peaks): 1447, 1111, 762, 746, 730, 696, and 679 cm.$^{-1}$. The F^{19} n.m.r. spectrum was obtained on a benzene solution of the solid. In spite of low solubility and low fluorine content, satisfactory spectra were obtained by carefully optimizing the radiofrequency field, receiver gain, and sweep rate settings. A doublet with a chemical shift of -39.2 p.p.m. (from trifluoroacetic acid as external reference) and a J_{PF} of 667 c.p.s. was observed (lit.[5] -39 p.p.m. and 695 c.p.s. for the neat liquid).

Anal. Calcd. for $C_{18}H_{15}F_2P$: C, 71.99; H, 5.03; F, 12.65; P, 10.32. Found: C, 71.90; H, 5.33; F, 12.0; P, 10.25.

The same product was formed in a similar reaction in which anhydrous ethyl ether was substituted for chlorobenzene and when triphenylphosphine was heated at 91° with excess tetrafluorohydrazine. However, the product from the latter reaction showed additional weak bands at 878 and 785 cm.$^{-1}$ in its infrared spectrum and had a lower melting point (141–150°) than the products prepared in solution.

Reaction of Triphenylphosphine with Sulfur Tetrafluoride.—An approximately 550-ml. Pyrex glass reactor was charged with 1.87 g. (7.1 mmoles) of triphenylphosphine. The reactor was evacuated and 10 ml. of chlorobenzene was charged by vacuum transfer from a bulb containing phosphorus pentoxide into the reactor. Excess sulfur tetrafluoride (*ca.* 20 mmoles) was condensed into the reactor with a liquid nitrogen bath. The reactor was closed and the bath was removed. After 10 min. magnetic stirring was started and continued for 0.5 hr. The volatiles were then removed, leaving a solid residue. The infrared spectrum (mineral oil mull) of the solid and the corresponding spectrum of the product from tetrafluorohydrazine were identical.

The solid was washed out of the reactor with anhydrous benzene, filtered, washed with anhydrous ethyl ether, and dried. The yield of pale yellow solid was 1.1 g. (3.7 mmoles, 52%); m.p. 154–158°.[8]

Some of the solid was recrystallized from hot benzene using polypropylene centrifuge tubes to carry out the recrystallization. The hot solution was decanted from a small amount of yellow, insoluble material (presumably sulfur). The recrystallized material was treated with reagent grade methanol and dried; m.p. 159.6–160.6°.[8] The treatment with methanol removed an impurity, absorbing weakly at 1145 cm.$^{-1}$, in the benzene-recrystallized product.

Hydrolysis of Difluorotriphenylphosphorane.—Difluorotriphenylphosphorane was stirred overnight with an excess of a 10% solution of sodium hydroxide in 1:1 ethanol–water. The solvents were largely distilled and the solid product was filtered and washed with water to give a 67% yield of triphenylphosphine oxide, identified by its m.p. of 156–156.4° (lit.[11a] 152–153°; lit.[11b] 156°) and its infrared spectrum.[12] A fluoride determination on the filtrate found 0.62 mequiv. (86%).

In another experiment difluorotriphenylphosphorane in a polyethylene container was dissolved in 96% sulfuric acid (fumes of presumed hydrogen fluoride were evolved) and the solution was poured into water. The insoluble solid which formed was triphenylphosphine oxide.

Reaction of Tetrafluorohydrazine with Diphenylphosphine.—Tetrafluorohydrazine (7.7 mmoles, 87% pure,[10] 6.7 mmoles of N_2F_4) was allowed to diffuse over a stirred solution of diphenylphosphine (1.1 g., 6.1 mmoles) in 30 ml. of 1,2,3-trichloropentafluoropropane. Nitrogen gas was removed periodically by cooling most of the system in liquid nitrogen and pumping off the noncondensables. After 24 hr., 3.5 mmoles of nitrogen (identified by mass spectrometry) had been evolved. The solvent was distilled at 25° from an amber oil, which was then distilled bulb-to-bulb to give 0.8 g. (54%) of trifluorodiphenylphosphorane.

The infrared and F^{19} n.m.r. spectra of the phosphorane were essentially the same as those of a sample which we prepared by the published method of Smith.[7,13] The infrared spectrum showed the presence of P–F absorption at 870 cm.$^{-1}$ but no P–H absorption at 2380 cm.$^{-1}$. The F^{19} n.m.r. spectrum of the neat liquid showed a doublet of doublets of chemical shift -43.68 p.p.m. and a doublet of triplets of chemical shift $+1.15$ p.p.m. (from trifluoroacetic acid as an external standard). The reported values are -44 and $+1.2$ p.p.m., respectively.[5]

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[12] We wish to thank Dr. A. K. Hoffmann for the sample of triphenylphosphine oxide which was used for comparison.

[13] The assistance of Mr. S. W. Grant in this preparation is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS

Kinetics of the Reduction of Halopentaamminecobalt(III) Complexes by Chromium(II)

BY JOHN P. CANDLIN AND JACK HALPERN

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Earlier attempts[1] to measure the rates of reduction of the halopentaamminecobalt(III) complexes by chromium(II)

$$(NH_3)_5CoX^{2+} + Cr^{2+}(aq) + 5H_3O^+ \longrightarrow Co^{2+}(aq) + (H_2O)_5CrX^{2+} + 5NH_4^+$$

(where X = F, Cl, Br, I) were unsuccessful because the reactions were too fast for the stopped-flow procedure employed. By modifying the procedure, we have now succeeded in measuring these rates, which are reported in the present paper.

The essential features of the experimental method, the stopped-flow apparatus, and the preparation of materials have all been described earlier.[1] The present modification consisted of substituting a Beckman deuterium lamp for the tungsten lamp of the stopped-flow apparatus, thus making it possible to use the ultraviolet absorption bands of the halopentaamminecobalt(III) ions (λ_{max} ranging from 210 mμ for $(NH_3)_5CoF^{2+}$ to 287 mμ for $(NH_3)_5CoI^{2+}$), in place of the visible bands, to follow their disappearance. Because of the much higher extinction coefficients ($\sim 2 \times 10^4$) of these bands, the reactant concentrations could be lowered sufficiently to bring the rate measurement into the range of the stopped-flow apparatus ($t_{1/2} > 5 \times 10^{-3}$ sec.). The initial reactant concentrations were, typically, $[(NH_3)_5CoX^{2+}] \sim 5 \times 10^{-6}$ *M*, $[Cr^{2+}]$ ranging from 2×10^{-5} to 1.2×10^{-4} *M*. The kinetic data fitted the second-order rate law, $k[Cr^{2+}][(NH_3)_5CoX^{2+}]$,

[1] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

found earlier for the chromium(II) reduction of other pentaamminecobalt(III) complexes. The results of our rate measurements are summarized in Table I.

TABLE I

RATE CONSTANTS FOR THE REDUCTION OF HALOPENTAAMMINECOBALT(III) COMPLEXES BY CHROMIUM(II) AT 25°

Oxidant	k, M^{-1} sec.$^{-1}$ $\mu = 0.1^a$	k, M^{-1} sec.$^{-1}$ $\mu = 1.0^b$
$(NH_3)_5CoF^{2+}$	$(2.5 \pm 0.5) \times 10^5$	$(9 \pm 1) \times 10^5$
$(NH_3)_5CoCl^{2+}$	$(6 \pm 1) \times 10^5$	$(2.6 \pm 0.5) \times 10^6$
$(NH_3)_5CoBr^{2+}$	$(1.4 \pm 0.4) \times 10^6$	c
$(NH_3)_5CoI^{2+}$	$(3 \pm 1) \times 10^6$	c

[a] 0.1 M $HClO_4$. [b] 0.1 M $HClO_4$–0.9 M $NaClO_4$. [c] Too fast for measurement.

These electron-transfer reactions have previously been shown[2] to proceed by inner-sphere mechanisms, through bridged intermediates of the type $[(NH_3)_5Co\text{-}X\text{-}Cr(H_2O)_5]^{4+}$, resulting in transfer of the halide from cobalt to chromium. The electron-transfer step is thus presumably preceded by a substitutional step of the type

$$(NH_3)_5CoX^{2+} + Cr(H_2O)_6^{2+} \longrightarrow [(NH_3)_5Co\text{-}X\text{-}Cr(H_2O)_5]^{4+} + H_2O$$

leading to the formation of the bridged intermediate. In view of the very high rate constants reported above, the possibility that the rates of these electron-transfer reactions are determined by this substitutional step cannot be overlooked. In this connection it is of interest that the sequence of rates reported here with Cr^{2+} as reductant, *i.e.*, $(NH_3)_5CoI^{2+} > (NH_3)_5CoBr^{2+} > (NH_3)_5CoCl^{2+} > (NH_3)_5CoF^{2+}$, is the reverse of that found earlier for the much slower reductions of these complexes by Fe^{2+},[3] and Eu^{2+},[1] which are also believed to proceed through inner-sphere mechanisms. In the latter two cases, it seems likely that the order of rates is determined by the increasing stability of the product halide complex, *i.e.*, FeX^{2+} or EuX^{2+}, in going along the sequence X = I to X = F.

Acknowledgment.—Support of this work through a grant from the National Science Foundation is gratefully acknowledged.

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Correspondence

Infrared Spectra of, and Protonation Sites in, Solid Ethylenediaminetetraacetic Acid

Sir:

There is a controversy regarding the protonation sites in ethylenediaminetetraacetic acid (H_4Y) and its derivatives.[1–8] The interpretation of the infrared spectra which seems to be at the origin of much of the controversy has been limited mainly to the 1800–1500 cm.$^{-1}$ region.[1–7] We want to report some spectral data concerning solid H_4Y which support the assumption that the nitrogen atoms are protonated in the H_4Y crystal.

We have investigated the infrared spectra of the solid acid H_4Y, of its disilver salts, Ag_2H_2Y, and of its hydrochloride, $H_4Y \cdot 2HCl$, between 4000 and 250 cm.$^{-1}$. The spectra are shown on Figure 1 together with the spectrum of potassium hydrogen ditrichloroacetate, $KH(CCl_3COO)_2$, which has been recorded for comparison.

The disilver salt exhibits two very strong absorption bands at 1620 and 1392 cm.$^{-1}$, which are assigned to the antisymmetrical and symmetrical COO^- stretching vibrations, respectively. There is no C=O stretching band attributable to the COOH group. The structure of the H_2Y^{2-} ion of Ag_2H_2Y may then be represented just as in the case of the disodium salt,[3] by $(^-OOCCH_2)_2NH^+\text{-}CH_2CH_2\text{-}NH^+(CH_2COO^-)_2$.[9] The broad bands appearing in the 3000–2600 cm.$^{-1}$ region of the Ag_2H_2Y spectrum which are deuteration sensitive may then be assigned to the NH^+ groups. The sharp bands near 3000 cm.$^{-1}$, which are superimposed on the large ones, are not deuteration sensitive and are then due to the CH_2 groups.

Solid H_4Y shows only one broad band near 1690 cm.$^{-1}$ in the 1800–1500 cm.$^{-1}$ region. Chapman[1,5] has concluded that H_4Y must then be a normal carboxylic acid containing four COOH groups and therefore there is no protonation on the nitrogen atom. Langer[6] supports this view, saying that the single band near 1700 cm.$^{-1}$ observed for solid H_4Y is due to dimeric COOH groups attached to neutral nitrogen. If H_4Y is a normal acid it should show a normal acid spectrum over the entire infrared region. However, this is not the case.

In the 4000–2000 cm.$^{-1}$ region, for instance, the absorption pattern of H_4Y is much more similar to that of Ag_2H_2Y than to a normal carboxylic acid spectrum.[10] The broad bands which appear between 3000 and 2600

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