

Electron Transfer. 126. Reductions of Oxime-Bound Nickel(IV)¹

Subrata Mandal and E. S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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Solutions of the nickel(IV) complex of the dianion of 2,6-diacetylpyridine dioxime (chelate **II** in text) are stable enough at low pH values to allow redox studies involving aquametal cations as reductants. This Ni(IV) derivative is reduced cleanly to Ni(II) by aqueous solutions of Fe(II), Sn(II), I⁻, and U(IV) but reacts unobservably slowly with the 2e reductants H₃PO₂ and H₃AsO₃. There is no evidence for accumulation of the intermediate state Ni(III), even with the oxidant in large excess. Rate laws for reductions by Fe(II), Sn(II), and I⁻ feature prominent [H⁺]-dependent terms, reflecting partial protonation of the oxidant. The Sn(II) reduction is strongly catalyzed by Cl⁻, suggesting involvement of an unusually reactive chloro-substituted reductant. Reductions by U(IV) at [H⁺] below 0.02 M are catalyzed by UO₂²⁺; under these conditions, rates are proportional to ([U^{VI}][U^{IV}])^{1/2}. The overall kinetic picture of the Ni(IV)–U(IV) system supports a sequence in which the reactive intermediate, a U(V) species, may undergo one of two competing processes—reduction of Ni(IV) or reversible disproportionation to U^{VI} and U^{IV}. Each of the proposed steps is a single electron transfer. These results, taken together, bolster the view that conversions of Ni(IV) to Ni(II), a net 2e process, must entail pairs of 1e steps. Such is the case even for the (relatively slow) reduction by Sn(II), which appears to be initiated by formation of a Sn(III) species significantly stabilized via ligation by chloride.

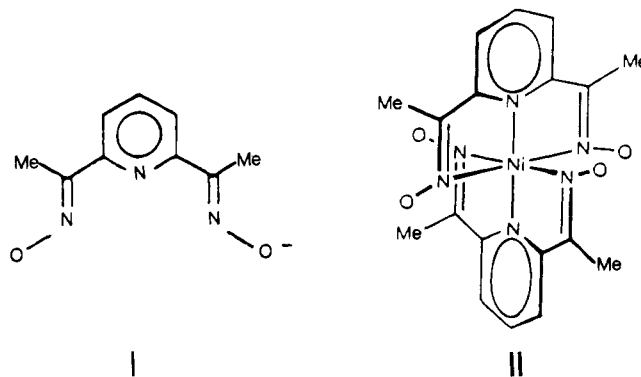
Before 1970, information concerning the redox reactions of nickel compounds in solution was indeed scarce. Then, as now, the chemistry of this element was heavily dominated by its dispositive state. The additional states Ni(0) (as in Ni(CO)₄) and Ni(III) (as in Ni₂O₃) had achieved industrial importance,² but these were not readily convertible to dissolved species. A handful of complexes featuring “atypical” oxidation numbers had been reported³ but were generally regarded as chemical curiosities.

During the last two decades, however, the roster of complexes of hypervalent nickel has expanded impressively. Over 300 derivatives of Ni(III) have been prepared and characterized, in addition to a more modest, but growing, array of Ni(IV) derivatives.⁴ An impetus for this augmentation is the increasing body of evidence⁵ that Ni(III) is involved in the action of several enzymes such as (NiFe)-hydrogenases and CO dehydrogenases.

The availability of such complexes, especially those dissolving in polar solvents, has been reflected in a flurry of mechanistic studies pertaining to their redox behavior.⁶ A key question concerning Ni(IV) is whether its reduction to Ni(II)

invariably proceeds through a Ni(III) intermediate or if there are circumstances favoring a direct 2e transaction for this conversion.

This report deals with reactions of the bis-chelated Ni(IV) derivative of the dianion (I) of 2,6-diacetylpyridine dioxime. This prototype Ni^{IV}N₆ complex⁷ was one of the first for which a detailed structure (II) was determined.⁸ Its solutions are substantially more stable at low pH values than those of other chelates of this type, allowing the use of aquametal cations as reductants. Note that the Ni(III) complex of I, although preparable with special care,^{5d} has been found to be much less accessible than the Ni(II) and Ni(IV) analogs.^{5a,7}



Experimental Section

Materials. 2,6-Diacetylpyridine, ammonium peroxydisulfate, tin(II) sulfate, nickel perchlorate, and iron(II) ammonium sulfate (Aldrich

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- (1) Sponsorship of this work by the National Science Foundation (Grant 9314113) is gratefully acknowledged.
- (2) See, for example: (a) Salkind, A. J.; Pearlman, E. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Grayson, M., Ed.; Wiley-Interscience: New York, 1978; Vol. 3, pp 596–621. (b) Antonsen, B. H. *Ibid.*, 1981; Vol. 15, pp 806–807.
- (3) See, for example: (a) Eastes, J. W.; Burgess, W. M. *J. Am. Chem. Soc.* **1942**, *64*, 1187. (b) Hofmann, A.; Erhardt, W. *Ber.* **1913**, *46*, 1457. (c) Jensen, K. A. *Z. Anorg. Allg. Chem.* **1936**, *229*, 275. (d) Nyholm, R. S. *J. Chem. Soc.* **1951**, 2602.
- (4) Reviews: (a) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 5, pp 287–300. (b) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87. (c) Haines, R. J.; McAuley, A. *Ibid.* **1981**, *39*, 77.
- (5) See, for example: (a) *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH Publishers: New York, 1988; Chapters 2–4. (b) Tan, S. L.; Fox, J. A.; Kojima, N.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3064. (c) Scott, R. A.; Wallin, S. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864. (d) Kruger, H.-J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955. (e) Lancaster, J. R., Jr. *Science*, **1982**, *216*, 1324.

- (6) See, for example: (a) Neogi, G.; Acharya, S.; Panda, R. K.; Ramaswami, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1233, 1239. (b) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530. (c) Macartney, D. H.; McAuley, A.; Olubuyide, O. *Inorg. Chem.* **1985**, *24*, 307. (d) Baral, S.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 2213. (e) Lappin, A. G.; Martone, D. P.; Oavath, P.; Marusak, R. A. *Inorg. Chem.* **1988**, *27*, 1863. (f) McAuley, A.; Macdonald, C. J.; Spencer, L.; West, P. R. *J. Chem. Soc., Dalton Trans.* **1988**, 2279. (g) Bhattacharya, S.; Ali, M.; Gangopadhyay, S.; Banerjee, P. *J. Chem. Soc., Dalton Trans.* **1994**, 3733.
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products) were used as received, as were hydroxylamine hydrochloride and nickel chloride hexahydrate (Fisher products), red uranium(VI) oxide (Alfa), and sodium iodide (J. T. Baker). Solutions of $\text{UO}_2(\text{ClO}_4)_2$ were prepared by dissolving UO_3 in 1 M HClO_4 at 60 °C with stirring and were analyzed spectrophotometrically.⁹ Solutions of U(IV) were prepared by reducing $\text{UO}_2(\text{ClO}_4)_2$ to U(III) with zinc amalgam¹⁰ and then treating the reduced mixture with air;¹¹ the resulting preparations were stored under N_2 .¹² Concentrations of Sn(II) were estimated by addition of excess KI_3 and then titration of the unreacted I_3^- with $\text{Na}_2\text{S}_2\text{O}_3$.¹³ All solutions used in kinetic and stoichiometric experiments involving Sn(II), Fe(II), and U(IV) were prepared in distilled water that had been boiled for at least 1 h and then sparged with N_2 for 4 h.

Bis(2,6-diacetylpyridine dioximato)nickel(IV) (complex **II**) was prepared by a modification of the method of Baucom and Drago.⁷ 2,6-Diacetylpyridine was converted to its dioxime as described by Hartkamp.¹⁴ Just 400 mg of the dioxime was dissolved in a mixture of 20 mL of acetone and 20 mL of 15 M aqueous ammonia. To this mixture was slowly added a solution of 240 mg (1.01 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 mL of water. Addition of 570 mg (2.5 mmol) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to the resulting wine-colored solution turned the color to blue-green. The stoppered preparation, on standing overnight, deposited well-formed violet needles, which were filtered off, washed with distilled water, and dried in air. Absorption peaks of the product, taken in DMF (at 305, 431, and 614 nm), corresponded to those reported by Kruger.^{5d} Although this complex is nearly insoluble in water, very dilute (supersaturated) solutions for redox experiments could be prepared by dissolving the powdered crystalline product in 1:1 water-methanol under reflux for 2 h with stirring, cooling, and then diluting with distilled water. Solutions used in kinetic studies contained 2–4% CH_3OH , but measured reaction rates were found to be independent of the methanol content within this range. Such solutions, which deteriorated slowly on standing, were prepared fresh for each set of runs. The low-energy maximum at 615 nm^{5d} is shifted⁷ to 572 nm ($\epsilon = 1.28 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in 98:2 $\text{H}_2\text{O}/\text{CH}_3\text{OH}$.

Stoichiometric Experiments. Stoichiometric determinations were carried out under N_2 . For reductions by Sn(II), Fe(II), and U(IV), measured deficient quantities of the reductant were added to a known excess of the Ni(IV) complex. After reaction had ceased, decreases in absorbance measured at 572 nm were compared with those resulting from addition of an excess of reductant. The stoichiometry of the reaction with excess I^- was estimated by measuring the absorbance of I_3^- liberated ($\epsilon_{\text{max}}^{462} = 1030 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁵

Results are summarized in Table 1.

Kinetic Studies. Reactions were carried out under N_2 and were generally monitored at 572 nm using either a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Ionic strength, which was regulated by addition of NaClO_4 and HClO_4 , was maintained at 0.10 M for most reactions. Reductions by U(IV) were, however, carried out at $\mu = 1.0 \text{ M}$, since optical artifacts immediately after rapid mixing, which were most troublesome in interpreting the complex patterns obtained with this reagent, appeared to be less pronounced at the higher concentrations of electrolyte. Because the Ni(IV) complex undergoes perceptible decomposition (in a manner not yet determined) at high acidities, stock solutions of this oxidant were prepared in aqueous NaClO_4 and redox reactions were carried out at $[\text{H}^+] < 0.10 \text{ M}$. Excess quantities of reductant were used in all kinetic runs with concentrations most often adjusted so that no more than 10% of the latter was consumed in reaction. Reductions by Fe(II), Sn(II), and I^- yielded simple exponential curves. Rate constants in such cases

Table 1. Stoichiometries of the Reductions of Oxime-Bound Nickel(IV)^a

reductant	waiting period	$[\text{Ni}^{\text{IV}}]$, $\text{M} \times 10^5$	[red], $\text{M} \times 10^4$	$\Delta[\text{Ni}^{\text{IV}}]$, $\text{M} \times 10^5$	$\Delta[\text{red}]$, $\text{M} \times 10^5$	$\Delta[\text{Ni}^{\text{IV}}]/\Delta[\text{red}]$
Sn(II)	20 min	7.3	0.60	5.7		0.95
		6.4	0.40	4.2		1.05
		4.6	0.20	2.3		1.15
		3.0	0.20	2.1		1.05
Fe(II)	15 min	7.0	0.40	1.94		0.49
		5.0	0.65	3.2		0.49
		3.9	0.40	2.2		0.55
		3.5	0.30	1.47		0.49
I^- ^b	5 min	8.0	203		16.2	0.49
		6.0	254		11.4	0.53
		5.0	152		9.6	0.52
		4.0	203		7.6	0.53
U(IV)	20 min	5.9	0.50	5.0		1.00
		4.2	0.30	3.3		1.10
	15 min	6.7	0.50	5.9		1.18 ^c
		6.0	0.40	4.5		1.13 ^c
		3.2	0.20	2.0		1.00 ^c

^a Reductions of the bis-chelated nickel(IV) complex (**II**) of 2,6-diacetylpyridine dioximate were carried out at 25 °C in 20/80 methanol-water; $\lambda = 572 \text{ nm}$. $[\text{H}^+] = 0.10 \text{ M}$ unless otherwise indicated. ^b Reactions were monitored at 462 nm; ϵ_{max} of $\text{I}_3^- = 1030 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁵ ^c $[\text{H}^+] = 0.010 \text{ M}$.

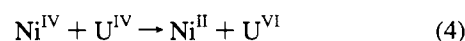
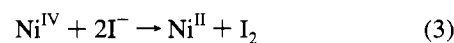
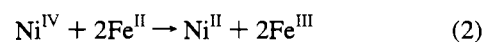
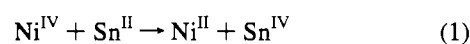
were obtained by nonlinear least squares fitting to the relationship describing first-order decay. Values calculated from replicate runs agreed to better than 4%. These reactions were first order in both redox partners. Kinetic patterns exhibited no indication of intermediates formed or destroyed on a time scale comparable to that for the disappearance of Ni(IV).

The character of decay profiles for reductions by U(IV), as monitored by stopped-flow, depended markedly on reaction conditions. At $[\text{H}^+] = 0.04\text{--}0.10 \text{ M}$, curves were nearly exponential, and the (relatively low) rates of decay were adjusted to take into account the slow unimolecular decomposition of the Ni(IV) chelate as well as its gradual loss from solution consequent to passage through the stopped-flow mixing jet.¹⁶ At lower acidities, more complex forms were obtained, and these featured both slow and rapid components (see Results and Discussion). Rates were independent of added Ni(II), but reductions at low acidities were accelerated by addition of UO_2^{2+} , and curves once again became exponential at concentrations of the latter $> 5 \times 10^{-5} \text{ M}$.

Additional Observations. Solutions of the Ni^{IV} chelate (**II**) did not react at a measurable rate with H_3PO_2 , H_3AsO_3 , NH_3OH^+ , or N_2H_5^+ under conditions employed for reductants in the previous section. Reactions of nitrite (at pH 2) and with VO_2^{2+} were observable, but the resulting complex decay profiles could not be meaningfully disentangled.

Results and Discussion

The stoichiometries of the redox reactions examined (Table 1) indicate that even with Ni(IV) in excess, we are observing reduction to Ni(II) in each case:



(16) We suspect that this effect, which was not observed in conventional mixing experiments, reflects nucleation and precipitation of a small portion of the Ni(IV) complex, which was added as a supersaturated solution. The quantity of precipitated material was too small to affect absorbance readings.

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Table 2. Representative Kinetic Data for Reductions of Oxime-Bound Nickel(IV) by Sn^{II} and I⁻^a

reductions by Sn ^{II}				reductions by I ⁻		
[Sn ^{II}], M × 10 ⁴ ^c	[H ⁺], M	[Cl ⁻], M × 10 ⁵	10 ² k, s ⁻¹ ^b	[I ⁻], M × 10 ⁴	[H ⁺], M	10 ² k, s ⁻¹ ^b
1.00	0.10	0	0.29 (0.32)	0.50	0.10	0.64 (0.60)
2.00	0.10	0	0.59 (0.64)	1.00	0.10	1.07 (1.19)
4.0	0.10	0	1.20 (1.28)	2.0	0.10	2.3 (2.4)
8.0	0.10	0	3.1 (2.6)	4.0	0.10	5.1 (5.8)
4.0	0.10	0	0.89 (0.96)	8.0	0.10	9.1 (9.5)
4.0	0.060	0	0.78 (0.80)	2.0	0.080	1.70 (1.66)
4.0	0.040	0	0.71 (0.64)	2.0	0.070	1.41 (1.35)
4.0	0.020	1.00	0.96 (0.98)	2.0	0.060	1.16 (1.06)
4.0	0.060	5.0	1.09 (1.06)	2.0	0.050	0.78 (0.81)
4.0	0.060	50	2.1 (2.0)	2.0	0.040	0.60 (0.59)
4.0	0.060	100	3.1 (3.0)	2.0	0.030	0.38 (0.39)
4.0	0.10	5.0	1.54 (1.38)	2.0	0.020	0.23 (0.23)
4.0	0.040	5.0	0.86 (0.90)			
4.0	0.020	5.0	0.74 (0.74)			
4.0	0.040	50	1.78 (1.82)			
4.0	0.020	50	1.60 (1.66)			

^a Reductions of the nickel(IV) complex of 2,6-diacetylpyridine dioximate (chelate **II**) were carried out at 25 °C; $\mu = 0.10$ M (HClO₄-NaClO₄); $\lambda = 572$ nm; 98/2 H₂O-CH₃OH; [Ni^{IV}] = 8×10^{-6} M. ^b Pseudo-first-order specific rates; parenthetical values were calculated using the rate laws and kinetic parameters listed in Table 3. ^c Added as SnSO₄.

Table 3. Rate Laws and Kinetic Parameters for Reductions of Oxime-Bound Nickel(IV)^a

reductant	rate law	eq no.	parameters
Fe ^{II}	[Ni ^{IV}][Fe ^{II}]($k_0 + k_1[H^+]$)	5	$k_0 = (7.5 \pm 0.8) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$; $k_1 = (7.4 \pm 0.3) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$
Sn ^{II}	[Ni ^{IV}][Sn ^{II}]($k_0 + k_1[H^+] + k_{Cl}[Cl^-]$)	6	$k_0 = 13 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$; $k_1 = 223 \pm 21 \text{ M}^{-2} \text{ s}^{-1}$; $k_{Cl} = (5.7 \pm 0.4) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$
I ⁻	[Ni ^{IV}][I ⁻]($k_1[H^+] + k_2[H^+]^2$)	7	$k_1 = (4.3 \pm 0.3) \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$; $k_2 = (7.6 \pm 0.5) \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$

^a Reductions of the Ni(IV) complex of 2,6-diacetylpyridine dioximate (chelate **II**) were carried out at 25 °C; $\mu = 0.10$ M (HClO₄-NaClO₄); $\lambda = 572$ nm; 98/2 H₂O-CH₃OH. Rate laws describe $-d[\text{Ni}^{\text{IV}}]/dt$.

No irregularities in patterns attributable to accumulation of Ni(III) were noted. Hence, if this state intervenes, its concentration must remain small.

Representative kinetic data, pertaining to the reductions by Sn(II) and I⁻, are collected in Table 2. Both reactions are seen to be accelerated by increases in acidity, with the [H⁺]-dependence more marked for the iodide reactions. In addition, the reduction by Sn(II) is perceptibly catalyzed by Cl⁻. Rate expressions and kinetic parameters for these reductions and for reductions by Fe²⁺, are assembled in Table 3. Observed rates are compared with those calculated using rate laws (6) and (7) in Table 2. Note particularly that reductions by Fe²⁺ are about 10² as rapid as those by Sn²⁺ (under comparable conditions) although formal potentials assigned to the two reductants¹⁷ tell us that the latter center is far more strongly reducing.

The [H⁺]-proportional terms observed for all three reductions may be attributed to partial conversion of the predominant Ni(IV) species to an extraprotonated form, for protonation of an oxidant generally increases its effectiveness. There is no indication of kinetic saturation with respect to [H⁺]; hence, the acidity constant applying to this protonation must lie well beyond the range examined (i.e., $pK_A \leq 0$). Kruger and Holm^{5d} have shown that the fully deprotonated form of this Ni(IV) chelate, which predominates above pH 8, is too weak an oxidant ($E^\circ = 0.49$ V vs NHE) to convert Fe(II) to Fe(III). We therefore conclude that the principal form of Ni(IV) at the low pH values examined is the monoprotonated species and that the protonation equilibrium associated with the [H⁺]-dependent terms involves

the mono- and diprotonated forms. The [H⁺]² term noted for reduction of I⁻ indicates that this reaction receives an additional kinetic boost from the contribution of a triprotonated cation. Since the concentration of the latter is necessarily very low, it must be exceptionally reactive.

The [Cl⁻]-dependent term seen for the Sn(II) reduction almost certainly arises from a component featuring SnCl⁺ rather than Sn(II)_{aq} as the reducing species. The bimolecular rate constant for this path may then be calculated by dividing k_{Cl} in eq 6 by Q_{assn} for this monochloro complex.¹⁸ The resulting value, $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, is 3×10^2 times that for k_0 , which pertains to reduction by Sn(II)_{aq}. This acceleration, resulting from substituting Cl⁻ for H₂O in the coordination sphere of the reductant, is much more marked than those observed^{19a} for a wide variety of reductions by Fe²⁺, Cr²⁺, and V²⁺ and suggests unusually strong stabilization, through chloride ligation, of the initial oxidation product (see below).

The nature of the kinetic profiles obtained in the reduction of Ni(IV) with U(IV) depends dramatically on the reaction medium. Data for reactions yielding exponential decay curves, carried out either at [H⁺] > 0.04 M or at lower acidities in the presence of added UO₂²⁺, are summarized in Table 4. Baes and Mesmer^{19b} have reviewed speciation data pertaining to U(IV)_{aq} and have pointed out the difficulties in obtaining a firm pK_A value for this cation, although there is no doubt that hydrolysis is significant between 0.04 and 0.10 M HClO₄. However, rates within this range are seen to vary only marginally with [H⁺], indicating that the protonated and

(17) Tabulated E° values are +0.15 V for Sn(II,IV) and +0.74 V for Fe(II,III). See, for example: Bard, A. J.; Parsons, R.; Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.

(18) The association constant for SnCl⁺ (25 °C, $\mu = 0.50$ M) is listed as 12 M^{-1} . See: Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5, p 420.

(19) See for example: (a) Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545. (b) Baes, C. F., Jr.; Mesmer, R. F. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; pp 174-181.

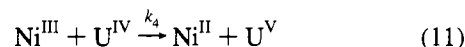
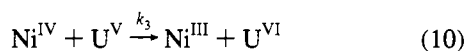
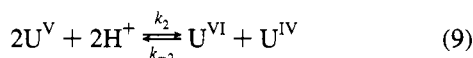
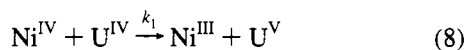
Table 4. Kinetic Data for Reduction of Oxime-Bound Nickel(IV) by Uranium(IV)^a

(A) redns at high acidity				(B) redns at low acidity			
[U ^{IV}], mM	[H ⁺], M	[U ^{VI}], mM	<i>k</i> , s ⁻¹ ^b	[U ^{IV}], mM	[H ⁺], M	[U ^{VI}], mM	<i>k</i> , s ⁻¹ ^c
0.25	0.10	0	0.028	1.00	0.010	0.025	19.9 (21)
0.50	0.10	0	0.057	1.00	0.010	0.050	30 (29)
1.00	0.10	0	0.114	1.00	0.010	0.100	42 (43)
1.00	0.10	0.05	0.119	1.00	0.010	0.40	87 (82)
1.00	0.10	0.50	0.121	0.50	0.010	0.20	37 (42)
2.00	0.10	0	0.23	1.00	0.010	0.20	62 (59)
4.0	0.10	0	0.45	2.00	0.010	0.20	88 (82)
8.0	0.10	0	0.93	1.00	0.0080	0.20	70 (73)
1.00	0.080	0	0.095	1.00	0.0120	0.20	50 (48)
1.00	0.060	0	0.117	1.00	0.0160	0.20	38 (36)
1.00	0.040	0	0.136	1.00	0.020	0.20	27 (29)

^a Reductions of the Ni(IV) complex of pyridine-2,6-bis(acetylloximate) (chelate II) were carried out at 25 °C; $\mu = 1.0$ M (HClO₄-NaClO₄); $\lambda = 572$ nm; 98/2 H₂O-CH₃OH; [Ni^{IV}] = 5×10^{-6} M. ^b Pseudo-first-order rate constants; values are adjusted to take into account the slow nonredox loss of the Ni(IV) oxidant from solution after stopped-flow mixing (see Experimental Section). ^c Pseudo-first-order rate constants; parenthetical values were calculated using equation 16 and taking $k_3(k_{-2}/k_2)^{1/2} = 1.30 \times 10^3$ s⁻¹.

deprotonated forms of this reductant have nearly the same reactivity. Reactions are seen to be markedly accelerated by U(VI) at lower acidities but not at high. Reductions at [H⁺] > 0.02 M give smooth curves (e.g., Figure 1) which, however, correspond to no monomial order.

The strong enhancement of reduction rates by UO₂²⁺, an oxidizing agent, indicates that U(VI) acts in this case by maintaining the steady-state concentration of a reducing intermediate which is much more reactive than the primary reductant, U(IV). The approach to half-order dependence on U(VI), and, in this region, a half-order dependence on U(IV) as well, is in accord with this description. The overall kinetic picture of the Ni(IV)-U(IV) system appears to be consistent with reaction sequence (8)-(11), in which the reac-



tive intermediate, a U(V) species, may undergo one of two competing transformations—reduction of Ni^{IV} (eq 10) or, alternatively, reversible disproportionation to U^{VI} and U^{IV} (eq 9). Note that each of the proposed steps is a single-electron transaction.

Differential equations generated by this sequence, in conjunction with application of the steady state approximation to intermediates U^V and Ni^{III}, then followed by rearrangement of terms, leads to rate law (12). At high acidities, the first term

$$\frac{-d[\text{Ni}^{\text{IV}}]}{dt} = k_1[\text{Ni}^{\text{IV}}][\text{U}^{\text{IV}}] + k_3[\text{Ni}^{\text{IV}}] \left[\frac{2k_1[\text{Ni}^{\text{IV}}][\text{U}^{\text{IV}}] + k_{-2}[\text{U}^{\text{VI}}][\text{U}^{\text{IV}}]}{k_2[\text{H}^+]^2} \right]^{1/2} \quad (12)$$

in (12) predominates, and reaction is very nearly first order in the added redox partners, under which conditions the data in Table 4A yield $k_1 = 114 \pm 3$ M⁻¹ s⁻¹. At lower acidities, and in the presence of added U^{VI}, rates become determined by the k_{-2} term in the numerator of (12), leading to rate expression

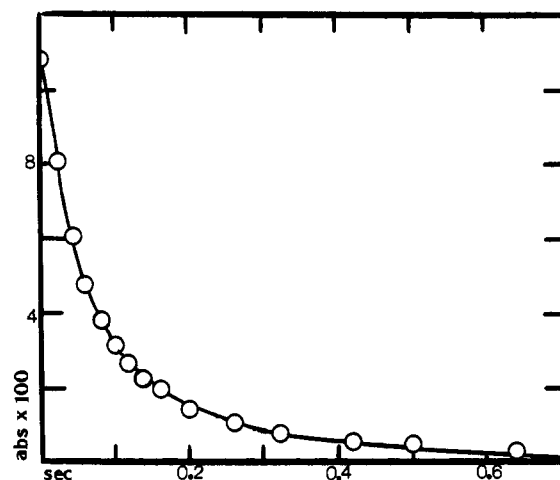


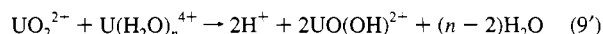
Figure 1. Kinetic profile at 572 nm for the reduction of the nickel(IV) complex of 2,6-diacetylpyridine dioximate (chelate II) (4.3×10^{-6} M) with uranium(IV) (1.00×10^{-3} M) at 24.0 °C: [H⁺] = 0.010 M; $\mu = 1.0$ M (NaClO₄). The solid line is the experimental curve, whereas the circles represent absorbances calculated from numerical integration of (16),²³ taking $k_1 = 114$ M⁻¹ s⁻¹, $a = 0.074$ s⁻¹, and the composite parameter $k_3(k_{-2}/k_2)^{1/2} = 1.88 \times 10^3$ s⁻¹. The extinction coefficient used for Ni^{IV} was 1.28×10^4 M⁻¹ cm⁻¹, and other species were considered to be negligibly absorbent. Optical path length = 2.0 cm.

(13). Refinement of data in Table 4B according to (13) yields a value of the composite parameter $k_3(k_{-2}/k_2)^{1/2} = (1.30 \pm 0.03) \times 10^3$ s⁻¹.

$$\frac{-d\ln[\text{Ni}^{\text{IV}}]}{dt} = \frac{k_3}{[\text{H}^+]} \left[\frac{k_{-2}[\text{U}^{\text{VI}}][\text{U}^{\text{IV}}]}{k_2} \right]^{1/2} \quad (13)$$

At low acidities with U^{IV} in excess, but in the absence of added U^{VI}, the profile for each run becomes nearly biphasic

(20) It is suggested that the disproportionation step (eq 9), in the pH range examined here involves 2 H⁺, rather than a single H⁺, in contrast to what is reported for this reaction at much higher acidities.²¹ An [H⁺]⁻¹ dependence for this step would result in overall rates inversely proportional to [H⁺]^{1/2}, contrary to the observed [H⁺]⁻¹ proportionality (Table 4B). We are indebted to a Reviewer who points out that the apparent 2H⁺ exchange associated with (9) implies a formulation of the U(V) intermediate as UO(OH)²⁺ (9').



Uncertainty in the hydrolysis constant of U(IV) in our medium^{19b} dictates caution in this assignment.

(21) See, for example: (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166. (b) Ekstrom, A. *Inorg. Chem.*, **1974**, *13*, 2237.

(eq 14), where k' is related to parameters in (12). In such

$$\frac{-d[\text{Ni}^{\text{IV}}]}{dt} = k_1[\text{Ni}^{\text{IV}}][\text{U}^{\text{IV}}] + k'[\text{Ni}^{\text{IV}}]^{3/2} \quad (14)$$

$$k' = \frac{k_3}{[\text{H}^+]} \left(\frac{2k_1[\text{U}^{\text{IV}}]}{k_2} \right)^{1/2} \quad (15)$$

cases, decay is nearly $3/2$ order in Ni(IV) shortly after mixing, but as the oxidant is depleted, dependency becomes less steep and the curve more nearly exponential. Integration of (14) in closed form is possible but relatively cumbersome. A more convenient alternative employed numerical integration^{22,23} with a 20-ms time interval chosen between kinetic points during the course of the reaction. The composite parameter $k_3(k_1/k_2)^{1/2}$ was allowed to vary, whereas $[\text{Ni}^{\text{IV}}]$, $[\text{U}^{\text{IV}}]$, $[\text{H}^+]$, and k_1 were assigned known values. Incorporation of $\epsilon_{\text{Ni(IV)}}$ (the only appreciable absorbing species under reaction conditions) yielded calculated optical densities of the reaction mixture at each point. Optimum agreement between calculated and observed values (e.g., Figure 1) was reached with $k_3(k_1/k_2)^{1/2} = 1.88 \times 10^3 \text{ s}^{-1}$. Dividing the latter by the product $k_3(k_2/k_1)^{1/2}$ (derived from the experiments with U^{VI}) yields the ratio $k_1/k_2 = 1.90$, whence

(22) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. *Tech. Chem. (N.Y.)* **1974**, *6*, 764. (c) This procedure was accomplished by a FORTRAN-IV program, INTEGRAL, and was executed on an IBM 9121 mainframe system. We thank Professor Gilbert Gordon (Miami University, Oxford, OH) for this program.

(23) In practice, the integration procedure was applied to (16), which was obtained by combining (14) and (15)

$$\frac{-d[\text{Ni}^{\text{IV}}]}{dt} = [\text{Ni}^{\text{IV}}](k_1[\text{U}^{\text{IV}}] + a) + \frac{(2[\text{U}^{\text{IV}}])^{1/2}}{[\text{H}^+]} k_3 \left(\frac{k_1}{k_2} \right)^{1/2} [\text{Ni}^{\text{IV}}]^{3/2} \quad (16)$$

and adjusting (term a) for the slow $[\text{U}^{\text{IV}}]$ -independent loss of Ni^{IV} in the stopped-flow system (see Experimental Section).

k_{-2} (pertaining to the U(IV,VI) comproportionation reaction) may be estimated as $60 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 1.0 \text{ M}$).

Our results from the Ni(IV)–U(IV) reaction (despite the complexity of the system), when considered in concert with the reductions by Fe(II) and I^- and the inactivity of Ni(IV) toward H_3PO_2 and H_3AsO_3 , bolster the view, already expressed by others,^{6d–f,24} that conversion of Ni(IV) to Ni(II), a net 2e process, must proceed in single-electron steps. The reductions by Sn(II) stand out, however, for although this is generally taken to be a 2e donor, evidence is accumulating that sufficiently strong oxidants, specifically those derived from Co(III)²⁵ and Cr(VI)²⁶ centers, can remove a single electron (although this requires breakage of a complete 5s subshell). Such transactions should be favored by the absence of bridging functions, for transfers of two oxidation units cannot proceed by simple outer-sphere paths.

If, as we suspect, the Ni(IV)–Sn(II) reaction is initiated by the transfer of a single electron, the marked sensitivity of this reaction to added Cl^- (rate law 6), which cannot enter the coordination sphere of the oxidant to form a new redox bridge, may be attributed to a high degree of stabilization, through ligation, of Sn(III), a product of the initial step. The implication here is that searches for this unusual odd-electron state are likely to be best carried out on chloride-rich systems.

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