state does not lead to significantly better agreement. On the other hand, for a complex with a $^2A_{1g}$ ground state the direct participation of the metal 4s orbital is allowed by symmetry, and this is expected to have an effect opposite in sign to that of the polarized core electrons.[21] For $K_2Zn[Cu]F_4$ a much better agreement with experiment is obtained with $K = 0.20$, yielding $A_z = 85 \times 10^{-4}$ cm^{-1} and $A_{xy} = 23 \times 10^{-4}$ cm^{-1}. This corresponds to a contribution $K = -0.23$ due to direct 4s participation in the ground state. The calculated value of the isotropic hyperfine splitting due to unit unpaired spin density in a copper 4s orbital is 0.2003 cm^{-1},[12] so that the above estimate of K implies a fractional occupany of the 4s orbital by the unpaired electron of ~(0.23 × 0.77 × 0.036/0.2003) or ~3.2%. This is similar to the value derived from the analysis of the metal hyperfine parameters of low-spin cobalt(II) complexes having the more common tetragonally elongated Jahn–Teller distortions in which the unpaired electron occupies a $^2A_{1g}(d_{z^2})$ orbital[24] and also to the 4s mixing coefficient deduced from the energy of the $^2A_{1g}(d_{z^2})$ excited state of planar four-coordinate copper(II) complexes.[25]

The metal hyperfine parameters $|A_z| = 645 \times 10^{-4}$ cm^{-1} and $|A_{xy}| = 697 \times 10^{-4}$ cm^{-1} of the CuF_2 molecule[17] are almost isotropic and far higher than those of $K_2Zn[Cu]F_4$, or almost all other copper(II) complexes, clearly implying a significant unpaired spin density in the copper 4s orbital. The g_{xy} value of 2.601 suggests an orbital contribution $\mu = 0.112$ for CuF_2, yielding "best fit" estimates of the hyperfine constants $A_z = 684 \times 10^{-4}$ cm^{-1} and $A_{xy} = 657 \times 10^{-4}$ cm^{-1} using a value of $K = -1.5$. This implies an occupancy of the 4s orbital of ~33%, some 10 times that in $K_2Zn[Cu]F_4$. Simple theory suggests that the $3d_{z^2}$/4s mixing coefficient in tetragonally distorted complexes is proportional to the difference in metal–ligand bonding between the axial and in-plane ligands,[26] so that a significantly greater 4s participation is indeed expected for the linear CuF_2 molecule compared with the axially compressed CuF_6^{4-} ion.

Acknowledgment. The receipt of a Humboldt research fellowship to M.A.H. is gratefully acknowledged.

Registry No. K_2ZnF_4, 37732-22-2; CuF_6^{4-}, 20581-14-0; Cu, 7440-50-8.

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(24) Rockenbauer, A. R.; Budó-Zakoryi, E.; Sinándi, L. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1729.

(25) Hitchman, M. A.; Cassidy, P. J. *Inorg. Chem.* **1979**, *18*, 1745.

(26) Smith, D. W. *Inorg. Chim. Acta* **1977**, *22*, 107.

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Redox Reactivity of Photogenerated $Cr(CO)_5$ Species: Formation of $[Cr^{III}(o\text{-semiquinone})_3]$ Complexes

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The mechanism of the formation of $[Cr^{III}(o\text{-semiquinone})_3]$ complexes by complete photochemical oxidative substitution of $Cr(CO)_6$ with *o*-quinones (*o*-chloranil, 3,5-di-*tert*-butyl-1,2-benzoquinone) was studied by both stationary and flash photolysis in aromatic hydrocarbon solvents. The photogenerated coordinatively unsaturated $Cr(CO)_5$ species was found to undergo a rapid oxidative addition of the *o*-quinone molecule, resulting in a strong labilization of Cr–CO bonds and launching a series of very fast reactions that ultimately produce the CO-free Cr(III) complex $[Cr(o\text{-semiquinone})_3]$. The rate of its formation was found to be determined by the rate of the solvent molecule dissociation from the primary photoproduct, the $Cr(CO)_5(solv)$ species, producing the reactive $Cr(CO)_5$ intermediate; $k_1 = 1.1 \times 10^{-5}$ s^{-1}. Prospects of oxidative substitutions of group VIB (6) metal carbonyls are briefly discussed.

Introduction

Chromium hexacarbonyl, $Cr(CO)_6$, is a well-known coordinatively saturated and substitution-inert compound, which can be only hardly oxidized or reduced at rather extreme values of electrode potentials: $E_p^{Ox} = +1.53$ V, $E_p^{Red} = -2.66$ V (vs. SCE, measured in tetrahydrofuran), respectively.[1]

$Cr(CO)_6$ is well-known to undergo fast photochemical substitutions with Lewis bases in solution producing, $Cr(CO)_5L$ or $Cr(CO)_4L_2$ complexes.[2,3] Photosubstitution of more than two CO ligands is very difficult[4] and occurs only with some fluorophosphines under prolonged irradiation[4] (often for several days or even weeks). All hitherto described solution photosubstitutions of $Cr(CO)_6$ take place without any change of the oxidation state of the chromium central atom.

Recently, we have described[5] a photochemical synthesis of $[Cr^{III}(o\text{-semiquinone})_3]$ complexes by irradiation of mixtures of $Cr(CO)_6$ and the appropriate *o*-quinone, particularly *o*-chloranil, in benzene solution. This reaction represents not only a convenient preparative method but also a very interesting mechanistic problem. It is a unique process among the huge amount of simple photosubstitutions of one or two CO ligands in $Cr(CO)_6$, as all six CO ligands are very readily replaced by three quinone molecules, which are reduced to corresponding semiquinone radical anions, whereas the Cr(0) central atom is concomitantly oxidized to the oxidation state III. This reaction represents a new type of $Cr(CO)_6$ reactivity, which can be described as a *complete photochemical oxidative substitution.*

Elucidation of its mechanism may thus afford a better understanding of the reactivity of group VIB (6)[42] metal carbonyls which are now often employed as photocatalysts.[6,7]

We have thus undertaken a mechanistic study of the photochemical reaction between $Cr(CO)_6$ and various *o*-quinones

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(1) Picket, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879.

(2) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401.

(3) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(4) Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1972**, *11*, 1858.

(5) Šmídová, I.; Vlček, A., Jr.; Vlček, A. A. *Inorg. Chim. Acta* **1982**, *64*, L63.

(6) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* **1981**, *4*, 171.

(7) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. *Pure Appl. Chem.* **1979**, *41*, 671.

(8) Brown, D. G.; Johnson, W. L., III *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 712.

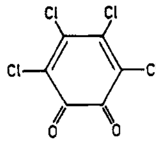
(9) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.

(10) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552.

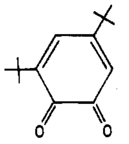
(11) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(12) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* **1956**, *235*, 518.

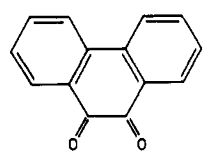
(13) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.



CQ



DBQ



PQ

with the aim of getting a better understanding of the nature of the photochemical step(s), the nature of the primary redox step, and the mechanism of the facile labilization of all six CO ligands. The possibilities of the preparative and catalytic utilization of the photochemical oxidative substitutions of group VIB metal carbonyls are also briefly discussed.

Experimental Section

$Cr(CO)_6$, 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-chloranil, CQ), and 9,10-phenanthrenequinone (PQ) were obtained from Fluka. These compounds as well as 3,5-di-*tert*-butyl-1,2-benzoquinone (DBQ, from EGA-Chemie) were used without further purification. CQ, DBQ, and PQ are common abbreviations for these quinones. Their one-electron-reduced forms, semiquinone radical anions, are denoted as CSQ, DBSQ, and PSQ, where Q and SQ stand for an unspecified *o*-quinone and its radical anion, respectively. Benzene and toluene (Lachema, Brno, Czechoslovakia) were purified by repeated vigorous stirring with H_2SO_4 and then by distillation with P_2O_5 and finally with $LiAlH_4$.

$Cr(CSQ)_3 \cdot CS_2 \cdot {}^1/_2C_6H_6$ complex was prepared by a photochemical method developed previously in this laboratory.[5] The product was recrystallized from CS_2, affording samples whose spectral properties and analyses are identical with those described previously for this complex.[5,14–16] In the visible spectral region this complex is well characterized by its absorption at 774 nm ($\epsilon = 3.85 \times 10^3$ $M^{-1} \cdot cm^{-1}$) and 529 nm ($\epsilon = 1.53 \times 10^4$ $M^{-1} \cdot cm^{-1}$).

The $Cr(DBSQ)_3$ complex was also synthesized photochemically: 0.5 g of $Cr(CO)_6$ and 1.5 g of DBQ (molar ratio 1:3) in 150 mL of dry benzene flushed with argon was irradiated for 110 min by the light of a 125-W medium-pressure mercury-arc lamp in the Pyrex glass immersion well apparatus. The solvent was then evaporated to dryness, and the dark residue was recrystallized from the 1:1 (v/v) mixture of ethanol and benzene. $Cr(DBSQ)_3$ is produced as a very dark microcrystalline solid whose IR and UV–vis spectra are completely identical with those reported[8–10] for $Cr(DBSQ)_3$. Photochemically prepared samples are not contaminated by free *o*-DBQ as are the thermally prepared ones.[8] However, overirradiation should be avoided as it may produce another unidentified impurity absorbing around 700 nm. Extinction coefficients of UV–vis absorption bands of $Cr(DBSQ)_3$ were determined: 4.1×10^3 and 1.9×10^4 $M^{-1} \cdot cm^{-1}$ (±10%) for the absorption maxima at 780 and 525 nm, respectively. These values are somewhat higher than those reported[8] for thermally synthesized samples, reflecting different solvent content[11] and better purity of photochemically prepared $Cr(DBSQ)_3$.

Electronic absorption spectra in the UV–vis region were measured on a Unicam SP-800B spectrophotometer. A Perkin-Elmer Model 257 instrument was used for the measurement of IR absorption spectra, whereas EPR spectra were obtained with Varian E-4 spectrometer.

Quantum yields of the $Cr(SQ)_3$ formation were measured with employment of the 313-nm Hg spectral line, which was selected by appropriate glass filters (Carl Zeiss, Jena) from the focused light of the medium-pressure 250-W mercury-arc lamp. In a typical experiment, a stirred 10^{-3} M solution of $Cr(CO)_6$ with a corresponding amount of quinone in toluene was irradiated in a 1-cm spectral cell under an argon atmosphere. The incident light was totally absorbed by the solution. Its intensity was measured by ferrioxalate actinometry[12,13] in a separate experiment immediately before and after proper quantum yield measurement. The absorbed light intensity was corrected for the partial absorption of $Cr(CO)_6$ at 313 nm. The concentration of the $Cr(SQ)_3$ formed during irradiation was determined spectroscopically by the absorption change at 774 nm for $Cr(CSQ)_3$ whereas the absorption band at 780 nm was used in the case of $Cr(DBSQ)_3$. The concentration of $Cr(SQ)_3$ photoproducts was found to increase linearly with the irradiation time. A clear isosbestic point was observed in diluted solutions with low quinone concentration. (At higher concentrations or in the presence of an excess of quinones the isosbestic point falls into the spectral region where the absorbance is well above 2.) Quantum yields were determined with good reproducibility (±3%).

Conventional flash photolytic measurements were performed with use of an instrument constructed in this laboratory employing a quartz flash lamp with flash duration of approximately 5 μs. The wavelength range 240–370 nm was selected from the flash by an appropriate filter. The intensity of the analyzing light beam transmitted by the photolyzed solution was measured with use of a photomultiplier whose signal was digitalized with the transient recorder DL 905. All measurements were performed at 293 K under an argon atmosphere in cylindrical 5-cm quartz cells with use of purified toluene as solvent and a low concentration of $Cr(CO)_6$, typically 5×10^{-5} M. The concentration of DBQ ranged from 2.5×10^{-5} to 2.5×10^{-4} M. Kinetic measurements were performed with use of 535 ± 2 nm analyzing light wavelength. The rate constants were obtained with reproducibility better than ±10%, typically ±6%.

Results

The $Cr(SQ)_3$ complexes were previously reported to be prepared thermally[9,14–16] by long-term refluxing of $Cr(CO)_6$ with the appropriate *o*-quinone. We have successfully reproduced this procedure for DBQ and PQ. However, all attempts to synthesize the $Cr(CSQ)_3$ complex thermally failed. Instead, we have found[5] that this complex, as well as $Cr(DBSQ)_3$, may be prepared by facile and convenient photochemical method according to overall reaction 1. Qualitatively the same photochemistry has been

$$\mathrm{Cr^0(CO)_6 + 3Q \xrightarrow{h\nu} Cr^{III}(SQ)_3 + 6CO} \qquad (1)$$

observed in various solvents like benzene, toluene, hexane, and CH_3CN.

Both $Cr(CSQ)_3$ and $Cr(DBSQ)_3$ complexes undergo a slow photodecomposition in solution, producing species characterized by a new absorption at 690–710 nm. Excessive irradiation should thus be avoided in the synthesis of the $Cr(DBSQ)_3$ complex, whereas $Cr(CSQ)_3$ is protected against photodecomposition by its immediate precipitation.[5] On the other hand, all attempts to photochemically prepare the $Cr(PSQ)_3$ complex failed as its photodecomposition is very fast (see below).

Spectroscopic study of the preparative reactions revealed that no thermal reaction between $Cr(CO)_6$ and CQ, DBQ, or PQ takes place at room temperature. The photochemical formation of $Cr(SQ)_3$ complexes also immediately ceased when the irradiation was interrupted.

As both $Cr(CO)_6$ and *o*-quinones are potentially photoactive species, it was necessary to determine the nature of the photoactive component. No reaction takes place when the solutions of $Cr(CO)_6$ (10^{-3} M) and CQ or DBQ (5×10^{-3} M) were irradiated at 436 or 405 nm, where only quinones absorb. On the other hand, the formation of $Cr(SQ)_3$ complexes occur readily under irradiation by the 313-nm light, which is absorbed by both reactants. As no ground-state adduct formation between $Cr(CO)_6$ and *o*-quinones was observed, it may be concluded that the only photoactive species involved is $Cr(CO)_6$.

Quantum yields of the $Cr(CSQ)_3$ and $Cr(DBSQ)_3$ formation were found to be independent both of incident light intensity in the studied range 4.6×10^{-11}–9.7×10^{-10} einstein·s^{-1} and of quinone concentration ranging from 2×10^{-3} to 10^{-2} M, the $Cr(CO)_6$ concentration being 10^{-3} M. At given experimental conditions, only one photochemical step may thus be involved, all following thermal reaction steps that are first or zero order with respect to quinone. No kinetically significant competitive side reactions deactivating any of the reaction intermediates take place. The measured overall quantum yield of the $Cr(SQ)_3$ formation has thus to be equal to the quantum yield of the primary photochemical step.

The value of the quantum yield of $Cr(CSQ)_3$ formation, 0.67 ± 0.02, is equal to the quantum yield of the usual photosubstitutions of $Cr(CO)_6$.[17,18] It may thus be concluded that the primary photochemical step of the $Cr(CSQ)_3$ formation is identical with that of $Cr(CO)_6$ photosubstitutions.

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(14) Pierpont, C. G.; Downs, H. H.; Rukavina, T. G. *J. Am. Chem. Soc.* **1974**, *96*, 5573.

(15) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1976**, *98*, 4834.

(16) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.

(17) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215.

(18) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237.

It has been found[19,20] that $Cr(CO)_6$ undergoes primary photodissociation of one CO ligand, producing excited trigonal-bipyramidal $Cr(CO)_5$, which adds with two-thirds probability a solvent molecule from the solvent cage, producing the solvated $Cr(CO)_5S$ complex within 25 ps after photoexcitation of $Cr(CO)_6$.[21] The solvated $Cr(CO)_5$(solv) complexes are known to be in equilibrium with very reactive naked $Cr(CO)_5$ species.[20,22-26] This coordinatively unsaturated complex was found to add various Lewis bases present in the solution. Using this picture of photochemical substitution of $Cr(CO)_6$ and combining it with our results on stationary photolysis and on quantum yield measurements, it is possible to formulate the reaction scheme shown by Scheme I, where solv′ stands for the solvent molecule present in the solvation shell of the $Cr(CO)_6$ species at the moment of excitation.

Scheme I

$$Cr(CO)_6 \xrightarrow{h\nu,\ \text{solv}'} Cr(CO)_5(\text{solv}) + CO \tag{2}$$

$$Cr(CO)_5(\text{solv}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr(CO)_5 + \text{solv} \tag{3}$$

$$Cr(CO)_5 + Q \xrightarrow{k_2} Cr(CO)_5Q \tag{4}$$

$$Cr(CO)_5Q \xrightarrow[-5CO]{+2Q} Cr(SQ)_3 \tag{5}$$

The quantum yield of $Cr(DBSQ)_3$ formation has been found somewhat lower (0.54). This may be partly due to some inherent irreproducibility in the evaluation of extinction coefficient caused by different solvent contents in $Cr(DBSQ)_3$ samples (vide supra). Secondary photodecomposition of $Cr(DBSQ)_3$ mentioned above may also partly account for this decrease in ϕ. Nevertheless, it may be still well argued that the formation of the $Cr(DBSQ)_3$ complex follows also the mechanism proposed in Scheme I.

Flash photolysis was employed to confirm the reaction scheme (Scheme I) and to obtain data on the rates of individual reaction steps. The unfavorably high partial absorption of CQ at both excitation and analyzing wavelengths prevented the study of the reaction between $Cr(CO)_6$ and CQ. Only the reaction with DBQ was thus studied in detail; all conclusions may be applied to the reaction with CQ as well.

A typical experiment consisted of excitation of a toluene solution containing $Cr(CO)_6$ and DBQ, the latter being always in large excess over the $Cr(CO)_5$(solv) formed by the excitation flash and thus also over the $Cr(CO)_5$ reactive intermediate.

The transmitted analyzing light intensity, I_t, was found to decrease exponentially and very rapidly from its original value, I_0, to the constant final value, I_∞. Essentially the same behavior was observed at various analyzing light wavelengths ranging from 480 to 650 nm. A difference absorption spectrum of the final photolytic product taken as a plot of log $(I_0/I_\infty) = A_\infty - A_0$ (A_∞ and A_0 being final and initial solution absorbances, respectively) against the analyzing light wavelength confirms the formation of $Cr(DBSQ)_3$ following the photolytic flash. No evidence for any transient absorption due to some reaction intermediate has been found. (Expected absorption of $[Cr(CO)_5(\text{tol})]$ (tol = toluene) in the 450–480-nm range[21] is overlapped by much stronger absorption of the reaction product and, partially, of free quinone. Nevertheless, some indication of an increase of the absorption at 470 nm during the flash was observed that might be accounted for by the formation of the $Cr(CO)_5$(solv) intermediate.) The changes of the transmitted analyzing light intensity may thus be directly attributed to the formation of final reaction product, $Cr(DBSQ)_3$.

Table I. Rate Constants of $Cr(DBSQ)_3$ Formation

[DBQ], mol·L^{-1}	$10^{-4}k_{app}$, s^{-1}	[DBQ], mol·L^{-1}	$10^{-4}k_{app}$, s^{-1}
2.5×10^{-5} [a]	2.22	2.0×10^{-4} [a]	7.09
5.0×10^{-5} [a]	3.55	2.5×10^{-4} [a]	7.79
1.0×10^{-4} [a]	5.52	2.5×10^{-4} [b]	7.92
1.5×10^{-4} [a]	6.40		

[a] $[Cr(CO)_6] = 5 \times 10^{-5}$ mol·L^{-1}. [b] $[Cr(CO)_6] = 10^{-4}$ mol·L^{-1}.

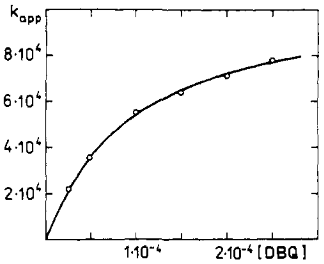

Figure 1. Dependence of apparent rate constant of $Cr(DBSQ)_3$ formation on DBQ concentration.

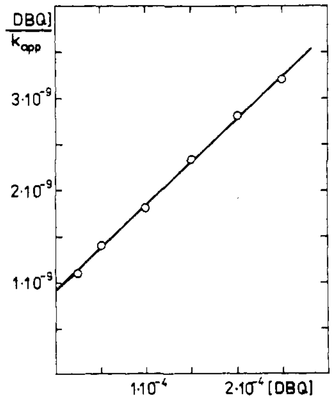

Figure 2. Analysis of the dependence of apparent rate constant k_{app} on DBQ concentration according to eq 7.

Kinetic measurements revealed that $Cr(DBSQ)_3$ is formed in a very rapid smooth process following a simple single-exponential kinetics, $c = c_\infty(1 - e^{-k_{app}t})$, c and c_∞ being the immediate and final concentrations of $Cr(DBSQ)_3$, respectively. Corresponding analysis of experimental data shows that the dependence of ln log $(I/I_\infty) = \ln (A_\infty - A)$, I and A being immediate transmitted light intensity and solution absorbance, respectively, on time is perfectly linear with correlation coefficients higher than 0.992 (typically 0.998–0.9993).

Apparent rate constants, k_{app}, were evaluated as slopes of these plots (Table I). It has been found that k_{app} does not depend on the wavelength of the analyzing light beam in the studied range 495–550 nm. Its value is also unchanged when the $Cr(CO)_6$ concentration is doubled. The dependence of k_{app} on quinone concentration is nonlinear, exhibiting saturation at high quinone concentrations (Table I, Figure 1).

The observed simple kinetic picture of reaction 1 is virtually in contradiction with its obvious complexity: substitution of six ligands by three chelates accompanied by changes of oxidation states inevitably has to be a very complicated process involving several intermediates and several reaction steps. However, all observed experimental data are in full agreement with the reaction mechanism described by Scheme I provided that all reaction steps following equilbrium 3 are sufficiently fast so that the steady-state approximation can be used for $Cr(CO)_5$ and $Cr(CO)_5Q$ species as well as for all, experimentally unresolvable, intermediates of

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(19) Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

(20) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271.

(21) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.

(22) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; von Gustorf, E. K. *J. Organomet. Chem.* **1974**, *69*, 259.

(23) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(24) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

(25) Hermann, H.; Grevels, F. W.; Henne, A.; Schaffner, K. *J. Phys. Chem.* **1982**, *86*, 5151.

(26) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381.

process 5. In such a case the analysis of Scheme I, assuming pseudomonomolecularity of reactions 4 and 5, gives eq 6 for the apparent rate constant, k_{app}. Figure 2 shows that the experimental

$$k_{app} = \frac{k_1 k_2[Q]}{k_{-1}' + k_2[Q]} \qquad k_{-1}' = k_{-1}[solv] \tag{6}$$

$$\frac{[Q]}{k_{app}} = \frac{1}{k_1}[Q] + \frac{k_{-1}'}{k_1 k_2} \tag{7}$$

data follow exactly eq 7, thus confirming thus the reaction mechanism described by Scheme I. The value of the rate constant of the $Cr(CO)_5(solv)$ dissociation, k_1, has been found to be $k_1 = 1.1 \times 10^5\ s^{-1}$. Equation 7 allows also the evaluation of the term $k_{-1}'/k_1k_2 = 1/k_2K = 9.2 \times 10^{-10}$ M·s, K being the dissociation constant of $Cr(CO)_5(solv)$, whose value is unknown. The value of k_2 thus cannot be determined from our experiment. However, the value of the ratio $k_2/k_{-1} = 10^5$ may be readily calculated, showing that the addition of *o*-quinone to $Cr(CO)_5$ is much faster than the addition of toluene.

Flash photolytic measurements thus confirm the reaction mechanism outlined in Scheme I, prove the presence of equilibrium 3, and reveal that the rate of $Cr(SQ)_3$ formation is determined by the rate of $Cr(CO)_5(solv)$ dissociation into $Cr(CO)_5$. As the assumptions used in the derivation of eq 6 are obviously met, the kinetic measurements also prove, more exactly than the quantum yield measurements, that $Cr(CO)_5$ undergoes very fast reaction with one quinone molecule (eq 4) and that all following reaction steps embraced in eq 5 are either first or zero order with respect to the quinone.

Alternative mechanisms involving redox reactions between excited $Cr(CO)_6$ or ground-state $Cr(CO)_5(solv)$ and quinones are ruled out by flash photolysis as they predict linear dependence of k_{app} on quinone concentration.

Reaction in CH_3CN. The $Cr(SQ)_3$, SQ = CSQ, DBSQ, complexes are formed in CH_3CN photochemically in the same way as in toluene. However, this reaction is much slower as the rate-determining dissociation of the $Cr(CO)_5(solv)$ species (reaction 3) is approximately 10^7 times slower in CH_3CN.[22]

The $Cr(SQ)_3$ complexes are also slowly (in 1 h) formed when quinone is added in the dark to the previously irradiated solution of $Cr(CO)_6$ in CH_3CN containing the $[Cr(CO)_5(CH_3CN)]$ complex, which was spectroscopically detected (λ_{max} = 396 nm). This compound is only very slightly dissociated into naked $Cr(CO)_5$ species. No reaction intermediates except $[Cr(CO)_5(CH_3CN)]$ were observed spectroscopically in CH_3CN due to reactions 4 and 5 of Scheme I, whose rate is much faster than that of rate-determining dissociation of $[Cr(CO)_5(CH_3CN)]$. The reaction in CH_3CN was not studied in more detail due to the instability of $Cr(SQ)_3$ complexes in this solvent. However, the behavior observed in CH_3CN qualitatively agrees with the reaction mechanism in Scheme I.

EPR Measurements and Reaction with PQ. Recently, Weir and Wan assumed the formation of the $[Cr(CO)_2(PQ)_2]\cdot$ stable radical complex by a photochemical reaction of $Cr(CO)_6$ with PQ in benzene.[27] This finding is in apparent contradiction with our mechanism depicted above (Scheme I). Our own EPR investigation confirmed the formation of EPR-active species under intense irradiation of $Cr(CO)_6$ with CQ, DBQ, or PQ in toluene solution inside the EPR cavity. These species are identical with those described by Wan:[27] EPR parameters found for the product of the reaction with PQ, $g = 1.9698$ and $a_{Cr} = 2.7$ mT, correspond well with those reported by Wan,[27] $g = 1.9692$ and $a_{Cr} = 2.69$ mT. EPR signals observed for CQ and DBQ are quite similar. However, completely identical EPR spectra were observed when pure toluene solutions of $Cr(SQ)_3$ complexes were irradiated. As in this case no $Cr(CO)_6$ was present, the observed spectra cannot be attributed to $[Cr(CO)_2(Q)_2]\cdot$ species but to a product of the decomposition of $Cr(SQ)_3$ complexes, which were, in Weir and Wan's experiments, formed during the irradiation of $Cr(CO)_6$ in the presence of *o*-quinones. The $Cr(SQ)_3$ photodecomposition is now under further investigation.

By spectroscopy in the UV–vis region as well as by EPR, it was found that the $Cr(PSQ)_3$ complex is much more photolabile than $Cr(CSQ)_3$ or $Cr(DBSQ)_3$. The dark violet $Cr(PSQ)_3$ solutions turn immediately light yellow under irradiation in the UV–vis region. Spectroscopic investigation of the photoreaction of $Cr(CO)_6$ with PQ reveals fast formation of a very low concentration of $Cr(PSQ)_3$ complex, which remains almost constant and drops only after prolonged irradiation. It may thus be concluded that $Cr(CO)_6$ reacts with PQ also according to Scheme I, producing the $Cr(PSQ)_3$ complex, which undergoes very fast photodecomposition. This instability also prevents the photochemical synthesis of the $Cr(PSQ)_3$ complex.

Discussion

All experimental evidence points to the mechanism outlined above (Scheme I); i.e., the primary photoreaction of $Cr(CO)_6$ produces $Cr(CO)_5(solv)$, which reversibly dissociates, generating, in the rate-determining step, the $Cr(CO)_5$ species, which adds very rapidly one *o*-quinone molecule. This mechanism is formally identical with that of simple photosubstitutions of group VIB metal carbonyls.[17,18,26] However, contrary to these simple photosubstitutions by Lewis bases, the addition of the first *o*-quinone molecule to $Cr(CO)_5$ is not the final reaction step but it launches a series of very fast thermal reactions (eq 5) producing ultimately carbonyl-free complexes, $Cr(SQ)_3$, containing a Cr central atom in the oxidation state III, which was confirmed already by other investigations.[9,11,16,40,41] To account for the strong labilization of Cr–CO bonds, the addition of *o*-quinone to $Cr(CO)_5$ cannot be regarded as a simple Lewis acid–base interaction but rather as an oxidative addition producing a semiquinone complex of Cr(I)

$$Cr^0(CO)_5 + Q \rightarrow Cr^I(CO)_5(SQ') \tag{8}$$

where SQ′ stands for the monodentate *o*-semiquinone ligand. As semiquinone complexes containing a monodentate *o*-semiquinone ligand usually undergo fast intramolecular chelate ring closure,[28] reaction 8 should be followed by the reaction

$$Cr(CO)_5(SQ') \rightarrow Cr(CO)_4(SQ) + CO \tag{9}$$

Oxidation of the Cr^0 central atom in reaction 8 causes a strong labilization of Cr–CO bonds due to diminution of π back-bonding. This effect is amplified by chelate ring formation (eq 9), as chelated *o*-semiquinone radical ligands are capable of strong π interaction with metal orbitals.[11,28] This labilization of M–CO bonds upon oxidation of metal carbonyls is quite typical, and for $Cr(CO)_5L$ species it has been demonstrated also electrochemically.[1,29] The $Cr^I(CO)_4(SQ)$ species may be thus well disposed to easily dissociate further CO ligands and to oxidatively add a further *o*-quinone molecule. The formation of $Cr^{III}(SQ)_3$ ultimate product may be then simply explained by repeating the CO dissociation and *o*-quinone oxidative addition. This sequence of one-electron oxidative additions should be accompanied by an increase of the energy of antiferromagnetic interaction between semiquinone and chromium unpaired electrons, which may thus contribute to the driving force of the overall process. This strong antiferromagnetic interaction is typical for all *o*-semiquinone complexes with paramagnetic transition metals.[11,16,30]

The coordinatively unsaturated $Cr(CO)_5$ species is a very strong Lewis acid whose redox reactivity is quite unusual. *o*-Quinones are Lewis bases and may thus be easily coordinated to the Cr central atom via the interaction between their oxygen lone electron pair and empty a_1 (essentially chromium d_{z^2}) orbital of $Cr(CO)_5$. At the same time, a strong interaction between occupied e (essentially chromium d_{xz}, d_{yz}) orbitals of $Cr(CO)_5$ and the low-lying π^* LUMO of the quinone takes place, resulting in the electron density transfer from the chromium d_π orbitals to the quinone π^*

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(27) Weir, D.; Wan, J. K. S. *J. Organomet. Chem.* **1981**, *220*, 323.

(28) Vlček, A., Jr.; Klíma, J.; Vlček, A. A. *Inorg. Chim. Acta* **1983**, *69*, 191.

(29) Bond, A. M.; Carr, S. W.; Colton, R.; Kelly, D. P. *Inorg. Chem.* **1983**, *22*, 989.

(30) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038.

orbital. The latter is strongly antibonding with respect to the quinone C–O bonds, and it has a significant contribution from the oxygen 2p$_z$ orbital. However, oxygen-bound quinones are not usually π acceptors but rather oxidizing ligands whose complete reduction alters significantly both their electronic and molecular structure[11,28,31] and strengthens also their bonding to the central metal atom.[11] This $d_\pi \rightarrow \pi^*$(LUMO) electron transfer concerted with the formation of a Cr–O(quinone) σ bond may thus be regarded as a net electron transfer in accordance with the formulation of the addition of *o*-quinones as an oxidative addition (eq 8).

The photochemical formation of Cr(SQ)$_3$ complexes represent the first well-characterized example of photochemical oxidative substitution of group VIB metal carbonyls in solution. However, this process might be of more general and practical importance as is shown e.g. by polymerizations photosensitized by various metal carbonyls in the presence of CCl$_4$.[32] These processes seem to be initiated by various radicals formed in the photoredox reactions of CCl$_4$ with metal carbonyls (including Cr(CO)$_6$). Our preliminary results show formation of CrCl$_3$ when Cr(CO)$_6$ is irradiated in pure CCl$_4$.

Analogously Cr$_2$O$_3$ is slowly formed by an oxidative substitution of [Cr(CO)$_5$(CH$_3$CN)] in the presence of dioxygen.[33] Recent low- temperature matrix isolation studies[34,35] show the formation of mixed-carbonyl–oxygen complexes by the photochemical reaction of M(CO)$_6$ (M = Cr, Mo, W) with dioxygen at 10 K. Moreover, a number of very slow thermal reactions between group VIB metal carbonyls and oxidizing substrates, producing M(III) complexes, has been described.[36–38] Compounds containing active reducible protons (β-diketonates, carboxylic acids, or Schiff bases)[36,37] and also compounds containing S–S bonds[38] were employed as oxidizing substrates. Some of these synthetic reactions were also recently carried out photochemically.[39]

It might thus be argued that photochemical oxidative substitutions of group VIB metal carbonyls represent a more general class of processes that may be widely used in synthesis and, perspectively, in photocatalysis, especially in the case of Mo and W carbonyls, where low-valent mixed-carbonyl–ligand complexes may be expected to be produced by the irradiation of Mo(CO)$_6$ or W(CO)$_6$ with suitable oxidizing substrates at ambient or low temperatures.

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Registry No. Cr(CO)$_6$, 13007-92-6; CQ, 2435-53-2; DBQ, 3383-21-9; Cr(CO)$_5$, 26319-33-5; Cr(DBSQ)$_3$, 64020-84-4; PQ, 84-11-7.

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(31) Vlček, A., Jr.; Klíma, J.; Vlček, A. A. *Inorg. Chim. Acta* **1982**, *58*, 75.

(32) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.

(33) Strohmeier, W.; Gerlach, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15B*, 622.

(34) Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 651.

(35) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051.

(36) Dunne, T. G.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 263.

(37) Calderazzo, F.; Floriani, C.; Henzi, R.; L'Eplattenier, F. *J. Chem. Soc. A* **1969**, 1378.

(38) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1964**, *86*, 2799.

(39) Thomas, P.; Schreckenbach, J.; Hennig, H. *Z. Chem.* **1984**, *24*, 413.

(40) Downs, H. H.; Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1736.

(41) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907.

(42) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Resonance Raman Spectroscopy of the Lowest Excited State of Derivatives of Tris(2,2′-bipyridine)ruthenium(II): Substituent Effects on Electron Localization in Mixed-Ligand Complexes

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The one-electron nature of the lowest electronic excited state of $[\mathrm{RuL}_n\mathrm{L'}_{3-n}]^{2+}$ (L, L′ = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy), 4,4′-dibromo-2,2′-bipyridine (Br$_2$bpy); *n* = 0, 1, 2, 3) as the PF$_6^-$ salts in CH$_3$CN at 25 °C has been investigated by optical absorption and emission spectral studies and by resonance Raman spectroscopy. For the Raman studies, a high concentration of excited species was produced by the leading edge of a frequency-tripled Nd:YAG laser pulse (~18 ns; 354.7 nm; ~3 mJ) and the Raman scattering from the trailing edge of the pulse was monitored. For all $[\mathrm{RuL}_3]^{2+}$ species the data are interpreted as revealing a lowest excited state that has the excited electron localized on one of the three equivalent ligands, as previously established for $[\mathrm{Ru(bpy)}_3]^{2+}$. Generally, for the mixed-ligand complexes the excited electron is localized on the more easily reduced ligand, on the time scale of the probe (~18 ns). However, the complexes $[\mathrm{Ru(bpy)(Me_2bpy)_2}]^{2+}$ and $[\mathrm{Ru(bpy)_2(Br_2bpy)}]^{2+}$ show excited-state Raman spectra consistent with a mixture of excited species, only a fraction with the excited electron localized on the more easily reduced ligand. Optical emission spectra show that substituent effects can be important, even though the substituent variation occurs in a ligand that is not the ligand on which the excited electron is localized. For example, $[\mathrm{Ru(bpy)(Me_2bpy)_2}]^{2+}$ emits at lower energy (~450 cm^{-1}) than $[\mathrm{Ru(bpy)_3}]^{2+}$, though both excited species involve an excited electron localized on the 2,2′-bipyridine ligand. The lower energy excited state is due to the destabilization of the d-π(HOMO) orbital in the ground-state 4,4′-dimethyl-2,2′-bipyridine species. Consistent with such an interpretation, the $E°'$ for the $[\mathrm{Ru(Me_2bpy)_3}]^{3+/2+}$ redox couple is ~0.2 V negative of that for the 2,2′-bipyridine analogue.

In this paper we present new information concerning ligand substituent effects on the electron distribution in the lowest electronic excited state of $[\mathrm{Ru(bpy)_3}]^{2+}$. In particular, we demonstrate that the mixed-ligand complexes $[\mathrm{RuL}_n\mathrm{L'}_{3-n}]^{2+}$ (L, L′ = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy), 4,4′-dibromo-2,2′-bipyridine (Br$_2$bpy); *n* = 0, 1, 2, 3) can be probed by excited-state Raman spectroscopy. This work was undertaken to establish the effect of substituents in directing the extent of electron localization on a given ligand and to assess the substituent effect on the excited-state energy.

The lowest $[\mathrm{Ru(bpy)_3}]^{2+}$ excited state is Ru → π^*(bpy) charge transfer (MLCT) in character and has been well established as such.[1–6] The excited state can be viewed, in the one-electron

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