3), whereas the symmetrical species $Cu_4OCl_6(nmp)_4$ is catalytically *inactive*, clearly suggests that Cu(1) of the present structure is actively involved in the catalytic cycle. Further work is, however, required before the detailed steps of the mechanism are elucidated. Such steps might involve replacement of the aquo ligand by dioxygen or deprotonation of the aquo ligand. Also, the precise molecular geometry of the species "$(nmp)_3Cu_4Cl_4O_2$" has still to be ascertained.

Each of the copper(II) atoms is in a (slightly distorted) trigonal-bipyramidal coordination geometry, with chloride ligands in the three equatorial sites and oxygen atoms bonded at the axial sites. The distortions of the $CuCl_3O_2$ moieties from D_{3h} symmetry are clearly indicated by planes I–IV of Table VII. In each case the central Cu(II) ion is displaced outward (i.e., away from O(50)) from the plane defined by the three equatorial chloride ligands.

Finally, we note that all distances and angles within the nmp ligands are in the expected ranges.

Acknowledgment. We thank Professor Geoffrey Davies for providing the sample and for his continuing interest in these studies. This work was supported by the National Science Foundation (Grant CHE77-04981, to M.R.C.) and by a generous allocation of computer time from the Computing Center at the State University of New York at Buffalo.

Registry No. $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$, 68630-24-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(24) Throughout the text, esd's on individual distances, etc., are shown in parentheses. Esd's on average distances, which are calculated as shown in footnote *b* to Table V, are distinguished by being written in the form ±x.xxx Å, etc.

Notes

Contribution from Centro di Studio sulla Stabilità e Reattività
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Nickel(0) Complexes with the Hybrid Bidentate Ligand 1-(Thioethyl)-2-(diphenylphosphino)ethane. Synthesis and Catalytic Properties of the Related Nickel Hydride Derivative

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The chemistry of the zerovalent complexes of nickel with phosphite and phosphine ligands (L) has been extensively studied in recent years in view of their relevance in homogeneous catalysis. It has been recognized that the reactivity of the NiL_4 complexes is particularly influenced by their tendency to give coordinatively unsaturated NiL_3 and NiL_2 species in solution.[1-3] Also, in the case of the hydrido derivative $[NiHL_4]^+$, which can be easily obtained by protonation of the corresponding nickel(0) complex,[4-8] the reactivity appears strictly dependent on the possibility of dissociating one ligand to give a free coordination site at the nickel atom.[2,9-11]

Since the nature of donor atoms can have a profound influence on the ease with which the ligands undergo dissociation, we have attempted to prepare $Ni(L-L')_2$ and $[NiH(L-L')_2]^+$ complexes with hybrid bidentate ligands (L–L′) containing both phosphorus and sulfur donor atoms. It seemed likely, in fact, that these complexes could become coordinatively unsaturated in solution since the sulfur end of the chelate would easily be displaced from the metal atom. In particular, we have chosen ligands of the type $(C_6H_5)_2PCH_2CH_2SR$ (R = CH_3, C_2H_5, C_6H_5) since previous investigations on their coordinating properties have shown that in their complexes of nickel(II) the dissociation of the thioether group can occur quite readily.

This paper reports the synthesis and chemistry of some nickel(0) derivatives with the ligand 1-(thioethyl)-2-(diphenylphosphino)ethane ($(C_6H_5)_2PCH_2CH_2SC_2H_5$, abbreviated P-SEt). Moreover we describe the preparation of the nickel hydride $[NiH(P\text{-}SEt)_2]^+$ and its catalytic behavior in olefin isomerization reactions.

Experimental Section

All operations involving air-sensitive complexes were performed under argon. Melting points were determined in evacuated, sealed capillaries and were uncorrected. Tetrahydrofuran was distilled from $LiAlH_4$. Other solvents were dried in the usual manner. All solvents were purged with argon. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer and GLC's on a Hewlett-Packard 5750 gas chromatograph. ^1H NMR spectra were taken using a Bruker 90-MHz instrument. Elemental analyses were performed

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by Mr. L. Turiaco, Instituto di Chimica Analitica, University of Padua.

Preparation of the Complexes. The ligand **P-SEt** was prepared as described earlier.[12]

[Ni(P-SEt)$_2$](BF$_4$)$_2$. The ligand (2.75 g, 10 mmol) dissolved in dichloromethane (10 mL) was added to a boiling solution of $Ni(BF_4)_2 \cdot 6H_2O$ (1.7 g, 5 mmol) in 2-propanol (100 mL). The precipitate obtained was recrystallized from dichloromethane/2-propanol to give 3.7 g (95%) of yellow crystals, mp 244 °C dec. Anal. Calcd for $C_{32}H_{38}B_2F_8NiP_2S_2$: C, 49.21; H, 4.90. Found: C, 49.26; H, 5.06.

Reduction of [Ni(P-SEt)$_2$](BF$_4$)$_2$. In an argon atmosphere [Ni(P-SEt)$_2$](BF$_4$)$_2$ (2.34 g, 3 mmol) suspended in benzene (50 mL) was stirred with sodium amalgam (0.14 g of metallic sodium in 6 mL of mercury) until the nickel complex dissolved with a color change from yellow to red. After filtration, the solvent was removed under vacuum to give an orange solid. It was not found possible to purify this material (probably Ni(P-SEt)$_2$), and no acceptable analysis could be obtained.

Ni(FN)(P-SEt)$_2$ (FN = Fumaronitrile). A benzene solution of "Ni(P-SEt)$_2$" was prepared under argon by Na–Hg reduction of [Ni(P-SEt)$_2$](BF$_4$)$_2$ (2.34 g, 3 mmol) in dry benzene (40 mL). After filtration, the solution was treated with 0.23 g (3 mmol) of FN in 5 mL of benzene. The mixture was stirred for 0.5 h, and then *n*-hexane (50 mL) was slowly added. The red crystals which separated were filtered off, washed with *n*-hexane, and dried in vacuo to give 1.34 g (65%) of Ni(FN)(P-SEt)$_2$, mp 116–117 °C dec. IR (Nujol): ν(CN) 2180 cm^{-1}. ^{1}H NMR (C_6D_6): τ 2.67, 2.99 (m, C_6H_5), 6.83 (br s, CH), ~7.5 (m, P-CH$_2$-(CH$_2$-S), 7.54 (q, S-CH$_2$), 8.95 (t, CH$_3$). Anal. Calcd for $C_{36}H_{40}N_2NiP_2S_2$: C, 63.07; H, 5.88; N, 4.09. Found: C, 62.50; H, 6.00; N, 4.10.

Ni(CO)$_2$(P-SEt)$_2$. A red solution of "Ni(P-SEt)$_2$" (prepared as described above) was treated with 1 atm of carbon monoxide. A colorless solution was immediately formed from which a white solid was obtained by removing the solvent under vacuum. The residue was extracted with 50 mL of *n*-hexane, and the extract was concentrated to ca. 10 mL and cooled at −20 °C for 1 h. The resulting white crystalline solid was collected at −20 °C, washed with cold *n*-hexane, and dried in vacuo to give 1.2 g (60%) of Ni(CO)$_2$(P-SEt)$_2$, mp 89–90 °C. IR (Nujol): ν(CO) 1995 and 1945 cm^{-1}. ^{1}H NMR (C_6D_6): τ 2.6, 2.9 (m, C_6H_5), ~7.5 (m, P–CH$_2$–CH$_2$–S), 7.77 (q, S–CH$_2$), 9.02 (t, CH$_3$). Anal. Calcd for $C_{34}H_{38}NiO_2P_2S_2$: C, 61.55; H, 5.77. Found: C, 62.08; H, 5.76.

[NiH(P-SEt)$_2$]B(C$_6$H$_5$)$_4$. A benzene solution of "Ni(P-SEt)$_2$" was prepared under argon by Na–Hg reduction of [Ni(P-SEt)$_2$](BF$_4$)$_2$ (1.67 g, 2 mmol) in dry benzene (25 mL). After filtration, the solution was cooled at 0 °C and was treated dropwise with an ethereal solution of HBF$_4$ (obtained by tenfold dilution with diethyl ether of a 50% aqueous solution of HBF$_4$). Orange crystals were immediately formed, and addition of HBF$_4$ was stopped when the red color of the solution disappeared. The product was filtered off, washed with *n*-hexane, and dried in vacuo. Attempts to recrystallize this complex led to decomposition. The orange solid was suspended in absolute ethanol (10 mL) and treated with NaB(C$_6$H$_5$)$_4$ (0.7 g). After 20 min of stirring, the crude product was filtered off, recrystallized from anhydrous acetone/ethanol, and dried in vacuo to give 1.1 g (60%) of [NiH(P-SEt)$_2$]B(C$_6$H$_5$)$_4$, mp 108 °C dec. IR (Nujol): ν(NiH) 1917 cm^{-1}. ^{1}H NMR (acetone-d_6): τ 2.25, 2.43 (m, C_6H_5), 6.94 (br s, P–CH$_2$–CH$_2$–S), 8.11 (q, S–CH$_2$), 9.02 (t, CH$_3$), 27.6 (t, Ni–H, J_{PH} = 49 Hz). Anal. Calcd for $C_{56}H_{59}BNiP_2S_2$: C, 72.50; H, 6.41. Found: C, 71.78; H, 6.47.

Isomerization of Olefins by [NiH(P-SEt)$_2$]B(C$_6$H$_5$)$_4$. Owing to the sensitivity of the nickel hydride to oxygen and water, all reactions were performed under argon using anhydrous solvents distilled immediately before use. The isomerization reactions were carried out at 20 °C in a three-necked glass flask. In all cases the solid nickel hydride (0.1 g) was added, under argon, through a special valve to 10 mL of a 0.22 M olefin solution previously deoxygenated by freeze–pump–thaw cycles. The solution was stirred magnetically, and samples for IR or GLC analysis were withdrawn by a syringe through a rubber cap. The isomerization of the substituted olefins was followed by recording the infrared spectra of the solutions. GLC analysis of reaction mixtures containing C_5H_{10} isomers was done at 30 °C using a 4-m column filled with dimethylsulfolane on Chromosorb (20%). The olefins used both as reagent and standard compounds were high-purity Schuchard or Fluka products and were used as received.

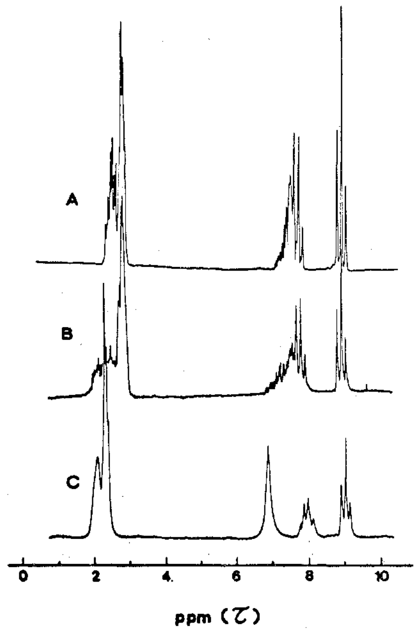
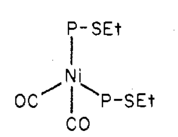


Figure 1. Proton NMR spectra: A, P-SEt in C_6D_6; B, Ni(CO)$_2$(P-SEt)$_2$ in C_6D_6; C, [Ni(CN)(P-SEt)$_2$]BF$_4$ in CDCl$_3$.

Results and Discussion

The ligand P-SEt reacts with nickel tetrafluoroborate to form the square-planar [Ni(P-SEt)$_2$](BF$_4$)$_2$ complex. Reduction of this complex with sodium amalgam in benzene suspension (Na/Ni molar ratio of 2) gives red solutions, which probably contain the zerovalent nickel complex Ni(P-SEt)$_2$. Efforts to isolate this product in pure form were unsuccessful. Also, a spectroscopic investigation of the solution was prevented by slow formation of whitish insoluble materials. However, the presence of the complex Ni(P-SEt)$_2$ in solution is supported by a number of chemical evidences.[13]

When the solution is treated with CO, the red color immediately disappears, and a carbonyl derivative with stoichiometry corresponding to Ni(CO)$_2$(P-SEt)$_2$ can be isolated from the reaction mixture. This complex, which is very soluble in aliphatic hydrocarbons, shows carbonyl absorptions at 2008 and 1945 cm^{-1} (*n*-hexane solution). The position of the bands, similar to those of the Ni(CO)$_2$(PPh$_2$Et)$_2$ complex,[14] together with the known tendency of d^{10} ions to give a tetracoordinate unit, suggests the structure **1** in which the P-SEt ligand acts as monodentate.



1

as monodentate. This is the expected product for a carbonylation reaction on Ni(P-SEt)$_2$, since the thioethyl groups are likely to undergo easier substitution than the better π-acceptor phosphine arms. An IR spectrum of the reaction mixture shows, in addition to the carbonyl absorption of **1**, less intense bands at 2000 and 2080 cm^{-1} which are consistent with the formation of some amount of the tricarbonyl derivative Ni(CO)$_3$(P-SEt).[15]

Examination of the NMR spectra of the free ligand[16] and of a number of metal complexes,[17] in which P-SEt is coordinated only through the phosphorus atom, shows that the resonances of aliphatic protons of the ligand are practically unaffected by coordination of the phosphine arm (Figure 1). On the contrary, when the ligand acts as bidentate, significant changes occur especially on the CH$_2$ resonance of the aliphatic chain. This signal, which in the free ligand consists of a complex multiplet partially overlapping with the CH_2 quartet of the ethyl group, collapses on formation of the chelate ring to a broad singlet (Figure 1C).[17] In the case of the complex $Ni(CO)_2(P\text{-}SEt)_2$ the ^1H NMR spectrum is very similar to that of free P-SEt, thus confirming structure **1** with phosphorus-bonded P-SEt ligands.

The formation of $Ni(P\text{-}SEt)_2$ in the Na–Hg reduction of $[Ni(P\text{-}SEt)_2](BF_4)_2$ is also confirmed by reaction with fumaronitrile (FN). The reduced solution reacts immediately with an equimolar amount of FN to give a dark red solution, from which $Ni(FN)(P\text{-}SEt)_2$ (**2**) can be obtained on addition of *n*-hexane. The IR spectrum of **2** shows a strong sharp $\nu(CN)$ band at 2180 cm^{-1} (60 cm^{-1} lower than in the uncoordinate FN) which is assigned to π-bonded dinitrile. In agreement with a four-coordinate structure, in which the thioethyl arms are displaced from metal, the NMR resonances of the protons of the P-SEt ligand in **2** are in the same position as those of the free ligand. The FN proton's signal occurs as a broad singlet at τ 6.83. The coordinated olefin can be easily displaced from complex **2** by carbon monoxide to give the carbonyl derivative **1**, together with a small quantity of tricarbonyl $Ni(CO)_3(P\text{-}SEt)$.

Addition of a stoichiometric amount of aqueous fluoboric acid (diluted in diethyl ether) to the benzene solution of $Ni(P\text{-}SEt)_2$ leads to the immediate precipitation of the orange hydride complex $[NiH(P\text{-}SEt)_2]BF_4$. This product, which retains water, cannot be purified. However, treatment of an alcohol suspension with $NaB(C_6H_5)_4$ gives the corresponding $[NiH(P\text{-}SEt)_2]B(C_6H_5)_4$ complex (**3**), which can be obtained in the pure form and fully characterized. The infrared spectrum (Nujol mull) of **3** shows a weak, broad Ni–H absorption at 1917 cm^{-1}. In the ^1H NMR spectrum the hydride resonance, which is not temperature dependent, appears at τ 27.6 as a triplet with $J = 49$ Hz. Moreover, the CH_2 resonance of the alkyl chain of P-SEt appears as a broad singlet, thus suggesting a five-coordinate structure in which both P-SEt molecules act as bidentate ligands. In agreement with this conclusion the low-field spectrum of **3** is indistinguishable from that (Figure 1C) of the five-coordinate $[Ni(CN)(P\text{-}SEt)_2]^+$.[12] Complex **3**, which is stable in the solid state under inert atmosphere, slowly decomposes in solution according to the sequence

$$NiH(P\text{-}SEt)_2{}^+ \rightleftharpoons Ni(P\text{-}SEt)_2 + H^+ \qquad (1)$$

$$NiH(P\text{-}SEt)_2{}^+ + H^+ \rightarrow Ni(P\text{-}SEt)_2{}^{2+} + H_2 \qquad (2)$$

similar to that proposed to explain the decay of $[NiH(P(OR)_3)_4]^+$ in CH_3OH.[7] The ^1H NMR spectrum of a CH_2Cl_2 solution of **3** shows that the hydride resonance at τ 27.6 decreases with time (50% for 0.2 M solution after 0.5 h) without the appearance (even on cooling) of resonances assignable to other hydridic species. In these solutions there is also a slow subsequent formation of the complex $[NiCl(P\text{-}SEt)_2]^+$, as shown by the appearance in the visible spectrum of a band at 20 000 cm^{-1}.[12] In agreement with step 2 strong acids react with **3** giving $[Ni(P\text{-}SEt)_2]^{2+}$ quantitatively with H_2 evolution. Moreover, when solutions of **3** are treated with CO, a mixture of the nickel(0) derivatives $Ni(CO)_2(P\text{-}SEt)_2$ and $Ni(CO)_3(P\text{-}SEt)$ is formed together with some amount of $[Ni(P\text{-}SEt)_2]^{2+}$.

It is known that the nickel hydride cations of the type $[NiHL_4]^+$ react with dienes to form cationic π-allyl (syn or anti) derivatives according to the sequence

$$NiHL_4{}^+ + \text{diene} \xrightarrow{-L} \underset{\text{red}}{(\pi\text{-allyl})NiL_3{}^+} \overset{-L}{\rightleftharpoons} \underset{\text{yellow}}{(\pi\text{-allyl})NiL_2{}^+}$$

$$L = P(OR)_3$$

The similar complex $[NiH(Ph_2PCH_2CH_2PPh_2)_2]^+$ reacts in an analogous manner, but the reaction is considerably slower owing to a greater difficulty in creating a free coordination site at the nickel atom.[10]

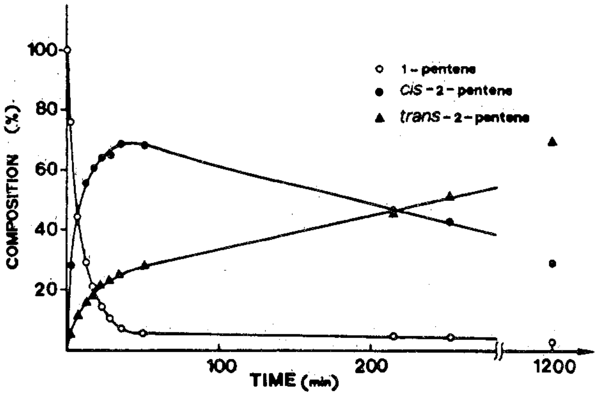


Figure 2. Profile for the $[NiH(P\text{-}SEt)_2]B(C_6H_5)_4$-catalyzed isomerization of 1-pentene in CH_2Cl_2 solution.

It is interesting in this regard that solutions of $[NiH(P\text{-}SEt)_2]^+$ react rapidly (even at −78 °C) with 1,3-butadiene with a color change from orange to dark red. The red color then gradually fades, and the solution becomes yellow. Attempts to isolate the red species or the final product were unsuccessful. NMR experiments show that when **3** and butadiene are mixed in a 1:1 molar ratio, the resonances characteristic of the hydride at τ 27.6 immediately disappear with simultaneous formation of new resonances in the τ 4–9 region. The overall feature of the NMR spectrum suggests the formation of a π-allyl derivative, but the occurrence in the same region of resonances of the P-SEt ligand does not allow a complete identification of the product.

Isomerization of Olefins Catalyzed by $[NiH(P\text{-}SEt)_2]^+$. We have briefly investigated the catalytic activity of complex **3** in olefin isomerization. The reactions were carried out in CH_2Cl_2 or tetrahydrofuran solution with a catalyst concentration of 0.015 M and a molar olefin/hydride ratio of 15. In these conditions **3** catalyzes, for example, the isomerization of allylbenzene to *trans*-propenylbenzene, of allyl alcohol to propionoaldehyde, of allyl cyanide to crotonitrile, and of 1-pentene to *trans*- and *cis*-2-pentene.

We have examined in some detail the isomerization of 1-pentene, and the profile of isomer distribution for this reaction in CH_2Cl_2 is reported in Figure 2. As shown, the initial cis/trans isomer ratios are controlled by kinetic factors; the *cis*-2-pentene concentration reaches a maximum (70%) before declining toward its equilibrium figure. A stereoselectivity factor of 3.5 in favor of the cis isomer was found at about 25% conversion. Addition of 1-pentene to the solution of **3** does not cause any appreciable variation in the intensity of the hydride resonance; at the same time the NMR spectrum does not show evidence for any catalytic intermediate. Gas chromatographic analysis of the final solution also reveals the presence of small amounts of pentane (1%) probably arising from cleavage of an alkylmetal intermediate which is spectroscopically not detectable.

The catalytic activity of the solution decreases with time owing to decomposition of **3**, and this has prevented a complete kinetic study of the system. However, it is likely that, as found[2,11] for other nickel-catalyzed olefin isomerizations, the reaction involves the formation of an olefin–metal hydride adduct which rearranges first to a metal alkyl then to a metal hydrido complex of the isomeric olefin. Since coordination of the olefin must occur to a coordinatively unsaturated hydrido complex, it appears that the facility for dissociation of the thioethyl arms may be a significant factor in determining the catalytic activity of complex **3**.

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Registry No. **1**, 68307-35-7; **2**, 68307-37-9; **3**, 68307-39-1; $[Ni(P\text{-}SEt)_2](BF_4)_2$, 68307-40-4; $Ni(P\text{-}SEt)_2$, 68307-41-5; $[Ni(CN)(P\text{-}SEt)_2]BF_4$, 68307-42-6; 1-pentene, 109-67-1.

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(13) The electrochemical behavior of $Ni(P\text{-}SEt)_2^{2+}$ has been investigated with the mercury electrode. The reduction is characterized by two one-electron waves which suggest stepwise formation of the nickel(I) and nickel(0) complexes $Ni(P\text{-}SEt)_2^+$ and $Ni(P\text{-}SEt)_2$: M. Martelli, P. Rigo, G. Pilloni, and G. Zotti, unpublished results.
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(16) The ^{1}H NMR spectrum of P-SEt in C_6D_6 shows resonances at τ 26.29 (m, C_6H_5), ~7.5 (m, P–CH_2–CH_2–S), 7.77 (q, S–CH_2), and 9.02 (t, CH_3).
(17) P. Rigo, unpublished results.

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Pulse Radiolytic Study of the Oxidation of Vitamin B_{12r} by Dibromide Ions[1a]

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Received July 28, 1978

Bromine oxidizes one-equivalent reducing agents such as divalent metal complexes in general[2,3] and Co(II) complexes including vitamin B_{12r}[2] in particular to the trivalent state in a noncomplementary fashion, the net process consuming 2 mol of M(II)/mol of bromine. The rate equation for a large number of complexes shows a first-order dependence on both reducing agent and bromine, consistent with an initial one-equivalent process.

Detailed mechanisms for the first and rate-limiting step have been considered;[2,3] it is likely[4] that the dibromide ion $Br_2^-\cdot$ is formed in this step (or immediately thereafter).

$$M^{II} + Br_2 \rightarrow Br_2^-\cdot + M^{III} \quad (\text{or } Br\cdot + Br\text{–}M^{III}) \qquad (1)$$

We have undertaken for the system $M^{II} = Co^{II}$(corrin) or vitamin B_{12r} a study of the requisite second major reaction, that by which $Br_2^-\cdot$ is consumed, a process necessarily very rapid compared to the first. Margerum[3] points out two plausible sequences which can be invoked to complete the overall reaction, both consistent with the data at hand.

These alternatives consist of direct oxidation, whether by an inner-sphere or outer-sphere mechanism (eq 2), and of

$$Br_2^-\cdot + M^{II} \rightarrow Br^- + Br\text{–}M^{III} \quad (\text{or } Br^- + M^{III}) \qquad (2)$$

$$Br_2^-\cdot + Br_2^-\cdot \rightarrow Br_2 + 2Br^- \qquad (3)$$

dibromide disproportionation (eq 3). The present work seeks to resolve these possibilities for the oxidation of vitamin B_{12r}.

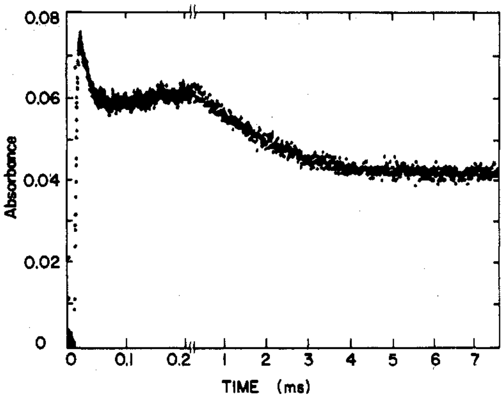

Figure 1. Kinetic data from a pulse radiolysis experiment showing the change in absorbance (optical path 2 cm) at 365 nm with time in a run with $[B_{12r}]_0 = 15\ \mu M$ and $[Br^-] = 11$ mM. The initial rapid decrease corresponds to the reaction of dibromide ion (eq 4), the small increase to eq 7, and the final, slower decrease to aquation of bromocobalamin, eq 5.

Table I. Kinetic Data Reactions of $Br_2^-\cdot$ with Vitamin B_{12r}[a]

conditions			$Br_2^-\cdot$ + [Co(II)] $10^{-9}k_4$/ dm^3 mol^{-1} s^{-1}	second k/s^{-1}	Br–[Co(III)] aquation $10^{-2}k_d$/ s^{-1} [b]
$10^5 \times [B_{12r}]_0$/M	$[Br^-]$/M	λ/nm			
1.5	0.011	365	2.8		6.2
		380	3.7		5.4
3.0	0.010	350	4.5	~5 × 10^3	
		365	3.8		7.2
		365	3.7		7.9
3.0	0.011	365		1.9 × 10^4	6.0
		380	3.0		5.4
3.0	0.11	365		2.4 × 10^4	6.6
		380	2.4		6.9

[a] At $T = 22 \pm 1$ °C, $\mu = [Br^-]$ in solutions saturated with N_2O at pH ~4.5. [b] From eq 6 with $K_5 = 1.8\ M^{-1}$.

Results and Discussion

Pulse radiolysis of solutions of sodium bromide saturated with N_2O produces[6] the dibromide ion $Br_2^-\cdot$, which in the absence of oxidizable substrate disappears by disproportionation[6] ($2k_3 = 3.3 \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$). We find that with B_{12r} present at pH 4.5, the rate of disappearance of the absorption due to $Br_2^-\cdot$ (ϵ_{365} 7800 ± 200 $dm^3\ mol^{-1}\ cm^{-1}$)[6] is accelerated while a new absorption at λ 365 nm of an unstable intermediate appears. After two further steps a permanent absorption spectrum due to stable products (vitamin B_{12a}, aquocobalamin) is observed.

The timed sequence of three successive changes at 365 nm is shown in Figure 1. The first reaction occurring is

$$Br_2^-\cdot + [Co(II)] \rightarrow Br^- + Br\text{–}[Co(III)] \qquad (4)$$

The kinetics of this first step were evaluated from runs in which B_{12r} was varied in the range (1.5–3.0) × 10^{-5} M; the best data were obtained at 380 nm with other runs at 350 and 365 nm. The data correspond to half-times between 3.4 and 14 μs; the results are summarized in Table I and give $k_4 = (3.4 \pm 0.6) \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$.

The final reaction stage with $t_{1/2} \sim 1$ ms corresponds to the much slower aquation of bromocobalamin, reaction 5,

$$(H_2O)\text{–}[Co(III)]^+ + Br^- \underset{d}{\overset{f}{\rightleftarrows}} Br[Co(III)] + H_2O \qquad (5)$$

for which Thusius[7] has reported kinetic and thermodynamic data. Since the formation constant for bromocobalamin is