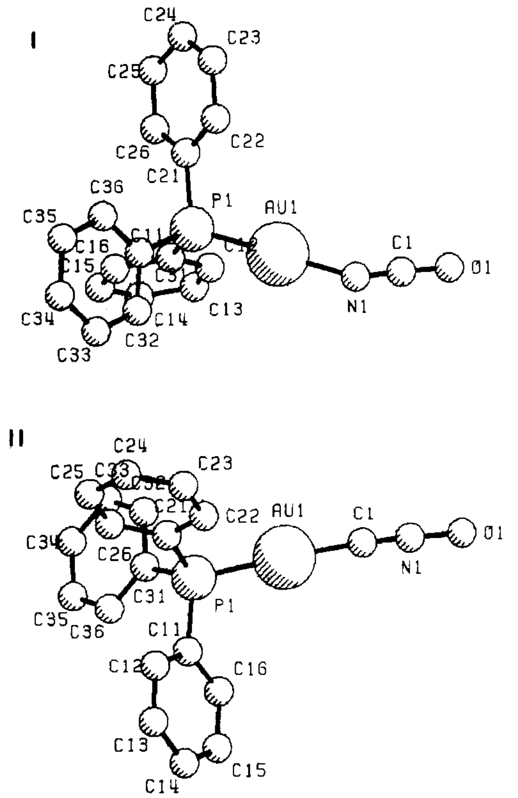

Figure 2. Crystallographic atomic numbering scheme: (I) isocyanato compound; (II) fulminato compound (molecules in minimum overlap position.

is probably caused by the decomposition that took place during the measurements.

Difference Fourier syntheses show significant rest-electron densities (up to 2 e/Å^3) in the neighborhood of the Au–CNO moiety. Therefore, the estimated standard deviations are not reliable. Refinement problems were also noted by others in solving the structures of the bis(fulminato)gold complex $AsPh_4[Au(CNO)_2]$[14] and AgCNO,[15] the only two other fulminates of which the crystal structures were determined. To investigate this problem, we exposed crystals of $AuPPh_3CNO$ to X-ray radiation for 24 h. The rotation photographs and the IR spectra of the crystal taken before and after the exposure did not show any significant changes, and we could not draw any conclusions about a possible rearrangement of the gold fulminate moiety during the decomposition. The bond lengths in the fulminate agree well with other known fulminates, (see Table V). In $AuPPh_3CNO$ the gold–carbon distance (1.939 (14) Å) is slightly shorter than in $AsPh_4[Au(CNO)_2]$ (2.01 (2) Å). This can be attributed to a trans effect of the triphenylphosphine. The same effect is observed when the Au–C distances of $KAu(CN)_2$ and $AuPPh_3CN$ are compared. Here a shortening is found from 2.12 to 1.85 Å.[16] In case of the fulminate this trans effect is apparently less pronounced.

Surprisingly the angle Au–C–N in $AuPPh_3CNO$ is 162.9 (11)°. One would expect this compound to be linear as is found for $AsPh_4[Au(CNO)_2]$. Due to this nonlinearity, the fulminate is isomorphous with the isocyanate. No unusual short intermolecular distances are found in $AuPPh_3CNO$. In this respect it is interesting that studies on fulminic acid, HCNO, have shown a remarkably low energy difference between the linear and bent structures.[17]

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Registry No. $AuPPh_3NCO$, 24169-91-3; $AuPPh_3CNO$, 98875-32-2; $AuPPh_3NO_3$, 14897-32-6; CO, 630-08-0.

Supplementary Material Available: Lists of structure factors, coordinates of hydrogen atoms, and anisotropic parameters (56 pages). Ordering information is given on any current masthead page.

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Pulse-Radiolysis Study of the Reduction of VO^{2+} by the Hydrated Electron[1]

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The hydrated electron, e_{aq}^-, produced by the irradiation of water with an electron beam is a strong reductant. The half-cell potential of $H^+ + e_{aq}^- \rightarrow H$ is −2.3 eV.[3] This reductant reacts with a number of d and f transition-metal ions[4,5] and their compounds at rates that are essentially diffusion-controlled.

When the reduced species has a primary coordination sphere that is markedly altered from that of the original reactant, the initial product of the electron transfer may be formed in an excited electronic state and/or in an inappropriate coordination configuration. We have previously studied the change of coordination in the linear $O–^+Np–O$ ion upon reduction to the hydrated $Np^{4+}{}_{aq}$ ion[6] using transient conductivity detection. The results were interpreted in terms of a reaction scheme wherein there occurred a step in which the initial [O–Np–O] product rearranged to a hydrolyzed $Np^{4+}{}_{aq}$ ion. The present study was undertaken to determine if a similar process could be identified in the case of a d transition element where the bonding between metal ion and coordinated oxygen is markedly altered. The ion of choice, $VO^{2+}{}_{aq}$, has one "yl"-type oxygen, which has a relatively slow rate of exchange with bulk H_2O,[7] four equatorial H_2O molecules with residence times of 10^{-3} s,[8] and a trans H_2O molecule that is very labile.

Experimental Section

The preparation and standardization of the stock VO^{2+} perchlorate solutions have been previously described.[9] Fresh, unbuffered solutions of (2–5) × 10^{-4} M $VO(ClO_4)_2$ were prepared under an Ar atmosphere. Ethanol, 0.01–0.05 M, or *tert*-butyl alcohol, 0.12 M, was added to scavenge the OH radicals. The pH was adjusted to values between 3.8 and 4.6 by the addition of appropriate amounts of $HClO_4$.

The solutions were irradiated with 0.25-μs pulses from a 15-MeV linac. The dose (ca. 1.4 krad/pulse) was monitored for each pulse. The temperature was kept constant at 25 ± 0.2 °C during the measurement. The transient conductivity change was measured with an improved system described in ref 10. These changes were predominantly in the design of the irradiation cell assembly and improved shielding, which resulted in markedly improved signal-to-noise ratios.

Results and Discussion

When water is subjected to a pulse of ionizing radiation, a positive transient conductivity signal is observed as a result of the formation of H^+, e_{aq}^-, and OH^-. In the absence of a reducible ion, this signal decays rapidly to zero due to the reactions

$$H^+ + OH^- \rightarrow H_2O \qquad (1)$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (2)$$

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(3) Schwartz, H. A. *J. Chem. Educ.* **1981**, *58*, 101.

(4) M. Anbar, In *Solvated Electron*; Advances in Chemistry 50; American Chemical Society: Washington, DC, 1965.

(5) Sullivan, J. C.; Gordon, S.; Cohen, D.; Mulac, W.; Schmidt, K. H. *J. Phys. Chem.* **1976**, *80*, 1684.

(6) Schmidt, K. H.; Gordon, S.; Thompson, R. C.; Sullivan, J. C. *J. Inorg. Nucl. Chem.* **1980**, *42*, 611.

(7) Johnson, M. D.; Murman, R. K. *Inorg. Chem.* **1983**, *22*, 1068.

(8) Reuben, J.; Fiat, D. *Inorg. Chem.*, **1967**, *6*, 579.

(9) Watkins, K. O.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1974**, *13*, 1712.

(10) Schmidt, K. H.; Gordon, S.; Thompson, M.; Sullivan, J. C.; Mulac, W. A. *Radiat. Phys. Chem.* **1983**, *21*, 321.

0020-1669/86/1325-2096$01.50/0

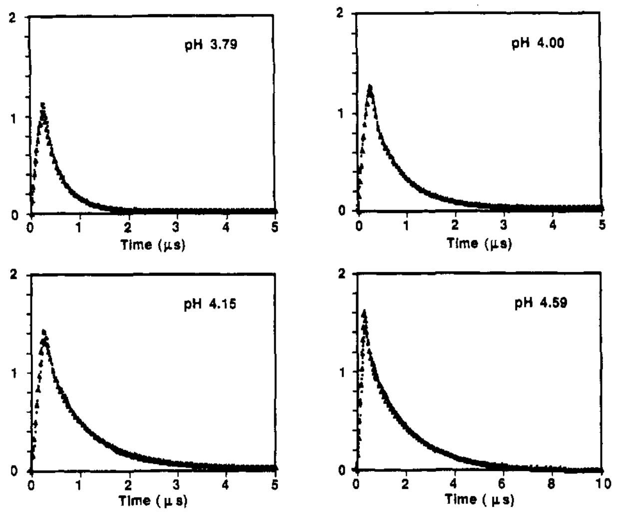

Figure 1. Conductivity signals obtained for the reduction of VO^{2+} by e_{aq}^- at different pHs: squares, experimental results; triangles, calculated signals (see text). Vertical scale: conductivity change, 1 × 10^{-6} S cm^{-1}/division.

In the presence of such an ion, in our case VO^{2+}, the hydrated electron disappears mainly by

$$e_{aq}^- + VO^{2+} \rightarrow VO^+ \quad (3)$$

leaving a positive balance of H^+, which causes a positive residual conductivity signal. The ensuing loss of the "yl" oxygen must be accompanied by the consumption of two protons if V^{3+} is the product. In the pH range studied by us (3.8–4.6), the predominant form of the trivalent vanadium ion is VOH^{2+} (see eq 5 below), so that the loss is reduced to approximately one proton. According to this stoichiometry, the initially positive conductivity signal should decay to nearly zero, and the decay rate would reflect the kinetics of the transition from VO^+ to VOH^{2+}.

Figure 1 shows examples of measured conductivity transients. The signal shapes are as expected, and we observe a decay rate increasing with $[H^+]$.

With the aid of a kinetic program originally described in ref 11, which was recently modernized and installed on a VAX 11/780 computer, we calculated a model curve for each experiment, based essentially on reaction 3 and

$$VO^+ + H^+ \rightarrow VOH^{2+} \quad (4)$$

For k_3, we used our optically measured value of 8 × 10^{10} M^{-1} s^{-1}. k_4 was adjusted to obtain the best fit at all pH values. Our final value was $k_4 = 1.5 \times 10^{10}$ M^{-1} s^{-1}, with an estimated accuracy of ~10%. Other parameters needed were taken from the literature: $k_1 = 1.43 \times 10^{11}$ M^{-1} s^{-1};[12] $k_2 = 2.2 \times 10^{10}$ M^{-1} s^{-1};[13] the radiation yield $G(e_{aq}^-) = 2.8$ particles/100 eV.[14] The equilibrium

$$VOH^{2+} + H^+ \rightleftharpoons V^{3+} + H_2O \quad (5)$$

with its pK_a of 2.26[15] has a slight effect at the lower end of the pH range covered and was therefore included in the calculation.

More difficult was the inclusion of the equilibrium

$$VOOH^+ + H^+ \underset{b}{\overset{a}{\rightleftharpoons}} VO^{2+} + H_2O \quad (6)$$

with a pK_a of 5.79[15] which significantly altered the kinetics at pH 4.59, and slightly at 4.15. We had to add to our model system the following postulated reactions (all diffusion-controlled):

$$e_{aq}^- + VOOH^+ \rightarrow VOOH \quad (7)$$

$$VOOH + H^+ \rightarrow V(OH)_2^+ \quad (8)$$

$$V(OH)_2^+ + H^+ \rightarrow VOH^{2+} + H_2O \quad (9)$$

We estimated $k_7 = 6 \times 10^{10}$ M^{-1} s^{-1} (from k_3, assuming the same diffusion coefficient and reaction radius, but correcting for the different charge of the cation), and by the same procedure, $k_8 = 3.5 \times 10^{10}$ M^{-1} s^{-1} and $k_9 = 1.5 \times 10^{10}$ M^{-1} s^{-1} (both from k_4). Calculations showed that all three values were much less critical than the value chosen for k_{6a}. The best fit for pH 4.59 was achieved by using $k_{6a} = 7.5 \times 10^9$ M^{-1} s^{-1}.

The asymptotic level of the conductivity signals depends somewhat on the difference in ionic equivalent conductance, $\lambda_{VOH^{2+}} - \lambda_{VO^{2+}}$. Since no values are known, we adjusted this difference to 10 by using estimated values of $\lambda_{VO^{2+}} = \lambda_{VO^+} = 40$ and $\lambda_{VOH^{2+}} = 50$ (all in S cm^2 $equiv^{-1}$). Other ionic equivalent conductance values were taken from the literature: $\lambda_{H^+} = 350$, $\lambda_{OH^-} = 198$, and $\lambda_{e_{aq}^-} = 185$, with the same units. No other parameter was adjusted. The shape of the electron pulse and the system response time (ca. 50 ns) were also taken into account. The theoretical curves in Figure 1 were calculated by using the entire reaction system described above for all four pH values.

The excellent agreement between the calculated and the measured decay rates and signal amplitudes leads to the conclusion that assumption of a $[H^+]$-independent rearrangement reaction such as

$$VO^+{\cdot}5H_2O \rightarrow V(OH)_2^+{\cdot}4H_2O \quad (10)$$

is not necessary to interpret the experimental results. The "yl"-type oxygen in the VO^{2+} evidently does not retain its unequal bonding after the one-electron reduction. This is analogous to results of ^{18}O exchange experiments wherein the partial hydrolysis of VO^{2+} causes an internal electronic rearrangement that destroys the unique (V=O) structure. The marked difference between these results and those previously reported for Np(V) (i.e., an apparent rate-determining rearrangement step in the reaction scheme) have dictated an attempt to reproduce our original findings.

Registry No. VO^{2+}, 20644-97-7; H_2O, 7732-18-5.

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(11) Schmidt, K. H. *Argonne Natl. Lab.* [Rep.], *ANL* **1966**, ANL-7199; **1970**, *ANL-7693.*

(12) Ertl, G.; Gerischer, H. *Z. Elektrochem.* **1962**, *66*, 560.

(13) *NBS Handbook* **1973**, NSRDS-NBS43.

(14) Michael, B. D.; Hart, E. J.; Schmidt, K. H. *J. Phys. Chem.* **1971**, *75*, 2798.

(15) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; p 202.

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Structure of $[\mu\text{-}(CH_3)_2PCH_2P(CH_3)_2]_2Ni_2(CO)_4$

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Recently, the reaction of $Ni(CO)_4$ with the small-bite bidentate ligand bis(dimethylphosphino)methane (abbreviated as dmpm) has been reported in this journal to yield a white precipitate **1**, which was assumed to be "(dmpm)$Ni(CO)_2$" with dmpm as a chelating ligand.[1] Besides two strong terminal infrared ν(CO) frequencies at 1991 and 1927 cm^{-1}, **1** exhibits in the phosphorus-31 NMR spectrum a single resonance at −15.1 ppm, a surprisingly high-field chemical shift. The authors state that "the volatilities of mononuclear metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ are generally sufficient for purification by vacuum sublimation and observation of their mass spectra". This contrasts with their

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(1) King, R. B.; RaghuVeer, K. S. *Inorg. Chem.* **1984**, *23*, 2482.