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Synthetic and Spectroscopic Studies on the Hexakis(aryl isocyanide) Complexes of Ruthenium(II) $[Ru(CNAr)_6](PF_6)_2$

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Received September 8, 1986

Several studies have revealed that d^6 isocyanide complexes exhibit ligand photosubstitution reactions analogous to those of metal carbonyls.[1–4] However, due to their more extended electronic structure, complexes of isocyanide ligands are expected to exhibit more varied behavior. While ligand field, or d–d*, states dominate the absorption spectrum and the photochemistry[3] of $[Fe(CNCH_3)_6]^{2+}$, aryl isocyanide complexes of low-valent metal centers exhibit a series of low-lying metal-to-ligand charge-transfer (CT) states.[2,4] In the case of hexakis(aryl isocyanides) of W(0), viz. $W(CNAr)_6$, a CT state occurs as the lowest energy excited state, and it appears to undergo associative ligand substitution reactions.[2] The isoelectronic Re(I) systems are more photoactive,[4] but the photochemistry occurs from a d–d* state that is either the lowest energy excited state or one that is readily populated at thermal energies.[4]

In the present work we have examined a series of Ru(II) complexes of aryl isocyanides that are isoelectronic with the aforementioned W(0) and Re(I) species. These compounds are of interest because the CT states should be shifted to higher energy (relative to the energies of W(0) and Re(I)) due to the increased charge of the central metal. At the same time, intraligand (IL) excited states may be expected to be more prominent in the photochemistry and photophysics. This study became possible following our development of a synthetic route to alkyl isocyanide complexes of the type $[Ru(CNR)_6](PF_6)_2$[5] and, subsequently, our modification of this procedure to afford the hexakis(aryl isocyanide) analogues.

Experimental Section

The diruthenium(II,III) acetate $Ru_2(O_2CCH_3)_4Cl$ was prepared as described in the literature.[6] The isocyanide ligands *p*-tolyl isocyanide (*p*-tolNC) and 2,4,6-trimethylphenyl isocyanide (mesNC) were prepared by using the method described by Weber et al.,[7] while 2,6-dimethylphenyl isocyanide (xylNC) was purchased from Fluka AG. Potassium hexafluorophosphate was purchased from Alfa Products and recrystallized from water before use. The dichloromethane and methanol solvents that were used in the spectroscopic characterizations were distilled-in-glass grade from Burdick and Jackson. Absolute ethanol was obtained from U. S. Industrial Chemicals Co. All other reagents were obtained from commercial sources and were used without subsequent purification. Solvents used in the synthetic procedures were reagent grade and were deoxygenated prior to use. All reactions were carried out under an atmosphere of nitrogen.

Preparative Procedures. Reactions of $Ru_2(O_2CCH_3)_4Cl$ with Aryl Isocyanides. (i) $[Ru(CNxyl)_6](PF_6)_2$. A mixture comprising $Ru_2(O_2CCH_3)_4Cl$ (0.119 g, 0.251 mmol), KPF_6 (0.3 g), $Pb(NO_3)_2$ (0.3 g), and xylyl isocyanide (0.561 g, 4.3 mmol) was treated with 10 mL of methanol and refluxed for 18 h. The brown mixture was cooled to room temperature and evaporated to dryness and the residue extracted with CH_2Cl_2. The insoluble residue consisted of potassium and lead salts. The brown filtrate was taken to dryness, redissolved in a minimum volume of CH_2Cl_2, and treated with diethyl ether to precipitate the off-white $[Ru(CNxyl)_6](PF_6)_2$. This complex was purified by recrystallization from CH_2Cl_2/diethyl ether and the crystals washed with diethyl ether and vacuum dried for 30 min; yield 0.30 g (51%). Anal. Calcd for $C_{54}H_{54}F_{12}N_6P_2Ru$: C, 55.05; H, 4.63, N, 7.14. Found: C, 55.06; H, 4.61; N, 7.09.

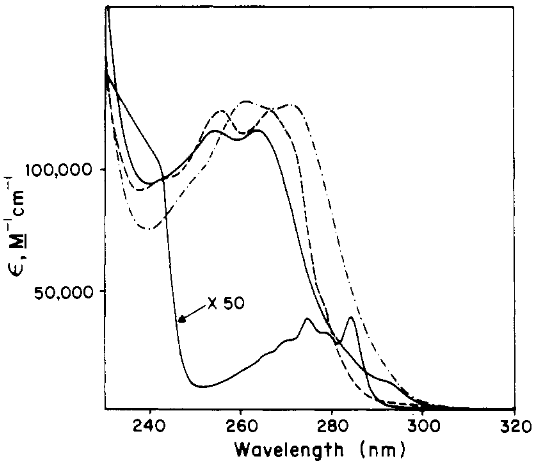

Figure 1. Electronic absorption spectra of xylNC (—, ×50), $[Ru(CNxyl)_6]^{2+}$ (—), $[Ru(CN\text{-}p\text{-}tol)_6]^{2+}$ (- - -), and $[Ru(CNmes)_6]^{2+}$ (–·–). The solvent is CH_2Cl_2, and $T = 20$ °C.

Other complexes of the type $[Ru(CNAr)_6](PF_6)_2$ (Ar = *p*-tol, mes) were prepared by a method very similar to that above.

(ii) $[Ru(CN\text{-}p\text{-}tol)_6](PF_6)_2$: yield 72%. Anal. Calcd for $C_{48}H_{42}F_{12}N_6P_2Ru$: C, 52.70; H, 3.88. Found: C, 53.09; H, 3.99.

(iii) $[Ru(CNmes)_6](PF_6)_2$: yield 65%. Anal. Calcd for $C_{60}H_{66}F_{12}N_6P_2Ru$: C, 57.09; H, 5.27. Found: C, 57.01; H, 5.88.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates or on CH_2Cl_2 solutions with an IBM Instruments IR/32 Fourier transform (4000–400 cm^{-1}) spectrometer. The electronic absorption spectra were obtained with a Perkin-Elmer Lambda 4C UV/vis spectrophotometer. Emission spectra were acquired with a Perkin-Elmer MPF-44B spectrofluorometer; the emission lifetimes were obtained on the same instrument with the use of a rotating-can phosphoroscope. The photolysis equipment has been described previously.[4] Electrochemical measurements were carried out on dichloromethane or acetonitrile solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{p,c}$ values were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. ^1H NMR spectra were recorded at 90 MHz with a Perkin-Elmer R32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer. Resonances were internally referenced to residual protons (δ +2.05) in the $(CD_3)_2CO$ solvent. Conductivities were measured with an Industrial Instruments Inc. Model RC 16B2 conductivity bridge on solutions of the complexes ($\sim 1.0 \times 10^{-3}$ M) in acetonitrile. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

Synthesis of $[Ru(CNAr)_6](PF_6)_2$ and Preliminary Characterization Studies. We have previously reported that the alkyl isocyanide complexes $[Ru(CNR)_6](PF_6)_2$ (R = $CHMe_2$, CMe_3, C_6H_{11}) can be prepared in quite high yield through the reaction of $Ru_2(O_2CCH_3)_4Cl$ with an excess of RNC and KPF_6 in hot methanol.[5] An extension of this procedure to the aryl isocyanides ArNC (Ar = *p*-tolyl, xylyl, mesityl) gave the analogous $[Ru(CNAr)_6](PF_6)_2$ complexes as colorless crystals in yields exceeding 50%. Solutions of these complexes in acetonitrile (ca. 1×10^{-3} M) possess conductivities typical of 1:2 electrolytes,[8] viz., Λ_m = 260–290 Ω^{-1} mol^{-1} cm^2. Like their alkyl isocyanide analogues, solutions of $[Ru(CNAr)_6](PF_6)_2$ in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ showed no significant electrochemical response in the potential

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(1) Geoffroy, G. L.; Wrighton, M. S. *Organic Photochemistry*; Academic: New York, 1979; Chapter 2.

(2) Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. *Adv. Chem. Ser.* **1978**, *No. 168*, 44.

(3) Costanzo, L. L.; Giuffrida, S.; DeGuidi, G.; Condorelli, G. *Inorg. Chim. Acta* **1985**, *101*, 71.

(4) Stacy, N. E.; Conner, K. A.; McMillin, D. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3649.

(5) Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 3363.

(6) Mitchell, R. W.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 846.

(7) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(8) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

0020-1669/87/1326-0966$01.50/0

Table I. Absorption and Emission Data

	absorption[a]		emission[b]		
syst	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϕ[c]	τ, ms[d]
xylNC	284	780	381	1.0	7000
	279	650	390		
	275	760	398 sh		
	271	580	405		
	266	480	412		
$[Ru(CNxyl)_6]^{2+}$	264	116 000	392	2.7	22
	255	116 000	400		
			410 sh		
			417		
			427		
			437		
$[Ru(CN\text{-}p\text{-}tol)_6]^{2+}$	267	124 000	390	1.8	20
	256	123 000	402 sh		
			408		
			414		
			421 sh		
			428		
			435		
$[Ru(CNmes)_6]^{2+}$	272	127 000	398	3.3	25
	262	128 000	406		
			414 sh		
			422		
			432		

[a] In CH_2Cl_2 solution at 20 °C. [b] In 4:1 EtOH/MeOH glass at 77 K; excited at 268 nm. [c] Relative to xylNC phosphorescence yield; error estimate ±10%. [d] Error estimate ±10%.

range +1.8 to −1.8 V vs. Ag/AgCl although in 0.1 M *n*-Bu_4NPF_6/CH_3CN they displayed irreversible reductions below ca. −1.6 V.[9] The Nujol mull IR spectra of these three salts showed a single intense ν(CN) mode at 2190 ± 2 cm^{-1} (an additional feature at 2213 m cm^{-1} was present in the case of the mesNC derivative). Related measurements on CH_2Cl_2 solutions of $[Ru(CNAr)_6](PF_6)_2$ showed ν(CN) at 2188 vs and 2182 vs cm^{-1} in the case of Ar = xylyl and mesityl, respectively.[10]

Electronic Absorption and Emission Spectra. The absorption spectra of the free xylNC ligand and the three homoleptic aryl isocyanide complexes of Ru(II) are presented in Figure 1. Absorption maxima are compiled in Table I. The near-UV spectrum of the xylNC ligand (Figure 1) consists of a relatively weak π–π^* absorption band that appears to exhibit multiple vibrational progressions. The two most prominent vibronic maxima in the absorbance spectrum are separated by ca. 1200 cm^{-1}. The spectra of the $[Ru(CNAr)_6]^{2+}$ species exhibit much more intense absorption bands (Figure 1). In each case, two bands of approximately equal intensity are resolved with shoulders apparent on the high- and low-energy sides. The intensities and the energies of these bands are sensibly related to metal-to-ligand charge-transfer (CT) transitions previously observed in the W(0)[2] and Re(I)[4] analogues, and a similar assignment is indicated.

Emission spectra, measured in a 4:1 ethanol/methanol (v/v) glass at 77 K, for the series are presented in Figure 2. The emission lifetimes and relative emission quantum yields, as obtained by the method of Parker and Rees,[11] are also listed in Table I. The phosphorescence spectrum of the xylNC ligand is highly structured in the glass at 77 K, and the lifetime indicates that the emission is from a $^3\pi\pi^*$ state. However, neither the relative intensities nor the vibrational frequencies that are resolved are readily related to those in the absorption spectrum. A structured fluorescence emission is also observed in the region of 280–310 nm, analogous to that of phenyl isocyanide,[12] but the fluorescence is not considered further since it is effectively quenched in the emission spectra of the ruthenium complexes. Nalepa and Laposa[12] have studied the phosphorescence from phenyl isocyanide in frozen matrices and have assigned the main progression at 1595 cm^{-1} to the totally symmetric ring breathing vibration. The analogous splitting in the phosphorescence spectrum of xylyl isocyanide is associated with a frequency of 1560 cm^{-1}.

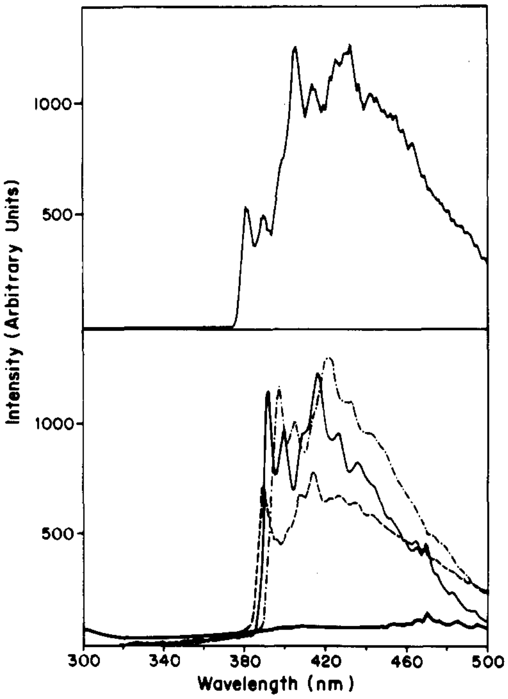

Figure 2. Luminescence spectra: (top) xylNC; (bottom) $[Ru(CNxyl)_6]^{2+}$ (—, thin trace), $[Ru(CN\text{-}p\text{-}tol)_6]^{2+}$ (- - -), $[Ru(CNmes)_6]^{2+}$ (-·-), solvent blank (—, thick trace). Spectra were run in a 4:1 EtOH/MeOH glass at 77 K. The excitation monochromator was set to a particular wavelength between 265 and 270 nm and was optimized for each sample; the excitation and emission slits were set at 3 nm. The intensities are not to scale.

Although the pattern of vibronic intensities is altered, similar vibrational structure is present in the emission from each of the $[Ru(CNAr)_6]^{2+}$ salts; hence, the emission is attributed to the analogous $^3\pi\pi^*$ states. The emission lifetimes are significantly decreased for the complexes compared with the free xylyl isocyanide, presumably because of the presence of the heavy metal center.

Photochemistry. The xylNC complex was chosen as a representative system and irradiated at 260 nm in CH_2Cl_2 and CH_3OH solutions. Spectral changes occurred, but the photoproducts have not yet been identified. The analogous $[Fe(CNMe)_6]^{2+}$ complex undergoes photoinduced ligand substitution, which has been attributed to a reactive d–d* excited state.[3] The energies of the d–d* excited states of our systems are unknown, but within the related series $[Fe(CN)_6]^{4-}$,[13] $[Fe(CNMe)_6]^{2+}$,[3] and $[Ru(CN)_6]^{4-}$,[13] the d–d* absorption occur at similar energies. This correlation is of interest because $[Ru(CN)_6]^{4-}$[14] and the isoelectronic $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ systems[15] undergo photoaquation upon irradiation with UV light. Moreover, the 0–0 energies of the reactive d–d* states of the Rh(III) and Ir(III) hexacyanide complexes are estimated to be 2.5 μm^{-1} (400 nm) and 2.65 μm^{-1} (373 nm), respectively,[15] close to the energies of the highest energy vibronic components of the $^3\pi\pi^*$ states studied here. Hence, the photochemistry of $[Ru(CNAr)_6]^{2+}$ may be difficult to unravel since

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(9) For Ar = *p*-tolyl, $E_{p,c}$ = −1.73 and −1.93 V, for Ar = xylyl, $E_{p,c}$ = −1.60 V (with a product wave at $E_{p,c} \simeq -0.65$ V), and for Ar = mesityl, $E_{p,c}$ = −1.80 V vs. Ag/AgCl.

(10) ^1H NMR spectral measurements on solutions of $[Ru(CNAr)_6](PF_6)_2$ in $(CD_3)_2CO$ showed the samples to be spectroscopically pure. These spectral data, which displayed the correct integrated relative intensities, are as follows (s = singlet, d = doublet, and m = multiplet): Ar = *p*-tolyl, δ +2.42 (s, $-CH_3$), +7.41 (d, C_6H_5), +7.72 (d, C_6H_5); Ar = xylyl, δ +2.60 (s, $-CH_3$), +7.43 (m, C_6H_3); Ar = mesityl, δ +2.35 (s, *p*-CH_3), +2.55 (s, *o*-CH_3), +7.20 (s, C_6H_2).

(11) Parker, C. A.; Rees, W. T. *Analyst* (*London*) **1960**, *85*, 587.

(12) Nalepa, R. A.; Laposa, J. D. *J. Lumin.* **1974**, *8*, 429.

(13) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984; pp 463–465.

(14) Emschwiller, G. *C. R. Hebd. Seances Acad. Sci.* **1959**, *248*, 959.

(15) Frink, M. E.; Ford, P. C. *Inorg. Chem.* **1985**, *24*, 3494.

it is possible that the ^{3}dd* states and the $^3\pi\pi^*$ states react in parallel.

Acknowledgment. We thank the National Science Foundation for the support of this work through grants to R.A.W. (Grant No. CHE85-06702) and D.R.M. (Grant No. CHE84-14267).

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Manganese(III)-Induced Electron Transfer in Pentaamminecobalt(III) Complexes of α-Hydroxy Acids and in Unbound Ligands

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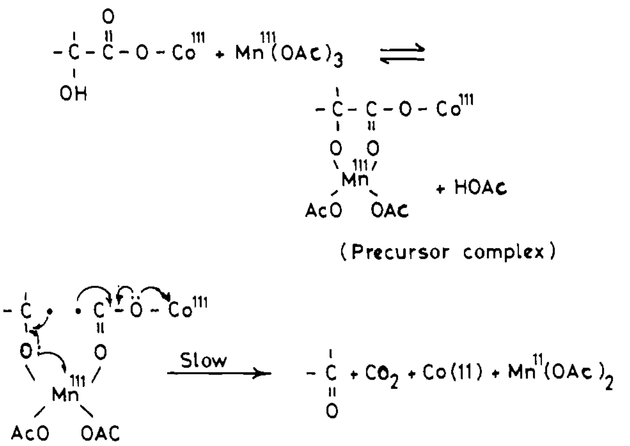
Received February 12, 1986

The oxidation of glycols,[1] α-hydroxy acids,[2] α-hydroxy ketones,[3] and several other organic substrates[4] by manganese(III) pyrophosphate are well documented. Also manganese(III) sulfate was used as an oxidant in the reactions with formic acid,[5] formaldehyde,[5] and α-hydroxy acids[6,7] wherein it has been shown that it behaves as a carbon–carbon bond cleaving agent. The report on the oxidation of glycolic acid by the Mn^{3+}(aq) ion also lends support for such a bond-cleavage action.[8] But the reports of reactions with manganese(III) acetate as oxidant are limited,[3,9–13] and its behavior toward hydrazine[10] has been shown to be exceptional. Hence the present study on the manganese(III) acetate and manganese(III) perchlorate induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids and oxidation of unbound ligands has been undertaken.

Experimental Section

Manganese(III) acetate dihydrate was prepared by following the procedure in the literature,[14] and the sample was of 99% purity as evidenced from the estimation of the purity of a solution in acetic acid by an iodometric procedure. Manganese(III) perchlorate solution was prepared when necessary by following the modified procedure. To about 10 g of manganese(II) perchlorate kept at 0 °C was added 15 mL of 12 M $HClO_4$. Then 20 mL of a saturated solution of $KMnO_4$ in water was added slowly with stirring until it becomes decolorized. The solution was then filtered, and the manganese(III) perchlorate in the filtrate was estimated by an iodometric procedure. Reactions with manganese(III) acetate were performed in solutions with 76% aqueous acetic acid[15a] whereas reactions with manganese(III) perchlorate were performed in 60% aqueous acetic acid.[15b] The cobalt(III) complexes of lactic and benzilic acids were prepared as their perchlorates by following the procedure of Butler and Taube,[16a] and the corresponding derivative of mandelic acid was prepared by the method of Fan and Gould.[16b]

Scheme I



Rates of manganese(III) acetate reactions with cobalt(III) complexes and unbound ligands were estimated spectrophotometrically (Carl Zeiss VSU2-P instrument) from the observed decrease in absorbance at 350 nm for Mn(III). In the case of manganese(III) perchlorate, specific rates were evaluated spectrophotometrically from the decrease in absorbance at 380 nm.[17] The disappearance of cobalt(III) was followed spectrophotometrically from the decrease in absorbance at 502 nm. Conversions were followed for at least 4 half-lives. Specific rates from successive half-lives agreed within ±7%, and the average values did not differ from those obtained from a logarithmic plot of changes in absorbance vs. time. Temperatures were kept at 28 ± 0.2 °C during the entire series of experiments.

One of the products of manganese(III) induced electron transfer in cobalt(III) complexes of α-hydroxy acids, Co(II), was estimated after 9 half-lives, by diluting the reaction mixture by a factor of 10 with concentrated HCl, allowing the evolution of chlorine to cease, and then measuring the absorbance of chloro complex of cobalt(II) at 692 nm (ϵ = 560 M^{-1} cm^{-1}).[18] Optical density measurements with corresponding amounts of manganese(III) were used as a blank and the corrections applied were less than 5% of the total absorbance. The amount of carbonyl compound formed, in the manganese(III) reaction with cobalt(III) complexes of α-hydroxy acids or unbound ligands, was estimated by neutralizing the reaction mixture, after 9 half-lives, with saturated $KHCO_3$ solution, and the organic product from the filtrate was separated by extracting in ether. The amount of benzaldehyde and benzophenone formed were determined by following an earlier procedure.[20] The amount of acetaldehyde formed from manganese(III)–lactato complex (or) lactic acid reaction was estimated from the amount of 2,4-dinitrophenylhydrazone derivative (mp 168 °C).[19] The amount of CO_2 evolved in each reaction was estimated by following an earlier procedure.[20]

Table I summarizes the yield of products of manganese(III) acetate and manganese(III) perchlorate induced electron transfer in pentaamminecobalt(III) complexes of mandelic acid. The above results suggested that, for 1 mol of manganese(III), nearly 1 mol of cobalt(II), 1 mol of CO_2 and 1 mol of carbon–carbon cleavage product (carbonyl compound) were formed. The reactivity of manganese(III) compounds toward these cobalt(III) complexes seems to resemble that of Ce(IV)[20] (except with the benzilato complex). Table II includes stoichiometric data for the manganese(III) oxidation of mandelic acid. With unbound ligands, 1 mol of α-hydroxy acid or a keto acid like pyruvic acid reacts with nearly 2 mol of manganese(III) compound, yielding nearly 1 mol of CO_2 and 1 mol of carbon–carbon cleavage product, suggesting nearly

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(1) Drummond, A. Y.; Waters, W. A. *J. Chem. Soc.* **1953**, 3119.
(2) Levesley, P.; Waters, W. A. *J. Chem. Soc.* **1955**, 217.
(3) Griegee, R.; Kraft, L.; Rank, B. Justus *Liebigs Ann. Chem.* **1933**, *507*, 159.
(4) Wiberg, K. B. *Oxidation in Organic Chemistry*, Part A; Academic: New York, 1973, p 185.
(5) Kemp, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 339.
(6) Littler, J. S. *J. Chem. Soc.* **1962**, 2190.
(7) Kemp, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 1192.
(8) Metha, M.; Nagori, R. R.; Kumar, A.; Mehrotra, R. N. *Indian J. Chem., Sect. A* **1982**, *21A*, 777.
(9) Julian, K. D. Phil. Thesis, University of Oxford, Oxford England, 1962 (as cited in ref 4, p 195).
(10) Cuy, E. J.; Rosenberg, M. E.; Bray, W. C. *J. Am. Chem. Soc.* **1924**, *46*, 1796.
(11) Zonis, S. A.; Kornilova, Yu. I. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1950**, *20*, 130.
(12) Rindone, B.; Scolastico, C. *Tetrahedron Lett.* **1974**, 3379.
(13) Gilmore, J. R.; Mellor, J. M. *J. Chem. Soc. C* **1971**, 2355.
(14) (a) Andrulis, P. J., Jr.; Michael, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 5473. (b) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138.
(15) (a) The dissociation/disproportionation of manganese(III) acetate is at a minimum in 76% aqueous acetic acid. (b) Manganese(III) perchlorate solution remains stable in 60% aqueous acetic acid.
(16) (a) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. (b) Fan, F. R. R.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.
(17) Since the rate of manganese(III) perchlorate oxidation of benzilic acid is very fast, only a stoichiometry study has been made.
(18) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.
(19) Vogel, A. I. *Textbook of Practical Organic Analysis*; Longman: London, 1978; p 1191.
(20) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 208.