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Metalation of Thiobenzophenones by Rhenium Carbonyl. Isolation of the Reaction Intermediate

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Received August 21, 1975 AIC50623F

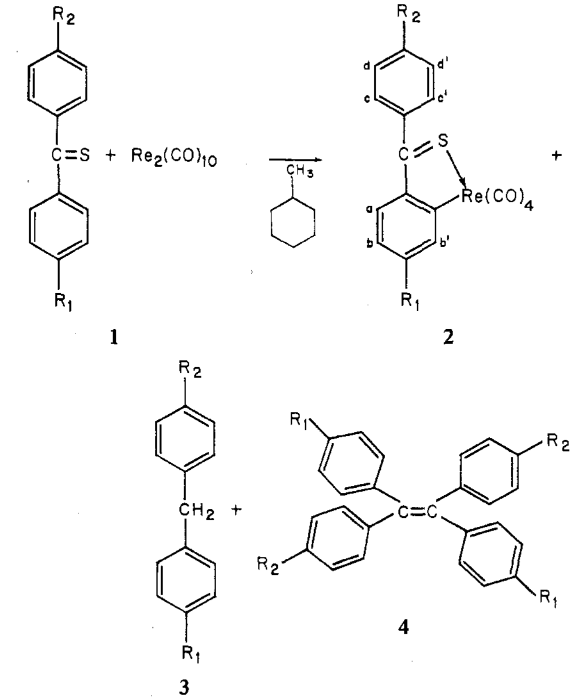
Treatment of thiobenzophenones with dirhenium decacarbonyl in hot methylcyclohexane affords the first examples of sulfur-donor ligand ortho-metalated complexes of rhenium. Irradiation of thiobenzophenones with dirhenium decacarbonyl gave thiobenzophenone–dirhenium nonacarbonyl complexes in almost quantitative yield. Thermolysis of the latter complexes in methylcyclohexane resulted in conversion to the corresponding ortho-metalated complexes.

Thiobenzophenones have proved to be a very useful source for sulfur-donor ligand ortho-metalated complexes, by reaction of the thiones with $Fe_2(CO)_9$,[1] $Ru_3(CO)_{12}$,[2] and MCl_4^{2-} [M = Pd, Pt].[3] The presence of a highly activating group [e.g., $N(CH_3)_2$] on the benzene ring of the thiobenzophenone is required for effecting electrophilic ortho metalation with dimanganese decacarbonyl.[4] Olefin formation results when less activating substituents [e.g., CH_3, OCH_3] are present on the aromatic ring(s) of the thione.

It was of considerable interest to learn (i) if ortho metalation and/or desulfurization would occur on treatment of the thiones with dirhenium decacarbonyl [$Re_2(CO)_{10}$] and (ii) how the substituent effect differs, if at all, for the two group 7 metal carbonyls.

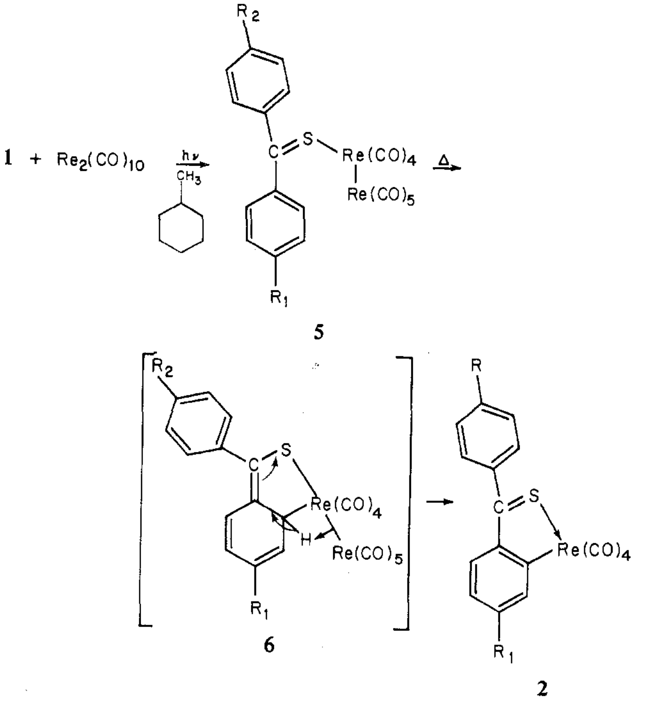
Results and Discussion

Reaction of 4,4'-dimethoxythiobenzophenone [**1**, $R_1 = R_2 = OCH_3$], 4-methoxythiobenzophenone [**1**, $R_1 = OCH_3$, $R_2 = H$], or 4,4'-bis(dimethylamino)thiobenzophenone [**1**, $R_1 = R_2 = N(CH_3)_2$] with an equimolar amount of $Re_2(CO)_{10}$ in refluxing methylcyclohexane afforded the mononuclear sulfur-donor ligand ortho-metalated complexes **2** [$R_1 = R_2 = OCH_3$, $N(CH_3)_2$; $R_1 = OCH_3$, $R_2 = H$], identified on the basis of analytical and spectral data (see eq 1). Four terminal metal carbonyl stretching bands were observed in the infrared region [$CHCl_3$] at 2082–2089 (m), 1987–1992 (vs), 1970–1980 (vs), and 1921–1935 (s) cm^{-1}, in good agreement with data for other ortho-metalated complexes of rhenium.[5-9] Proton magnetic resonance spectra for **2** were similar to those of the corresponding manganese complexes.[4] All of the complexes gave molecular ion peaks in the mass spectra, followed by successive loss of four carbonyl groups.



(1)

Scheme I



Also formed in all of the reactions described above was a small amount of diarylmethanes (**3**). 4,4'-Dimethoxythiobenzophenone [**1**, $R_1 = R_2 = OCH_3$] gave a trace quantity of tetrakis(*p*-methoxyphenyl)ethylene, **4**, $R_1 = R_2 = OCH_3$.

Thiobenzophenone [**1**, $R_1 = R_2 = H$] and 4,4'-dimethylthiobenzophenone [**1**, $R_1 = R_2 = CH_3$] failed to react with $Re_2(CO)_{10}$ in refluxing methylcyclohexane, even after reaction times of 8 days. However, metalation could be achieved by a simple two-step procedure (below).

The author previously proposed that ortho metalation of thiobenzophenones by $Mn_2(CO)_{10}$ occurs by initial carbon monoxide displacement to afford a thiobenzophenone–dimanganese nonacarbonyl complex.[4] Good evidence has now been obtained for the involvement of such dimetal nonacarbonyl complexes in metalation of rhenium and manganese systems.

Irradiation of **1** [$R_1 = R_2 = OCH_3$, CH_3] with $Re_2(CO)_{10}$ in methylcyclohexane for 90–120 min (medium-pressure mercury lamp) afforded the corresponding thiobenzophenone–dirhenium nonacarbonyl complex **5** [$R_1 = R_2 = OCH_3$, CH_3] in 93–98% yield, as purple, reasonably air-stable complexes (see Scheme I). The ir spectrum of **5** displayed five terminal metal carbonyl stretching absorptions in the region of 1925–2095 cm^{-1}, but no bridging carbonyls were present (see Experimental Section). These complexes gave molecular ion peaks in the mass spectrum, the fragmentation showing successive loss of nine carbonyls, and a band due to the thione ligand. There were small changes in the NMR spectrum of the thiobenzophenone on conversion to the sulfur-donor ligand complex **5**.

The thione ligand likely occupies an axial position in **5**, since the ir carbonyl stretching bands occur at similar frequencies to the values reported for $Re_2(CO)_9[P(C_6H_5)_3]$. The triphenylphosphine ligand in the latter is axial.[10]

When **5**, $R_1 = R_2 = OCH_3$, was refluxed in methylcyclohexane for 24 h [i.e., thermal conditions used for ortho metalation], clean conversion occurred to the ortho-metalated complex **2**, $R_1 = R_2 = OCH_3$. The 4,4'-dimethyl complex [**2**, $R_1 = R_2 = CH_3$] was similarly obtained on thermolysis of **5**, $R_1 = R_2 = CH_3$. Complex **6** may be involved in the transformation of **5** to **2**.

In conclusion, sulfur-donor ligand ortho-metalated complexes of rhenium can be readily synthesized by photochemical or thermal reactions of thiones with $Re_2(CO)_{10}$. The intermediacy of thiobenzophenone–dirhenium nonacarbonyls [or, by analogy, (thione)$Mn_2(CO)_9$] in the ortho metalation of group 7 metal carbonyls has been clearly demonstrated.

Experimental Section

General Data. Melting points were determined using a Fisher-Johns apparatus and are uncorrected. Infrared spectra were obtained using a Beckman IR20A spectrometer, equipped with a calibration standard. Proton NMR spectra were recorded on a Varian T60 or HA100 spectrometer, using tetramethylsilane as internal standard. Mass spectral analyses were determined on a Varian MS902 spectrometer. Elemental analyses were performed by Drs. F. Pascher and E. Pascher, Microanalytical Laboratory, Bonn, West Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn. Irradiation experiments were carried out with a Hanovia medium-pressure mercury lamp.

Dirhenium decacarbonyl was purchased from Pressure Chemical Co. and used as received. Solvents were purified by standard techniques. All reactions were run under a dry nitrogen atmosphere.

Reaction of 1, $R_1 = R_2 = OCH_3$, $N(CH_3)_2$, or 1, $R_1 = OCH_3$, R_2 = H,[11] with $Re_2(CO)_{10}$. An equimolar mixture of the thione **1** (2.00 mmol) and $Re_2(CO)_{10}$ in methylcyclohexane (45–65 ml) was refluxed with stirring for 6.5–7.0 days. The solution was cooled and filtered, and the filtrate was evaporated to give a residue which was worked up as follows in the individual cases.

(a) 1, $R_1 = R_2 = OCH_3$. The resulting semisolid was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene gave 0.024 g (5.2%) of di-*o*-methoxyphenylmethane [**3**, $R_1 = R_2 = OCH_3$], identified by comparison of spectral data with those for an authentic sample.[12] Elution with benzene–ether (20:1) gave 0.49 g (54.4%) of the orange-red ortho-metalated complex **2** [$R_1 = R_2 = OCH_3$], mp 90–92 °C.

Anal. Calcd for $C_{19}H_{13}O_6SRe$: C, 41.08; H, 2.36; S, 5.77. Found: C, 41.01; H, 2.38; S, 6.05.

Ir ($CHCl_3$), ν_{CO}: 2082 (m), 1990 (vs), 1980 (vs), 1935 (s) cm^{-1}. PMR ($CDCl_3$): δ 3.73, [s, $R_1 = OCH_3$], 3.85 [s, $R_2 = OCH_3$], 6.60 [d, $H_{dd'}$, J_{cd} = 9 Hz], 6.85 [d (br), H_b, J_{ab} = 9 Hz], 6.95 [d, $H_{cc'}$], 7.40 [s (br), $H_{b'}$], 7.73 [d, H_a]. Mass spectrum (*m/e*): 555 $[M]^+$, 527 $[M - CO]^+$, 499 $[M - 2CO]^+$, 471 $[M - 3CO]^+$, 443 $[M - 4CO]^+$.

The methylcyclohexane-insoluble solid was chromatographed on neutral alumina. Elution with benzene gave 4 mg of a yellow organic solid of unknown structure. Further elution with benzene or elution with benzene–ether (9:1) afforded 7–8 mg of tetrakis(*p*-methoxyphenyl)ethylene [**4**, $R_1 = R_2 = OCH_3$], mp 184–185 °C (lit.[4] mp 183.5–184.5 °C).

(b) 1, $R_1 = R_2 = N(CH_3)_2$. The resulting solid was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene gave unreacted $Re_2(CO)_{10}$, followed by 0.040 g (7.0%) of bis(dimethylamino)diphenylmethane [**3**, $R_1 = R_2 = N(CH_3)_2$], mp 89–90.0 °C (lit.[4] mp 90–92 °C).

Elution with 3:1 benzene–methylene chloride gave the orange-red ortho-metalated complex, contaminated with a trace of 4,4'-bis(dimethylamino)benzophenone [oxidation of unreacted thione on work-up]. Pure ortho-metalated complex **2**, $R_1 = R_2 = N(CH_3)_2$ (0.47 g, 40%), was isolated by treatment of the solid with 200 ml of petroleum ether (bp 30–60 °C), filtering, and evaporating the filtrate; mp 168–171 °C.

Anal. Calcd. for $C_{21}H_{19}N_2O_4SRe$: C, 43.37; H, 3.29; S 5.51. Found: C, 42.90; H, 3.39; S, 5.64.

Ir ($CHCl_3$), ν_{CO}: 2089 (m), 1987 (vs), 1970 (vs), 1921 (s) cm^{-1}. PMR ($CDCl_3$): δ 2.90 [s, $R_1 = N(CH_3)_2$], 3.05 [s, $R_2 = N(CH_3)_2$], 6.51 [dd, H_b, J_{ab} = 8.5 Hz, $J_{bb'}$ = 2.0 Hz], 6.70 [d, $H_{dd'}$, J_{cd} and $J_{c'd'}$ = 9.0 Hz], 7.42 [d, $H_{b'}$], 7.55 [d, $H_{cc'}$], 7.78 [d, H_a]. Mass spectrum (*m/e*): 582 $[M^+]$, 554 $[M - CO]^+$, 526 $[M - 2CO]^+$, 498 $[M - 3CO]^+$, 470 $[M - 4CO]^+$.

(c) 1, $R_1 = OCH_3$, R_2 = H. The residue was dissolved in benzene and chromatographed on Florisil. Elution with benzene afforded unreacted $Re_2(CO)_{10}$, followed by 0.018 g (4.5%) of (*p*-methoxyphenyl)phenylmethane.[12] Elution with 1:1 benzene–chloroform gave a mixture of 4-methoxybenzophenone [oxidation of unreacted thione on work-up] and the ortho-metalated complex **2**, $R_1 = OCH_3$, R_2 = H. The latter mixture was chromatographed on neutral alumina. Elution with 50:1 benzene–ether gave 0.317 g (30%) of the ortho-metalated complex **2**, $R_1 = OCH_3$, R_2 = H, as an orange-red oil.

Anal. Calcd. for $C_{18}H_{11}O_5SRe$: C, 41.14; H, 2.11; S, 6.10. Found: C, 41.20; H, 1.95; S, 6.54.

Ir ($CHCl_3$), ν_{CO}: 2084 (m), 1992 (vs), 1976 (vs), 1930 (s) cm^{-1}. PMR ($CDCl_3$): δ 3.67 [s, $R_1 = OCH_3$], δ 6.60–7.90 [m, aromatic protons]. Mass spectrum (*m/e*): 525 $[M]^+$, 497 $[M - CO]^+$, 469 $[M - 2CO]^+$, 441 $[M - 3CO]^+$, 413 $[M - 4CO]^+$.

Attempted Thermal Reaction of Thiobenzophenone [1, $R_1 = R_2$ = H] and 4,4'-Dimethylthiobenzophenone [1, $R_1 = R_2 = CH_3$] with $Re_2(CO)_{10}$. Exposure of thiobenzophenone[13] or 4,4'-dimethylthiobenzophenone[13] to $Re_2(CO)_{10}$ in refluxing methylcyclohexane for 6–8 days gave recovered starting materials in 90–93% yield [some of the thione was oxidized during work-up].

Photolysis of 4,4'-Dimethoxythiobenzophenone [1, $R_1 = R_2 = OCH_3$] and $Re_2(CO)_{10}$. A mixture of 0.516 g (2.00 mmol) of 4,4'-dimethoxythiobenzophenone and 1.305 g (2.00 mmol) of $Re_2(CO)_{10}$ in methylcyclohexane (260 ml) was irradiated for 1.5–2 h. The solution was filtered, and the filtrate was evaporated in vacuo to give a beautiful purple oil. The oil was dissolved in hexane and chromatographed on Florisil. Elution with hexane gave a trace of $Re_2(CO)_{10}$. Elution with 30:1 hexane–ether gave 1.64 g (93%) of 4,4'-dimethoxythiobenzophenonedirhenium nonacarbonyl [**5**, $R_1 = R_2 = OCH_3$]. This purple oil slowly crystallized after being kept either in the freezer or in the vacuum desiccator for 3 weeks; mp 60–62 °C.

Anal. Calcd for $C_{24}H_{14}O_{11}SRe_2$: C, 32.65; H, 1.59; S, 3.63. Found: C, 32.77; H, 1.63; S, 3.84.

Ir ($CHCl_3$), ν_{CO}: 2095 (ms), 2036 (ms), 1995 (vs), 1959 (m), 1928 (m) cm^{-1}. PMR ($CDCl_3$): δ 3.87 [s, methoxy groups], 6.92 [d, *J* = 9 Hz, protons ortho to methoxy-bearing carbons], 7.50 [d, protons meta to methoxy-bearing carbons]. Mass spectrum (*m/e*): 883 $[M]^+$, 855 $[M - CO]^+$, 827 $[M - 2CO]^+$, 799 $[M - 3CO]^+$, 771 $[M - 4CO]^+$, 743 $[M - 5CO]^+$, 715 $[M - 6CO]^+$, 687 $[M - 7CO]^+$, 659 $[M - 8CO]^+$, 631 $[M - 9CO]^+$, 373 $[Re_2]^+$, 258 [4,4'-dimethoxythiobenzophenone(1+)].

Conversion of 4,4'-Dimethoxythiobenzophenonedirhenium Nonacarbonyl [5, $R_1 = R_2 = OCH_3$] to the Ortho-Metalated Complex 2, $R_1 = R_2 = OCH_3$. The dirhenium nonacarbonyl complex **5** [$R_1 = R_2 = OCH_3$] (0.883 g, 1.00 mmol) was dissolved in methylcyclohexane (110 ml) and refluxed for 24 h. The orange-red solution was cooled somewhat and the solvent was then flash evaporated. The residue was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene gave a small amount of $Re_2(CO)_{10}$ [possibly formed from $HRe(CO)_5$]. Elution with 10:1 benzene–ether gave 0.420 g (76%) of the ortho-metalated complex **2**, $R_1 = R_2 = OCH_3$, identical in all respects with the complex obtained by direct thermal reaction of 4,4'-dimethoxythiobenzophenone with $Re_2(CO)_{10}$.

Photolysis of 4,4'-Dimethylthiobenzophenone [1, $R_1 = R_2 = CH_3$] and $Re_2(CO)_{10}$. Irradiation of a mixture of **1**, $R_1 = R_2 = CH_3$, and $Re_2(CO)_{10}$, and subsequent work-up as described for the photolysis of **1**, $R_1 = R_2 = OCH_3$, gave 4,4'-dimethylthiobenzophenonedirhenium nonacarbonyl as an intense purple oil.

Anal. Calcd for $C_{24}H_{14}O_9SRe_2$: C, 33.89; H, 1.65. Found: C, 34.17; H, 1.93.

Ir ($CHCl_3$), ν_{CO}: 2092 (ms), 2035 (ms), 1993 (vs), 1956 (m), 1929 (m) cm^{-1}. Mass spectrum (*m/e*): 851 $[M]^+$, 823 $[M - CO]^+$, 795 $[M - 2CO]^+$, 767 $[M - 3CO]^+$, 739 $[M - 4CO]^+$, 711 $[M - 5CO]^+$, 683 $[M - 6CO]^+$, 655 $[M - 7CO]^+$, 627 $[M - 8CO]^+$, 599 [M –

9CO]+, 372 [Re_2]+, 226 [4,4'-dimethylthiobenzophenone].

Thermolysis of 4,4'-Dimethylthiobenzophenonedirhenium Nonacarbonyl [5, $R_1 = R_2 = CH_3$]. A methylcyclohexane solution (100 ml) of the dirhenium nonacarbonyl complex **5** [$R_1 = R_2 = CH_3$] was refluxed for 24 h. Work-up as described for **5**, $R_1 = R_2 = OCH_3$, gave the orange-red ortho-metalated complex **2**, $R_1 = R_2 = CH_3$, as an oil in 68% yield.

Anal. Calcd for $C_{19}H_{13}O_4SRe$: C, 43.58; H, 2.50; S, 6.10. Found: C, 43.99; H, 2.57; S, 6.06.

Ir ($CHCl_3$), ν_{CO}: 2085 (m), 1988 (vs), 1975 (vs), 1928 (s) cm^{-1}. Mass spectrum (*m/e*): 523 [M]+, 495 [M − CO]+, 467 [M − 2CO]+, 439 [M − 3CO]+, 411 [M − 4CO]+.

Acknowledgment. The author is grateful to the National Research Council of Canada and to Imperial Oil Ltd. for support of this research. I am also indebted to Messrs. Jake Blair and Hector Seguin for recording mass spectra and to Mr. R. Capoor for running 100-MHz PMR spectra.

Registry No. $Re_2(CO)_{10}$, 14285-68-8; **2** ($R_1 = R_2 = OCH_3$), 57652-82-1; **2** ($R_1 = R_2 = N(CH_3)_2$), 57652-83-2; **2** ($R_1 = OCH_3$; $R_2 = H$), 57652-84-3; **5** ($R_1 = R_2 = OCH_3$), 57652-85-4; **5** ($R_1 = R_2 = CH_3$), 57652-86-5; **2** ($R_1 = R_2 = CH_3$), 57652-87-6; **1** ($R_1 = R_2 = N(CH_3)_2$), 1226-46-6; **1** ($R_1 = R_2 = OCH_3$), 958-80-5; **1** ($R_1 = R_2 = CH_3$), 1141-08-8; **1** ($R_1 = OCH_3$; $R_2 = H$), 1141-07-7.

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Kinetics and Mechanism of the Complexation Reactions of Pervanadyl Ion with Some Aminopolycarboxylates

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Received July 2, 1975 AIC50526M

The kinetics of the complex formation reaction of pervanadyl ion with ethylenediamine-*N*,*N*'-diacetic acid (EDDA), *N*-methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA) has been studied spectrophotometrically by means of a stopped-flow technique. The rate of formation of the pervanadyl aminopolycarboxylate is expressed as $d[VO_2Y^{1-n}]/dt = k^+[VO_2^+][H_mY^{m-n}] - k^-[VO_2Y^{1-n}][H^+]^m$, where $k^+ = 10^{8.03}$ M^{-1} s^{-1}, $k^- = 10^{3.16}$ M^{-1} s^{-1}, $m = 1$, and $n = 2$ for EDDA; $k^+ = 10^{3.39}$ M^{-1} s^{-1}, $k^- = 10^{2.76}$ M^{-1} s^{-1}, $m = 1$, and $n = 2$ for MIDA; $k^+ = 10^{5.13}$ M^{-1} s^{-1}, $k^- = 10^{2.70}$ M^{-2} s^{-1}, $m = 2$, and $n = 3$ for NTA, all at 25 °C and $I = 1.0$ M ($NaClO_4$). Lower rate constants for the reaction of VO_2^+ with protonated MIDA and NTA are interpreted by the relatively slow step of proton migration from protonated nitrogen. In the case of VO_2^+–EDDA, the reaction proceeds with the loss of the first water molecule from the aquated VO_2^+ as a rate-determining step. Mechanisms are proposed for the complexation reactions of the protonated ligands and some discussions are made on the difference in the reactivities of these ligands.

Introduction

Because of the lack of information concerning the solution equilibria of the vanadium(V) cation (pervanadyl ion is represented as VO_2^+ in acidic solution), few studies of complexation kinetics involving pervanadyl ion have been undertaken. Only the kinetics of complexation reactions with hydrogen peroxide[1] and ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetic acid[2] have been reported so far. The reaction of pervanadyl ion does not seem to be well understood; we hoped to obtain information about the characteristics of this oxo cation from studies on complexation kinetics.

We have studied the hydrolysis reaction of pervanadyl ion[3] and the complexation equilibria with some aminopolycarboxylates.[4] The present paper describes the kinetic results on the complexation reaction

$$VO_2^+ + Y' \rightleftharpoons VO_2Y$$

where Y' refers to aminopolycarboxylate ion such as ethylenediamine-*N*,*N*'-diacetate (EDDA), *N*-methyliminodiacetate (MIDA), and nitrilotriacetate (NTA). We have utilized the stopped-flow technique to study the reaction.

Experimental Section

Reagents. Methods of preparation and standardization of the reagents (pervanadyl perchlorate, EDDA, MIDA, NTA, sodium perchlorate, and sodium hydroxide) have been described previously.[4]

Measurements. All experiments were carried out in a room thermostated at experimental temperature to ±0.5 °C. The ionic strength was maintained at 1.0 M with sodium perchlorate. Hydrogen ion concentration was determined by a Radiometer pH meter (PHM 22 Type) with a calomel electrode filled with saturated sodium chloride as an internal solution instead of saturated potassium chloride. A 1.000×10^{-2} M perchloric acid solution containing 0.99 M sodium perchlorate was employed as a standard of hydrogen ion concentration ($-\log [H^+] = 2.000$) and the liquid junction potential was taken into consideration.[4]

The kinetics of complexation were studied spectrophotometrically by means of a stopped-flow analyzer, RA 1100 (Union, Ltd., Hirakata, Japan) equipped with a transient recorder (Union RA 108 S). The pervanadyl and the aminopolycarboxylate solutions were brought to temperature equilibrium in a bath kept at a given temperature to ±0.1 °C and then transferred to the thermostated mixing syringes. The changes in absorbance at 270 nm were recorded as a function of reaction time. In all kinetic studies aminopolycarboxylates were present in sufficient excess to ensure the pseudo-first-order reaction.

Results

Under the present experimental conditions the complex formation equilibrium is written as[4]

$$VO_2^+ + Y' \underset{k^{-}_{\mathrm{o(H,Y)}}}{\overset{k^{+}_{\mathrm{o(H,Y)}}}{\rightleftharpoons}} VO_2Y \qquad (1)$$