Bonding through the terminal nitrogen would not be expected to greatly alter the change in dipole moment of the PN absorption.[23-28] The observed decrease in area of the PN mode in the adduct and the tentative assignment of a PB stretch[21] indicate that the best representation of the adduct is attachment of the borane group to the phosphorus atom and not to one of the nitrogens; however, until a ^{11}B nmr can be obtained showing $^{31}P-^{11}B$ coupling the bonding site of the adduct is uncertain.

Experimental Section

Materials and General Techniques.—The PF_2Br, PF_2I,[29] and B_2H_6[30] were prepared by literature methods. NaN_3 and LiN_3 were obtained from Matheson Coleman and Bell and Eastman Organics.

High-vacuum techniques were used throughout.[31] Although no explosions occurred with PF_2N_3, secondary products are highly explosive (HN_3, $P(N_3)_3$, etc.)[7,32,33] and proper precautions should be followed. Several explosions have occurred in this laboratory during transfer and disposal of side products and a violent explosion occurred during transfer of $PF_2N_3BH_3$.

Infrared spectra were recorded at a sample pressure of 10 mm on a Perkin-Elmer 137 NaCl spectrophotometer and a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. The mass spectrum was obtained on a Varian M60-6 (70 eV), while nmr spectra for ^{19}F were recorded on a Jeolco JNM-C-60 HL operating at 56.4 MHz. Chemical shifts refer to CF_3COOH by tube interchange.

Synthesis of PF_2N_3.—After allowing a 15.0-mmol sample of LiN_3 to sit at ambient temperature in moist air, we placed it in a 500-cm³ reaction bulb and evacuated the bulb for several minutes. A slight excess of PF_2Br (16.0 mmol) was condensed on the LiN_3 at −196°. The reactants then were alternately warmed to room temperature and refrozen at −196°; this procedure was repeated several times. We cooled the reaction mixture to −78° in a Dry Ice–acetone slush and allowed it to sit 18 hr. The material was then distilled through traps held at −110, −135, and −196°. The material at −110°, a mixture of PF_2HO[34] and several explosive azides (HN_3, etc.),[7,32,33] was identified by ir and then carefully discarded. Small amounts of PF_3 at −196° were also discarded. The trap at −135° contained PF_2N_3, very small amounts of F_2POPF_2,[35] and unreacted PF_2Br. This material was condensed on an excess of ZnF_2 and warmed and refrozen several times. The latter procedure converted the PF_2Br to PF_3 which could be removed by distillation. The products from this reaction were led through traps held at −110, −135, and −196°. Again the material at −110 and −196° was discarded with care, while the −135° trap contained 9.0 mmol of PF_2N_3, contaminated by very small amounts of F_2POPF_2. Separation of these two compounds was extremely difficult, but samples of PF_2N_3 could be obtained fairly pure by careful distillation through traps held at −112 and −196° (see mass spectra). PF_2N_3 was trapped in the −112° trap.

If the LiN_3 was very carefully dried, no reaction occurred. PF_2I could be substituted for PF_2Br and NaN_3 could be substituted for LiN_3.

Properties of PF_2N_3.—Difluorophosphine azide is a colorless spontaneously flammable gas at room temperature. No detonations were observed with the pure compound.

Difluorophosphine azide was characterized by its gas molecular weight at 23° (found, 111.6; calcd for PF_2N_3, 111.0) and the mass spectrum splitting pattern. Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of PF_2N_3: 154 ($PF_2OPF_2^+$), 2.2; 111 ($PF_2N_3^+$), 72.3; 92 (FPN_3^+), 8.2; 88 (PF_3^+), 1.6; 85 (PF_2O^+), 1.1; 83 (PF_2N^+), 30.4; 69 (PF_2^+), 100; 64 (PFN^+), 16.9; 50 (PF^+), 15.8; 47 (PO^+), 1.6; 45 (PN^+), 3.8; 43 (HN_3^+), 2.7; 42 (N_3^+), 6.0; 32 (PH^+), 2.7; 31 (P^+), 3.8; 28 (N_2^+), 11.4.

Synthesis of $PF_2N_3 \cdot BH_3$.—PF_2N_3 (6.53 mmol) was condensed with 14.0 mmol of B_2H_6 at −196° in a 500-cm³ reaction bulb. The mixture was allowed to warm and then sit for 6 hr at room temperature. The reaction mixture was distilled through traps held at −67, −110, −140, and 196°. The material at −67° (small amounts of unidentified solids) and −140° (0.1 mmol of PF_2N_3) was discarded. The −196° trap held 10.9 mmol of unreacted B_2H_6, while the −110° trap contained 6.02 mmol of $PF_2N_3 \cdot BH_3$. The yield of the adduct was 95% and PF_2N_3 and BH_3 combined in the ratio 0.99:1.0.

Properties of $PF_2N_3 \cdot BH_3$.—Difluorophosphine azide–borane is a colorless liquid at room temperature. A violent explosion was experienced on transferring this compound.

The borane was characterized by its infrared spectrum given earlier, mass spectrum, and its molecular weight at 20° and 175 mm (found, 125.3; calcd for $PF_2N_3BH_3$, 124.8). The following are the mass numbers (species) and relative abundances of the major ions in the mass spectrum of $PF_2N_3BH_3$: 125 ($PF_2N_3{}^{11}BH_3^+$), 2.81; 124 ($PF_2N_3{}^{11}BH_2^+$), 17.5; 123 ($PF_2N_3{}^{11}BH$), 8.5; 112 ($PF_2N_3H^+$), 3.1; 111 (PF_2N_3), 48.3; 95 ($PF_2N{}^{11}BH^+$), 2.44; 94 ($PF_2N{}^{11}B^+$), 20.8; 93 ($PF_2N{}^{10}B^+$), 5.3; 92 (PFN_3^+), 8.3; 83 (PF_2N^+), 12.2; 76 ($PFN{}^{11}BH^+$), 3.9; 64 (PF_2N^+), 72.1; 51 (PFH^+), 5.7; 50 (PF^+), 10.0; 49 (PNH_4^+), 7.8; 46 (PNH^+), 12.8; 33 (NF^+), 3.0; 32 (PH^+), 5.3; 31 (P^+), 8.6; 30 ($^{11}BH^+$), 2.8; 28 (N_2^+), 9.8; 18 (H_2O^+), 6.7; 13 ($^{11}BH_2^+$), 4.9.[36]

Acknowledgment.—The authors are grateful for the assistance of John Gray with the nmr and Roy Jones with the mass spectrometer. We also thank the Air Force for the use of a Jeolco 60-MHz nmr at Robins Air Force Base and gratefully acknowledge the Petroleum Research Fund administered by the American Chemical Society for support of this work.

---

[23] E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946).

[24] M. F. Shostakovskii, N. I. Shergina, N. V. Komarov, and Yu. V. Maroshin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1515 (1964).

[25] H. Buchert and W. Zeil, *Spectrochim., Acta*, **18**, 1043 (1962).

[26] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 1575 (1957).

[27] F. Cotton, R. Francis, and W. J. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).

[28] P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950).

[29] J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

[30] H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, **80**, 1552 (1958).

[31] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[32] L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

[33] A. M. Buswell, G. W. McMillan, W. H. Rodebush, and F. T. Wall, *J. Amer. Chem. Soc.*, **61**, 2809 (1939).

[34] L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, **7**, 1005 (1968).

[35] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966).

[36] NOTE ADDED IN PROOF.—Since acceptance of this note a paper has appeared by S. R. O'Neill and J. M. Shreeve [*Inorg. Chem.*, **11**, 1629 (1972)] describing the preparation of PF_2N_3 by a similar route. Although we did not experience any explosions with PF_2N_3 their work suggests caution.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILLINOIS 60616

A Novel and Improved Synthesis of $[IrCl(NO)(P(C_6H_5)_3)_2]^+$. A Nitrosyl Analog of Vaska's Compound

BY RONALD J. FITZGERALD* AND HSIU-MEI WU LIN

Received January 3, 1972

There has been a great deal of interest lately, by ourselves[1] and others,[2] in the synthesis and properties of the complex $[IrCl(NO)(P(C_6H_5)_3)_2]^+$.

We report here a novel and greatly improved preparation for the complexes $[IrX(NO)(P(C_6H_5)_3)_2]^+$ (X = Cl, Br) beginning with the readily available com-

---

[1] R. J. Fitzgerald and A. A. El-Awady, submitted for publication.

[2] (a) M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, **93**, 1591 (1963); (b) C. A. Reed and W. R. Roper, *J. Chem. Soc. D*, 155 (1969); (c) C. A. Reed and W. R. Roper, *ibid.*, 1459 (1969).

plexes $[IrX(CO)(P(C_6H_5)_3)_2]$ (X = Cl, Br). This synthesis involves only two steps, in contrast to the usual six-step process,[1] and results in substantially improved yields.

A preliminary report of the chemical reactivity of this complex with several Lewis acids is also presented. The complex shows decreased chemical reactivity in comparison to its carbonyl analog[3] in agreement with previous reports.[2c]

Experimental Section

Apparatus and Techniques.—All of the infrared spectra of compounds were recorded on a Perkin-Elmer 257 grating infrared spectrophotometer using Nujol mulls and calibrated with polystyrene. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and M-H-W Laboratories, Garden City, Mich. All reactions were carried out under a nitrogen atmosphere.

Reactions and Solutions.—*trans*-$[IrX(CO)(P(C_6H_5)_3)_2]$ (X = Cl, Br, I) were purchased from Strem Chemicals Inc., Danvers, Mass., and were used without further purification. Tetracyanoethylene and fumaronitrile were purchased from Aldrich Chemical Inc. and sublimed prior to use. *p*-Nitrobenzoyl azide was purchased from Eastman Organic Chemical Distillation Products Inc. and was recrystallized prior to use. Nitrosyl tetrafluoroborate (95% pure) was purchased from Alfa Inorganics Ventron and was used without further purification. All solvents, methanol, chloroform, absolute ethanol, and *n*-hexane, were dried over 4A molecular sieves and were degassed by passing a stream of nitrogen through the solvent with a filtered bubbling tube for 0.5 hr and then cooling to 0° before use.

Preparation of the Complexes. Preparation of $IrCl(N_2)(P(C_6H_5)_3)_2$.—This complex was prepared from $IrCl(CO)(P(C_6H_5)_3)_2$ and *p*-nitrobenzoyl azide using a previously reported procedure.[4]

Preparation of $IrBr(N_2)(P(C_2H_5)_3)_2$.—A magnetic stirring bar and 0.31 g (0.37 mmol) of $IrBr(CO)(P(C_6H_5)_3)_2$ were placed in a Schlenk apparatus which was flushed with nitrogen by alternatively applying a vacuum and refilling with nitrogen in a drybag filled with nitrogen gas. The apparatus was cooled in a ice bath and 5 ml of ice-cold chloroform was injected through the stopcock by means of a hypodermic syringe. After the magnetic stirrer was turned on, a precooled solution of (0.081 g, 0.42 mmol) *p*-nitrobenzoyl azide in 2 ml of chloroform was injected.

Within 2–3 min, the yellow suspension became a clear yellow solution. After a total reaction time of 10 min, 30 ml of cold methanol was immediately injected to precipitate the nitrogen complex. At least 10 min should be allowed to complete the precipitation. The yellow, crystalline complex was collected on the filter and washed with a 20-ml portion of cold methanol. The product was dried *in vacuo* for 1 hr.

The infrared band at 1960 cm^{-1} (carbonyl stretching frequency) disappeared completely and a new band at 2095 cm^{-1} attributed to the nitrogen stretching frequency appeared. This band was identical with that previously reported[4] for the chloro analog, $IrCl(N_2)(P(C_6H_5)_3)_2$. The yellow, microcrystalline solid gave 0.22 g (70% yield).

Attempted Preparation of $IrI(N_2)(P(C_6H_5)_3)_2$.—This complex was prepared from $IrI(CO)(P(C_6H_5)_3)_2$ in a manner analogous to that used to prepare the bromo complex, except that the reaction time was limited to 3 min. The product was a mixture of $IrI(N_2)(P(C_6H_5)_3)_2$ and a trace of $IrI(CO)(P(C_6H_5)_3)_2$. The infrared spectrum exhibited an intense absorption at 2095 cm^{-1} attributed to the nitrogen stretching frequency in $IrI(N_2)(P(C_6H_5)_3)_2$ and a very weak band at 1960 cm^{-1} attributed to the carbonyl stretching frequency in $IrI(CO)(P(C_6H_5)_3)_2$. Due to the air sensitivity of $IrI(CO)(P(C_6H_5)_3)_2$ and $IrI(N_2)(P(C_6H_5)_3)_2$, which is unstable even in the solid state at room temperature, we found it impossible satisfactorily to separate the products of this mixture.

Preparation of $[IrCl(NO)(P(C_6H_5)_3)_2]BF_4$.—Solid 95% $NOBF_4$ (0.0016 g, 0.0132 mmol) was added to an ice-cold solution of 0.1 g (0.0129 mmol) of $IrCl(N_2)(P(C_6H_5)_3)_2$ in 10 ml of chloroform. The color of the solution changed from yellow to red in 10 min and was filtered to remove any remaining solid. The red solution was evaporated in a vacuum desiccator and the product was recrystallized from a chloroform–*n*-hexane mixture. The red crystals gave 0.10 g (90% yield). *Anal.* Calcd for $IrNOClP_2BF_4C_{36}H_{30}$: C, 49.74; H, 3.45; N, 1.61. Found: C, 49.09; H, 3.83; N, 1.39. The infrared spectrum is identical with that previously reported[1,2b,c] for $[IrCl(NO)(P(C_6H_5)_3)_2]ClO_4$ prepared by other methods with $\nu(NO)$ at 1902 cm^{-1}.

Preparation of $[IrBr(NO)(P(C_6H_5)_3)_2]BF_4$.—This complex was prepared in a manner analogous to that used for the chloro complex, *vide supra*, except that $IrBr(N_2)(P(C_6H_5)_3)_2$ was used as a starting material. *Anal.* Calcd for $IrNOBrP_2BF_4C_{36}H_{30}$: C, 47.32; H, 3.28; N, 1.53. Found: C, 46.95; H, 3.53; N, 1.25. The infrared spectrum yielded an intense band attributed to $\nu(NO)$ at 1902 cm^{-1}.

Attempted Preparation of $[IrI(NO)(P(C_6H_5)_3)_2]BF_4$.—This complex was prepared in a manner analogous to that used for the chloro complex, *vide supra*, except that $IrI(N_2)(P(C_6H_5)_3)_2$ was used as a starting material. Since the starting material contained a trace of $IrI(CO)(P(C_6H_5)_3)_2$, the product obtained was probably a mixture of $[IrI(NO)(P(C_6H_5)_3)_2]BF_4$ and $[IrI(CO)(NO)(P(C_6H_5)_3)_2]BF_4$. The infrared spectrum yielded a strong band at 2040 cm^{-1} attributed to $\nu(CO)$ in $[IrCl(CO)(NO)(P(C_6H_5)_3)_2]BF_4$.[5]

Preparation of $[IrCl(NO)(P(C_6H_5)_3)_2 \cdot TCNE]ClO_4$.—The complex $[IrCl(NO)(P(C_6H_5)_3)_2]ClO_4$ was dissolved in a small volume of absolute ethanol at room temperature and up to a fivefold excess of TCNE (C_6N_4) was added. The red color of the solution disappeared and a pale yellow solid precipitated. The solid was filtered, washed with absolute ethanol, and dried in a vacuum desiccator. *Anal.* Calcd for $IrCl_2P_2O_5N_5C_{42}H_{30}$: C, 49.94; H, 2.97. Found: C, 52.07; H, 3.88. The infrared spectrum exhibited a strong band at 1590 cm^{-1} attributed to $\nu(NO)$.

Attempted Preparation of $[IrCl(NO)(P(C_6H_5)_3)_2 \cdot FUM]BF_4$.—This adduct was prepared in a manner analogous to that used to prepare the TCNE adduct, *vide supra*, except that fumaronitrile ($C_4N_2H_2$) was used as a Lewis acid and tetrafluoroborate was the counterion. There was no color change or precipitation after a reasonable period, indicating no reaction had occurred, and the infrared spectrum yielded a strong band at 1902 cm^{-1} attributed to $\nu(NO)$ in the starting material.

Results and Discussion

The route for the synthesis of *trans*-$[IrX(NO)(P(C_6H_5)_3)_2]BF_4$ (X = Cl, Br, I) from *trans*-$[IrX(CO)(P(C_6H_5)_3)_2]$ (X = Cl, Br, I) is given by eq 1. The

$$trans\text{-}[IrX(CO)(P(C_6H_5)_3)_2] \xrightarrow[\text{under } N_2]{RN_3} IrX(N_2)(P(C_6H_5)_3)_2 \xrightarrow{NOBF_4} [IrX(NO)(P(C_6H_5)_3)_2]BF_4 \quad (1)$$

results of our infrared studies and some properties of these complexes are presented in Table I. The synthesis of the nitrosyl complexes by this method results in a substantial saving in time and labor and also produces a higher yield.

TABLE I

PROPERTIES OF IRIDIUM COMPLEXES

Complex	Color	Ir bands, cm^{-1}
$IrCl(N_2)(P(C_6H_5)_3)_2$	Bright yellow	$\nu(NN)$ 2095
$IrBr(N_2)(P(C_6H_5)_3)_2$	Yellow	$\nu(NN)$ 2095
$IrI(N_2)(P(C_6H_5)_3)_2$	Yellow	$\nu(NN)$ 2095
$[IrCl(NO)(P(C_6H_5)_3)_2]ClO_4$	Red	$\nu(NO)$ 1902
$[IrCl(NO)(P(C_6H_5)_3)_2]BF_4$	Red	$\nu(NO)$ 1902
$[IrBr(NO)(P(C_6H_5)_3)_2]BF_4$	Red	$\nu(NO)$ 1902
$[IrI(NO)(P(C_6H_5)_3)_2]BF_4$	Pale red	$\nu(NO)$ 1895
$[IrCl(NO)(P(C_6H_5)_3)_2TCNE]ClO_4$	Pale yellow	$\nu(NO)$ 1595, $\nu(CN)$ 2131

The infrared criteria for distinguishing between NO^+ and NO^- have been a matter of controversy for some years.[6] Recently, Ibers and coworkers have deter-

---

(3) W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 3705 (1968).

(4) J. P. Collman and J. W. Kang, *ibid.*, **88**, 3549 (1966).

(5) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *ibid.*, **90**, 4486 (1968).

(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970, pp 200–202.

mined the structures of a number of complexes with coordinated nitric oxide.[7] On the basis of their X-ray data and infrared stretching frequencies they[7c] have proposed the following criteria: NO$^+$ complexes have ν(NO) in the range 1600–1845 cm^{-1} and for NO$^-$ complexes ν(NO) is in the range 1525–1720 cm^{-1}. Therefore, it is inadequate to use ν(NO) solely to determine the mode of coordination in the region 1600–1720 cm^{-1}. We may conclude, however, that NO is coordinated as NO$^+$ in our nitrosyl complexes.

Reactions of tetracyanoethylene and fumaronitrile with IrX(CO)(P(C$_6$H$_5$)$_3$)$_2$ (X = Cl, Br, I) have been studied extensively.[3] A number of new compounds have been isolated and characterized in these and similar reactions.

TCNE will add to [IrCl(NO)(P(C$_6$H$_5$)$_3$)$_2$]$^+$ to give [IrCl(NO)(P(C$_6$H$_5$)$_3$)$_2$TCNE]ClO$_4$. There is a change in the bonding of NO to iridium upon coordiation as evidenced by the change in ν(NO) from 1902 to 1595 cm^{-1}. It seems plausible that this structure would be similar to the bent coordinated NO as determined crystallographically in [IrCl(CO)(NO)(P(C$_6$H$_5$)$_3$)$_2$]BF$_4$[5] and that NO is coordinated as NO$^-$ here. However, such proposals must be vindicated by crystallographic study.

The addition of the weaker Lewis acid fumaronitrile to [IrCl(NO)(P(C$_6$H$_5$)$_3$)$_2$]$^+$ produced no reaction, in contrast to [IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$] which forms a stable compound.[3] This decrease in chemical reactivity is consistent with previous reports on this complex.[2c] The decrease in apparent chemical reactivity is probably due to the positive charge on the complex and the resultant decrease in electron density on the metal. For example, this complex shows no tendency to combine with O$_2$,[2c] whereas the uncharged complex RuCl(NO)(P(C$_6$H$_5$)$_3$)$_2$ forms an irreversible adduct with O$_2$.[8]

Acknowledgment.—We are indebted to Professor Abbas A. El-Awady for helpful discussions throughout the course of this research.

[7] (a) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971); (b) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971); (c) D. M. P. Mingos and J. A. Ibers, *ibid.*, **10**, 1479 (1971).

[8] K. R. Laing and W. R. Roper, *ibid.*, **7**, 1556 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Free Radical Mechanism in the Acid-Catalyzed Redox Decomposition of Tris(oxalato)cobaltate(III) Ion in Aqueous Solution[1]

BY NANCY S. ROWAN, RONALD M. MILBURN,*
AND MORTON Z. HOFFMAN

Received January 11, 1972

Although there has been some dispute concerning the detailed path by which the acid-catalyzed redox decomposition of Co(C$_2$O$_4$)$_3$$^{3-}$ is initiated,[2] there has been general agreement up to now that the overall mechanism involves production of a free radical (C$_2$O$_4$$^-$ or CO$_2$$^-$) which reattacks the substrate to form additional Co^{2+}.[3-9] In simplest terms this process may be represented

$$\mathrm{Co(C_2O_4)_3^{3-}} \xrightarrow{k_1} \mathrm{Co^{2+}} + \mathrm{C_2O_4^-} + 2\mathrm{C_2O_4^{2-}} \tag{1}$$

$$\mathrm{C_2O_4^-} + \mathrm{Co(C_2O_4)_3^{3-}} \xrightarrow{k_2} \mathrm{Co^{2+}} + 2\mathrm{CO_2} + 3\mathrm{C_2O_4^{2-}} \tag{2}$$

where Co(C$_2$O$_4$)$_3$$^{3-}$ may be taken here to include protonated and ring-opened forms, C$_2$O$_4$$^{2-}$ includes HC$_2$O$_4$$^-$ and H$_2$C$_2$O$_4$, and C$_2$O$_4$$^-$ includes its protonated form (or CO$_2$$^-$ and CO$_2$H). The basis for this free radical mechanism appears to have arisen largely by analogy to the photochemical decomposition[3,4] and to other oxalate reactions[10] in which free radicals have been implicated. Some additional support has been offered by the observation that the thermal decomposition leads to other processes which are accepted as involving free radicals, such as vinyl polymerization.[3]

Recently Hin-Fat and Higginson[11] have advanced the hypothesis that the thermal decomposition does not involve free radicals at all. The key observation, cited by these authors for both Co(C$_2$O$_4$)$_3$$^{3-}$ and Co(C$_2$O$_4$)$_2$(H$_2$O)$_2$$^-$, is a deviation from first-order behavior as seen by curvature in plots of log $(A_t - A_\infty)$ *vs.* time (where A = absorbance). The fact that wholly linear plots could be obtained by addition of a term inverse in complex concentration, together with the effect of changes in reaction conditions on the magnitude of this term, led these authors[11] to favor a mechanism involving a concerted three-center redox reaction between the substrate and a ring-opened species.

At appropriate relative concentrations of the reactive species, with O$_2$ as an added scavenger, reactions 3 and 4 can predominate over (2), where $2k_4 = 1 \times 10^9\ M^{-1}$

$$\mathrm{C_2O_4^-} + \mathrm{O_2} \xrightarrow{k_3} 2\mathrm{CO_2} + \mathrm{O_2^-} \tag{3}$$

$$2\mathrm{C_2O_4^-} \xrightarrow{k_4} 2\mathrm{CO_2} + \mathrm{C_2O_4^{2-}} \tag{4}$$

sec^{-1}[12] and (3) is assumed to be very efficient by analogy to the CO$_2$$^-$–O$_2$ reaction.[13] In highly acidic solution, the O$_2$$^-$ radical will exist in its H$_2$O$_2$$^+$ form[14] which does not appear to be effective in reducing simple Co(III) complexes.[15] Thus, the formation of Co^{2+} in the presence of O$_2$ from secondary radical reactions is of negligible contribution.[16] Here, in the slow thermal

[1] Supported by the National Science Foundation through Grants GP 19878 and GP 11213.

[2] A detailed discussion, which makes it clear that the initiation process occurs in steps, will be fully presented in a separate communication.

[3] T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955).

[4] A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

[5] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

[6] I. G. Margulescu and T. Oncescu, *Z. Phys. Chem.* (*Leipzig*), **214**, 238 (1960).

[7] W. Schneider, *Helv. Chim. Acta*, **46**, 1863 (1963).

[8] (a) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964); (b) J. Aggett and A. L. Odell, *J. Chem. Soc. A*, 1415 (1968).

[9] H. G. Kruszyna and R. M. Milburn, *Inorg. Chem.*, **10**, 1578 (1971).

[10] H. Taube, *J. Amer. Chem. Soc.*, **70**, 1216 (1948).

[11] L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 2836 (1970).

[12] N. Getoff, F. Schwörer, V. M. Markovic, K. Sehested, and S. O. Nielsen, *J. Phys. Chem.*, **75**, 749 (1971). Reaction 4 for the protonated radical is slower ($2k < 10^7\ M^{-1}$ sec^{-1}) although $2k$(CO$_2$H + CO$_2$H) = $4 \times 10^9\ M^{-1}$ sec^{-1}.

[13] A. Fojtik, G. Czapski, and A. Henglein, *J. Phys. Chem.*, **74**, 3204 (1970).

[14] B. H. J. Bielski and J. M. Gebicki, *Advan. Radiat. Chem.*, **2**, 177 (1970).

[15] N. Zevos, *J. Phys. Chem.*, **72**, 1506 (1968).

[16] I. M. Kolthoff, E. J. Meehan, and M. Kimura [*J. Phys. Chem.*, **75**, 3343 (1971)] report that decomposition of acidic solutions of Co(C$_2$O$_4$)$_3$$^{3-}$ in the presence of oxygen leads to the production of H$_2$O$_2$, which is presumed to arise from the disproportionation of HO$_2$.