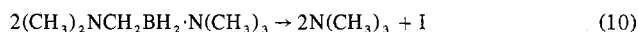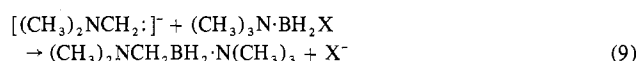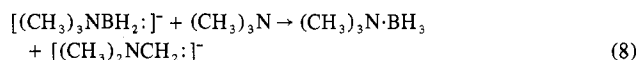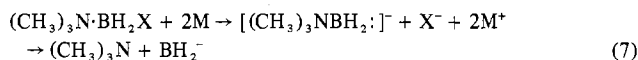Also, deuteration experiments show that the $(CH_3)_3N \cdot BH_3$ produced in the reaction probably abstracts a proton from solvent and not from coordinated $(CH_3)_3N$.

Thus, an alternate proposal for the production of I from the reduction of $(CH_3)_3N \cdot BH_2X$ ($X^- = I^-$, Br^-) with Na–K alloy seems to be in order. The presence of free $(CH_3)_3N$ in the system is a requirement for the production of I. The sequence of reactions 7–10 leading to the production of I satisfies this

$$(CH_3)_3N \cdot BH_2X + 2M \rightarrow [(CH_3)_3NBH_2:]^- + X^- + 2M^+$$
$$\rightarrow (CH_3)_3N + BH_2^- \qquad (7)$$

$$[(CH_3)_3NBH_2:]^- + (CH_3)_3N \rightarrow (CH_3)_3N \cdot BH_3$$
$$+ [(CH_3)_2NCH_2:]^- \qquad (8)$$

$$[(CH_3)_2NCH_2:]^- + (CH_3)_3N \cdot BH_2X$$
$$\rightarrow (CH_3)_2NCH_2BH_2 \cdot N(CH_3)_3 + X^- \qquad (9)$$

$$2(CH_3)_2NCH_2BH_2 \cdot N(CH_3)_3 \rightarrow 2N(CH_3)_3 + I \qquad (10)$$

requirement. This side reaction would be most evident when the concentration of $(CH_3)_3N$ was as high as possible. Thus, the highest yields of I should have been produced when $(CH_3)_3N$ was used as the solvent. This was exactly the trend observed.

Improved Synthesis for 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratocyclohexane. The present authors sought to improve the synthesis of I by using the iodide salt of bis-(trimethylamine)dihydroboronium ion which is more easily obtained than the anhydrous chloride salt.[8,9]

It is evident from the reaction sequence in which II is produced that $[:CH_3]^-$ abstracts a proton from $[(CH_3)_3N]_2BH_2^+I^-$ readily. Thus, the ideal reaction setup to produce I would be to use a Bronsted base with reasonable

stability whose counterion is a cation that does not form complexes with reaction intermediates as can occur when butyllithium[9] is used. The reaction of $NaNH_2$ with $[(CH_3)_3N]_2BH_2^+I^-$ in 1,2-dimethoxyethane in a 1:1 molar ratio gave a 25% yield of cyclic dimer.

This reaction is an improvement over present procedures in several ways. The boronium salt used is easier to obtain than the Cl^- salt, no particular precautions as to stoichiometry are indicated, and vacuum-line techniques and equipment are not necessary. The yields of I are essentially the same for both reactions.

References and Notes

(1) B. M. Graybill and J. K. Ruff, *J. Am. Chem. Soc.*, **84**, 1062 (1962).
(2) W. R. Deever and D. M. Ritter, *J. Am. Chem. Soc.*, **89**, 5073 (1967).
(3) W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).
(4) E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **10**, 939 (1971).
(5) W. R. Deever, F. M. Miller, E. R. Lory, and D. M. Ritter, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M215.
(6) D. M. Ritter, personal communication, 1971.
(7) T. H. Hseu and L. A. Larson, *Inorg. Chem.*, **14**, 330 (1975).
(8) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).
(9) N. E. Miller, M. D. Murphy, and D. L. Reznicek, *Inorg. Chem.*, **5**, 1832 (1966).
(10) R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).
(11) S. G. Shore, *J. Am. Chem. Soc.*, **93**, 3798 (1971).
(12) R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kirby, *J. Am. Chem. Soc.*, **85**, 487 (1963).
(13) G. Wittig and M. Wetterling, *Justus Liebigs Ann. Chem.*, **557**, 193 (1974).
(14) G. Wittig and R. Polster, *Justus Liebigs Ann. Chem.*, **599**, 1 (1956).
(15) B. R. Gragg and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **96**, 4717 (1974).

Formation of Nickel Acetate Complexes

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In aqueous solutions of nickel acetate two relaxation effects are observed with $\tau_I = (0.2–0.5) \times 10^{-3}$ s depending on concentration and $\tau_{II} = 2.7 \times 10^{-8}$ s independent of concentration at 10 °C. The effects are explained by the formation of the complexes $NiAc^+$ and $NiAc_2$. Kinetic and thermodynamic parameters of these reactions are evaluated and discussed.

Introduction

Kinetic methods—especially chemical relaxation methods—have been used frequently to investigate the formation of metal complexes[1] and elucidate the mechanism of the reactions. Furthermore, if several complexes are formed in a chemical reaction, they probably form at different rates; thus a kinetic is superior to a thermodynamic (=static) method in predicting the existence of these species. In this contribution, chemical relaxation measurements on aqueous solutions containing nickel and acetate ions are reported.

Experimental Section

The kinetic measurements have been performed using several chemical relaxation techniques: a pressure-jump method with conductometric recording,[2] an ultrasonic resonator method, and a modified ultrasonic-pulse method.[3] Solutions were prepared using doubly distilled water and $NiAc_2$ and $Ni(NO_3)_2$ of analytical reagent quality ($Ac^- = CH_3COO^-$).

Results

Using the pressure-jump relaxation technique, aqueous solutions of $NiAc_2$ have been investigated for the concentration

Table I. Relaxation Time τ_I, Its Temperature Dependence, and Relaxation Amplitude $X = (\delta\kappa/\kappa)_{relax}$ as a function of the Analytical Concentration $c°$ of $NiAc_2$ at 10 °C and a Pressure Jump of $\delta P = 130$ Atm

$c°$, M	0.01	0.02	0.05	0.1	0.2	0.5	0.7	1.0
$10^6 \tau_I$, s	495	456	385	343	315	269	248	235
$-10^{-3} \partial \ln \tau_I^{-1}/\partial T^{-1}$, K	6.5	6.8	6.7	7.6	7.1	7.0	6.6	6.7
$10^3 X$		2.3	3.6	5.6	5.6	7.6	8.0	9.8	8.8

range from 5×10^{-3} to 1 M and for the temperature range from 1 to 35 °C. All measurements showed a single relaxation effect in the time range of this method (50×10^{-6} s $< \tau <$ 100 s). Table I summarizes the observed relaxation times and relaxation amplitudes at $T = 10$ °C and d ln $\tau^{-1}/$ dT^{-1}, the temperature dependence of the relaxation time (10 °C has been chosen as the reference temperature, since the accuracy of the measurements has its maximum at this value). The relaxation amplitude X is defined as the relative change in electrical conductivity κ caused by the relaxation effect for a pressure jump of $\delta P = 130$ atm. Relaxation times are independent of the pH as has been shown for a 0.2 M $NiAc_2$ solution in the range of $4.8 < pH < 6.9$. The probable errors
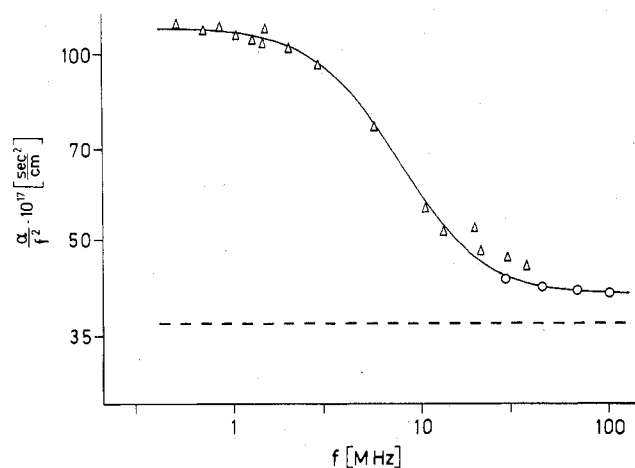
Figure 1. Double logarithmic plot of α/f^2 vs. f for 0.2 M NiAc$_2$ at 10 °C: $\triangle$, measured with the resonator method; $\circ$, measured with the pulse method. The curve is calculated according to eq 1 with $\tau_{II} = 2.6 \times 10^{-8}$ s, $A = 69.4 \times 10^{-17}$ s^2 cm^{-1}, and $B = 40.6 \times 10^{-17}$ s^2 cm^{-1}. The dashed line shows the absorption of water at 10 °C: $\alpha f^{-2} = 36.7 \times 10^{-17}$ s^2 cm^{-1}.

Table II. τ_{II} and A Obtained by a Best Fit of the Ultrasonic Absorption Measurements to Eq 2 for Different Analytical Concentrations [Ni]° and [Ac]°

[Ni]°, M	0.2	0.4	0.6	0.4	0.8
[Ac]°, M	0.4	0.4	0.4	0.6	0.4
$10^8 \tau_{II}$, s	2.6	2.5	2.6	2.9	2.9
$10^{17}A$, s^2/cm	64	91	107	146	144

are ±2% for τ, ±10% for $\partial \ln \tau^{-1}/ \partial T^{-1}$, and ±10% for X.

The ultrasonic absorption of solutions containing Ni^{2+} and Ac$^-$ ions has been determined in the frequency range 0.3–110 MHz, also at 10 °C. The solutions were prepared by dissolving suitable quantities of the salts NiAc$_2$ and Ni(NO$_3$)$_2$. Within the error width the results fit the expression

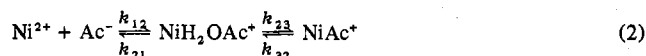$$\frac{\alpha}{f^2} = \frac{A}{1 + 4f^2\pi^2\tau_{II}^2} + B \tag{1}$$

where α is the absorption coefficient, f is the frequency, and A, B, and τ_{II} are constants. This indicates the existence of a single relaxation effect in this frequency range. The value of B is significantly higher than the corresponding value for pure water so that a third relaxation effect may be expected at frequencies above 100 MHz.

As an example, the absorption is shown for a 0.2 M solution of NiAc$_2$ in Figure 1. The results are summarized in Table II. Since the amplitude A is relatively small, reliable measurements could not be performed with diluted solutions. The probable error is 7% both for τ and for A. In the range studied, the results are independent of concentration and pH (6 < pH < 7). No relaxation effect could be observed in 0.5 M aqueous solutions of Ni(NO$_3$)$_2$ or NaAc (contradicting the results quoted in ref 4).

Treatment of Data

(a) Pressure-Jump Measurements. The slower relaxation process can be attributed to the formation of the complex NiAc$^+$. The reaction can be described by the Eigen mechanism

$$Ni^{2+} + Ac^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} NiH_2OAc^+ \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} NiAc^+ \tag{2}$$

where the first very fast step is the formation of a solvent separated ion pair (outer-sphere complex NiH$_2$OAc$^+$) and the second much slower one, the formation of the contact complex
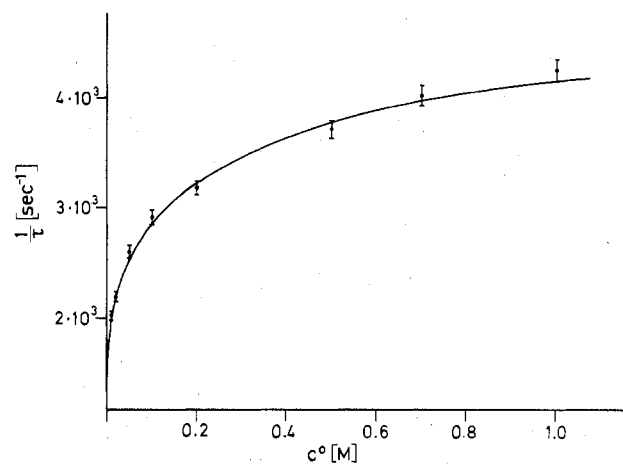
Figure 2. $1/\tau_I$ vs. c° at 10 °C; the curve is calculated according to eq 7 with $k_{32} = 1.5 \times 10^3$ s^{-1}, $k_{23} = 3.0 \times 10^3$ s^{-1}, and $K_{12} = 20$ M^{-1}. The error indicated is ±2%.

(inner-sphere complex NiAc$^+$).

In order to evaluate the results, the activity coefficients f are determined using Davies' equation[5]

$$-\log f = 0.5z^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right) \tag{3}$$

where I is the ionic strength. That means $f_{NiAc} = f_{NiH_2OAc} = f_{Ac}$, and the equilibrium concentrations are determined by the stability constants

$$K_{12} = [NiH_2OAc]/[Ni]f_{Ni}[Ac] \tag{4}$$

$$K_{23} = k_{23}/k_{32} = [NiAc]/[NiH_2OAc] \tag{5}$$

These are related to the overall association constant by

$$K_a = K_{12}(1 + K_{23}) \tag{6}$$

The relaxation time for the slow process is given by

$$\frac{1}{\tau_I} = k_{32} + k_{23}\frac{K_{12}f_{Ni}(\gamma_{Ni}[Ac] + [Ni])}{1 + K_{12}f_{Ni}(\gamma_{Ni}[Ac] + [Ni])} \tag{7}$$

f_{Ni} is the activity coefficient of the Ni^{2+} ion and γ_{Ni} is defined by

$$\gamma_{Ni} = 1 + \frac{d \ln f_{Ni}}{d \ln [Ni]} \tag{8}$$

From eq 3 we obtain

$$\gamma_{Ni} = 1 - 4.6[Ni]\left(\frac{1}{\sqrt{I}(1 + \sqrt{I})^2} - 0.6\right) \tag{9}$$

Equation 7 contains the three unknown constants k_{23}, k_{32}, and K_{12}, since the other variables can be calculated by eq 3, 4, 5, and 9. By a least-squares fit of the relaxation times (Table I) to eq 7 the following values are obtained: $k_{32} = (1.5 \pm 0.2) \times 10^3$ s^{-1}, $k_{23} = (2.9 \pm 0.2) \times 10^3$ s^{-1}, $K_{12} = 20 \pm 7$ M^{-1}. The agreement between the relaxation times calculated with these constants and the measured ones is shown in Figure 2.

The activation energies E_A^{23} and E_A^{32} can be obtained from the temperature dependence of the relaxation times. At the lowest concentrations measured the second term on the right-hand side of eq 7 is small compared to the first one.

Thus, we obtain for small concentrations

$$\frac{\mathrm{d}\ln\tau_{\mathrm{I}}^{-1}}{\mathrm{d}T^{-1}} \approx \frac{\mathrm{d}\ln k_{32}}{\mathrm{d}T^{-1}} = -\frac{E_{\mathrm{A}}^{32}}{R} \tag{10a}$$

At the highest concentrations measured, the fraction in eq 7 is close to unity and

$$\frac{\mathrm{d}\ln\tau_{\mathrm{I}}^{-1}}{\mathrm{d}T^{-1}} \approx \frac{\mathrm{d}\ln(k_{32}+k_{23})}{\mathrm{d}T^{-1}} = -\frac{E_{\mathrm{A}}^{32}}{R} - \frac{K_{23}}{1+K_{23}}\frac{\Delta H_{23}}{R} \tag{10b}$$

$\Delta H_{23} = E_{\mathrm{A}}^{32} - E_{\mathrm{A}}^{23}$ is the enthalpy of reaction. As shown in Table I, d ln $\tau_{\mathrm{I}}^{-1}/\mathrm{d}T^{-1}$ = -6.800 K ± 10%, independent of concentration. Therefore, by comparing eq 10a and 10b, it follows that ΔH_{23} is small compared to E_{A}^{32} and so we obtain $E_{\mathrm{A}}^{32} \approx E_{\mathrm{A}}^{23}$ = 13.5 ± 1.5 kcal mol^{-1}.

Finally, the volume of reaction can be estimated from the amplitude of the relaxation effect. The change in concentration caused by the slow relaxation process of eq 2 is given by

$$\delta[\mathrm{Ni}] = \frac{[\mathrm{NiAc}]+[\mathrm{NiH_2OAc}]}{1+x}\frac{\delta P}{RT}K_{23}\left(\frac{\Delta V_{12}}{1+K_{23}+x}\right.$$
$$\left.+\frac{\Delta V_{23}}{1+K_{23}}\right) \tag{11}$$

where $x = K_{a}f_{\mathrm{Ni}}([\mathrm{Ni}] + [\mathrm{Ac}]\gamma_{\mathrm{Ni}})$ and ΔV_{12} and ΔV_{23} are the volumes of reaction for the two steps free ions $\rightleftharpoons$ outer-sphere complex and outer-sphere complex $\rightleftharpoons$ inner-sphere complex, respectively.

Since no inert electrolyte is added, the electrical conductivity of the solutions is

$$\kappa = \sum_i z_i f_{\lambda_i} \lambda_i^0 \tag{12}$$

with i = $\mathrm{Ni^{2+}}$, $\mathrm{Ac^-}$, $\mathrm{NiH_2OAc^+}$, or $\mathrm{NiAc^+}$. f_{λ_i} are the conductivity coefficients and λ_i^0 the mobilities of the ions at infinite dilution. With the assumptions (i) that λ_i^0 has the same value for all ions involved and (ii) that the conductivity coefficients are equal for the monovalent ions, the relative change in κ is given by

$$\frac{\delta\kappa}{\kappa} = \frac{f_{\lambda_{\mathrm{Ni}}}\delta[\mathrm{Ni}] + [\mathrm{Ni}]\delta f_{\lambda_{\mathrm{Ni}}} + c^0\delta f_{\lambda_{\mathrm{NiAc}}}}{[\mathrm{Ni}]f_{\lambda_{\mathrm{Ni}}} + c^0 f_{\lambda_{\mathrm{Ac}}}} \tag{13}$$

δf_{λ_i} has been estimated from Onsager's formula, and by combining eq 11 and 13 with the value of the relaxation amplitude we get, for c^0 = 0.01 M, $\Delta V_{12} + \Delta V_{23} = 7 \pm 2$ cm^3 mol^{-1}. Only the sum of the volumes of reaction can be obtained which corresponds to the overall reaction free ions $\rightleftharpoons$ inner-sphere complex. It is not possible to separate them by evaluating the amplitudes at different concentrations, since the estimation of δf_{λ_i} becomes doubtful at higher concentration.

(b) Ultrasonic Absorption Measurements. The relaxation effect in the 1–10-MHz region has already been observed by Atkinson et al.[6] and by Yasunaga.[7] According to reaction 2 a second relaxation is expected which is caused by the reaction free ions $\rightleftharpoons$ outer-sphere complex. However, the relaxation effect we observe cannot be due to this reaction, since (i) the τ value is larger than expected for the formation of the outer-sphere complex[6,8] and (ii) with K_{12} = 20 ± 7 M^{-1} the relaxation time for this process is

$$1/\tau_{\mathrm{I}} = k_{21}(1 + K_{12}f_{\mathrm{Ni}}([\mathrm{Ni}] + [\mathrm{Ac}]\gamma_{\mathrm{Ni}})) \tag{14}$$

demanding a strong dependence of the relaxation time on

concentration, in contradiction to the results shown in Table II. Therefore, the formation of the outer-sphere complex should be observed at frequencies higher than 150 MHz which is out of the range of our present equipment. This third relaxation effect may be expected at higher frequencies, since the measured value of B is higher than the corresponding value for pure water (see Figure 1).

Since no concentration dependence of the relaxation time is observed, we have to study the concentration dependence of the relaxation amplitude to get information about the stoichiometry of the reaction involved. For $[\mathrm{Ni}]^\circ:[\mathrm{Ac}]^\circ$ = 0.4:0.4, the amplitude factor is A = 91 × 10^{-17} s^2/cm; for $[\mathrm{Ni}]^\circ:[\mathrm{Ac}]^\circ$ = 0.6:0.4, it is A = 107 × 10^{-17} s^2/cm; for $[\mathrm{Ni}]^\circ:[\mathrm{Ac}]^\circ$ = 0.4:0.6, it is increased to A = 146 × 10^{-17} s^2/cm. Thus, a change in the concentration of $\mathrm{Ac^-}$ influences the amplitude much more than a change in the concentration of $\mathrm{Ni^{2+}}$. This indicates that this reaction involves more $\mathrm{Ac^-}$ than $\mathrm{Ni^{2+}}$. The formation of $\mathrm{NiAc_2}$ is the most simple and most probable process satisfying this requirement. Therefore, the relaxation effect observed is attributed to the reaction

$$\mathrm{NiAc^+ + Ac^- \underset{k_{\mathrm{II}}}{\overset{k_{\mathrm{II}}}{\rightleftharpoons}} NiAc_2} \tag{15}$$

The equilibrium constant K_{II} can be calculated from the amplitude factor A (eq 1) with the assumption that the volume of reaction is ΔV = 4 ± 2 cm^3 mol^{-1} (somewhat smaller than the value for the formation of $\mathrm{NiAc^+}$). We obtain for the stability constant

$$K_{\mathrm{II}} = \frac{[\mathrm{NiAc_2}]}{[\mathrm{NiAc}][\mathrm{Ac}]f_\pm^2} = 1 \pm 0.5 \text{ M}^{-1} \tag{16}$$

The relaxation time for eq 15 is given by

$$1/\tau_{\mathrm{II}} = k_{\mathrm{II}}'[1 + K_{\mathrm{II}}C] \tag{17}$$

where

$$C = f_\pm^2 \left\{ [\mathrm{Ac}]\gamma_{\mathrm{NiAc}} \right.$$
$$\left. + [\mathrm{NiAc}]\gamma_{\mathrm{Ac}}\frac{[\mathrm{Ac}]([\mathrm{NiH_2OAc}]\gamma_{\mathrm{Ni}} + [\mathrm{Ni}])}{[\mathrm{NiH_2OAc}]([\mathrm{Ac}]\gamma_{\mathrm{Ni}} + [\mathrm{Ni}]) + [\mathrm{Ac}][\mathrm{Ni}]} \right\}$$

Calculating C for the different concentrations used, we get C = 0.15 ± 0.05 M, in agreement with the fact that the relaxation time τ_{II} does not change measurably with concentration. τ_{II} = 2.7 × 10^{-8} s yields for the rate constants k_{II}' = (3.2 ± 0.4) × 10^7 s^{-1} and k_{II} = (3.2 ± 1.6) × 10^7 s^{-1} M^{-1}.

The existence of the complex $\mathrm{NiAc_2}$ has not been taken into account in the evaluation of the pressure-jump measurements. Its consideration changes the fraction in eq 7 by less than 2% and therefore may be neglected safely as far as the slower reaction is concerned.

Discussion

(a) Pressure-Jump Measurements. The formation of nickel(II) complexes has been studied using many different ligands, and the results of these kinetic investigations have been reviewed and thoroughly discussed.[9,10] Reaction 2 has always been used to interpret the results, but instead of eq 7 the linearized equation

$$1/\tau = k_{32} + k_{23}K_{12}f_{\mathrm{Ni}}(\gamma_{\mathrm{Ni}}[\mathrm{L}] + [\mathrm{Ni}]) \tag{18}$$

has been used to evaluate the measurements. That means, the assumption made has been that in the concentration range studied the denominator in eq 7 is close to unity, i.e.

$$K_{12}f_{Ni}(\gamma_{Ni}[L] + [Ni]) \ll 1 \qquad (19)$$

(Moreover, the activity corrections could be neglected in most cases since the measurements were performed at constant ionic strength.) Therefore, only the product $k_{23}K_{12}$ has been obtained from the relaxation measurements and K_{12} has to be known in order to evaluate k_{23}. In all systems, K_{12} has been estimated by the Fuoss formula,[11] except in $Ni^{2+}-SO_4^{2-}$ and $Ni^{2+}-CH_3PO_4^{2-}$ where it has been obtained from sound absorption measurements.[8]

Our kinetic results for the $Ni^{2+}-Ac^-$ systems cannot be made to fit eq 18 irrespective of the values of k_{23}, k_{32}, and K_{12}. The deviations between the measurements and a best least-squares fit of these measurements with eq 18 are up to $\pm15\%$, whereas the accuracy of the measurements is $\pm2\%$. These deviations cannot be explained by the uncertainty in the activity corrections, since they occur if only the measurements at concentrations $c^\circ \leq 0.2$ M are considered in the range where eq 3 has been shown to be reliable.[5]

Thus, eq 17 has to be used and by a least-squares fit of the relaxation rates all three constants k_{23}, k_{32}, and K_{12} are obtained separately. This is the first time, for a Ni^{2+} complex, that all of these data are evaluated from only the relaxation process obtained from P-jump or T-jump measurements, and we shall now compare them with the results for other ligands.

The kinetic and thermodynamic constants derived in the previous section for 10 °C are $K_{12} = 20 \pm 7$ M^{-1}, $K_{23} = 1.9 \pm 0.2$, $k_{23} = (2.9 \pm 0.2) \times 10^3$ s^{-1}, $k_{32} = (1.5 \pm 0.2) \times 10^3$ s^{-1}, $E_A^{32} = 13.5 \pm 1.5$ kcal mol^{-1}, $E_A^{23} = 13.5 \pm 1.3$ kcal mol^{-1}, and $\Delta V_{12} + \Delta V_{23} = 7 \pm 2$ cm^3 mol^{-1}. From the values of k_{23} and E_A^{23} we obtain $k_{23}(25$ °C$) = (1.5 \pm 0.3) \times 10^4$ s^{-1}. For the formation of other Ni^{2+} complexes rate constants between 0.5×10^4 and 4×10^4 s^{-1} and activation energies of about 13 kcal mol^{-1} are reported.[9,10] This again shows that replacement of a water molecule in the inner solvation sphere of a cation is nearly independent of the entering ligand.

The outer-sphere equilibrium constant K_{12} can be estimated from Fuoss' formula to be $K(Fuoss) = 6 \pm 1$ M^{-1} for a distance of closest approach of $r = 5 \pm 1$ Å. This value differs at least by a factor of 2 from our experimentally determined constant. This difference is not surprising taking into consideration the crude approximation made for the derivation of Fuoss' formula.[12] For nickel acetate the product $k_{23}K_{12} = 1.5 \times 10^5$ M^{-1} s^{-1} has been measured by Hoffmann and Yeager (quoted in ref 13). The difference from our value $k_{23}K_{12} = (3.0 \pm 1.0) \times 10^5$ M^{-1} s^{-1} (at 25 °C) may be due to the fact that they evaluated their measurement according to eq 18 also at high concentrations of NiAc$_2$.

The association constant K_a has been determined for nickel acetate at 25 °C and ionic strength $I \rightarrow 0$ by different authors (quoted in ref 14) who obtained values between $K_a = 13$ M^{-1} and $K_a = 63$ M^{-1} (both values determined using the same technique). From our measurements we obtain $K_a = K_0(1 + K_i) = 60 \pm 20$ M^{-1}, so that the lower values quoted in the literature seem to be less reliable.

Reaction volumes have only been determined for the formation of a nickel complex with the SO_4^{2-} anion with the result that $\Delta V_{12} + \Delta V_2^3 = 17 \pm 3$ cm^3 mol^{-1}.[8] This value is about twice as large as the corresponding value of the $Ni^{2+}-Ac^-$ system which has to be expected, since in the former case more charges are neutralized causing a larger change in electrostriction.

(b) Ultrasonic Absorption Measurements. The concentration dependence of rate and amplitude of the relaxation effect can be explained by the formation of a complex from one Ni^{2+} and two Ac^- ions. The rate is very high compared with that of the formation of the NiAc$^+$ inner-sphere complex. If the second acetate ion is also bound in the inner solvation shell of the cation, this increase in reaction rate means that the inner hydration sphere of the cation is strongly labilized by the first ligand. It can also be assumed that the second acetate ion is bound in the outer solvation sphere and stabilized by hydrogen bonding.

Thus, from these measurements the only result that can be obtained is that a second complex is formed between Ni^{2+} and Ac^- ions, which is most probably of the stoichiometry Ni:Ac = 1:2. The existence of this complex has already been postulated from several thermodynamic measurements.[14] An analogous complex CaAc$_2$ has also been predicted from ultrasonic measurements.[6]

References and Notes

(1) M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, No. 49, 55 (1965).
(2) W. Knoche and G. Wiese, *Chem. Instrum.*, **5**, 91 (1973–1974).
(3) F. Eggers and Th. Funck, *Rev. Sci. Instrum.*, **44**, 696 (1973).
(4) M. Krishnamaruthi and M. Suryanarayana, *J. Phys. Soc. Jpn.*, **15**, 345 (1960).
(5) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).
(6) G. Atkinson, M. M. Emara, and R. Fernandez-Prini, *J. Phys. Chem.*, **78**, 1913 (1974).
(7) T. Yasunaga, paper presented at the International Summer School on Relaxation Spectrometry, Salford, U.K., 1974.
(8) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).
(9) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **7**, 107 (1968).
(10) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
(11) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
(12) M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes", Interscience, New York, N.Y. 1968.
(13) H. Hoffman, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969).
(14) R. Fuentes, L. O. Morgan, and N. A. Matwiyoff, *Inorg. Chem.*, **14**, 1837 (1975).