

tion coefficients. With quinoline as the stationary phase (5 cm<sup>3</sup>/tube), 10 g of benzene-cyclohexane mixture (1:1) was separated in one run, the efficiency being equivalent to slightly more than one plate per tube (tube number = 20; room temperature).

To get a separation with the least possible number of tubes, use should also be made of the fact that the separation factor  $a^*$  for two compounds (1 and 2) increases with the absolute value of their distribution constants towards the limiting value given by the ratio of the distribution constants ( $k_1$  and  $k_2$ ):

$$a^* = \frac{n_1}{n_2} = \frac{V_g/V_L + k_2}{V_g/V_L + k_1} \quad (2)$$

( $V_g$  and  $V_L$  are the gas and the liquid volumes;  $n_1$  and  $n_2$  are the tubes containing the maxima of compounds 1 and 2, respectively). Eqn. (2) is easily derived from the formula  $V_R = n(V_g + kV_L)$ , where  $V_R$  is the retention volume<sup>4</sup>. Eqn. (2) also applies if  $a^*$  is considered as the ratio between the retention volumes. The effect of the absolute values of the distribution constants, and of the volume ratio between the mobile and the stationary phases, upon the separation is exemplified by the separation of ethyl ether and *n*-pentane (Fig. 3a, b). With water as the stationary phase, their separation factor was 2.7, while with air it was about 19.

From the distribution coefficients determined, the number of plates required for a given separation is obtained by use of the following expression:

$$n_2 = \left( \frac{b}{a^* - 1} \right)^2 \quad (3)$$

$$\text{and } n = \sqrt{n_1 n_2} = \left( \frac{b}{a^* + (1/a^*) - 2} \right)^2 \quad (4)$$

Here,  $n_2$  is the plate containing the maximum of the slower component, and  $b$  is the number of standard deviations that separates the two maxima from each other. Eqn. (3) is obtained by putting  $n_1 - n_2 = b\sqrt{n_2}$  and eliminating  $n_1$  with the aid of (2).

Purnell<sup>5</sup> has given a formula for the number of plates required in GLC to just separate a pair of compounds.

This formula gives higher values for the required plate number than (4). However, with the apparatus described here, experi-

mental agreement with formula (4) has been obtained.

This work is being continued.

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## A Method for Kinetic Study of "Moderately Fast" Reactions. Rate of Dissociation of Monoammine-nickel(II) Ion in Aqueous Solution

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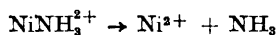
Rates of formation and dissociation of labile complex ions are often too great at room temperature to follow by conventional methods. Semi-quantitative studies<sup>1,2</sup> of such reactions in methanol at low temperatures (*e.g.*, -75°C) have given useful information. For certain systems and purposes it is also desirable to investigate reactions in aqueous solution. Although excellent methods exist for the study of such "moderately fast" reactions, *e.g.*, the stopped-flow and quenched-flow methods, they involve the construction and calibration of complicated apparatus.

We report here a method adaptable for many reactions and especially useful for kinetic and equilibrium studies of formation and dissociation reactions of ammine and amine metal complexes, using only commercially available instruments. The principle is to use an appropriate non-complexing salt to depress the freezing

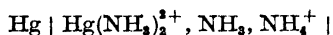
\* John Simon Guggenheim Fellow, 1960, on leave from the University of California, Los Angeles.

point of water to a temperature low enough to increase the reaction half-time to at least *ca.* 20 seconds, and to inject quickly into the equilibrium reaction system a small volume of a reagent, *e.g.* acid, which displaces the equilibrium and then to measure with a suitable detector the time rate of change to the new equilibrium state. As detector a Radiometer TTT-1 titrator has been used in conjunction with a micro syringe, electronic relay and recorder (Radiometer SBR2 Titrigraph) functioning as a potentiostat to determine the rate of addition of acid required to titrate the amine as it is released by a dissociating metal complex and thereby maintain constant the pH in the solution. This requires that a suitable EMF cell be devised that will respond rapidly to changes in the amine concentration at the low temperatures involved.

This method has been used to determine the rate constant *k* of the reaction:



in aqueous solution at  $-25^\circ\text{C}$ . Of those salts tested for depression of the freezing point, the most satisfactory was  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , which has a eutectic point at  $-29^\circ\text{C}$ , and which does not form complexes with  $\text{NH}_3$  to a considerable extent ( $K_1 \sim 2$ )<sup>4</sup>. Glass electrodes are not usable for our purpose at  $-25^\circ\text{C}$ \*, therefore a specially constructed mercuric half-cell:



was used in combination with a modified calomel reference electrode (KCl solution replaced with 8.0 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in 10 ml water, usable at  $-29^\circ\text{C}$ ); this cell was found to respond rapidly at  $-25^\circ\text{C}$  to changes in  $p[\text{NH}_3]$  as well as in pH at constant ammonium ion concentration. Reaction solutions (30 ml) were made with the following molar total concentrations:  $C_{\text{Ni}(\text{NO}_3)_2} = 0.100$ ,  $C_{\text{NH}_3} = 0.00624$ ,  $C_{\text{NH}_4\text{NO}_3} = 0.10$ ,  $C_{\text{Hg}(\text{NO}_3)_2} = 0.000095$ ,  $C_{\text{Mg}(\text{NO}_3)_2} = 2.7$  at  $-25^\circ\text{C}$ , and from the data of Bjerrum<sup>4</sup> ( $K_1/K_2 = 3.6$ ) estimated to have  $[\text{NiNH}_3^{2+}] = 0.0058$ ,  $[\text{Ni}(\text{NH}_3)_2^{2+}] \sim 0.0001$ . To solutions of this composition 0.091 ml 0.198 M  $\text{HNO}_3$ , 2.7 M  $\text{Mg}(\text{NO}_3)_2$  were rapidly injected to displace the equilibrium (pH drops abruptly from *ca.* 6 to

*ca.* 3, and EMF changes by *ca.* 130 mV). The  $\text{Hg}(\text{NH}_3)_2^{2+}$  present as potential indicator for  $\text{NH}_3$  is only 1.7 % of the  $\text{NiNH}_3^{2+}$  concentration, and is furthermore practically unchanged during the reaction ( $K_1 \sim 10^9$ ,  $\beta_2 \sim 10^{18}$ ,  $\beta_3 = 10^{18}$ )<sup>4</sup>. The rate of addition of  $\text{HNO}_3$  (equal to the rate of dissociation of  $\text{NiNH}_3^{2+}$ ) required to keep the pH constant was recorded by the Titrigraph. For a first-order dissociation the Titrigraph volume reading (% of syringe capacity) at time *t* can be shown to be

$$V\% = (100 C_0 V_R / M V_S) (1 - e^{-kt}),$$

where  $C_0$  = initial concentration of  $\text{NiNH}_3^{2+}$ ,  $M$  = molarity of  $\text{HNO}_3$  titrating agent,  $V_R$  = volume (ml) of reaction solution, and  $V_S$  = volume (ml) delivered by syringe in moving from 0 to 100 % on Titrigraph volume scale. Hence, the dissociation rate constant *k* can be evaluated from the Titrigraph curve. Equivalently, values of the dissociation half-time  $t_{1/2}$  can be read directly off the Titrigraph curve by noting the times required for *V*% to go half-way from different arbitrary values to the infinite-time value. Since, the reaction was not carried to completion, the rate constant obtained is ( $k + k'$ ), where  $k'$  is the pseudo first-order rate constant for the association reaction at constant  $p[\text{NH}_3]$ . From the complexity constant for  $\text{NiNH}_3^{2+}$  at  $-25^\circ$ , estimated from the data of Bjerrum<sup>4</sup> to be  $K_1 = 10^{8.1}$ ,  $k'$  ranges from  $10^{-1.4}k$  to  $10^{-4.1}k$  between  $p[\text{NH}_3] = 4.5$  and 7.2; thus the observed ( $k + k'$ ) is essentially *k* itself.

Values of  $t_{1/2}$  (sec) found at the pH given inside parentheses were: 70 (3.1), 70 (3.7), 64 (4.8), 54 (5.4), 70 (5.8), 59 (5.8), 63 (5.8). There is no clear trend of  $t_{1/2}$  with pH; the range of values more likely corresponds to random errors arising from technical problems (including diffusion of reaction solution through the sintered-Pyrex disc of the reaction vessel) which could be reduced with improved design. The average  $t_{1/2} = 64$  sec, corresponding to  $k = 0.011 \text{ sec}^{-1}$  at  $-25^\circ\text{C}$ .

Wilkins<sup>6</sup> has recently studied the dissociation of  $\text{NiNH}_3^{2+}$  at  $25^\circ$  and  $5^\circ$  using a stopped-flow method with spectrophotometric detection. Under his conditions of  $C_{\text{Ni}(\text{NO}_3)_2} = 0.18$ ,  $C_{\text{NH}_3} = 0.10$ ,  $C_{\text{NH}_4\text{NO}_3} = 0.04$ ,  $C_{\text{Mg}(\text{NO}_3)_2} = 0$ , 0.8 or 1.5 M,  $t_{1/2} = 0.12$  sec at  $25^\circ$  and the Arrhenius activation energy  $E_a = 14.3$  kcal. Extrapolation to

\* Modified glass and calomel electrodes for use down to  $-30^\circ$  have been reported recently<sup>6</sup>.

$-25^\circ$  gives  $t_{1/2} = 16$  sec. Wilkins estimates his errors such that  $t_{1/2} \leq 32$  sec at  $-25^\circ$ , so there is an apparent discrepancy between his and our values. We estimate the nickel ammine concentrations in his solutions to be  $[\text{NiNH}_3^{2+}] = 0.07$ ,  $[\text{Ni}(\text{NH}_3)_2^{2+}] = 0.014$ . Aside from the somewhat different conditions (especially the much higher relative concentration of  $\text{Ni}(\text{NH}_3)_2^{2+}$  and lower ionic strength in Wilkins' experiments), the discrepancy may arise from a nonlinear Arrhenius plot and the long extrapolation to  $-25^\circ$ ; accurate experiments on first-order reactions in aqueous solution show that  $dE_a/dT$  is negative<sup>7</sup>, which would be in the right direction to account for the difference in the two  $k$  values (ca. 30% increase in  $E_a$  would be required). Either  $k$  value shows that the dissociation of  $\text{NiNH}_3^{2+}$  in aqueous solution is faster, as expected, than dissociation of other Ni(II) monoamines, such as  $\text{Ni}(\text{en})^{2+}$ ,  $\text{Ni}(\text{bn})^{2+}$ , etc.<sup>8</sup>

*Experimental.* The reaction vessel was a Pyrex half-cell having a Pt-wire electrode sealed in through the bottom and a side arm equipped with a stopcock and a G4 sintered-Pyrex disc separating the side arm from the rest of the vessel. The side arm was filled with 2.7 M  $\text{Mg}(\text{NO}_3)_2$ , 0.14 M  $\text{NH}_4\text{NO}_3$  solution up to the disc, then 5.00 ml Hg delivered into the vessel and the reaction solution synthesized by careful delivery of the necessary amounts of stock solutions of  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ni}(\text{NO}_3)_2$ , and  $\text{NH}_3$ , then water on top of the Hg (with care to avoid solution getting below the Hg meniscus) up to a mark so calibrated that, after mixing and adding the necessary amount of  $\text{Hg}(\text{NO}_3)_2$  solution and cooling to  $-25^\circ\text{C}$ , the volume would be 30.0 ml. The vessel was next connected via its side arm to a vial containing  $\text{Mg}(\text{NO}_3)_2$  solution and stoppered with a 3-hole stopper containing the calomel electrode and a vertical tube which allowed for volume change in the vial and half-cell side arms on cooling to  $-25^\circ\text{C}$ . Stopcocks in the side arms were left closed until the entire assembly, immersed in a thermostated bath at  $-25.0 \pm 0.2^\circ\text{C}$ , came to bath temperature (ca. 20 min). The 0.5-mm ID capillary delivery tube of the 0.45-ml syringe burette (Radiometer SBU1), already filled with 0.4956 M  $\text{HNO}_3$ , 2.7 M  $\text{Mg}(\text{NO}_3)_2$ , was then inserted through a 3-hole rubber stopper into the reaction solution with the delivery tip ca. 5 mm above the Hg surface; at the same time a

stirring propeller was placed through a second hole of the stopper into the reaction solution next to the delivery tip (placement of both tip and stirrer is fairly critical for proper action of the potentiostat). With the stirrer on and the potentiostat set for operation at a predetermined voltage (corresponding to a given pH), and after a further 10-min temperature equilibration (during which the EMF remained constant to  $< 1$  mV), 0.091 ml 0.198 M  $\text{HNO}_3$ , 2.7 M  $\text{Mg}(\text{NO}_3)_2$  "initiator" was injected quickly from a micropipette into the reaction solution and the Titrigraph recording switch turned to "pH-STAT-ON" and the Titrigraph allowed to maintain constant pH by controlled delivery of  $\text{HNO}_3$  into the reaction solution at a recorded rate corresponding to the rate of release of  $\text{NH}_3$  by the dissociating  $\text{NiNH}_3^{2+}$ . Recording was continued until no further  $\text{HNO}_3$  was added by the Titrigraph. The Titrigraph was operated with chart gear A = 10 mm/rev, chart motor B = 4 rpm, pen motor C = 30 rpm and pen gear D = 2 or 4 %/rev (4 1-cm chart divisions/min, checked with a stop watch). Change in volume of the reaction solution during a run was  $< 1.5$  %, and change in temperature from the added titrating agent was negligible. The pH at which the reaction was run could be varied by setting the controlling EMF of the potentiostat accordingly.

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