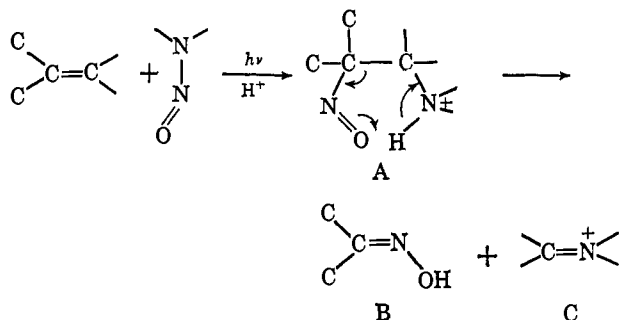


The observed pattern of orientation predicts that the photoaddition of a nitrosamine to an unsymmetrically disubstituted or more complex olefin should give an adduct (A) in which the nitroso group can no longer tautomerize to an oxime. An intramolecular proton transfer followed by redistribution of bonding electrons



(see A) would offer an alternative pathway resulting in cleavage of the original olefin bond to give B and C. Such an expectation has now been unambiguously borne out by our experiments, providing a new, yet remarkably simple, technique of cleaving a carbon-carbon double bond.

Using N-nitrosopiperidine as the reagent,  $\alpha$ -methylstyrene was cleaved to acetophenone oxime (91%) and dipiperidinomethane (82%) while tetramethylethylene gave acetone and its oxime. The latter photolysate was hydrolyzed to acetone and identified as the 2,4-dinitrophenylhydrazone (87%). For 1-methylcyclohexene, where the cleavage product possess both B and C moieties in interacting proximity, N-nitrosodimethylamine in 30% aqueous tetrahydrofuran was found to afford, after a mild hydrolysis, 6-ketoheptanal (59%), b.p. 102–105° (13 mm.); 2,4-DNP m.p. 181–182°. *Anal.* Found: C, 46.95; H, 4.25; N, 22.71.

A mixture of *dl*-camphene (10 g.), N-nitrosopiperidine (5.15 g.), concentrated hydrochloric acid (6 ml.), and methanol (300 ml.) was placed in a water-jacketed Pyrex photocell and cooled externally in an ice bath. While a slow stream of nitrogen was bubbled through, the solution was irradiated with a 250-w. Hanovia mercury lamp until the nitrosamine absorption at 348  $m\mu$  disappeared. Methanol and excess camphene were evaporated under vacuum and the residue was extracted with ether. The usual workup of the ether solution gave a crystalline residue which was recrystallized to give *dl*-camphenilone oxime, m.p. 102–103° (14.6 g.), lit.<sup>7</sup> m.p. 105–107°. The aqueous layer was basified and extracted with ether to give dipiperidinomethane, b.p. 48° (0.2 mm.) (67%), lit.<sup>8</sup> b.p. 115° (15 mm.).

The present cleavage reaction is similar to ozonolysis in the net results except that the two cleavage products derived from an olefin possess different functional groups. An olefin carrying functional groups, particularly those photolabile ones, may conceivably alter the reaction pattern at some stage. The scope and the limitation of this photocleavage reaction will be further investigated. In comparison to the similar photocleavage reported by Büchi and Ayre<sup>9</sup> the present method provides good yields and a simpler reaction.

(7) G. Kommpa, *Ann.*, **366**, 71 (1909).

(8) E. Knoevenagel, *Ber.*, **31**, 2585 (1898).

(9) G. Büchi and D. A. Ayre, *J. Am. Chem. Soc.*, **78**, 690 (1956).

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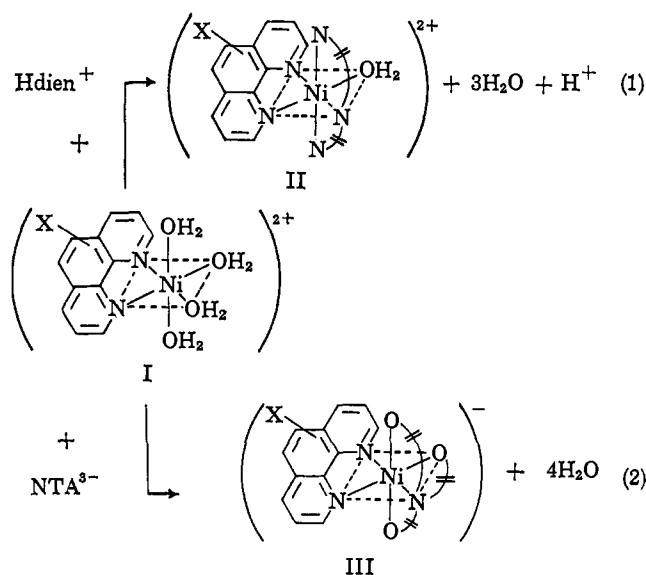
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Received July 9, 1965

### Remote Ligand Substituents in Nickel(II) Complexes Affecting the Rate of Loss of Coordinated Water

Sir:

Substituents on position 5 of the ligand in mono(1,10-phenanthroline)nickel(II) complexes influence the rate of replacement of water molecules coordinated to the nickel. Reactions were studied with diethylenetriamine (dien) and with nitrilotriacetate (NTA) leading to the formation of mixed complexes without displacement of the 1,10-phenanthroline or 5-substituted 1,10-phenanthroline (eq. 1 and 2).



Crystalline salts of the phenanthroline complexes were prepared, and in each kinetic experiment fresh solutions of these salts were used to avoid the presence of bis- and tris(1,10-phenanthroline)nickel(II) complexes. The mixed complexes II and III were characterized in solution by spectrophotometric and pH measurements which showed that in the initial reactions the phenanthroline was not displaced from nickel and that dien and NTA were coordinated to nickel. A recording spectrophotometer was used for the reaction in eq. 1 and a stopped-flow apparatus was used for the reaction in eq. 2. The reactions were first order in the Ni(phen)<sup>2+</sup> complex and first order in dien and NTA, respectively. The acid dependence of reaction 1 was resolved and showed Hdien<sup>+</sup> to be the primary reactant at pH 6–7.

The substituents are quite remote from the reaction site and their kinetic effect (Table I) cannot be due to steric factors but must be due to changes in metal-ligand electron density. Excellent Hammett free energy relationships were obtained for both reactions (Figure 1). The  $\sigma$  values were calculated from the acid dissociation

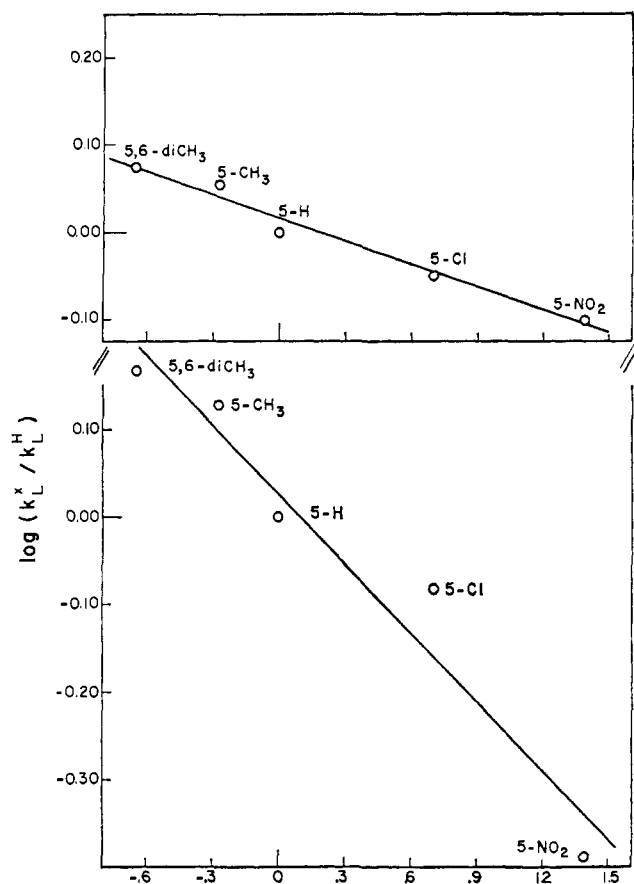


Figure 1.

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

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

Substituent	$pK_a$	$k_{\text{Hdien}}^a$	$k_{\text{NTA}}^b$
5,6-Di- $\text{CH}_3$	5.6	426	$4.15 \times 10^6$
5- $\text{CH}_3$	5.23	408	$3.78 \times 10^6$
5-H	4.96	359	$2.82 \times 10^6$
5-Cl	4.26	327	$2.34 \times 10^6$
5- $\text{NO}_2$	3.57	281	$1.15 \times 10^6$

<sup>a</sup> Ionic strength = 0.13. <sup>b</sup> 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.<sup>1</sup> 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.<sup>2,3</sup> 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.<sup>4</sup> 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  $\text{Hdien}^+$  and  $\text{NTA}^{3-}$  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  $\text{NTA}^{3-}$  is believed to involve substitution of an equatorial water (in the plane of Ni and phen), while the reaction with  $\text{Hdien}^+$  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.

*Acknowledgment.* This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 134-65.

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

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Received August 19, 1965

### Selective Labilizing of $\alpha$ -Hydrogen Atoms by Chelation of $\alpha$ -Aminocarboxylic Acids

Sir:

While the action of metal ions to increase the reactivity of  $\alpha$ -methylene hydrogens has been observed,<sup>1,2</sup> 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  $\text{D}_2\text{O}$  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  $22^\circ$ . 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.<sup>3</sup> 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).