and O 2p AO's. Basis functions for the W atom were derived for a +1 oxidation state with the 6s and 6p exponents fixed at 1.8.[40] An exponent of 1.16 was used for the H 1s atomic orbital.[41]

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**Registry No.** $W_4(O\text{-}i\text{-}Pr)_{12}$, 104911-26-4; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $W_2(O\text{-}i\text{-}Pr)_6$, 71391-16-7; $W_2(NMe_2)_6$, 54935-70-5; $W_4(\mu\text{-}OH)_4(OH)_8$, 110825-38-2; W, 7440-33-7.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, bond distances, and bond angles (4 pages); listing of $F_o$ and $F_c$ values (11 pages). Ordering information is given on any current masthead page.

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# Studies of Hypervalent Iron in Aqueous Solutions. 1. Radiation-Induced Reduction of Iron(VI) to Iron(V) by $CO_2^-$

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**Abstract:** Iron(VI) can be reduced in aqueous solutions to iron(V) by pulse radiolytically generated $CO_2^-$, $k_3 = (3.5 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$. The respective UV and visible spectra for these hypervalent oxidation states of iron are reported. It was found that formate reacts $10^5$ times faster with Fe(V) than with Fe(VI). Other kinetic rate measurements include the following: $k_4[O_2^- + Fe(VI)] = (5.71 \pm 0.17) \times 10^3$, $k[NADH + Fe(VI)] = 77.1 \pm 4.4$, $k[HCOONa + Fe(VI)] = (2.33 \pm 0.4) \times 10^{-2}$, $k[EtOH + Fe(VI)] = (1.47 \pm 0.7) \times 10^{-3}$, $k[DTPA + Fe(VI)] = (8.53 \pm 0.32) \times 10^{-4}$, $k[HCOONa + Fe(V)] = (2.48 \pm 0.32) \times 10^3\ M^{-1}\ s^{-1}$. The results are discussed in terms of their possible role in Fe(VI) oxidation processes.

Despite considerable evidence for the involvement of Fe(IV)/Fe(V) in iron-catalyzed oxidation/hydroxylation processes, little tangible information has been forthcoming concerning these oxidation states in the field of aqueous inorganic chemistry.[1-12] While the chemistry of Fe(VI) in aqueous solutions is well reviewed,[13,14] similar information on Fe(V) is, with exception of a short report from this laboratory,[15] scant and limited to research reports on high-temperature melts and the solid state.

Iron ferrates ($K_2FeO_4$, $BaFeO_4$, etc.) are easily prepared in relatively pure form.[16,17] They are very stable, safe, and strong oxidizing agents. In several reactions they were shown to display a high degree of selectivity.[2-4,6-8,11,18] In aqueous solutions Fe(VI) is present as the $FeO_4^{2-}$ ion, believed to have a tetrahedral structure similar to its geometry in the solid state.[19,20] The four oxygens in the molecule were shown to be equilvalent and apparently exchange in water slowly.[20] While aqueous $FeO_4^{2-}$ solutions are relatively stable in the pH range between 9 and 10.5, they deteriorate rapidly in more acidic media with evolution of oxygen. The decomposition process is accelerated by ferric oxides/hydroxides, which accumulate and precipitate as the reaction progresses. In basic media $FeO_4^{2-}$ apparently decomposes by a complex disproportionation mechanism.[13,21-23] Recent determinations of the p*K*'s of $FeO_4^{2-}$ ($pK_1 = 3.5$; $pK_2 = 7.8$) and its decomposition rates over a very broad pH range (2–9.5) have significantly advanced the understanding of the aqueous chemistry of Fe(VI).[13] $E°$'s have been estimated to be near −2.20 V in acid media and −0.72 V in alkaline solutions.[24]

Until recently, formation of Fe(V) had been observed only in high-temperature melts.[25-28] X-ray studies of isolated crystals from such melts suggest that the iron is present in the $FeO_4^{3-}$ form.[26] Although there are claims that stable solutions of $K_3FeO_4$ were prepared in cold alkaline solutions by dissolving the salt isolated from melts,[29] pulse radiolytically generated $FeO_4^{3-}$ in 5 N NaOH at ambient temperatures has a relatively short lifetime ($k_{decay} = 4\ s^{-1}$).[15]

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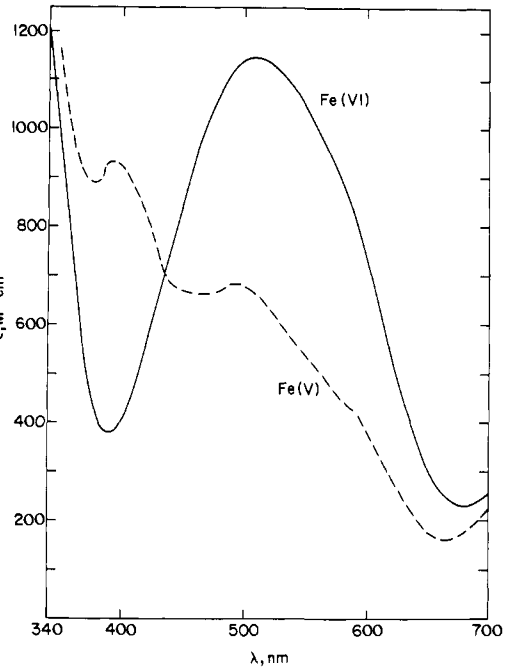

**Figure 1.** Visible absorption spectra of $FeO_4^{2-}$ and $FeO_4^{3-}$ in aqueous solutions containing 0.02 M sodium formate, 40 μM DTPA, and 0.02 M $N_2O$ at pH 9.5–10.5, 24 °C.

The present investigation (1) establishes the kinetic parameters for the reduction of Fe(VI) to Fe(V) by the $CO_2^-$ radical, (2) confirms the recently reported visible spectrum of Fe(V)[15] and presents spectral data in the UV range, (3) compares the rates of reaction of formate with Fe(VI) and Fe(V), and (4) searches for compounds that reduce Fe(VI) to Fe(V) at rates that would allow mechanistic studies of the latter to be carried out in a stopped-flow spectrophotometer.

## Experimental Section

**Chemicals.** All solutions were prepared with water, which, after distillation, had been passed through a Millipore ultrapurification system (MQ water). The pHs of solutions were adjusted by the addition of perchloric acid (double distilled from Vycor; GFS Chemical Co.) or potassium hydroxide (Apache Chemicals, Inc., ultrapure, 99.998%). Either oxygen or nitrous oxide (ultrapure, Matheson Co., 99.99%) was used when appropriate. Diethylenetriaminepentaacetic acid (DTPA; Aldrich Chemical Co., Inc.) was recrystallized 4 times from MQ water before use. Sodium formate was recrystallized twice from 1 mM DTPA solution, followed by two additional recrystallizations from pure MQ water. Potassium ferrate ($K_2FeO_4$) was synthesized according to the method of Thompson et al.[16] The samples were of 96% purity with respect to Fe (Fe was determined by atomic absorption spectroscopy), the impurity being $K_2CO_3$. At pH 10.0 the spectrum of $K_2FeO_4$ shows a maximum at 510 nm ($\epsilon = 1150 \pm 25$ M$^{-1}$ cm$^{-1}$) and a shoulder between 275 and 320 nm (see Figures 1 and 2).

**Equipment.** The pulse-radiolysis experiments were carried out with the BNL 2-MeV Van de Graaff accelerator according to procedures described earlier.[30] Doses were computed by the KSCN dosimeter, with the assumption that $G[(SCN)_2^-] = 6.13$. $G$ values (the number of radicals/molecular products formed per 100 eV of energy dissipated in the medium) are given in parentheses in eq I.[31] Optical path lengths were

$$H_2O \rightsquigarrow e_{aq}^-\ (2.65),\ H\ (0.65),\ OH\ (2.75),\ H_2O_2\ (0.72),\ H_2\ (0.45) \qquad (I)$$

2.0 or 6.1 cm as required, and the solutions were thermostated at 25 °C. $^{60}Co$ γ-ray experiments were carried out with a 1.85 krad/min source. The source was calibrated with the ferrous dosimeter, with the assumption that $G(Fe^{3+}) = 15.5$.[32] Routine UV–visible spectra were recorded on a Cary 210 spectrophotometer. Some kinetic measurements were made on a Durrum 110 stopped-flow spectrophotometer at ambient temperatures (23–25 °C). The optical path length was 2 cm.

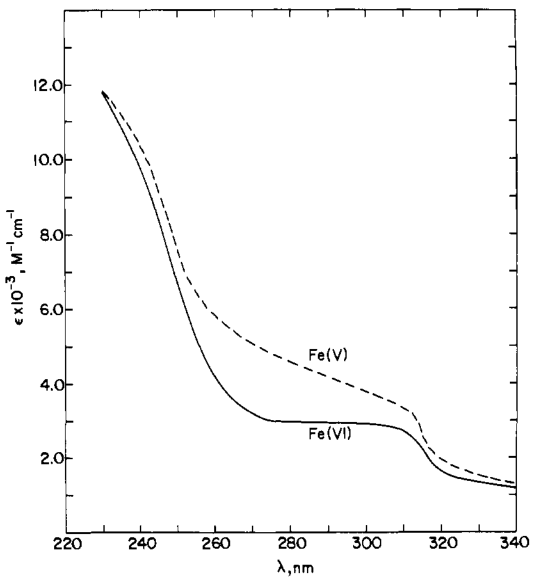

**Figure 2.** UV spectra of $FeO_4^{2-}$ and $FeO_4^{3-}$ in aqueous solutions containing 0.02 M sodium formate, 40 μM DTPA, and 0.02 M nitrous oxide at pH 9.5–10.5, 24 °C.

**Table I.** Reactivity of $FeO_4^{2-}$ (230 μM) with Formate (Concentration Variable) at pH 10.5 in the Presence of DTPA (600 μM) at 25 °C[a]

| $t_{1/2}$, s | [HCOONa], M | $k$, M$^{-1}$ s$^{-1}$ |
|---|---|---|
| 800 | 0.00 | $8.53 \times 10^{-4}$ |
| 600 | 0.05 | $2.31 \times 10^{-2}$ |
| 120 | 0.25 | $2.31 \times 10^{-2}$ |
| 60 | 0.50 | $2.32 \times 10^{-2}$ |
| 29 | 1.00 | $2.39 \times 10^{-2}$ |

[a] Measured $k_{av} = (2.33 \pm 0.04) \times 10^{-2}$ M$^{-1}$ s$^{-1}$. The spontaneous rate at which Fe(VI) disappears under these conditions is the rate with free DTPA, $k = 8.53 \times 10^{-4}$ M$^{-1}$ s$^{-1}$.

**Preparation and Use of $K_2FeO_4$ Solutions.** Fe(VI) solutions were prepared by dissolving crystalline samples of $K_2FeO_4$ in MQ water and adjusting the pH by addition of KOH. In carefully cleaned glass vessels, solutions containing up to 1 mM $FeO_4^{2-}$ are stable for several hours. The natural pH of 50–200 μM $K_2FeO_4$ solutions ranges from 9.5 to 10.5. Because of the high stability of ferrate solutions in this pH range, most experiments were carried out at pH 10.0–10.5, unless stated otherwise. Measured absorbance changes at 510 nm show a decay, approximately 2.5% during the first hour. The deterioration of the solutions accelerates as decomposition products (various forms of ferric oxide/hydroxide) accumulate. Hence all experiments were carried out with fresh solutions, which were discarded after 1 h. To avoid the formation of interfering precipitates during pulse and/or stopped-flow experiments, small amounts of DTPA (50–100 μM) were added to chelate Fe(III) and thereby prevent precipitation of iron hydroxides.

## Results

**Reactivity of $K_2FeO_4$ with Formate.** Since one of the objectives of this project is the reduction of $FeO_4^{2-}$ by the $CO_2^-$ radical, generated in situ by radiolysis of formate, the reactivity of formate with ferrate had to be established. The reaction was measured at 510 nm on a Cary 210 under pseudo-first-order conditions over a large concentration range of formate (0–1 M) (Table I). The observed first-order rates in the presence of 600 μM DTPA are proportional to the formate concentration and yield, after appropriate corrections for the spontaneous decay of $FeO_4^{2-}$, a rate constant of $k = (2.33 \pm 0.4) \times 10^{-2}$ M$^{-1}$ s$^{-1}$. To avoid complications from this reaction, an apparatus was built that allows the premixing of $N_2O$-saturated solutions of formate and ferrate 4–5 s before the mixture is pulse irradiated with the electron beam.

**Reactivity of $K_2FeO_4$ with Ethanol.** The rate of reaction of ferrate with ethanol was monitored under pseudo-first-order conditions at 510 nm on a Cary 210 spectrophotometer at pH 10.5 and 24 °C in solutions containing 32.8–71.9 μM $FeO_4^{2-}$, 1.03–2.06

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**Table II.** Reactivity of $FeO_4^{2-}$ (59.7–168 μM) with Fe(III)–DTPA in the Presence of Excess DTPA (15 mM) at pH 10.5[a]

| Fe(III)–DTPA, μM | *k*, $M^{-1}\ s^{-1}$ | Fe(III)–DTPA, μM | *k*, $M^{-1}\ s^{-1}$ |
|---|---|---|---|
| 100.0 | 1.23 | 500.0 | 0.90 |
| 200.0 | 0.99 | 1000.0 | 0.97 |

[a] All rates are corrected for the reactivity of $FeO_4^{2-}$ with free DTPA ($k = (8.53 \pm 0.32) \times 10^{-4}\ M^{-1}\ s^{-1}$). The reactions were monitored at 510 nm on a Cary 210 in 1-cm cells at 24 °C.

M EtOH, and 105 μM DTPA. The corresponding second-order rate constant found is $k = (1.47 \pm 0.07) \times 10^{-3}\ M^{-1}\ s^{-1}$.

**Reactivity of $K_2FeO_4$ with DTPA.** When Fe(VI) reacts with other compounds, it is reduced at some stage during the overall process to iron(III) hydroxide, which precipitates in alkaline solutions. The precipitates not only interfere with the optical measurements but also accelerate the spontaneous decomposition of Fe(VI). Precipitation of iron hydroxides can be avoided by addition of a strong Fe(III) chelating agent such as DTPA. Since DTPA is itself attacked by Fe(VI) and/or its reduction products, e.g. Fe(V)/Fe(IV), it became necessary to determine not only the rate of reaction of Fe(VI) with DTPA but also with Fe(III)–DTPA. The latter reactions are very slow and were determined on a Cary 210 spectrophotometer at 510 nm under pseudo-first-order conditions. The experimental details and results are summarized in Table II. As is apparent, the reactivity of $FeO_4^{2-}$ with Fe(III)–DTPA ($k = 1.02 \pm 0.14\ M^{-1}\ s^{-1}$) is 3 orders of magnitude faster than the corresponding reaction with DTPA ($k = (8.53 \pm 0.32) \times 10^{-4}\ M^{-1}\ s^{-1}$).

**Reduction of $K_2FeO_4$ by $CO_2^-$.** The control experiments for formate, ethanol, and DTPA have shown that their respective reactivities with Fe(VI) are sufficiently low not to interfere even at high concentrations when used with the described premixing apparatus, which has a dead time of approximately 4–5 s. In the present study the ferrate (40–200 μM) was reduced to Fe(V) by the $CO_2^-$ radical, which was generated in a $N_2O$-saturated (0.02 M) formate solution (0.02 M) containing 40 μM DTPA (eq 1–3).

$$e_{aq}^- + N_2O + H_2O \rightarrow OH + OH^- + N_2 \qquad (1)$$

$$OH + HCOO^- \rightarrow CO_2^- + H_2O \qquad (2)$$

$$CO_2^- + FeO_4^{2-} \rightarrow FeO_4^{3-} + CO_2 \qquad (3)$$

The $CO_2^-$ radical reduces $FeO_4^{2-}$ with $G = 6.05$ and at a rate $k_3 = (3.5 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$ at pH 9.5–10.5. Although most of the studies were carried out in the pH range from 9.5 to 10.5 because of the stability of ferrate solutions in this pH range, a series of experiments were extended up to pH 12.3. The values obtained for $k_3$ were similar within experimental error, which suggests that the above reported value represents a true rate constant. The *G* value for the disappearance of ferrate under pulse-radiolytic conditions was confirmed by $^{60}Co$ γ-ray studies. The latter experiments were carried out with solutions containing 0.02 M formate, 0.02 M $N_2O$, 40 μM DTPA, and variable amounts of $K_2FeO_4$ (43–85 μM). The solutions were irradiated for 30-s intervals and checked for absorbance changes at 510 nm on a Cary 210. The computed $G(FeO_4^{2-}) = 6.10 \pm 0.10$ is based on $G(Fe^{3+}) = 15.5$, in good agreement with the value obtained under pulse-radiolytic conditions. The UV and visible spectra of $FeO_4^{2-}$ and $FeO_4^{3-}$ shown in Figures 1 and 2 are not affected by pH changes between 9.5 and 10.5 nor are they affected by the addition of DPTA.

**Reduction of $K_2FeO_4$ by $O_2^-$.** That radiation-generated $O_2^-$ is capable of reducing ferrate had been suggested in an earlier $^{60}Co$ γ-ray study of $K_2FeO_4$ solutions.[23] In the present study the superoxide radicals were generated photolytically in oxygen-saturated 1–5 mM formate or ethanol solutions (eq 4) by a Xe plasma lamp in a stopped-flow spectrophotometer.[33] The rates

$$FeO_4^{2-} + O_2^- \rightarrow FeO_4^{3-} + O_2 \qquad (4)$$

of reaction were determined at 510 nm, and it was found that they are independent of pH in the range investigated (10.5–12.35). The experiments were carried out at constant $[O_2^-] = 5 \pm 1$ μM and $[FeO_4^{2-}] = 50.6$–$97.5$ μM at 24 °C in the presence of 50 μM DTPA, yielding $k_4 = (5.71 \pm 0.17) \times 10^3\ M^{-1}\ s^{-1}$.

**Table III.** Rates of Reaction for $K_2FeO_4$ with a Number of Compounds and Radicals

| reactants | pH | *k*, $M^{-1}\ s^{-1}$ | ref |
|---|---|---|---|
| formate | 10.5 | $(2.33 \pm 0.40) \times 10^{-2}$ | *a* |
| formate | 8.0 | $4.00 \times 10^{-1}$ | 13[b] |
| DTPA | 10.5 | $(8.53 \pm 0.32) \times 10^{-4}$ | *a* |
| Fe(III)–DTPA | 10.5 | $1.02 \pm 0.14$ | *a* |
| ethanol | 10.5 | $(1.47 \pm 0.70) \times 10^{-3}$ | *a* |
| ethanol | 8.0 | $8.00 \times 10^{-2}$ | 13[b] |
| NADH | 11.0 | $(7.70 \pm 0.44) \times 10^1$ | *a* |
| $CO_2^-$ | 9.5–10.5 | $(3.50 \pm 0.15) \times 10^8$ | *a* |
| $O_2^-$ | 9.5–10.5 | $(5.71 \pm 0.17) \times 10^3$ | *a* |

[a] This study. [b] Studies were carried out in 0.1 M phosphate buffer, pH 8.0 at 25 °C.

**Oxidation of NADH by $K_2FeO_4$.** The reactivity of $FeO_4^{2-}$ with reduced nicotinamide adenine dinucleotide (NADH) was monitored spectrophotometrically at 340 nm (24 °C, pH 11.0). While the ferrate concentration was kept constant at 50 μM, the [NADH] was varied from 0.25 to 1.0 mM. The initial disappearance of NADH followed pseudo-first-order kinetics and was shown to be proportional to the concentration of NADH over the concentration range studied. The corresponding second-order rate constant $k = 77.1 \pm 4.4\ M^{-1}\ s^{-1}$ is surprisingly low. There was no indication of a possible $H^-$ or equivalent 2-electron step reduction reaction.

**Reaction of Formate with Fe(V).** The rate of reaction of $FeO_4^{3-}$ with formate was studied by pulse radiolysis at pH 10.5 and 24 °C. The Fe(V) was generated by reduction of Fe(VI) with $CO_2^-$ as described above. When the formate concentration (10–500 mM) at constant $[FeO_4^{2-}] = 53$ μM was varied, the reaction of Fe(V) with $HCOO^-$ could be followed by observing the pseudo-first-order disappearance of Fe(V) at its absorption maximum at 390 nm. These experiments were carried out in the absence of DTPA and corrected for the spontaneous disappearance of Fe(V) in the absence of formate. The spontaneous disappearance of Fe(V) was determined earlier in solutions in which the Fe(VI) was reduced with the hydrated electron ($k = 2.0 \times 10^{10}\ M^{-1}\ s^{-1}$). The computed second-order rate constant for the reaction of $FeO_4^{3-}$ with $HCOO^-$ is $k = (2.48 \pm 0.32) \times 10^3\ M^{-1}\ s^{-1}$.

## Discussion

The rate constants for the reaction of $FeO_4^{2-}$ with a number of compounds and radicals are given in Table III. A comparison of our numerical values for formate and ethanol with those reported earlier[13] shows a small difference. The discrepancy is most likely due to the fact that the measurements were taken under different experimental conditions, e.g. different pH's and chelating agents (phosphate vs DTPA). Overall, these rates are low and do not interfere with the measurement of the rates of interest with $CO_2^-$ and $O_2^-$.

The reduction of $FeO_4^{2-}$ by $CO_2^-$ has the advantage over the earlier reported reduction with the hydrated electron[15] in that the yield $G(CO_2^-) = 6.05$ is 2.3 times that of the hydrated electron $G(e_{aq}^-) = 2.65$, which experimentally, results in a significant increase in the observed absorbance for an equivalent dose. The $CO_2^-$ radical was generated in micromolar quantities in the presence of such quantities of $FeO_4^{2-}$ that all of it was consumed in reaction 3, yielding an equivalent amount of $FeO_4^{3-}$. This is possible only because of its very high rate of reaction ($k_3 = 3.5 \times 10^8\ M^{-1}\ s^{-1}$). Although the visible spectrum of $FeO_4^{3-}$ shown in Figure 1 is similar in shape to the one reported earlier,[15] the molar absorbances reported here are more accurate. The corresponding UV spectrum show in Figure 2 has not been reported before.

When the concentration of formate was varied in a series of experiments, it was possible to determine its rate of reaction with $FeO_4^{3-}$ ($k = 2.5 \times 10^3\ M^{-1}\ s^{-1}$). This rate is 5 orders of magnitude

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larger than the corresponding rate for $FeO_4^{2-}$. Preliminary studies in this laboratory with other organic compounds indicate that Fe(V)/Fe(IV) indeed react orders of magnitude faster than Fe(VI). This suggests that Fe(VI) oxidation processes may be significantly accelerated if carried out in the presence of appropriate one-electron-reducing agents.

The reduction of $FeO_4^{2-}$ by $O_2^-$ is relatively slow ($k_4 = 5.7 \times 10^3$ $M^{-1}$ $s^{-1}$) and does not show evidence of hypervalent iron transients. In this case, if Fe(V) and Fe(IV) react orders of magnitude faster than Fe(VI) with the superoxide radical, one would not expect to observe these transients. Since the reaction between Fe(III) and $O_2^-$ is fast ($k = 1.5 \times 10^8$ $M^{-1}$ $s^{-1}$),[34] one would expect similar or higher rates for the reaction(s) of superoxide radical with Fe(V) and/or Fe(IV).

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**Registry No.** NADH, 58-68-4; DTPA, 67-43-6; $FeO_4^{2-}$, 16836-06-9; $FeO_4^{3-}$, 37114-36-6; $CO_2^-$, 14485-07-5; ethanol, 64-17-5; formate, 64-18-6.

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# Dialkylamino Phosphorus Metal Carbonyls. 4. Novel Phosphorus-Bridging Carbonyl Derivatives and Triphosphine Derivatives from Reactions of Tetracarbonylferrate(−II) with (Dialkylamino)dichlorophosphines[1-4]

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**Abstract:** Reactions of $R_2NPCl_2$ (R = isopropyl, cyclohexyl) with $Na_2Fe(CO)_4$ give orange $(R_2NP)_2COFe_2(CO)_6$ as the major product in diethyl ether solution and orange $(R_2NP)_3Fe_2(CO)_6$ as the major product in tetrahydrofuran solution. X-ray diffraction on $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (monoclinic, $P2_1/n$; $a = 10.197$ (3), $b = 31.403$ (13), $c = 9.170$ (3) Å; $\beta = 112.18$ (2)°; $Z = 4$) indicates a structure in which an iron–iron bond (2.603 (2) Å) in an $Fe_2(CO)_6$ unit is bridged by two phosphorus atoms and these two phosphorus atoms are bridged by one of the seven carbonyl groups, thereby suggesting a novel migration of a carbonyl group from iron to phosphorus. X-ray diffraction on $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (monoclinic, $P2_1/n$; $a = 11.554$ (2), $b = 14.294$ (6), $c = 20.405$ (4) Å; $\beta = 90.96$°; $Z = 4$) indicates an $Fe_2(CO)_6$ unit (Fe–Fe = 2.602 (2) Å) bridged by a triphosphine chain. Minor products from the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in diethyl ether include an orange trinuclear derivative $(R_2NP)_2Fe_3(CO)_9$ and an unstable diphosphene complex $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$. The latter product adds water upon attempted chromatography to give $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ shown by X-ray diffraction (monoclinic, $P2_1/n$; $a = 15.682$ (3), $b = 14.458$ (3), $c = 13.044$ (8) Å, $\beta = 99.80$ (4)°; $Z = 4$) to have an oxo-bridged structure (P–O–P = 136.4 (3)°), axially substituted trigonal-bipyramidal $LFe(CO)_4$ units, and no iron–iron bond. Minor products from the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in tetrahydrofuran include $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ as well as orange $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ shown by X-ray diffraction (monoclinic, $P2_1/a$; $a = 14.910$ (5), $b = 12.064$ (6), $c = 19.733$ (10) Å; $\beta = 105.31$ (4)°; $Z = 4$) to have a structure similar to that of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ but with a carbonyl group inserted into the triphosphine chain. Reaction of $Et_2NPCl_2$ with $Na_2Fe(CO)_4$ in diethyl ether gives totally different types of products arising from migrations of diethylamino groups. The initial major product, isolated when the temperature is kept below 0 °C, is a deep orange solid of stoichiometry $(Et_2NP)_3Fe_3(CO)_{12}$ shown by X-ray diffraction (monoclinic, $P2_1/n$; $a = 17.071$ (7), $b = 19.116$ (8), $c = 10.853$ (3) Å; $\beta = 96.82$°) to have a four-membered $FeP_3$ ring bonded to two isolated $Fe(CO)_4$ groups, a four-membered FePOC ring formed by a diethylcarbamoyl group bridging an Fe–P bond, an $(Et_2N)_2P$ unit formed by diethylamino migration, but no Fe–Fe bonds. This complex undergoes facile decarbonylation in solution at room temperature to give an orange solid of stoichiometry $(Et_2NP)_3Fe_3(CO)_{11}$. Structure determination of this decarbonylation product by X-ray diffraction (monoclinic, $P2_1/n$; $a = 9.054$ (4), $b = 38.752$ (34), $c = 19.737$ (8) Å, $\beta = 104.05$ (3)°; $Z = 8$) indicates that this decarbonylation reaction involves conversion of a bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group, formation of an Fe–Fe bond, and formation of a new Fe–P bond. The products formed from reactions of $R_2NPCl_2$ with $Na_2Fe(CO)_4$ can be rationalized by schemes involving the terminal (dialkylamino)phosphinidene complex $R_2NP{=}Fe(CO)_4$ as a reactive intermediate, which can undergo a redox reaction with $Fe(CO)_4^{2-}$ in tetrahydrofuran but not in diethyl ether.

Recent interest in the chemistry of diphosphenes,[5] RP=PR, because of the presence of the phosphorus–phosphorus double bond, has led to numerous studies on their preparation by dehalogenation of $RPCl_2$ derivatives with diverse strong reducing agents. Such reactions with metal carbonyl anions as the reducing agents have yielded products that may be regarded as metal carbonyl complexes of the diphosphenes. In this connection reactions of the readily available[6,7] dianion $Fe(CO)_4^{2-}$ with diverse $RPCl_2$ derivatives, mainly those containing bulky R groups, have

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