for such a comparison. One result of the analysis is the emphasis on the interaction constant $f_{rr'}$, which reflects the interaction between the stretching of bonds that are trans to each other. It is this interaction that precludes satisfactory agreement between observed and calculated frequencies using a modified Urey–Bradley force field, and one may muse on the possible implications of this result in regard to phenomena which seemingly involve a trans effect.[39] Although the remaining interaction constants $f_{r\alpha}$, f_{rr}, and $f_{\alpha\alpha}$ are nontrivial to the degree that they are required in order to obtain the good fit observed in Table VI, they are small, and physical interpretation of them would be unwise. Values for the constants $f_{r\alpha}$, f_{rr}, $f_{\alpha\alpha'}$, and $f_{\alpha\alpha}$ from the chromium calculation are transferred to the cobalt analysis. Only the magnitudes of f_r, f_α, and $f_{rr'}$, to which the analysis is more sensitive, are varied. Significantly larger values are required for $Co(NH_3)_6{}^{3+}$ than for $Cr(NH_3)_6{}^{3+}$, and this may be interpreted as reflecting a somewhat firmer coordination bond in the former complex.[21] The stretching force constants should be singled out for comment, since reasonable estimates of their magnitudes are required in the Marcus–Hush theory of electron-transfer rates.[39–42] The constants (f_r = 1.60 mdyn/Å, $Cr(NH_3)_6{}^{3+}$ and f_r = 1.72 mdyn/Å, $Co(NH_3)_6{}^{3+}$) diverge widely from the values reported for K(M–N) from the Urey–Bradley treatment (K(Cr–N) = 0.84 mdyn/Å and K(Co–N) = 1.05 mdyn/Å).[20,21] However, they are remarkably similar to the values of the Urey–Bradley diagonal matrix element of the F_{1u} degenerate stretching coordinate (F_{dia}(CrN) = 1.55 mdyn/Å and F_{dia}(CoN) = 1.75 mdyn/Å), whose relation to the strength of the coordinate bond has been argued.[20,21,23] Also, Block[43] calculated a cobalt–nitrogen stretching force constant of 2.00 mdyn/Å based on a modified valence-force-field treatment of incomplete vibrational data, but including interaction between skeletal and ligand modes. The values of f_r derived from our analyses do not appear to be aberrational, therefore, and their incorporation in kinetic discussions would be feasible.

Photodecomposition. As discussed above, the laser-stimulated decomposition of $Cr(NH_3)_6{}^{3+}$ in aqueous solution is very likely identical with the stepwise photoaquation previously investigated.[4] For the reactions of the crystalline materials, it is not possible to distinguish between a photochemical substitution process and thermal decomposition, since local heating from the focused laser beam could occur. However, there is little reason to believe that the solid-state process is not directly analogous to the aqueous solution reaction with photosubstitution by the outer-sphere anion for an ammine ligand. The occurrence of this substitution process in thermal decompositions of chromium(III) ammines has been well documented,[44,45] and a direct photochemical parallel is available in the reaction of crystalline trisethylenediaminechromium(III) salts.[24] For $Cr(NH_3)_6(NO_3)_3$, the infrared spectrum of the decomposition product is consistent with the formation of a complex in which a nitrate resides in the first coordination sphere of the Cr(III). Once again, the involvement of the ^2E_g state in photosubstitution reactions of Cr(III) is indicated,[5,11–13,34] since this is the state that is resonance populated by the He–Ne laser radiation.

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Autoxidation of a Coordinated Trialkylphosphine[1]

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Abstract: That the sole product of the slow but quantitative autoxidation of $CoCl_2(P(C_2H_5)_3)_2$ in several organic solvents is the phosphine oxide complex $CoCl_2(OP(C_2H_5)_3)_2$ is proven by mass balance and complete characterization[4] of the product. In its initial stages, the reaction is first order in oxygen and first order in complex. Azobisisobutyronitrile and hydroquinone have no effect. A dissociation mechanism is precluded since autoxidation of uncoordinated phosphines is a radical process giving mixed $R_nP(O)(OR)_{3-n}$ products.[5] The mechanism may involve the formation and rearrangement of an O_2 adduct of the cobalt complex. During the reaction in solution the redistribution equilibrium $CoCl_2(P(C_2H_5)_3)_2 + CoCl_2(OP(C_2H_5)_3)_2 \rightleftharpoons 2CoCl_2(P(C_2H_5)_3)(OP(C_2H_5)_3)$ is observed, with an equilibrium constant of about ten. Resolution of the components of the transiton $^4A_2 \rightarrow {}^4T_1(P)$ (T_d) is partial in the complexes $CoCl_2L_2$ (C_{2v}) and complete in the complex $CoCl_2LL'$ (C_s).

In the autoxidation of free trialkylphosphines,[5] intermediate phosphoranyl radicals $RO\dot{P}R_3$ can decompose to give phosphine oxides or to give trivalent phosphorus esters $ROPR_2$, susceptible to further oxidation.[6] In this way, a mixture of all the $R_nPO(OR)_{3-n}$ products is obtained. In a coordinated phosphine ligand, phosphorus is four coordinate and its lone pair is involved in the σ portion of the coordinate bond. In the autoxida-

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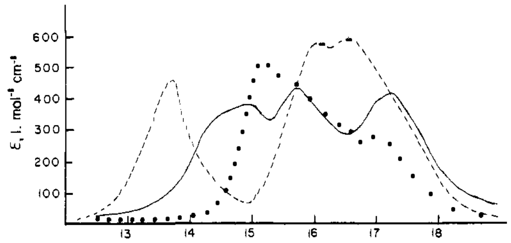

Figure 1. Visible spectra of cobalt complexes in benzene: - - -, $CoCl_2(P(C_2H_5)_3)_2$; ●, $CoCl_2(OP(C_2H_5)_3)_2$; —, 1:1 mixture.

tion of transition metal–phosphine complexes, examples have been reported of oxidation of the metal or of the phosphine or both, and of the formation of both reversible and irreversible oxygen adducts.[7–10] Jensen and coworkers[11] report that $CoCl_2(P(CH_3)_3)_2$ is oxidized to a cobalt(III) complex, while solid $CoCl_2(P(C_2H_5)_3)_2$ is said to be "easily oxidized on lying in the air . . . attains a lighter blue color and becomes insoluble in pentane, being transformed into a complex compound of the phosphine oxide." No experimental evidence is given. Some phosphine complexes, such as $Co(NCS)_2(P(C_2H_5)_3)_2$, react instantly with air,[12] while others, such as $NiBr_2(P(CH_3)_3)_3$, are scarcely affected.[13] The decomposition of dichlorobis(tri-*n*-butylphosphine)cobalt(II) in an oxygen–helium atmosphere at elevated temperatures has been described.[14]

A study of the autoxidation of dichlorobis(triethylphosphine)cobalt(II) is now reported. The characterization of the complete series of potential autoxidation products, $CoCl_2[(C_2H_5)_nPO(OC_2H_5)_{3-n}]_2$, has been reported previously.[4]

Results

Dichlorobis(triethylphosphine)cobalt(II) was found to be stable in dry air, in contrast to the previous report.[11] When the complex was stored under an atmosphere of pure oxygen at room temperature for 1 day, there was no change in pressure or in the weight, color, or pentane solubility of the complex. The complex is slightly hygroscopic, and presumably Jensen's observations were due to moisture. Autoxidation does take place in various organic solvents, slowly at room temperature, as is indicated by oxygen consumption, lightening of the blue color, and changes in the infrared spectrum. The sole product of quantitative autoxidation in benzene, *o*-dichlorobenzene, and *tert*-butylbenzene is dichlorobis(triethylphosphine oxide)cobalt(II) as is proven by the gain in weight (corresponding to exactly 1.00 mol of oxygen/mol of complex) and the elemental analysis, melting point, and infrared spectrum of the product,[4] as well as the isolation of triethylphosphine oxide in pure form following its displacement from the cobalt complex by pyridine.

Visible Spectra. A surprising result was found when visible spectra were obtained of samples removed at various times during the course of the autoxidation reaction in benzene. These spectra consist of three major peaks, the positions of which do not correspond to any of the peaks in the spectra of the starting material or of the final product. This anomaly was explained by the finding that mixtures of benzene solutions of the pure phosphine and phosphine oxide complexes do not obey Beer's law and show the same three-peak spectrum. Identical spectral behavior was found in *tert*-butylbenzene, but not in *o*-dichlorobenzene (*vide infra*). The spectra of benzene solutions of $CoCl_2(P(C_2H_5)_3)_2$, $CoCl_2(OP(C_2H_5)_3)_2$, and a 1:1 mixture of them are given in Figure 1. Continuous-variations plots[15] for benzene and *tert*-butylbenzene solutions are shown in Figure 2; these clearly indicate a 1:1 interaction of the two complexes, for which a redistribution equilibrium reaction may be written.

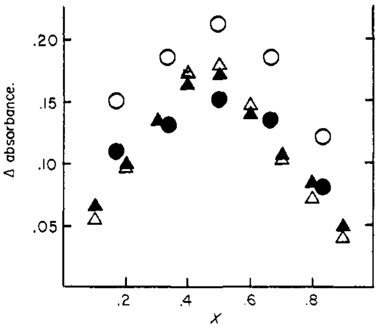

Figure 2. Continuous variations studies; X = $[CoCl_2(OP(C_2H_5)_3)_2]/\{[CoCl_2(P(C_2H_5)_3)_2] + [CoCl_2(OP(C_2H_5)_3)_2]\}$, [Co] = 1.00 × 10^{-3}. Benzene, 24°: ○, 700 nm; ●, 669 nm. *tert*-Butylbenzene, 700 nm: △, 36°; ▲, 65°.

$$CoCl_2(P(C_2H_5)_3)_2 + CoCl_2(OP(C_2H_5)_3)_2 \rightleftharpoons 2CoCl_2(P(C_2H_5)_3)(OP(C_2H_5)_3)$$

An accurate evaluation of the equilibrium constant from spectrophotometric data was not practical in this system owing to continuous overlap of the spectra of the components throughout the region of interest and to the low concentration range available because of solubility limitations. Approximate values were obtained[15] using Schaeppi and Treadwell's tangent method and Schwarzenbach's method modified for use with a nonlinear least-squares curve-fitting program.[16] In both solvents and at the several temperatures studied, values of the order of magnitudes of ten were obtained for the equilibrium constant.

Kinetic Studies. Volumetric measurements were made of the rate of absorption of oxygen gas by *tert*-butylbenzene solutions of dichlorobis(triethylphosphine)cobalt(II) at 36°. The oxygen pressure was held constant during each run. The agitation was sufficient that diffusion across the gas–liquid interface was nonlimiting. Autoxidation of the solvent was negligible. Plots of gas absorption *vs.* time are given in Figure 3. At constant oxygen pressure, doubling or tripling the concentration of complex increases the rate proportionally, while at constant complex concentration, doubling the oxygen pressure doubles the rate. Hence in the initial stages of the reaction the rate law is

$$d(\text{mol of } O_2)/dt = k[CoCl_2(P(C_2H_5)_3)_2]P_{O_2}$$

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Table I. Solvent Effects on the Visible Spectrum of $CoCl_2(P(C_2H_5)_3)_2$

Solvent	Absorption maxima, nm (extinction coefficient)[a]
Benzene	730 (460) s, 623 (580), 606 (590)
tert-Butylbenzene	730 (380) s, 622 (520), 603 (530)
n-Pentane	730 br, 610 sh, 590 sh, 580 br, 570 sh
Chloroform	716 (450) s, 613 (650)
Acetone	715 (350) s, 620 (430) sh, 600 (470)
o-Dichlorobenzene	690 (430), 654 (410), 640 (410), 608 (510)
o-Dichlorobenzene[b]	683 (500), 650 (480), 606 (480)
Carbon tetrachloride	668 ($>10^3$), 555 ($>5\times10^3$), 470 ($>5\times10^2$) sh

[a] Abbreviations: s = sharp, br = broad, sh = shoulder. [b] At 50°.

Pseudo-first-order plots were constructed as follows, of the function $\ln [CoCl_2(P(C_2H_5)_3)_2]/[CoCl_2(P(C_2H_5)_3)_2]_0$ *vs.* time. The number of moles of oxygen absorbed at each time was taken to represent conversion of phosphine complex to phosphine oxide complex, using the equation

$$CoCl_2(P(C_2H_5)_3)_2 + O_2 \longrightarrow CoCl_2(OP(C_2H_5)_3)_2$$

The concentration of original phosphine complex remaining was then calculated using approximate values of the equilibrium constant for the redistribution reaction. Data from experiments with three different starting concentrations of cobalt complex fell on the same pseudo-first-order curve, but this was linear only for the first quarter-life. It then bent upward, indicating retardation of the later stages of the reaction. Values of the redistribution equilibrium constant from 10 to 40 were tried; a higher order of magnitude would be needed to improve the linearity of the kinetic plot.

Also shown in Figure 3 are measurements of the rate of oxygen consumption of *tert*-butylbenzene solutions of dichlorobis(triethylphosphine)cobalt(II) at 65° containing azobisisobutyronitrile (AIBN), hydroquinone, and no additive. Data from the three experiments fell on the same curve.

Discussion

Spectra of the Cobalt(II) Complexes. The visible absorption is due to the transition $\nu_3 = {}^4A_2 \rightarrow {}^4T_1(P)$ in tetrahedral symmetry, which is decomposed to ${}^4A_2 \rightarrow {}^4A_2 + {}^4B_1 + {}^4B_2$ in microsymmetry C_{2v} (CoX_2L_2) and to ${}^4A'' \rightarrow {}^4A' + 2{}^4A''$ in microsymmetry C_s (CoX_2LL'). From Figure 1, it is seen that the approximation of an average ligand environment applies better to $CoCl_2(OP(C_2H_5)_3)_2$ than it does to $CoCl_2(P(C_2H_5)_3)_2$. That there is much less splitting of the transition in the phosphine oxide complex is reasonable in terms of the greater similarity of chloride to oxygen than to phosphorus in coordinate bond type and position in the spectrochemical series.

The spectrum of the phosphine complex has been reported previously in benzene solution[17] and in reflectance.[18] In the solution spectrum, resolution of the three components of the transition into a peak at 730 nm and a doublet at 623 and 606 nm is apparent. A very similar splitting, and its loss on dissolution in nitromethane, has been reported for the corresponding triphenylphosphine complex.[19] Some significant solvent effects on the visible spectrum of dichlorobis(triethylphosphine)cobalt(II) are demonstrated by the data of Table I. The spectra in the first five solvents listed are similar. Significant differences in *o*-dichlorobenzene may be attributed to partial ionic dissociation in this solvent; at room temperature the molar conductance of a 10^{-3} *M* solution was 0.27 ohm^{-1} cm^2 mol^{-1}, which may be compared to the value 1.43 ohm^{-1} cm^2 mol^{-1} found for tetra-*n*-butylphosphonium chloride in this solvent. In carbon tetrachloride, a 10^{-3} *M* solution could not be prepared at room temperature; the solubility appeared to be somewhat less than half of this. The very intense band at 555 nm of the deep violet solution suggests a rapid chemical change, perhaps a radical oxidation–reduction.[20]

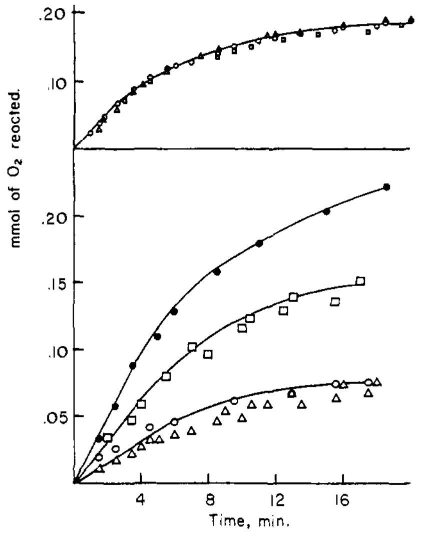

Figure 3. Reaction of O_2 with $CoCl_2(P(C_2H_5)_3)_2$ (40.0 ml of *tert*-butylbenzene solution). Bottom, 36°: ●, 1.95×10^{-2} *M* Co, 678 Torr; □, 1.31×10^{-2} *M* Co, 678 Torr; ○, 0.65×10^{-2} *M* Co, 678 Torr; △, 1.31×10^{-2} *M* Co, 339 Torr. Top, 65°, 1.31×10^{-2} *M* Co, 679 Torr: △, 0.76×10^{-3} *M* AIBN; □, 1.00×10^{-3} *M* hydroquinone; ○, no additive (duplicate runs).

With an order of magnitude of ten for the redistribution equilibrium constant, the mixed complex $CoCl_2(P(C_2H_5)_3)(OP(C_2H_5)_3)$ is the predominant solute species present in a 1:1 mixture of 10^{-3} *M* solutions of $CoCl_2(P(C_2H_5)_3)_2$ and $CoCl_2(OP(C_2H_5)_3)_2$. The resolution of the three components of the visible transition is seen from Figure 1 to be complete for this mixed complex of microsymmetry C_s. The approximate value of the equilibrium constant is reasonable statistically for a redistribution reaction in which coordinate bond energy changes are small.

The Autoxidation Reaction. A dissociative mechanism can be eliminated, since the autoxidation of uncoordinated tertiary phosphines gives a mixture of products, $R_nP(O)(OR)_{3-n}$, n = 0–3, and is subject to radical initiation and inhibition.[5] For the reaction

$$CoCl_2(PR_3)_2 + O_2 \longrightarrow CoCl_2(OPR_3)_2$$

it seems reasonable energetically that the formation of the two new P=O bonds should be closely associated with the rupture of the O—O bond. The formation and

$$CoCl_2(PR_3)_2 + O_2 \rightleftharpoons O_2CoCl_2(PR_3)_2 \qquad (1)$$

$$O_2CoCl_2(PR_3)_2 \longrightarrow CoCl_2(OPR_3)_2 \qquad (2)$$

subsequent rearrangement of an O_2 adduct[21] would be consistent with the results of the initial-rate studies.

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A "dissociative oxygen insertion" step of this type has been suggested previously.[22]

No evidence for an oxygen adduct in any measurable concentration was found in this work, and such a species might correspond to a transition state rather than an intermediate. The initial tetrahedral configuration around cobalt would not be expected to be as favorable to the formation of a stable adduct as square-planar and square-pyramidal geometries would be. However, carbon monoxide and nitric oxide adducts of dichlorobis(triethylphosphine)cobalt(II) have been isolated.[23]

After the reaction has proceeded for a short time, a mixture of complex solute species is present. Both the phosphine and phosphine oxide complexes, while stable, are expected to be labile.[24] The redistribution equilibrium should be established rapidly, with the mixed ligand complex becoming the major species present.

$$CoCl_2(P(C_2H_5)_3)_2 + CoCl_2(OP(C_2H_5)_3)_2 \rightleftharpoons 2CoCl_2(P(C_2H_5)_3)(OP(C_2H_5)_3) \quad (3)$$

The formation and rearrangement of a monomeric O_2 adduct of the mixed-ligand complex would not allow the formation of two new P═O bonds to compensate energetically for O—O bond rupture. However, an O_2-bridged binuclear complex[25] might be involved in an alternative slower route to the final product.

$$2CoCl_2(PR_3)(OPR_3) + O_2 \longrightarrow (R_3PO)(R_3P)Cl_2Co\text{-}O\text{-}O\text{-}CoCl_2(PR_3)(OPR_3) \quad (4)$$

$$(R_3PO)(R_3P)Cl_2Co\text{-}O\text{-}O\text{-}CoCl_2(PR_3)(OPR_3) \longrightarrow 2CoCl_2(OPR_3)_2 \quad (5)$$

The observed retardation of the reaction in its intermediate stages might possibly be due to the formation of similar binuclear bridged species involving the starting cobalt complex.

Violet Solutions. Such solutions, characterized by intense absorption in the 550–570-nm region, were obtained when unpurified hydrocarbon solvents were used, when dichlorobis(triethylphosphine)cobalt(II) solutions were exposed to the open air, or in the presence of benzoyl peroxide. Peroxides are known to react directly with tertiary phosphines and with their cobalt(II) halide complexes.[26] Free radicals could be present under the conditions where these intensely absorbing unknown species are present. The intensity and position of the absorption resemble those found in carbon tetrachloride solution (Table I). Peroxy radical containing complexes such as $RO_2^{\delta-}Co^{(2+\delta)+}$ might be involved.[27]

Experimental Section

Materials. The preparation of dichlorobis(triethylphosphine)cobalt(II) from its components in absolute ethanol[28] was found to be preferable to the synthesis in the absence of solvent;[18] mp 100–102° (lit.[29] mp 102°). *Anal.* Calcd for $CoCl_2C_{12}H_{30}P_2$: Co, 16.09. Found: Co, 16.11. Solvents were purified by standard methods. Solutions for spectral measurements, reaction studies, etc., were prepared under nitrogen in a drybox. Oxygen gas, USP, was passed through Drierite. Azobisisobutyronitrile and benzoyl peroxide were recrystallized. Hydroquinone (Matheson Coleman and Bell) was used as received.

Spectra and Analyses. These were obtained as previously described.[4]

Product of the Autoxidation Reaction. Solutions containing known amounts of the cobalt phosphine complex were placed in a one-piece glass apparatus consisting of a 500-ml flask with a gas dispersion tube extending to its bottom and surmounted by a long condenser. The flask was immersed in a hot mineral oil bath. Oxygen was bubbled exhaustively (1–2 weeks) through the apparatus and out through a bubbler trap.

With benzene as the solvent, the product was recovered quantitatively after removal of the solvent *in vacuo*. A 0.2489-g quantity of oxygen was taken up by 2.8512 g of complex, corresponding to a mole ratio of 0.999. Thus the product was $CoCl_2(OP(C_2H_5)_3)_2$. *Anal.* Calcd for $CoCl_2C_{12}H_{30}P_2O_2$: Co, 14.80; Cl, 17.81. Found: Co, 14.86; Cl, 17.85. The visible spectrum in benzene of the reaction product was identical with that previously reported[4] for authentic $CoCl_2(OP(C_2H_5)_3)_2$. A sample of the reaction product was treated with an excess of pyridine in a vacuum-line reaction bulb and allowed to stand for several days. The volatile components were then distilled through 0 and −23° traps into a −196° trap. The 0° trap contained a white solid, mp 51.5° (triethylphosphine oxide, lit.[30] mp 50°).

When *o*-dichlorobenzene was the reaction solvent, the blue solid recovered on evaporation of the solvent *in vacuo* was recrystallized from ethanol, mp 75–77° (dichlorobis(triethylphosphine oxide)-cobalt(II), lit.[4] mp 76–77°). *Anal.* Found: Co, 14.75; Cl, 17.81. The ethanol filtrate was evaporated to give a solid residue. *Anal.* Found: Co, 14.33; Cl, 17.59. Infrared spectra of both solids were identical with that of authentic $CoCl_2(OP(C_2H_5)_3)_2$, especially in the 940–1060-cm^{-1} region (absence of P–O–C ester groups) and the $\nu_{P=O}$ position (1100 cm^{-1}). These ir frequencies have been shown[4] to be diagnostic in the characterization of the $CoCl_2(OP(C_2H_5)_n(OC_2H_5)_{3-n})_2$ complexes.

The reaction product from *tert*-butylbenzene solution was identically characterized as the phosphine oxide complex by melting point and infrared spectrum.

Kinetic Measurements. The apparatus consisted of a manifold connected to a vacuum pump and an oxygen source by a three-way stopcock, and fitted with a manometer, a 50-ml gas buret and mercury leveling bulb, and a stopcock and tapered joint for the reaction flask. This vessel was a jacketed 50-ml erlenmeyer flask with four indentations in the wall to increase the agitation provided by a magnetic stirrer. The cobalt complex solution was introduced under nitrogen in the drybox. The reaction vessel was then attached to the manifold and evacuated. Water from a constant-temperature bath was circulated through the jacket. The manifold and attached gas volumetric apparatus was evacuated and filled with oxygen several times. The stopcock to the reaction flask was opened, the manometer level was quickly set using a cathetometer, and stirring was commenced (zero time). The absorption of gas was sufficiently slow to permit maintenance of constant pressure to within 1 mm by occasional manual adjustment of the leveling bulb. The number of moles of oxygen absorbed was calculated from gas volume changes using the ideal gas law, for which purpose room temperature was kept constant to within 1°. Unstirred solutions absorbed oxygen more slowly, but in the range of agitation used for the kinetic studies the rate of reaction was unchanged by changes in the rate of stirring. Blank runs established that oxygen absorption by the solvent was negligible under the conditions used.

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