

Rates of Protonation and Dissociation of Cyanoglycylglycinamidonickelate(II)

BY VINCENT T. BRICE and GORDON K. PAGENKOPF*

(Department of Chemistry, Montana State University, Bozeman, Montana 59715)

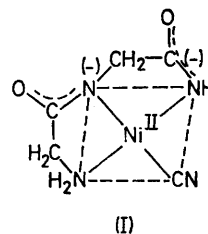
Summary The rate of dissociation of cyanoglycylglycinamidonickelate(II) is 38,000 times slower than that of aquoglycylglycinamidonickelate(II).

GLYCYLGLYCINAMIDE (H_2gga) ionizes its amide protons during the formation of the yellow, diamagnetic, square-planar complex with nickel(II), $Ni(gga)H_2O$.¹ Rates of proton transfer to this complex¹ and similar complexes of nickel(II) and copper(II) with triglycine (H_2ggg) [$Ni(ggg)^-$ and $Cu(ggg)^-$] are much slower than diffusion-controlled reactions.²

We have measured the rate of dissociation of the mixed complex $Ni(gga)CN^-$ and found that it is 38,000 times slower than the rate of dissociation for the corresponding aquo-complex $Ni(gga)H_2O$.¹

The cyanide complex was prepared by mixing nickel(II) with glycylglycinamide (1:2) and slowly adding base to pH 10.5, at which both amide protons have ionized to form

$Ni(gga)H_2O$. The three nitrogen donors of gga are coordinated and water occupies the fourth position in the square-planar co-ordination sphere of nickel. A stoicheio-



metric amount of cyanide was then added to form $Ni(gga)CN^-$. Excess of cyanide causes decomposition to $Ni(CN)_4^{2-}$.³ The structure of the complex is believed to be (I). The cyanide complex has λ_{max} 405 nm (ϵ 170) [*cf.* λ_{max} 452 nm (ϵ 136) for the aquo-complex, $Ni(gga)H_2O$]. These

complexes are weak acids, pK_a ca. 9. Attempts to determine the stability of the mixed complex were unsuccessful and we conclude that the stability constant must be greater than 10^7 .

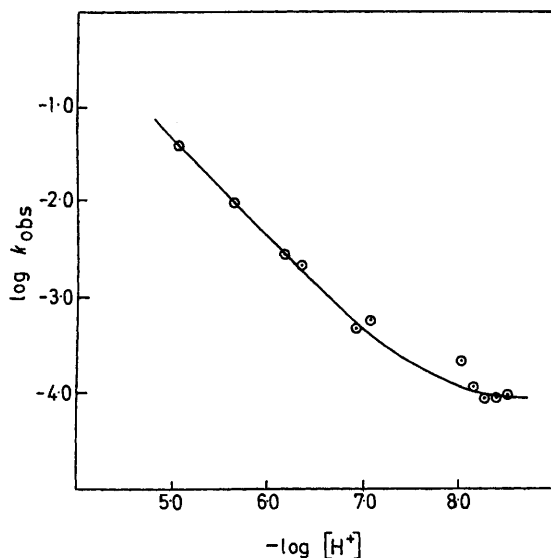
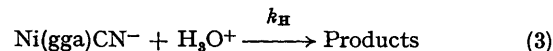
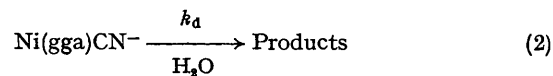


FIGURE. The observed rate constants for the decomposition of $Ni(gga)CN^-$ at different hydrogen ion concentrations.

Kinetic studies used the pH-jump method, which involves the rapid conventional mixing of a solution of the complex (pH ca. 10) with a buffer of desired pH. The buffer solution has to have sufficient buffer-capacity to maintain constant pH throughout the reaction; we used acetate, malonate, and tris(hydroxymethyl)aminomethane. A typical kinetic run had $[Ni(gga)CN^-] = 7.0 \times 10^{-6}$ M, $\mu = 0.1$ M ($NaClO_4$), $[Buffer] = 0.01$ M and $T = 25^\circ$. Disappearance of the complex was monitored at 246 nm. The decomposition was studied at a number of pH values and the results are shown in the Figure. Pseudo-first order kinetics were observed and the rate equation is shown in equation (1). A two-term rate equation has been

observed for other systems;² the proposed reactions to $-d[Ni(gga)CN^-]/dt = (k_d + k_H[H^+])[Ni(gga)CN^-]$ (1) explain the pH dependence are given in equations (2) and (3):



Another possible mechanism, loss of cyanide followed by rapid proton transfer, would not exhibit pseudo-first-order kinetics under our experimental conditions. As indicated by the Figure, the predominant reaction above pH 8 is simple dissociation as given by k_d . Below pH ca. 7 the predominant reaction is that of the proton transfer limited path as given by k_H . The solid line in the Figure is calculated using $k_d = 8.0 \times 10^{-5} s^{-1}$ and $k_H = 4.3 \times 10^3 l mol^{-1} s^{-1}$. The observed rate constant is the sum of the two terms shown in equation (4).

$$k_{obs} = k_d + k_H[H^+] \quad (4)$$

The rate of decomposition of $Ni(gga)H_2O$ is reported as $3.1 s^{-1}$ at pH ca. 9.¹ This value, obtained by extrapolation to low ligand and buffer concentrations and also independent of hydrogen ion concentration, can be compared to $k_d = 8.0 \times 10^{-5} s^{-1}$ for $Ni(gga)CN^-$ determined at the same pH and under similar conditions. This is a reduction in rate of nearly 40,000-fold for the cyanide complex. The k_H value for $Ni(gga)H_2O$ has not been measured; however, the k_H value for nickel-triglycine, $Ni(ggg)^-$ is $2.0 \times 10^5 l mol^{-1} s^{-1}$ which compares with $4.3 \times 10^3 l mol^{-1} s^{-1}$ for $Ni(gga)CN^-$, again a significant reduction. These rate constants indicate that cyanide is capable of exerting a large kinetic stabilizing influence in square-planar nickel(II) complexes. The effect does not appear to be a *trans*-effect since breaking of the imide-nickel bond opposite the cyanide group is not believed to be involved in the rate-determining step.¹⁻³

(Received, 20th August 1973; Com. 1196.)

¹ C. F. V. Mason, P. I. Chamberlain, and R. G. Wilkins, *Inorg. Chem.*, 1971, **10**, 2345.

² E. J. Billo and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 6811; G. K. Pagenkopf and D. W. Margerum, *ibid.*, 1968, **90**, 501; G. K. Pagenkopf and D. W. Margerum, *ibid.*, 1968, **90**, 6963; E. B. Paniago and D. W. Margerum, *ibid.*, 1972, **94**, 6704.

³ G. K. Pagenkopf, *J. Amer. Chem. Soc.*, 1972, **94**, 4359; G. K. Pagenkopf, *Inorg. Chem.*, submitted for publication.