture. Few studies have been made of the substitution reactions of tetrahedral complexes, but in general mechanisms involving an intermediate of expanded coordination number have been suggested.[3] Since Be^{2+} is a hard acid,[13] one would expect hard bases such as F$^-$, OAc$^-$, and OH$^-$ to be most effective in attacking Be(acac)$_2$. However, the data in Table IV indicate that, with the possible exception of hydroxylamine, the rate of hydrolysis is not affected by the addition of nucleophilic reagents.

Discussion

The kinetic data on acid hydrolysis of the metal acetylacetonates studied here are quite similar. The beryllium complex has an unusual rate profile with (H$^+$), and there is some indication that the vanadyl complex behaves in like fashion. In this latter case rapid increase in rate at high acid concentrations probably cancels any leveling effect that occurs, and the center portion of a rate profile similar to that of the beryllium complex does not appear. The data obtained at acid concentrations up to about 0.5 M suggest that the mechanism in which a half-bonded chelate is trapped by hydrogen ion[9b,11] is a general one for hydrolysis of acetylacetonates. The mechanism at high

acid concentrations is not so well characterized, but may be due to protonation in a preequilibrium step.

For dilute acid the form of the rate law has been obtained previously,[9b,11] and the discussion to follow will use the rate parameters of eq 6 in ref 9b. This rate law predicts a linear dependence of k_{obsd}^{-1} on (H$^+$)$^{-1}$. A good linear relation was obtained for Be-(acac)$_2$ over the interval $0.005 < $ (H$^+$) $ < 0.300$. From the straight line it is possible to calculate both k_1, the rate constant for initial ring opening, and the ratio of constants k_{-1}/k_2K_1. The constants refer to the processes

$$\text{Be(acac)}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Be(acac)(acac')} \qquad (5)$$

$$\text{Be(acac)(acac')} + \text{H}^+ \overset{K_1}{\rightleftharpoons} \text{Be(acac)(Hacac)} \qquad (6)$$

$$\text{Be(acac)(Hacac)} \overset{k_2}{\longrightarrow} \text{Be(acac)}^+ + \text{Hacac} \qquad (7)$$

The symbol acac' refers to a half-bonded acetylacetonate ligand and Hacac to the enol form of acetylacetone. The role of water is not shown in eq 5–7.

From the data of Table III, the constants of Table V were computed. The measured temperature dependence of k_1 was used to calculate an activation energy of 10 kcal/mole for the ring-opening step.

The hydrolysis of VO(acac)$_2$ and VO(acac)$^+$ does

(13) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

TABLE III

OBSERVED RATE CONSTANTS FOR ACID HYDROLYSIS OF Be(acac)$_2$
AND Be(acac)$^+$ AT SEVERAL TEMPERATURES (λ 3100 A)

Be(acac)$_2$ + H$^+$ + 2H$_2$O $\rightarrow$ Be(acac)(H$_2$O)$_2$$^+$ + Hacac

Be(acac)(H$_2$O)$_2$$^+$ + H$^+$ + H$_2$O $\rightarrow$ Be^{2+}(aq) + Hacac

H$^+$, M	k_{obsd}, sec^{-1} ^{a}	
	Be(acac)$_2$	Be(acac)$^+$
	25.0°	
0.0025	0.29 ± 0.02	0.27 ± 0.01
0.0049	0.56 ± 0.03	0.57 ± 0.03
0.0098	1.16 ± 0.04	1.04 ± 0.07
0.015	1.28 ± 0.09	1.40 ± 0.09
0.020	1.87 ± 0.07	1.71 ± 0.15
0.030	2.10 ± 0.15	2.42 ± 0.12
0.039	2.28 ± 0.16	2.53 ± 0.17
0.059	3.02 ± 0.14	3.47 ± 0.20
0.120	5.3 ± 0.3	...
0.200	5.9 ± 0.3	...
0.280	6.4 ± 0.4	...
0.360	7.0 ± 0.4	...
0.500	7.2 ± 0.3	...
1.00	8.3 ± 0.4^b	...
2.06	21.6 ± 2.5^c	...
2.58	72 ± 10^d	...
	35.0°	
0.0049	1.24 ± 0.04	...
0.0098	1.84 ± 0.07	...
0.020	3.12 ± 0.12	...
0.039	3.40 ± 0.48	...
0.079	6.21 ± 0.42	...
0.157	6.87 ± 0.45	...
0.236	10.0 ± 0.4	...
	45.0°	
0.0049	2.38 ± 0.07	...
0.0098	3.37 ± 0.25	...
0.020	6.6 ± 0.3	...
0.039	11.4 ± 0.2	...
0.079	13.3 ± 0.7	...
0.157	13.2 ± 1.2	...
0.236	17.1 ± 1.6	...

^{a} Ionic strength is 0.50 M except where noted. ^{b} I = 1.0 M. ^{c} I = 2.1 M. ^{d} I = 2.6 M.

not show the leveling-off effect. Accordingly one can only calculate the composite constant $k_1 k_2 K_1 / k_{-1}$. This is given in Table V also. The hydrolysis of VO(acac)$_2$ in the presence of added nucleophiles is very similar to that of the nickel complex.[11] That is, those anions which give rate increases are the same ones that form strong complexes with VO^{2+}, and none of the effects is large.

It has been reported[14] that VO(acac)$_2$ easily adds a sixth group to complete an octahedral coordination shell. Therefore the simplest explanation of how a nucleophile can increase the rate of hydrolysis is that it replaces water in the sixth coordination position of VO(acac)$_2$ or VO(acac)$^+$. This new complex then dissociates more rapidly than the hydrated species.

It is surprising that even hard bases such as F$^-$ and OAc$^-$ have little effect on the hydrolysis of Be(acac)$_2$. The explanation seems to be the small size of the beryllium ion. Tetrahedral coordination for such a small ion is as space filling as octahedral coordination for a larger ion. It should be mentioned that hydroxide

(14) R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Am. Chem. Soc.*, **83**, 1073 (1961).
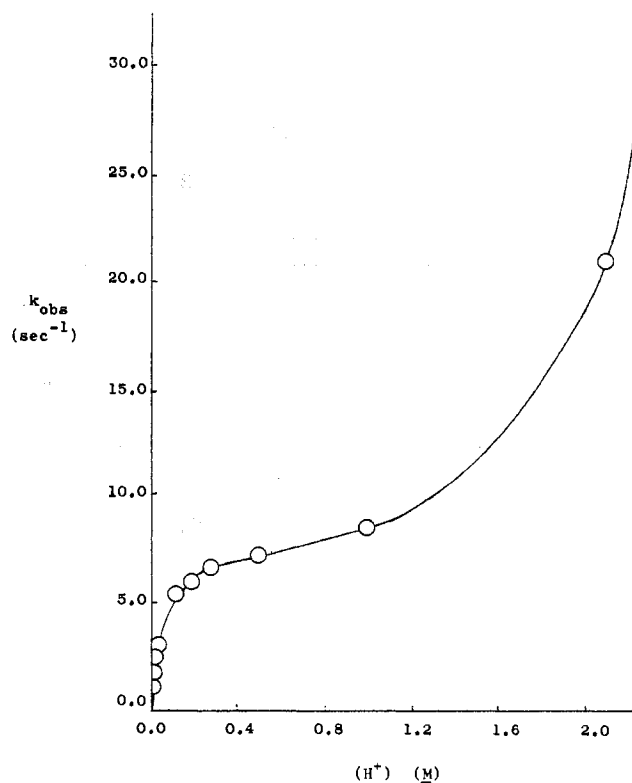

Figure 1.—Plot of k_{obsd} vs. hydrogen ion concentration for acid hydrolysis of Be(acac)$_2$ and Be(acac)$^+$.

TABLE IV

OBSERVED RATE CONSTANTS FOR HYDROLYSIS OF Be(acac)$_2$
IN THE PRESENCE OF ADDED NUCLEOPHILES AT 25° (λ 3100 A)

H$^+$, M	X, M		k_{obsd}, sec^{-1} ^{c}
0.005	0.00	SCN$^-$	0.59^a
0.005	0.01		0.59
0.005	0.16		0.64
8.4 × 10^{-5}	0.000	OAc$^-$	0.011^a ± 0.002
8.2 × 10^{-5}	0.005		0.028 ± 0.001
8.4 × 10^{-5}	0.010		0.027 ± 0.001
8.3 × 10^{-5}	0.020		0.027 ± 0.002
8.6 × 10^{-5}	0.030		0.029 ± 0.001
10.0 × 10^{-5}	0.0000	hx^b	0.013^a ± 0.002
6.6 × 10^{-5}	0.0006		0.018 ± 0.003
10.5 × 10^{-5}	0.0018		0.027 ± 0.003
0.010	0.000	Cl$^-$	1.16^a ± 0.04
0.010	0.005		1.49 ± 0.06
0.010	0.100		1.59 ± 0.09
0.010	0.000	Br$^-$	1.16^a ± 0.04
0.010	0.005		1.42 ± 0.04
0.010	0.100		1.44 ± 0.04
2.8 × 10^{-4}	0.00	F$^-$	0.036^a ± 0.005
2.8 × 10^{-4}	0.03		0.037 ± 0.005
2.7 × 10^{-4}	0.18		0.049 ± 0.006

^{a} Calculated from data in Table III. ^{b} hx = hydroxylamine. ^{c} Ionic strength is 0.50 M in all cases.

ion does cause a rapid hydrolysis of Be(acac)$_2$, as well as VO(acac)$_2$. However the kinetics are complex and not easy to interpret.[15]

It is significant that only Be(acac)$_2$, which has no labile ligands, appears indifferent to added nucleophiles. This supports the contention[11] that VO(acac)$_2$

(15) J. W. Moore, Ph.D. Dissertation, Northwestern University, 1964.

Complex	T, °K.	k_1, sec^{-1}	$k_1 k_2 K_1 / k_{-1}$, sec^{-1} M^{-1}
Be(acac)$_2$	298.2	6.5 ± 1.5	126 ± 34
and	308.2	10.4 ± 1.9	220 ± 51
Be(acac)$^+$	318.2	18.5 ± 2.5	472 ± 90
VO(acac)$_2$	298.2	$\ldots$	360 ± 50
VO(acac)$^+$	298.2	$\ldots$	2.37 ± 0.27

and Ni(acac)$_2$ are adding the nucleophile as a ligand in place of water before dissociation of the chelate occurs.

The rates of reaction of Ni^{2+}, VO^{2+}, and Be^{2+} with sulfate are characterized by interchange rate constants, k_{int}, of 10^4, 10^3, and 10^2 sec^{-1}, respectively.[16] These correlate reasonably well with the composite constant,

$$M(H_2O)_n{}^{2+}, SO_4{}^{2-} \xrightarrow{k_{int}} MSO_4(H_2O)_{n-1}, H_2O \qquad (8)$$

$k_1 k_2 K_1 / k_{-1}$, which has the values 8×10^5, 3.6×10^2, and 1.3×10^2 M^{-1} sec^{-1} for Ni(acac)$_2$, VO(acac)$_2$, and Be(acac)$_2$, respectively. The same ratios of constants for the mono complexes are 3.4×10^3, 2, and 1.3×10^2 for Ni(acac)$^+$, VO(acac)$^+$, and Be(acac)$^+$, respectively. The rate of hydrolysis of VO(acac)$^+$ is seen to be anomalously slow, or else Be(acac)$^+$ is anomalously fast. The successive stability constants do not show any large anomaly,[12] though the first and second constants are more nearly equal for Be^{2+} than for the other two ions.

(16) M. Eigen, *Ber. Bunsenges. Physik. Chem.*, **67**, 753 (1963); H. Strehlow and H. Wendt, *Inorg. Chem.*, **2**, 6 (1963).

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Perfluoromethylphosphine–Nickel Compounds, Including a New Volatile Heterocycle[1]

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The displacement of 3CO from Ni(CO)$_4$ by (CF$_3$)$_2$PF occurs as readily as the displacement of 2CO by CF$_3$PF$_2$, but this method arrives at pure (CF$_3$PF$_2$)$_4$Ni (mp $-84°$, bp estd 160°) far more easily than pure [(CF$_3$)$_2$PF]$_4$Ni (air-stable, mp 57.8°, bp estd 218°), for steric reasons such as prevent third-stage action by (CF$_3$)$_3$P. The infrared spectra suggest a slight increase of C–O bond strength as CF$_3$ replaces F in PF$_3$–Ni–CO compounds, and the effect is ascribed to minor differences in π bonding. The action of PF$_3$ upon (CF$_3$PF$_2$)$_4$Ni relates to the hypothesis that compounds of the type Li$_2$NiL$'_2$ often will be more stable than others having different proportions of the same ligands. The new chelate compound (CF$_3$)$_2$PC$_2$F$_4$P(CF$_3$)$_2$-Ni(CO)$_2$ (mp 30°, bp estd 179°) is more volatile but less stable than the similar C$_2$H$_4$-connected compound: complete displacement of the ligand (CF$_3$)$_2$PC$_2$F$_4$P(CF$_3$)$_2$ and one CO leads to the product [(CF$_3$)$_2$PC$_2$H$_4$P(CF$_3$)$_2$]$_2$NiCO with one bisphosphine unit acting unifunctionally.

The displacement of 4CO from Ni(CO)$_4$ by 4PF$_3$ has been verified,[2] but the more voluminous ligand (CF$_3$)$_3$P displaces only 2CO.[3,4] We now have found that repetitively used CF$_3$PF$_2$ can replace 4CO from Ni(CO)$_4$, making possible a quantitative synthesis of the new volatile compound (CF$_3$PF$_2$)$_4$Ni. The like action of (CF$_3$)$_2$PF occurs more easily for the first three CO, but the fourth-stage replacement is extremely difficult to complete. Thus steric interference is important for the third ligand in the series PF$_3$, CF$_3$PF$_2$, (CF$_3$)$_2$PF, (CF$_3$)$_3$P and becomes governing for the fourth.

However, the varying character of Ni–P bonding also may be significant. The P–F bond should have a small but not quite negligible F$_{2p}$→P$_{3d}$ π component, enhanced by the high polarity of the P–F σ bond—itself improved by the reverse polarity of the π bond. The F→P π bond also inductively aids the σ-dative P→Ni bond, but tends to suppress the Ni$_{3d}$→P$_{3d}$ π bonding. But let CF$_3$ replace F on P, and the less occupied P$_{3d}$ system will more effectively receive Ni$_{3d}$ π electrons. Thus, although PF$_3$ is a stronger π acceptor than most other phosphines,[5,6] CF$_3$PF$_2$ should be appreciably stronger.

Now if the Ni→P π electrons are more effectively moved toward P, those directed toward Ni→C π bonding in a Ni–C–O pattern in the same molecule will be less effective. Hence the O$_{2p}$–C$_{2p}$ π bond would be strengthened by using CF$_3$PF$_2$ as a ligand instead of PF$_3$. The resulting increase in the C=O stretching frequency is apparent as one compares the first two monocarbonyls in Table I.

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