**Table I.** Vibrational Spectra of $NF_4BrF_4$ and $NF_4BrF_4O$

| obsd freq, $cm^{-1}$, and rel intens[a] | | | | assignments (point group) | | |
|---|---|---|---|---|---|---|
| $NF_4BrF_4$ | | $NF_4BrF_4O$ | | | | |
| IR | RA | IR | RA | $NF_4^+$ ($T_d$) | $BrF_4^-$ ($C_{4v}$) | $BrF_4O^-$ ($C_{4v}$) |
| 1220 mw | | 1220 sh | | $2\nu_4$ ($A_1$ + E + $F_2$) | | |
| 1202 w | | 1216 mw | | | | |
| | 1182 (0.2) | | | | | |
| 1156 sh | 1158 (0.2) | 1165 s | 1165 (0.4) | $\nu_3$ ($F_2$), $\nu_{as}$ | | |
| 1147 vs | 1149 (0.2) | 1149 vs | 1152 sh | | | |
| | | 949 s | 953 (1.7) | | | $\nu_1$ ($A_1$), $\nu$(BrO) |
| | 851 (2.0) | | 853 (2.7) | $\nu_1$ ($A_1$), $\nu_s$ | | |
| 618 mw | 622 (0.5) | 614 w | 614 (2.0) | | | |
| 608 w | 608 (1.0) | 608 ms | 605 sh | $\nu_4$ ($F_2$), $\delta_{as}$ | | |
| 600 m | | 600 sh | | | | |
| (550 vw) | | | | | ? | |
| 530 sh | 535 (10) | | 506 (10) | | $\nu_1$ ($A_1$), $\nu_s$ | $\nu_2$ ($A_1$), $\nu_s$($BrF_4$) |
| 500 sh | 505 sh | 520 sh, br | 520 sh | | $\nu_6$ (E), $\nu_{as}$ | $\nu_7$ (E), $\nu_{as}$($BrF_4$) |
| 452 vs | | 470 vs | 470 (0.4) | | | |
| 430 sh | | 449 sh | 451 (1.4) | | | |
| | 466 (7.2) | 420 vw | 427 (7.5) | | $\nu_3$ ($B_1$), $\nu_s$ | $\nu_4$ ($B_1$), $\nu_s$($BrF_4$) |
| | 448 (0.8) | | 451 (3) | $\nu_2$ (E), $\delta_s$ | | |
| | | | 402 (0+) | | | $\nu_8$ (E), $\delta$($OBrF_4$) |
| | | 388 w | 389 (0.8) | | | |
| (363 vw) | | | 352 (0+) | | ? | ? |
| 325 vw | 320 (0.2) | | 304 (0.2) | | $\nu_2$ ($A_1$), $\delta_s$ out of plane | $\nu_3$ ($A_1$), $\delta_s$ out of plane |
| | 258 (1.0) | | 251 (0.7) | | $\nu_5$ ($B_2$), $\delta_s$ in plane | $\nu_6$ ($B_2$), $\delta_s$ in plane |
| | | | 225 (0+) | | | $\nu_5$ ($B_1$), $\delta_{as}$ out of plane |
| | 202 (0.5) | | 184 (0.5) | | $\nu_7$ (E), $\delta_{as}$ in plane | $\nu_9$ (E), $\delta_{as}$ in plane |
| | 129 (1.0) | | | lattice mode | | |

[a] Uncorrected Raman intensities (peak heights).

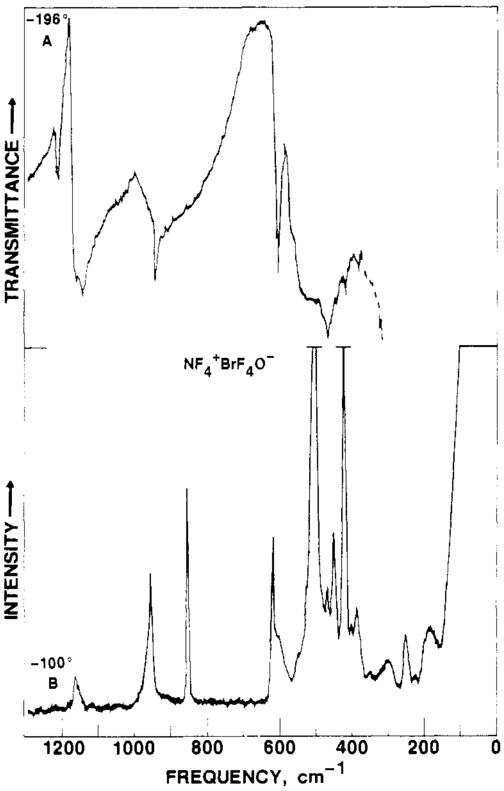

**Figure 2.** Vibrational spectra of solid $NF_4BrF_4O$: trace A, infrared spectrum; trace B, Raman spectrum.

agreement with those previously observed for $Cs^+BrF_4O^-$[3] and were assigned correspondingly.

In conclusion, the above results show that the $NF_4^+$ cation is capable of forming marginally stable salts with certain halogen fluoride or oxyfluoride anions. The synthesis of such salts is difficult and requires the use of a solvent that is (i) sufficiently polar to dissolve ionic salts, (ii) sufficiently volatile to allow solvent removal at low temperature, (iii) stable toward the strongly oxidizing $NF_4^+$ cation, and (iv) incapable of undergoing a solvolysis reaction with the starting materials. So far, the only solvent known to meet or approximate these requirements is $BrF_5$.

**Acknowledgment.** The authors are indebted to C. J. Schack, R. D. Wilson, and L. R. Grant for help and to the Army Research Office and the Office of Naval Research for financial support.

**Registry No.** $NF_4^+BrF_4O^-$, 101652-54-4; $NF_4^+BrF_4^-$, 101756-83-6; $CsBrF_4O$, 65391-03-9; $NF_4SbF_6$, 16871-76-4; $CsBrF_4$, 15705-88-1; $NF_3$, 7783-54-2; $BrF_3O$, 61519-37-7; $F_2$, 7782-41-4.

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# Photochemical Studies of [($\eta^5$-$C_5R_5$)M($\eta^6$-COT)]$PF_6$ and [($\eta^5$-$C_5R_5$)M($\eta^4$-1,5-COT)L]$PF_6$ Complexes of Iron and Ruthenium

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*Received October 9, 1985*

We have examined the photochemistry of a series of complexes of the form [($\eta^5$-$C_5R_5$)M($\eta^6$-COT)]$PF_6$ and [($\eta^5$-$C_5H_5$)M($\eta^4$-COT)L]$PF_6$ (R = H, $CH_3$; M = Fe, Ru; COT = cyclooctatetraene; L = CO, $P(OCH_3)_3$) to determine the potential for stepwise COT release through coordinatively unsaturated $\eta^2$ and $\eta^4$ intermediates. The cyclooctatetraene complexes were chosen because of the documented ability of COT to coordinate in both $\eta^6$ and $\eta^4$ configurations.[2]

## Experimental Section

**General Information.** The organic solvents used in this study were of spectroscopic grade and were dried over activated alumina or activated 4-Å molecular sieves prior to use. Cyclooctatetraene was purified by passage down a short alumina column. All other reagents were purchased as reagent grade and used as received. UV-vis spectra were obtained on either a Cary 17D spectrophotometer or a Hewlett Packard 8450A spectrophotometer. $^1H$ NMR were obtained either with a Varian CFT 20 spectrometer equipped with a 79.5-MHz proton accessory or on a Nicolet 300-MHz spectrometer.

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**Synthesis of Compounds.** All previously reported compounds were checked for purity by comparison of $^1$H NMR data with their literature values.

$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}COT)]PF_6$ was synthesized as reported by Gill and Mann[3] via the exchange reaction of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}ClC_6H_5)]PF_6$ via sunlight photolysis for 3 h at -8 °C.

$[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-}COT)]PF_6$ was synthesized as reported by Catheline and Astruc[4] by refluxing $[(\eta^5\text{-}C_5(CH_3)_5)Fe(CH_3CN)_3]PF_6$ with COT for 1 week. Recrystallization from $CH_2Cl_2$/ether gave large orange air-stable crystals.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$ was synthesized as reported by Gill and Mann[5] by stirring $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ with COT for 15 min.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)CO]PF_6$ was synthesized as reported by Gill and Mann[3] by addition of CO to $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ followed by addition of COT.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(P(OCH_3)_3)]PF_6$ was synthesized by reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(P(OCH_3)_3)]PF_6$ with COT. Full details of this synthesis will be reported in a subsequent paper.

**Photolysis Procedures.** Photolyses were carried out with a 100-W medium-pressure mercury lamp (Oriel) outfitted with an appropriate filter (436-nm interference filter for cyclopentadienyl iron complexes and Pyrex-filtered for ruthenium and pentamethylcyclopentadienyl iron complexes). Low-temperature photolyses were carried out either in dry ice/2-propanol (-75 °C) or $CH_3CN$/liquid-nitrogen (-45 °C) slush baths. Dark, control reactions confirmed the photochemical nature of all the reactants studied.

## Results and Discussion

**Photochemical Reactivity of the $\eta^6$-COT Complexes.** $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}COT)]PF_6$, $[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-}COT)]PF_6$, and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$ were studied under conditions thought amenable to the spectroscopic observation of coordinatively unsaturated complexes with $\eta^2$- or $\eta^4$-coordinated cyclooctatetraene ligands. We were unsuccessful in the direct, spectroscopic observation of such an intermediate, but the products obtained from the photochemical reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)CO]PF_6$ are consistent with the intermediacy of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)]^+$.

$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}COT)]PF_6$ was photolyzed at low temperature in acetone (-75 °C), methylene chloride (-75 °C), solutions of $P(OCH_3)_3$ in methylene chloride (-75 °C), and acetonitrile (-45 °C). In acetone and acetonitrile solutions, the only new product observed by $^1$H NMR spectroscopy was $[(\eta^5\text{-}C_5H_5)Fe(S)_3]PF_6$ where S = acetone[6] or acetonitrile.[7] In methylene chloride and methylene chloride solutions with 1 equiv of trimethyl phosphite present, no apparent reaction was observed by $^1$H NMR spectroscopy after several hours of photolysis. Similarly, photolysis of $[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-}COT)]PF_6$ in acetonitrile solutions under vacuum with Pyrex-filtered light gave, as the only observed product, $[(\eta^5\text{-}C_5(CH_3)_5)Fe(CH_3CN)_3]PF_6$.[4]

Acetonitrile solutions of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$ were photolyzed under nitrogen with Pyrex-filtered light at room temperature and at -45 °C. As in the case of the (pentamethylcyclopentadienyl)iron complex, the only product observed was the tris(acetonitrile) complex.[5] Photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$ with 1 equiv of trimethyl phosphite in methylene chloride gave exclusively phosphite decomposition products by $^1$H and $^{31}$P NMR analysis. However, with a large excess of phosphite present, photolysis yielded $[(\eta^5\text{-}C_5H_5)Ru(P(OCH_3)_3)_3]PF_6$[5] in addition to the phosphite decomposition products. No peaks indicative of an intermediate were observed in either the phosphite or the cyclopentadienyl region of the $^1$H NMR spectrum of the photolysis mixture. Under these conditions, the reaction is slow with about 5% conversion after 90 min of photolysis. In neat methylene chloride, no reaction was observed.

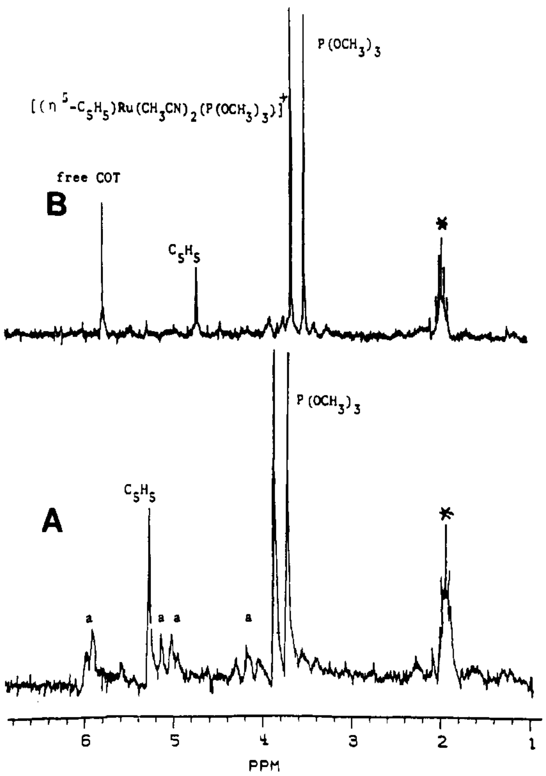
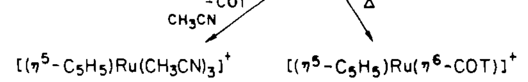


Figure 1. 79.5-MHz $^1$H NMR spectra obtained before (A) and after (B) 10 min of photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(P(OCH_3)_3)]PF_6$ in degassed $CD_3CN$. Peaks labeled a are due to the $\eta^6$-COT moiety in the starting complex. The starred peaks are due to the solvent.

**Photochemical Reactivity of the $\eta^4$-COT Complexes.** $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)L]PF_6$ (L = CO, $P(OCH_3)_3$) compounds were photolyzed at room temperature in acetonitrile solutions. The phosphite complex lost COT very efficiently with approximately 88% conversion to $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(P(OCH_3)_3)]PF_6$[5] after 5 min of photolysis. $^1$H NMR spectra before and after photolysis are presented in Figure 1. The much higher efficiency of this reaction as compared with the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]PF_6$ under similar conditions suggests that the $\eta^4$ complex is more photochemically labile than the $\eta^6$ complex, which required about 90 min of photolysis to reach 5% conversion under identical conditions.

Photolysis of the carbonyl complex in acetonitrile exhibited behavior significantly different from that exhibited by the $P(OCH_3)_3$ complex. Photolysis yields a mixture of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$. A series of $^1$H NMR spectra obtained during the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)(CO)]^+$ are shown in Figure 2. They may be explained by the following sequence of events:



The CO ligand is rapidly lost in the primary photochemical reaction to give coordinatively unsaturated $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}COT)]^+$. Then through competing pathways, either the $\eta^4$-COT converts to $\eta^6$-COT to give $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}COT)]^+$ or the $\eta^4$-COT ligand is lost to give the tris(acetonitrile) complex. Previously discussed experiments have shown that loss of COT

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(6) Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}arene)]^+$ (arene = *p*-xylene, benzene) in acetone at -80 °C also produces $[(\eta^5\text{-}C_5H_5)Fe(CH_3C(O)CH_3)_3]^+$ with a $^1$H NMR resonance at 4.18 ppm due to the coordinated $C_5H_5$ moiety: Schrenk, J. L. Ph.D. Thesis, University of Minnesota, 1985.

(7) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986.

(8) Photolysis of $P(OCH_3)_3$ in the absence of the ruthenium complex results in the formation of new $^1$H NMR resonances that are identical in position. The nature of these products have not been determined.

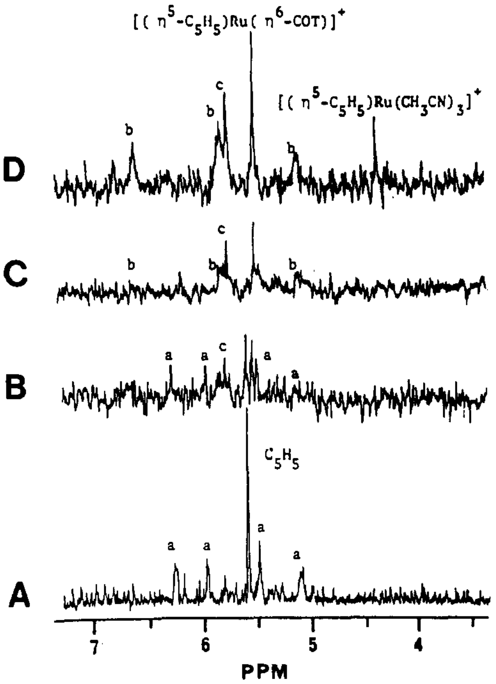

**Figure 2.** 79.5-MHz $^1$H NMR spectra obtained during the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(CO)]PF_6$ in $CD_3CN$: A, before photolysis; B, after 1 min of photolysis; C, after 6 min of photolysis; D, after 16 min of photolysis. Peaks labeled a are due to the $\eta^4$-COT moiety in the starting complex. Peaks labeled b are peaks due to $\eta^6$-COT in one of the products, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$. The peak labeled c is due to free COT.

from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ occurs too slowly (ie. 5% in 90 min) to be the source of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(CO)]^+$. Disappearance of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(CO)]^+$ is complete within 16 min of photolysis. Primary photochemical loss of $\eta^4$-COT is ruled out because no $^1$H NMR peak is observed for the stable $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(CO)]PF_6$ complex.

To insure that the $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ formed in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(CO)]^+$ was not formed via the synthetic reaction

$$[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+ + \text{COT} \rightarrow [(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+ + 3CH_3CN$$

the rate of this thermal reaction was studied. A 0.002 M solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ was photolyzed with unfiltered light for 4 h and monitored by UV–vis spectroscopy for the appearance of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ ($\lambda_{max}$ = 365 nm).[5] An absorbance change at 365 nm of 0.21 was observed after 4 h. The cell was then stored in the dark and monitored periodically for the loss of absorbance due to $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$. After 4 h, a change in absorption at 365 nm of 0.006 was observed, corresponding to less than 5% re-formation of the tris(acetonitrile) complex to form $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$. Data collected for the first 119 h of the recombination reaction exhibited (Figure 3) a linear dependence between $1/[[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+]$ and $t$ (second order, equal concentration kinetics). From the slope, a second-order rate constant of 8.9 (0.4) $\times 10^{-3}$ M$^{-1}$ s$^{-1}$ was obtained. The small value for this rate constant indicates that the slow rate for photochemical release of COT from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ is not due to the competitive back reaction of COT with the tris(acetonitrile) complex.

## Conclusions

In an attempt to observe the transformation from an $\eta^6$-COT to an $\eta^4$-COT configuration, solutions of $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-COT})]^+$ were photolyzed under a variety of conditions. No evidence for stable $\eta^4$ intermediates was obtained in any of these experiments. $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(L)]^+$ (L = CO, $P(OCH_3)_3$) were photolyzed to observe the reverse $\eta^4 \rightarrow \eta^6$ transformation. When L = $P(OCH_3)_3$, $\eta^4$-COT is lost in the primary photochemical step to give $[(\eta^5\text{-}C_5H_5)Ru(P(OCH_3)_3)(CH_3CN)_2]^+$. In contrast, when L = CO, CO is lost in the primary step to give ultimately $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$. The loss of $\eta^4$ COT from the putative intermediate $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})]^+$ is competitive with the $\eta^4 \rightarrow \eta^6$ collapse to form $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$. The slow back-reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ and COT precludes the formation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$ on the time scale of these experiments. Consequently the formation of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ in the photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(CO)]^+$ does not occur via secondary photolysis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$.

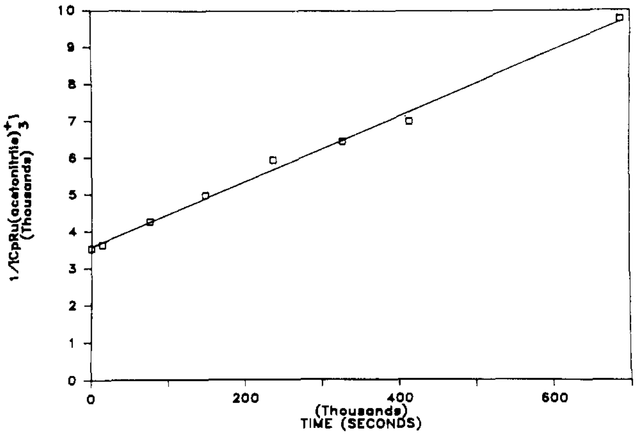

**Figure 3.** Plot of the reciprocal of $[[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+]$ vs. time for the 25 °C reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$ with COT. Squares represent experimental data; the least-squares line has intercept = 3580 M$^{-1}$, slope = $8.9 \times 10^{-3}$ M$^{-1}$ s$^{-1}$, and correlation coefficient = 0.9974.

**Acknowledgment.** Support of this work was through a grant from the U.S. DOE.

**Registry No.** $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-COT})]PF_6$, 79122-13-7; $[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-COT})]PF_6$, 86991-94-8; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]PF_6$, 80049-73-6; $[(\eta^5\text{-}C_5H_5)Fe(CH_3C(O)CH_3)_3]PF_6$, 101858-50-8; $[(\eta^5\text{-}C_5H_5)Fe(CH_3CN)_3]PF_6$, 99594-91-9; $[(\eta^5\text{-}C_5(CH_3)_5)Fe(CH_3CN)_3]PF_6$, 86991-88-0; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$, 80049-61-2; $[(\eta^5\text{-}C_5H_5)Ru(P(OCH_3)_3)_3]PF_6$, 71397-30-3; $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})CO]PF_6$, 80049-75-8; $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-COT})(P(OCH_3)_3)]PF_6$, 101834-68-8; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(P(OCH_3)_3)]PF_6$, 80049-65-6; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+$, 80049-60-1; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-COT})]^+$, 80049-72-5.

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# Rapid Pulse-Radiolytic Reduction of Iron(III) Complexes of Tetrakis(4-sulfonatophenyl)porphine Anion and Tetrakis(*N*-methylpyrid-4-yl)porphine Cation

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*Received January 15, 1986*

Pulse radiolysis of water generates the primary radicals $e_{aq}^-$, H, and OH. With appropriate conditions each can be examined separately or used to produce other reducing or oxidizing radicals.[1] The distinct advantage of the technique is in the very rapid production of the radicals and, because of this, in the observation of very labile intermediates that may be produced in the interaction of the radicals with substrates.[1] The porphyrins and their metal complexes have been popular targets for this approach (For recent literature, see ref 2–12). Complexes of both naturally occurring

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