

Figure 1.

constants of the substituted 1,10-phenanthrolium ions. The ρ values found were -0.089 for Hdien^+ and -0.264 for NTA^{3-} .

Table I. Rate Constants ($M^{-1} \text{ sec.}^{-1}$) at 25.0°

| Substituent | pK_a | k_{Hdien}^a | k_{NTA}^b |
|-----------------------|--------|----------------------|--------------------|
| 5,6-Di- CH_3 | 5.6 | 426 | 4.15×10^6 |
| 5- CH_3 | 5.23 | 408 | 3.78×10^6 |
| 5-H | 4.96 | 359 | 2.82×10^6 |
| 5-Cl | 4.26 | 327 | 2.34×10^6 |
| 5- NO_2 | 3.57 | 281 | 1.15×10^6 |

^a Ionic strength = 0.13. ^b Ionic strength = 0.16.

The substitution reactions for many octahedral complexes of nickel and other metals are governed by the characteristic first-order rate of loss of water as shown in a summary by Eigen and Wilkins.¹ The reactions of polyamines and aminocarboxylate ions with nickel(II) have been shown to have as the rate-determining step the loss of water and coordination of the first nitrogen bond.^{2,3} Therefore, reactions 1 and 2 are believed to have as their rate-determining step the loss of one of the four water molecules coordinated to nickel followed by rapid coordination to the incoming ligand. Electron-withdrawing or -donating

(1) M. Eigen and R. G. Wilkins, "Mechanism of Inorganic Reactions," Summer Symposium, Division of Inorganic Chemistry, American Chemical Society, University of Kansas, June 1964.

(2) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

(3) D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

groups on the 1,10-phenanthroline alter the electron density at the metal reaction site and thus change the characteristic rate of loss of coordinated water. This is consistent with the earlier observation that the type of groups coordinated to nickel has a greater influence on its substitution reaction than does the charge of the complex.⁴ However, this is believed to be the first example of ligand substituents altering the rate of loss of coordinated water.

The very large difference in rate constants for Hdien^+ and NTA^{3-} is consistent with their relative electron repulsion and attraction to $\text{Ni}(\text{phen})^{2+}$, which in turn affects the concentration of reactants in the immediate vicinity of each other when a coordinated water molecule is lost from the nickel.

The reaction with NTA^{3-} is believed to involve substitution of an equatorial water (in the plane of Ni and phen), while the reaction with Hdien^+ involves the substitution of an axial water as the rate-determining step. If this interpretation is correct, reaction at the equatorial position is more than twice as sensitive to substituents than reaction at the axial position.

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(4) D. W. Margerum and M. Eigen, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p. 289.

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Selective Labilizing of α -Hydrogen Atoms by Chelation of α -Aminocarboxylic Acids

Sir:

While the action of metal ions to increase the reactivity of α -methylene hydrogens has been observed,^{1,2} the magnitude and specificity of the effect is first shown by our p.m.r. examination of certain complexes. Glycinato- and alaninatobis(ethylenediamine)cobalt(III) and ethylenediaminetetraacetatocobaltate(III), $\text{Co}(\text{EDTA})^-$, ions illustrate these observations.

Nearly saturated solutions of $[\text{Co}(\text{en})_2(\text{glycine})](\text{NO}_3)_2$ and $[\text{Co}(\text{en})_2(\text{alanine})](\text{NO}_3)_2$ were prepared in acidic D_2O solutions, pD of approximately 3, and the p.m.r. spectra obtained using a Varian Associates A-60 spectrometer. In either complex the protons attached to the carbon atoms of the ethylenediamine rings occur in a broad resonance centered at 115 c.p.s. upfield from the water resonance, at 22° . The width of the resonance is 25 c.p.s. at half-height. Broad resonances of this nature have been observed for other *cis*- and *trans*-bis(ethylenediamine) complexes of cobalt(III) by Clifton and Pratt.³ These workers observed that the chemical shift of the hydrogen atoms attached to the nitrogen atoms was different for *cis* and *trans* isomers of these complexes. In the compounds studied here the protons attached to the nitrogens absorb in a

(1) D. E. Metzler, J. D. Longenecker, and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 639 (1954).

(2) M. Murakami and K. Takahashi, *Bull. Chem. Soc. Japan*, **32**, 308 (1959).

(3) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

very broad resonance located approximately 30 c.p.s. downfield from the water resonance. The intensity of this resonance suggests that about 60% of these protons have undergone exchange during the time required by sample preparation and recording of the spectrum.

The two α -methylene hydrogens of the glycine ring exhibit a triplet at 62 c.p.s. upfield from the water resonance, which has side bands of approximately one-third the intensity one normally expects. This splitting is due to those protons on the adjacent nitrogen atom. In the alanine complex, [Co(en)₂(alanine)](NO₃)₂, the single α -hydrogen exhibits a poorly defined quartet centered at the same location, and the methyl resonance is split into a doublet centered at 180 c.p.s. upfield with a splitting of 7 c.p.s. Second-order splitting is evident as the components of the doublet exhibit some additional splitting. The poor definition of the quartet at 62 c.p.s. (split by the three methyl hydrogen atoms) probably results from the same cause and also because of interaction with the protons of the nitrogen.

The addition of a drop of 2 *N* sodium hydroxide in D₂O, making the solution barely alkaline to litmus, causes the hydrogens on the nitrogen atom to undergo exchange but, of particular interest, brings about rapid exchange of the α -hydrogens. The weak triplet in the glycine complex and the quartet in the alanine, both at 62 c.p.s. upfield, disappear as do the resonances ascribed to the protons attached to the nitrogen atoms, at 30 c.p.s. downfield. In the alanine complex the methyl doublet collapses to a singlet, but in both cases the en ring hydrogens remain unexchanged. These observations serve as dramatic evidence of the electron-withdrawing action of the central metal ion upon the chelate ring to enhance the lability, as well as the acidity, of the α -methylene hydrogens. Observations of a similar but more subtle nature have been made on Co(EDTA)⁻.

Weagleim and Hoard⁴ have determined the structure of the Co(EDTA)⁻ ion in two of its salts, and the conformations of the chelate rings have been considered earlier.⁵ The glycine-like chelate rings in octahedral EDTA complexes exist as two distinct pairs of rings. These are most readily identified as mutually planar with the ethylenediamine chelate ring, the *in-plane* pair, and as not in that plane, the *out-of-plane* pair of rings.⁶ Day and Reilly⁷ correctly identified AB patterns with the methylene hydrogen atoms of each of these kinds of glycine-like chelate rings and we have independently achieved complete assignment of the p.m.r. spectrum of CoEDTA⁻.⁸ The two AB patterns are centered at $\delta_{av} = 39$ and 49 c.p.s. vs. H₂O at 22°. The AB pattern occurring at lower fields is assigned on the basis of its relative position in the spectrum and because of the environmental distinction between the two hydrogen atoms of the *out-of-plane* chelate rings. This is required by the fact that the *out-of-plane* rings are virtually strain free while the *in-plane* rings suffer

(4) H. A. Weagleim and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(5) D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961); D. H. Busch and K. Swaminathan, *ibid.*, **23**, 150 (1961).

(6) We avoid such titles as axial and polar because of prior use of these obvious terms for other purposes.

(7) R. J. Day and C. N. Reilly, *Anal. Chem.*, **36**, 1073 (1964).

(8) D. H. Williams, Thesis, The Ohio State University, Aug. 1964 (to be published).

severe valence angle distortions and substantial elongation of the Co-O bonds.

When solutions of Co(EDTA)⁻ in D₂O are carefully made basic and heated gently, the downfield AB pattern (*out-of-plane* rings) slowly decreases in intensity. After relatively long periods of time, the second AB pattern (*in-plane* rings) also shows a measurable diminution in intensity. Confirmation of the nature of the process has been provided by observing the appearance of the AB patterns when ethylenediaminetetra-perdeuterioacetatocobaltate(III) is allowed to undergo exchange with H₂O.

Although present data are semiquantitative at best, it can be concluded that the rates of exchange of the hydrogen atoms on the two kinds of glycine-like chelate rings are quite different. Since all the acetate functions of the free ligand are equivalent, it is seen that the metal ion that coordinates to EDTA in an octahedral manner may serve both to activate and to bring a sharp chemical distinction between pairs of these groups. The effect is at once stereochemical and electronic. It again serves to illustrate the decisive, very easily understood, yet kaleidoscopically varied effects that metal ions can exert on the properties and reactivities of molecules and ions that may serve as ligands.

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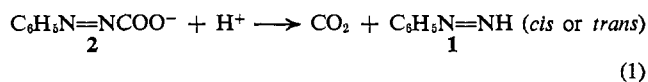
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Phenyldiimide

Sir:

Phenyldiimide (1) has been postulated as an intermediate in the oxidation of phenylhydrazine,¹ the hydrolysis of benzoylphenyldiimide, and the decarboxylation of phenylazoformic acid.² The sodium salt of 1 has been claimed as the product of the reaction of sodium amide and phenylazoformic acid amide,³ but no further report on this work has appeared.

We have now detected 1 as a somewhat unstable intermediate in the decarboxylation of phenylazoformic acid anion (2) according to eq. 1.



The anion 2 decomposes at a rate linear in hydrogen ion over the pH range 10.5–12.0 in a first-order process. The rate constant is independent of the concentration of 2 and only somewhat sensitive to ionic strength (see Figure 1). The rates are followed at 2830 Å. (the maximum for 2) with samples taken from *oxygen-free* solutions, quenched in 1.2 *N* sodium hydroxide, and extracted with *n*-heptane to remove strongly absorbing products.

A degassed solution of 2 in 0.6 *M* sodium hydroxide (0.9–1.6 × 10⁻² *M*, 50 μl.) is mixed with 5.0 ml. of degassed phosphate buffer, pH 7.10, in an all-glass system fitted with a quartz cell. Recording of spectra

(1) F. D. Chattaway, *J. Chem. Soc.*, **91**, 1323 (1907).

(2) S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965).

(3) A. Angeli and Z. Jolles, *Ber.*, **62**, 2099 (1929); cf. footnote 4.