evidenced in the rate constant $k_{2,0}$ ($k_{2,0}$ = 25 M^{-1} sec^{-1}) which is a factor of 4 greater than $k_{1,0}$. This difference is significant and definitely shows that substitution rates in low-spin nickel(II) are sensitive to the nature of the ligands coordinated in the other square-planar positions. The difference is probably much greater than 4 but because of electrostatic repulsions it is significantly reduced.

Other ligand exchange reactions with $NiH_{-2}L^-$ and $CuH_{-2}L^-$ are proton-transfer limited.[7,8] The rates observed in this work at pH 11 are less than what would be expected for a proton-transfer mechanism and thus indicating that the presence of cyanide in $NiH_{-2}L(CN^{2-})$ and $NiH_{-2}L(CN)_2^{3-}$ has a very pronounced effect upon the lability of the nickel–imide bonds. There is no hydrogen ion dependence in the pH 11–12 region; however, there is a significant contribution to path II from hydrogen cyanide at pH 9. Boric acid has no effect upon the observed rate and thus the reaction is not subject to general acid catalysis.

(7) E. J. Billo and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 6811 (1970).
(8) G. K. Pagenkopf and D. W. Margerum, *ibid.*, **90**, 6963 (1968).

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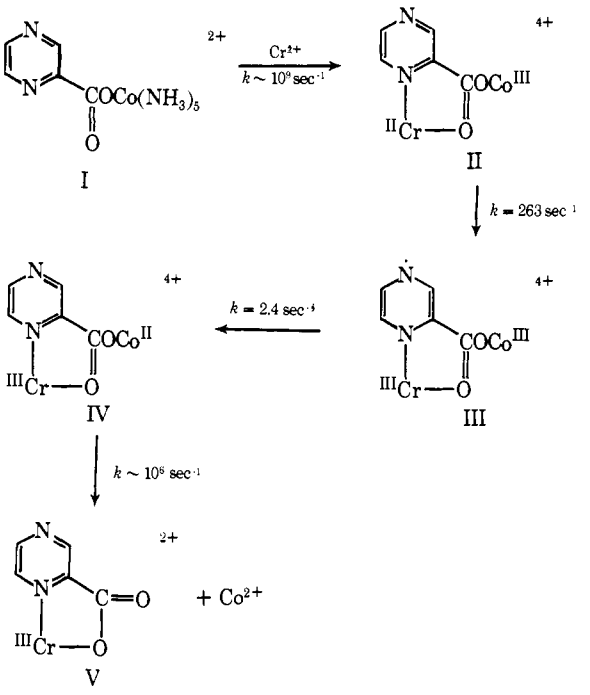
Electron Transfer through Organic Structural Units. XIII. Radical–Cation Intervention

Sir:

Radical species bound both to Co(III) and Cr(III) have been suggested as intermediates in the Cr(II) reductions of heterocyclic[1] and unsaturated carboxylato[2] derivatives of cobalt(III). The present communication describes a strongly absorbing intermediate appearing during the reduction of pyrazinecarboxylatopentaamminecobalt(III)[1b] (I) with Cr^{2+}; the behavior of this species corresponds to that of the suspected cation–radical intermediate.

Addition of excess Cr^{2+} (0.005–0.05 M) to oxidant I (7×10^{-5} M) in 1.2 M $HClO_4$ results in a very marked increase in absorbance throughout the range 400–660 nm during the first 0.01 sec after mixing, followed by a fading, during the next 1.4 sec, to an absorbance characterizing Co^{2+} and the chelated Cr(III) product V.[1b] Both changes are cleanly first order. Absorption maxima for the intermediate lie at 625 nm (ϵ 2400) and 430 (5100).[3] *The maximum concentration of the absorbing species, its rate of formation, and its rate of disappearance are independent of* (Cr^{2+}) in the range studied. The measured specific rates (25°, μ = 1.22) for these reactions, 263 ± 12 and 2.39 ± 0.06 sec^{-1}, are many orders of magnitude below known[4] substitution rates at Cr^{2+} (~10^9 sec^{-1}) and Co^{2+} (~10^6 sec^{-1}) centers; neither observed reaction can then reasonably be taken as the formation of the binuclear precursor complex II or the collapse of successor complex IV. Instead, it is suggested (Scheme I) that the increase in

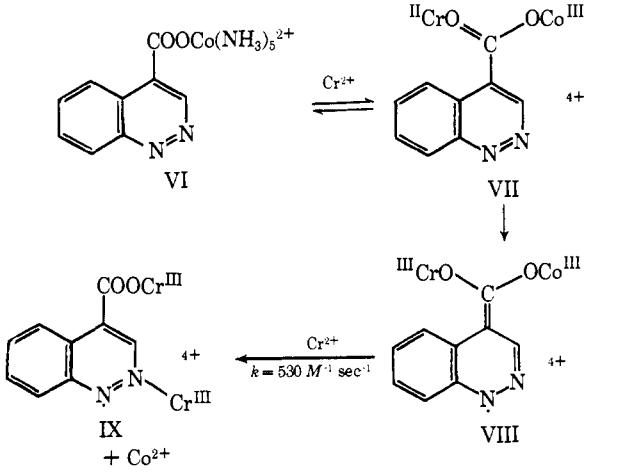
Scheme I



absorbance reflects internal electron transfer in precursor II to form radical–cation III and that the fading is due to further conversion to successor IV, which undergoes very rapid aquation. If this scheme is correct, the absence of (Cr^{2+}) dependency in the conversions II → III and III → IV demands that conversion of I to a Cr^{II} chelate be virtually complete, even in 1.2 M $HClO_4$.

A strongly absorbing intermediate intervenes also during the Cr^{2+} reduction of a 2.6×10^{-4} M solution of the 4-cinnolinecarboxylato derivative VI.[1b] The degree of conversion to this intermediate (ϵ_{360} 3400, ϵ_{580} 420, sh)[3] is again independent of (Cr^{2+}) when the latter exceeds 0.005 M, but in this case both formation (k = 2.4 ± 0.3 × 10^5 M^{-1} sec^{-1}) and disappearance (k = 530 ± 30 M^{-1} sec^{-1}) are first order in Cr^{2+}. The implications here (Scheme II) are different, and more

Scheme II



tentative, from those pertaining to the reduction of complex I. If the strongly absorbing intermediate is

(1) (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4730 (1965); (c) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).
(2) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).
(3) Extinction coefficients are calculated assuming complete conversion of complexes I and VI to the absorbing species.
(4) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, pp 152–155.

taken as the binuclear radical–cation VIII, formed *via* precursor complex VII (which cannot be chelated), the latter is present only at small steady-state concentrations, whereas conversion to VIII is very nearly complete. Intermediate VIII appears then, in the presence of excess Cr^{2+}, to be attacked by a second Cr^{2+} (very probably at one of the ring nitrogens).[5]

Complex VI is thus similar to I in that both heterocyclic systems readily accept an electron from Cr^{2+} to form a moderately stable radical–cation which can undergo internal electron transfer with reduction of Co(III). The cinnoline reduction is, however, complicated by the availability of an additional site at which further rapid external reductive attack may occur. Work is continuing in an effort to define the structural features within the ligand which favor one or the other type of behavior.[7,9]

Acknowledgments. Sponsorship of the Petroleum Research Fund, administered by the American Chemical Society under Grant 2868-A3, is gratefully acknowledged. Thanks go also to Professor William Movius for valuable discussions.

(5) Further elaboration of Scheme II is necessary to accommodate the earlier finding[1b] that when oxidant VI is in excess, just 1 equiv of Co^{2+} is eventually produced for each equivalent of Cr^{2+} taken. The alternatives appear to be a second, intramolecular path for reduction of Co(III) in VIII, which becomes important when only a deficiency of Cr^{2+} is taken, or, less likely, a slow reduction of Co(III) in VI by radical cation IX, in a manner similar to that proposed for radical–cations in the pyridine series.[6]

(6) C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, **93**, 4044 (1971); J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971).

(7) Although the rates of formation of the strongly absorbing intermediates derived from oxidants I and VI are independent of acidity in the (H^+) range 0.12–1.20 *M*, the rates of disappearance of these species are acid-dependent but in opposite directions. The fading of the intermediate from I is 0.7 times as rapid in 0.12 *M* $HClO_4$ (μ = 1.22) as in 1.2 *M* $HClO_4$, whereas the intermediate from VI disappears about twice as rapidly at the lower acidity. These trends correspond to those observed in the Cu^+ reductions of these complexes[8] and are in accord with the suggestion that protonation of the 4-nitrogen in the pyrazine complex facilitates electron transfer to Co(III) within a dinuclear intermediate, whereas with the cinnoline complex, H^+ and the reducing metal center compete for a basic "lead-in" site.

(8) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 5661 (1971).

(9) A similar, but much more short-lived, Co(III)-bound radical–cation intermediate has recently been characterized in the e_{aq}^- reduction of *p*-nitrobenzoatopentaamminecobalt(III) by M. Z. Hoffman and M. Simic, *ibid.*, **94**, 1757 (1972). These authors report a specific rate of 2600 sec^{-1} for internal electron transfer, at pH 5.5–7.7, but there is evidence[10] that this radical–cation may be greatly stabilized by conversion to its conjugate acid in 1.2 *M* $HClO_4$.

(10) E. S. Gould, *ibid.*, **88**, 2983 (1966).

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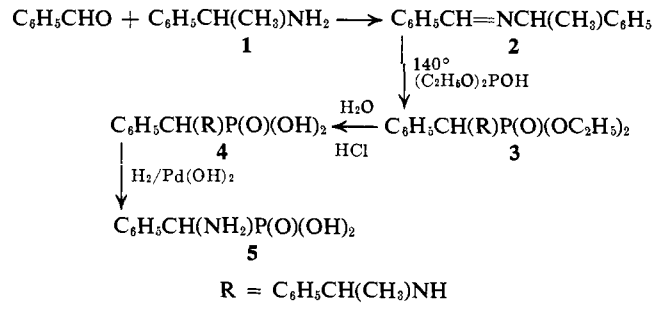
Synthesis of an Optically Active α-Aminophosphonic Acid

Sir:

Although various syntheses for α-aminophosphonic acids have been known for several years,[1-3] an optically active acid has not been reported to date. We wish to report the synthesis of the first optically active α-aminophosphonic acid. We have succeeded in preparing both enantiomers of α-aminobenzylphosphonic acid and we wish in further work to develop this synthesis into a general procedure for preparing the optically active phosphonic acid analogs of various amino acids.

The α-aminobenzylphosphonic acid enantiomers **5** were prepared by condensing benzaldehyde with either (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine (**1**) to form the respective Schiff's base **2**. The diethyl ester **3** was prepared by heating a mixture of **2** with diethyl hydrogen phosphonate at 140° for 1 hr.[4] The ester was hydrolyzed in concentrated HCl and evaporated to dryness. Treatment of the hydrochloride salt dissolved in a minimum amount of water with propylene oxide[5] gave **4**. The final product **5** was obtained by hydrogenolysis of the α-methylbenzyl group on a low-pressure Paar hydrogenator using 10% $Pd(OH)_2/C$[6] in glacial acetic acid at room temperature. Removal of the acetic acid gave a solid mass which was recrystallized from water–ethanol. Physical properties of both enantiomers were identical with the known racemic acid.[4c] Synthesis of **5** with (*S*)-(−)-α-methylbenzylamine gave the dextrorotatory enantiomer, $[\alpha]^{25}D$ +18.1° (*c* 2.0, 1 *N* NaOH), and the (*R*)-(+)-amine gave the levorotatory enantiomer, $[\alpha]^{25}D$ −18.1° (*c* 2.0, 1 *N* NaOH). Preliminary testing of each isomer with D-amino acid oxidase has failed to give an indication of absolute configuration.



Acknowledgment. We are grateful to the American Foundation for Pharmaceutical Education and the Research Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, for their support of this work.

(1) M. E. Chalmers and G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **75**, 5278 (1953).

(2) K. D. Berlin, R. T. Claunch, and E. T. Gaudy, *J. Org. Chem.*, **33**, 3090 (1968).

(3) J. R. Chambers and A. F. Isbell, *ibid.*, **29**, 832 (1964).

(4) (a) E. K. Fields, *J. Amer. Chem. Soc.*, **74**, 1528 (1952); (b) A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **83**, 865 (1952); *Chem. Abstr.*, **47**, 4299 (1953); (c) R. Tyka, *Tetrahedron Lett.*, 677 (1970).

(5) K. D. Berlin, N. K. Roy, R. T. Claunch, and D. Bude, *J. Amer. Chem. Soc.*, **90**, 4494 (1968).

(6) W. M. Pearlman in "Reagents for Organic Synthesis," L. F. Fieser and M. Fieser, Ed., Wiley, New York, N. Y., 1967, p 782.

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Biogenetically Patterned Approaches to Eudesmane Sesquiterpenes. A Total Synthesis of (±)-Junenol

Sir:

Nonenzymic cationic cyclizations of farnesol derivatives have been extensively investigated as a means for accomplishing biogenetic-type syntheses of sesquiterpenes.[1] While several representatives of sesquiterpene

(1) E. E. van Tamelen, *Fortschr. Chem. Org. Naturst.*, **19**, 242 (1961), and references therein.