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Preparation and Chemistry of $Mo(CO)_3(S_2PPh_2)_2$

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Molybdenum(II) and tungsten(II) are known to form an extensive series of 1,1-dithiolate complexes of the type $M(CO)_2L(\overline{SS})_2$ (M = Mo, W; $\overline{SS}$ = S_2CNR_2, S_2COMe, $S_2P(OEt)_2$, $S_2P(i\text{-}Pr)_2$; L = two-electron σ-donor ligand).[1-10] The parent tricarbonyl complexes are known for the cases of $Mo(CO)_3(S_2CNR_2)_2$,[4,11] $Mo(CO)_3(S_2P(i\text{-}Pr)_2)_2$,[3] and $W(CO)_3(S_2CNR_2)_2$.[8,10,12] A salient aspect of the reactivity of these d^4, 18-electron tricarbonyl systems is their ability to form the analogous isolable 16-electron dicarbonyl species via a reversible decarbonylation reaction as shown in eq 1.

$$M(CO)_3(\overline{SS})_2 \rightleftarrows M(CO)_2(\overline{SS})_2 + CO \qquad (1)$$

We report herein the preparation of $Mo(CO)_3(S_2PPh_2)_2$ (**1**), a complex that surprisingly shows no tendency to form an isolable $Mo(CO)_2(S_2PPh_2)_2$ species. Despite this anomalous behavior, **1** provides a convenient entry point to the synthesis of a number of bis(diphenyldithiophosphinato)molybdenum complexes.

Experimental Section

All reactions were performed either in vacuo or under a nitrogen atmosphere by using standard Schlenk techniques. All solvents were stored over appropriate drying agents and distilled directly into the reaction vessels. HS_2PPh_2 was purchased from Alfa Ventron and used as received. All other chemicals were reagent grade. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 1330 spectrophotometer and were calibrated with the use of a polystyrene film. ^1H (100.1 MHz) and ^{31}P (40.5 MHz) NMR spectra were obtained on a Varian XL-100 instrument and were referenced to internal Me_4Si and external 35% H_3PO_4/D_2O, respectively. ^{13}C (100.1 MHz) NMR spectra were obtained on an IBM/Bruker WM-400 instrument and were referenced to Me_4Si. All spectra were measured at 30 ± 1 °C. Elemental analyses were performed by Galbraith Laboratories. The complexes $Mo(CO)_4Br_2$[13] and $MoO_2(S_2PPh_2)_2$[14] were prepared according to the literature methods. Aryl azides were prepared from the reaction of the corresponding arenediazonium tetrafluoroborate salts with NaN_3 in an Et_2O/H_2O mixture and were purified by distillation at reduced pressure (ca. 10^{-4} torr).

$Mo(CO)_3(S_2PPh_2)_2$ (1). $MoBr_2(CO)_4$ (1.73 g, 4.7 mmol) was added to a stirred, filtered solution of HS_2PPh_2 (2.6 g, 10.4 mmol) in absolute methanol (40 mL) at room temperature. Immediate and vigorous gas evolution was observed, which was accompanied by the rapid formation of a burgundy-colored precipitate. After 20 min of stirring, the product was filtered, washed with 50 mL of absolute methanol, and dried in vacuo. The yield was 3.1 g (97%). Anal. Calcd for $C_{27}H_{20}O_3P_2S_4Mo$: C, 47.79; H, 2.95. Found: C, 47.70; H, 2.94. IR: ν(CO) 2022, 1952, 1918 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.61-8.13 ppm (complex multiplet). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 79.77 ppm (singlet). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 235.6 (CO, singlet), 136.5 (ipso, doublet, $^1J_{P-C}$ = 75 Hz), 131.5 (para, doublet, $^4J_{P-C}$ = 3.7 Hz), 129.5 (meta or ortho, doublet, J_{P-C} = 12.7 Hz), 127.8 ppm (ortho or meta, doublet, J_{P-C} = 13.4 Hz). $\bar{M}$ (CH_2Cl_2 solution; isopiestic method): calcd, 678; found, 675 ± 30.

$Mo(CO)_3(S_2PPh_2)_2$, ^{13}CO Enriched. A sample of $Mo(CO)_3(S_2PPh_2)_2$ in CH_2Cl_2 was stirred under ca. 600 mmHg pressure of ^{13}CO (90% ^{13}C, KOR) for 4 h at 40 °C and then stirred at ambient temperature for an additional 10 h. After the gases were removed in vacuo, this procedure was repeated. Evaporation of solvent left $Mo(CO)_3(S_2PPh_2)_2$ that was ca. 90% enriched in ^{13}CO as judged by infrared spectroscopy. IR: ν(CO) 2010, 1974, 1892 (sh), 1873 cm^{-1}.

$Mo(CO)_2(PPh_3)(S_2PPh_2)_2$ (2a). A portion of **1** (1.00 g, 1.47 mol) was dissolved in benzene (20 mL), and an excess of PPh_3 (0.77 g, 2.94 mmol) was added, causing immediate gas evolution and forming a purple precipitate. The reaction was stirred at ambient temperature for 1 h, then Et_2O (25 mL) was added, and the purple product was isolated by filtration, washed with an additional 30 mL of Et_2O, filtered out, and dried in vacuo. The complex is not very soluble in ordinary organic solvents. Anal. Calcd for $C_{44}H_{35}O_2P_3S_4Mo$: C, 57.89; H, 3.86. Found: C, 57.97; H, 4.01. IR: ν(CO) 1924, 1838 cm^{-1}.

$Mo(CO)_2(EtPh_2P)(S_2PPh_2)_2$ (2b). A sample of **1** (0.75 g, 1.1 mmol) was placed in a side arm that was attached to an evacuable flask containing ca. 0.1 mL of $EtPh_2P$. The vessel was evacuated, and ca. 30 mL of CH_2Cl_2 was introduced by distillation. The sample of **1** was added to the stirred $EtPh_2P$ solution at room temperature, causing immediate gas evolution and forming a rich burgundy-colored solution. After being stirred for 1 h, the solution was evaporated to dryness yielding a red-purple glassy residue. Et_2O (25 mL) was distilled into the system. Initially, the Et_2O acquired a deep red color, with little or no insoluble material remaining. After ca. 20 min, the Et_2O solution blanched and deposited a salmon-colored powder. This solid was stirred an additional 1 h and then was isolated by filtration. The salmon-colored product was washed with an additional 25 mL of Et_2O, filtered out, and dried in vacuo. IR: ν(CO) 1935, 1840 cm^{-1}. Anal. Calcd for $C_{40}H_{37}O_2P_3S_4Mo$: C, 55.42; H, 4.27. Found: C, 55.26; H, 4.30.

$Mo(CO)_2(py)(S_2PPh_2)_2$ (2c). A portion of **1** (0.40 g, 0.59 mmol) was placed in a side arm that was attached to an evacuable flask containing ca. 0.2 mL of pyridine. After evacuation, 25 mL of CH_2Cl_2 was introduced by distillation. The addition of **1** to the stirred pyridine solution led to modest gas evolution and the deposition of small amounts of a bright orange powder. After the reaction mixture was stirred for 3 h at room temperature, solvent volume was reduced to ca. 10 mL and the bright orange product was collected by filtration, washed with 30 mL of MeOH, and dried in vacuo. IR: ν(CO) 1924, 1845 cm^{-1}. Anal. Calcd for $C_{31}H_{25}NO_2P_2S_4Mo$: C, 51.03; H, 3.45; N, 1.92. Found: C, 50.92; H, 3.56; N, 1.95.

$Mo(CO)(PhC_2H)(S_2PPh_2)_2$. A portion of **1** (0.51 g, 0.75 mmol) was added to a stirred solution of phenylacetylene (0.082 g, 0.8 mmol) in CH_2Cl_2 (25 mL). Mild gas evolution was observed, and within 1 min the solution acquired a jade green color. After 1 h of stirring, solvent was evaporated and the green residue was triturated with hexane (30 mL). The green product was collected by filtration, washed with an additional 30 mL of hexane, and dried in vacuo. Anal. Calcd for $C_{33}H_{26}OP_2S_4Mo$: C, 54.69; H, 3.62. Found: C, 54.97, H, 3.86. IR: ν(CO) 1931 cm^{-1}. ^1H NMR (CD_2Cl_2): 12.54 (singlet, 1 H, $PhC_2\mathit{H}$), 7.95–7.20 ppm (complex multiplet, 25 H, $\mathit{Ph}C_2H$ + $S_2P\mathit{Ph}_2$). $^{13}C\{^1H$, gated$\}$ NMR (C_6D_6): 235.2 (singlet, CO), 209.5 ppm (doublet, $^1J_{C-H}$ = 218 Hz, $PhC{\equiv}\mathit{C}H$).

$Mo(Ntol)_2(S_2PPh_2)_2$ (3a). A sample of **1** (1.5 g, 2.2 mmol) was added to an evacuated, stirred solution of *p*-tolyl azide (0.625 g, 4.7 mmol) in CH_2Cl_2 (30 mL), causing prominent gas evolution and forming a dark orange solution. The evolved gases were periodically removed in vacuo over a 2-h period, and then the solution was stirred at room temperature for 16 h. The solvent volume was reduced to approximately 5 mL, and hexane (30 mL) was introduced, causing the deposition of a maroon powder. The product was collected by filtration, washed with 40 mL of hexane, and dried in vacuo. Anal. Calcd for $C_{38}H_{34}N_2P_2S_4Mo$: C, 56.71; H, 4.26; N, 3.48. Found: C, 55.72; H, 4.58; N, 3.05. ^1H NMR (CD_2Cl_2): 8.01–7.37 (complex

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(1) Abbreviations used herein: R = hydrocarbyl group, Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Ph = phenyl, tol = *p*-tolyl, Ar = aryl, py = pyridine, mes = 2,4,6-mesityl.

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multiplet, 20 H, S_2PPh_2), 6.90 (AB quartet, J_{AB} = 8 Hz, 8 H, $C_6H_4CH_3$), 2.32 ppm (singlet, 6 H), $C_6H_4CH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 65.75 ppm (singlet). $Mo(Ntol)_2(S_2PPh_2)_2$ may also be prepared by substituting $Mo(CO)_2(py)(S_2PPh_2)_2$ for $Mo(CO)_3(S_2PPh_2)_2$ in the above procedure.

$Mo(Nmes)_2(S_2PPh_2)_2$ (3b). This compound was prepared in a manner entirely analogous to that for $Mo(Ntol)_2(S_2PPh_2)_2$ as described above using **1** (0.89 g, 1.3 mmol) and 2,4,6-mesityl azide (0.47 g, 2.9 mmol). Anal. Calcd for $C_{42}H_{42}N_2P_2S_4Mo$: C, 58.59; H, 4.92; N, 3.25. Found: C, 57.39; H, 5.01; N, 2.94. ^1H NMR (CD_2Cl_2): 7.97–7.26 (complex multiplet, 20 H, S_2PPh_2), 6.62 (singlet, 4 H, $C_6H_2(CH_3)_3$), 2.21 ppm (singlet, 18 H, $C_6H_2(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 65.13 ppm (singlet).

Reaction of 1 and $MoO_2(S_2PPh_2)_2$. A portion of **1** (0.325 g, 0.48 mmol) was added to a solution of $MoO_2(S_2PPh_2)_2$ (0.30 g, 0.48 mmol) in 30 mL of CH_2Cl_2. An intensely purple solution formed immediately, accompanied by vigorous gas evolution. The reaction was stirred at ca. 40 °C for 1.5 h during which time the solution acquired a rich red color. The reaction was filtered and evaporated to dryness, yielding a lilac-colored product, which was shown to be $MoO(S_2PPh_2)_2$ by comparison of its IR and ^{31}P NMR spectra to those of an authentic sample prepared from $MoO_2(S_2PPh_2)_2$ and Ph_3P.[14] IR: ν(MoO) 980 cm^{-1}. $^{31}P\{^1H\}$ NMR(CD_2Cl_2): −33.85 ppm (singlet).

Thermal Decomposition of 1. A sample of **1** (1.00 g, 1.47 mmol) was dissolved in 30 mL of 1,2-dichloroethane and heated to 50 °C in a water bath. Gas was slowly and continuously evolved over a period of 24 h, and the solution gradually darkened to a brownish color. Evaporation of solvent left a very dark green powder. An IR spectrum of this material confirmed the loss of all CO ligands and, except for the appearance of a new medium-intensity band at 550 cm^{-1}, was otherwise similar to the spectrum of **1**. ^1H NMR (CD_2Cl_2): 7.97–7.13 ppm (complex multiplet). This material appears air stable both as a solid and in solution (as judged by its invariant infrared spectrum) although its solubility in common organic solvents was observed to decrease with time. A similar product is obtained when **1** is warmed to >40 °C in C_6H_6 solution.

Results and Discussion

The reaction between $Mo(CO)_4Br_2$ and HS_2PPh_2 in MeOH proceeds readily at ambient temperature as shown in eq 2.

$$Mo(CO)_4Br_2 + 2HS_2PPh_2 \rightarrow \underset{\mathbf{1}}{Mo(CO)_3(S_2PPh_2)_2} + CO + 2HBr \qquad (2)$$

The burgundy-colored solid thus obtained is air stable for months while room-temperature solutions of **1** appear stable to air for a few hours. **1** is monomeric in solution. The IR spectrum of **1** displays three strong absorptions assignable as ν(CO) at 2022, 1952, and 1918 cm^{-1}. These values are similar to those previously reported for the analogous $Mo(CO)_3(S_2P(i\text{-}Pr)_2)_2$[3] and $M(CO)_3(S_2CNR_2)_2$ (M = Mo,[11] W[8,10,12]) systems.

Neither solid **1** nor MeOH suspensions of **1** show any evidence for decarbonylation in vacuo to yield the expected $Mo(CO)_2(S_2PPh_2)_2$ species. This behavior was most surprising, given the relatively high CO stretching frequencies observed for **1** and considering the ease with which similar molybdenum systems lose CO.[3,4,9,11] Indeed, pure $Mo(CO)_3(S_2P(i\text{-}Pr)_2)_2$ is known only in solution and suffers spontaneous decarbonylation to $Mo(CO)_2(S_2P(i\text{-}Pr)_2)_2$ upon attempted isolation.[3] When benzene or 1,2-dichloroethane solutions of **1** are warmed to >40 °C, CO is slowly and continuously evolved over a period of ca. 24 h and a homogeneous green-brown solution results. Examination of the IR spectra of aliquots removed periodically from the reaction vessel during the thermolysis process showed that no new carbonyl-containing species were present. The IR spectrum of the dark green powder obtained by solvent evaporation was virtually identical with the spectrum of **1**, except for the loss of the three original CO absorptions and the appearance of a new medium-intensity band at 550 cm^{-1}. In fact, the IR spectrum (and color) of this material is remarkably similar to that of the recently reported $Mo_2(S_2PPh_2)_4$ species.[15] However, various physicochemical data obtained for the thermolysis product(s) of **1**, in particular its elemental analysis[16] and its observed solubility in ordinary organic solvents, preclude its formulation as $Mo_2(S_2PPh_2)_4$. Likewise, its $^{31}P\{^1H\}$ NMR spectrum was extraordinarily complex, displaying numerous resonances between 103 and 25 ppm. We have not been successful in purifying this material, and we remain unsure as to its composition.

The difference in stability between $Mo(CO)_3(S_2PPh_2)_2$ and $Mo(CO)_3(S_2P(i\text{-}Pr)_2)_2$ (and their corresponding dicarbonyl complexes) is puzzling. The basicities of dithiophosphinate anions, $R_2PS_2^-$, are virtually insensitive to the nature of R,[17] and thus an explanation based on steric effects is offered. Using Tolman's values[18] for the cone angles of metal–phenyl and metal–isopropyl groups (105 and 114° respectively), we calculate values of 111 and 120° for the cone angles of P–Ph and P–(i-Pr) groups, respectively.[19] Thus the observed instability of $Mo(CO)_3(S_2P(i\text{-}Pr)_2)_2$ may reflect unfavorable steric interactions between the CO ligands and the alkyl groups. Clearly, however, more complexes of this type must be investigated before firm conclusions can be drawn.

When solutions of **1** are warmed under an atmosphere of CO, the thermal decomposition process is suppressed and **1** may be recovered unchanged. Similarly, ^{13}CO-enriched **1** is produced by warming a solution of **1** under an atmosphere of ^{13}CO. σ-Donor ligands, such as organophosphines or pyridine, also react readily with solutions of **1** to afford substitution products as shown in eq 3. The IR spectra of compounds **2**

$$\underset{\mathbf{1}}{Mo(CO)_3(S_2PPh_2)_2} + L \rightarrow \underset{\substack{\mathbf{2a},\ L\,=\,Ph_3P\\ \mathbf{2b},\ L\,=\,EtPh_2P\\ \mathbf{2c},\ L\,=\,py}}{Mo(CO)_2L(S_2PPh_2)_2} + CO \qquad (3)$$

each show two strong ν(CO) absorptions at ca. 1930 and 1840 cm^1, in good agreement with previously reported values for similar systems.[2-10] The above results are understandable by assuming that **1** participates in a rapid preequilibrium wherein minute amounts of the reactive and unstable 16-electron species $Mo(CO)_2(S_2PPh_2)_2$ are produced via CO dissociation (eq 4). In the absence of added reagents, if the CO thus

$$Mo(CO)_3(S_2PPh_2)_2 \rightleftarrows Mo(CO)_2(S_2PPh_2)_2 + CO \qquad (4)$$

produced is allowed to escape, the nascent dicarbonyl species suffers decomposition (vide supra). The presence of a CO atmosphere forces the equilibrium of eq 4 even further to the left, effectively retarding the decomposition of the dicarbonyl species. Nucleophilic ligands L present in solutions of **1** serve as efficient scavengers for the emerging dicarbonyl species, and complexes $Mo(CO)_2L(S_2PPh_2)_2$ are produced (eq 3).

Solutions of **1** also react rapidly with phenylacetylene to afford jade green $Mo(CO)(PhC_2H)(S_2PPh_2)_2$ (eq 5), and

$$\mathbf{1} + PhC{\equiv}CH \rightarrow Mo(CO)(PhC{\equiv}CH)(S_2PPh_2)_2 + 2CO \qquad (5)$$

again we believe it is $Mo(CO)_2(S_2PPh_2)_2$ that is being intercepted by the alkyne, with subsequent CO expulsion affording

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the isolated monocarbonyl product. A variety of analogous species may be prepared via the interaction of **1** with various acetylenes.[20] The IR spectrum of $Mo(CO)(PhC{\equiv}CH)(S_2PPh_2)_2$ displays a strong $\nu(CO)$ absorption at 1931 cm^{-1} but does not show a carbon–carbon stretch of the coordinated alkyne. In the room-temperature ^1H NMR spectrum, the resonance due to the acetylenic hydrogen atom appears at 12.54 ppm, approximately 9.5 ppm downfield from the corresponding resonance in free phenylacetylene (3.05 ppm). Likewise, in the ^{13}C NMR of $Mo(CO)(PhC{\equiv}CH)(S_2PPh_2)_2$ the resonance of the $\equiv CH$ carbon atom is found at 209.5 ppm with $^1J_{C-H} = 218$ Hz. As noted by Templeton and Ward,[21] the ^{13}C NMR chemical shifts of coordinated alkynes provide a convenient qualitative assessment of the formal electron-donation number of these ligands. Applying this criterion and considering all of the above observations provide strong evidence that the alkyne ligand is acting as a formal 4-electron donor in $Mo(CO)(PhC{\equiv}CH)(S_2PPh_2)_2$, and thus an 18-electron configuration about the Mo atom is maintained.[22]

Equimolar amounts of **1** and $MoO_2(S_2PPh_2)_2$ react smoothly to produce 2 equiv of the oxo-transfer[23] product, $MoO(S_2PPh_2)_2$ (eq 6). Since the structures and reactivity patterns

$$\mathbf{1} + MoO_2(S_2PPh_2)_2 \rightarrow 2MoO(S_2PPh_2)_2 + 3CO \quad (6)$$

of transition-metal oxo and imido complexes are often similar,[24] it became of interest to investigate the possibility of synthesizing the species $Mo(NAr)(S_2PPh_2)_2$ via an analogous imido group transfer reaction. The requisite bis(imido) complexes $Mo(NAr)_2(S_2PPh_2)_2$ (**3**) were prepared by the treatment of **1** with aryl azides as shown in eq 7. However, when

$$\mathbf{1} + 2Ar{-}N_3 \rightarrow \underset{\substack{\mathbf{3a},\ Ar\,=\,p\text{-tolyl} \\ \mathbf{3b},\ Ar\,=\,2,4,6\text{-mesityl}}}{Mo(NAr)_2(S_2PPh_2)_2} + 3CO + 2N_2 \quad (7)$$

solutions containing equimolar amounts of **1** and **3a** are warmed, **1** simply decomposes (vide supra) and **3a** remains unchanged, as determined by IR and NMR spectroscopy. Apparently, the imido ligands are so strongly bound in **3a** that they are rendered insufficiently nucleophilic to participate in the ligand-transfer reaction. Likewise, the reaction between equimolar amounts of **1** and *p*-tolyl azide at room temperature failed to give the desired $Mo(Ntol)(S_2PPh_2)_2$ product. Instead, the reaction produced equimolar quantities of the bis(imido) species, **3a**, and unreacted **1** as shown in eq 8. While $Mo(Ntol)(S_2PPh_2)_2$ is a likely intermediate in this sequence, its rate of reaction with tolyl azide must be much faster than that of tolyl azide with **1**.

$$1.0\,tol{-}N_3 + 1.0\,\mathbf{1} \rightarrow 0.5\,\mathbf{3a} + 0.5\,\mathbf{1} + N_2 + {}^3/_2CO \quad (8)$$

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Registry No. **1**, 91327-59-2; **2a**, 91312-09-3; **2b**, 91312-10-6; **2c**, 91312-11-7; **3a**, 91312-13-9; **3b**, 91312-14-0; $Mo(CO)(PhC_2H)(S_2PPh_2)_2$, 91312-12-8; $MoO_2(S_2PPh_2)_2$, 29372-10-9; $MoO(S_2PPh_2)_2$, 59796-76-8; $MoBr_2(CO)_4$, 22172-30-1; *p*-tolyl azide, 2101-86-2; 2,4,6-mesityl azide, 14213-00-4.

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Franck–Condon Barriers to Outer-Sphere Reductive Cleavage

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Reductive cleavage as a fundamental mechanistic step permeates reaction chemistry. In organic chemistry, alkyl halides, for example, are cleaved by single-electron reducing agents.[1] In inorganic chemistry, reductive cleavage of peroxides and halogens may be cited. In many cases it is uncertain whether electron transfer and bond cleavage are concerted or sequential; the controversy in this regard is particularly prominent for reductive cleavage of alkyl halides, where it remains to be established whether the radical anions exist in solution.[2,3] Inorganic chemistry furnishes examples where the reduced products are clearly nonbonded, e.g., reduction of I_2^- to two iodide ions. The reverse process, oxidative bond formation, is less commonly observed, but it is, of course, of equivalent dynamic significance.

Both reductive cleavage and oxidative bond formation have been observed for reactions involving the $I_2^-/2I^-$ and $(SCN)_2^-/2SCN^-$ couples.[4,5] Oxidations of I^- and SCN^- by substitution-inert oxidants such as $IrBr_6^{2-}$ and $[Os(bpy)_3]^{3+}$ were found to have rate laws with terms first order in oxidant and second order in reducing agent. The following mechanism was proposed:

$$Ox + 2X^- \rightleftarrows Red + X_2^- \qquad k_1,\ k_{-1},\ K_{eq} \quad (1)$$

$$Ox + X_2^- \rightarrow Red + X_2 \qquad k_2 \quad (2)$$

Under the experimental conditions k_1 was rate limiting.[5] In another series of experiments the reverse (k_{-1}) paths were observed by generating the species X_2^- pulse radiolytically in the presence of Red.[4] The validity of the proposed mechanism was confirmed by the fact that the ratio of the two rate constants, k_1/k_{-1}, was equal to the equilibrium constant, K_{eq}, which was calculated independently on the basis of the established reduction potentials.[4]

At the time of these studies it was considered that this interpretation posed a dilemma.[5] Electron transfer was viewed as occurring in concert with bond formation (in the k_1 direction). The bond length in I_2^- was estimated to be 3.10 Å by applying Badger's rule to the vibrational frequency (obtained from a matrix-isolation Raman spectrum), while the

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[1] See, for example: Eberson, L. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 533.

[2] Bigot, B.; Roux, D.; Salem, L. *J. Am. Chem. Soc.* **1981**, *103*, 5271.

[3] Bowman, W. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 25.

[4] Nord, G.; Pedersen, B.; Floryan-Løvborg, E.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327.

[5] Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715.

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