soluble brown material, probably iron(III) oxide, was removed and the filtrate was acidified with a few drops of concentrated HCl. The solution immediately turned dark red and on standing and cooling it deposited dark green needles. These were washed with water and dried over phosphoric oxide. *Anal.* Calcd for $[FeB(NCS)_2]NCS$: C, 42.94; H, 4.60; N, 22.25; S, 19.11; Fe, 11.09. Found: C, 41.95; H, 4.51; N, 21.50; S, 18.47; Fe, 11.02.

$[FeBX_2]ClO_4$ (X = Cl, Br, I, or NCS).—The same general method of preparation was employed for all four complexes. A 2.18-g amount of $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ was dissolved in water with warming. The hot solution was acidified with 3–4 drops of 60% $HClO_4$ and filtered into a warm, aqueous solution of NaX (~0.01 mol). The bromide separated immediately; the other complexes separated on standing and cooling. They were recrystallized from hot water containing 1 drop of 60% $HClO_4$. *Anal.* Calcd for $[FeBCl_2]ClO_4$: C, 35.87; H, 4.48; N, 13.84; Cl, 20.99. Found: C, 36.07; H, 4.64; N, 14.02; Cl, 21.30. Calcd for $[FeBBr_2]ClO_4$: C, 30.48; H, 3.79; N, 11.71; Cl, 5.86; Br, 27.06. Found: C, 30.62; H, 3.94; N, 11.90; Cl, 6.02; Br, 27.16. Calcd for $[FeBI_2]ClO_4$: C, 26.40; H, 3.40; N, 10.29; I, 37.20. Found: C, 26.33; H, 3.43; N, 9.81; I, 38.20. Calcd for $[FeB(NCS)_2]ClO_4$: C, 37.50; H, 4.23; N, 18.0; S, 11.8; Cl, 6.51; Fe, 10.20. Found: C, 38.76; H, 4.38; N, 18.59; S, 12.10; Cl, 6.41; Fe, 10.54.

$[FeBCl_2]BF_4$.—The method of preparation was the same as that for $[FeB(NCS)_2]NCS$ except that $NaBF_4$ was used instead of NaNCS. Some insoluble material remaining after air oxidation was removed and the filtrate was acidified with a few drops of concentrated HCl. On standing, yellow crystals separated. They were recrystallized from hot water containing 1 drop of concentrated HCl. *Anal.* Calcd for $[FeBCl_2]BF_4$: C, 37.00; H, 4.76; N, 14.39; F, 15.61. Found: C, 35.83; H, 4.46; N, 14.00; F, 15.84

$[Fe_2B_2(NCS)_2O](ClO_4)_2$.—A 0.5-g amount of $[FeB(NCS)_2]ClO_4$ was dissolved in 50 ml of methanol and a 20% ethylenediamine solution was added dropwise until the red color disappeared, then 5 drops more were added. The filtered solution was set aside, and when the volume had fallen to about 10 ml, the brown crystals were isolated by filtering and washed with water, ethanol, and ether. *Anal.* Calcd for $[Fe_2B_2(NCS)_2O](ClO_4)_2$: C, 38.86; H, 4.69; N, 16.99; S, 6.48; Cl, 7.17; O, 14.55. Found: C, 38.44; H, 5.10; N, 16.36; S, 6.03; Cl, 7.10; O, 14.54.

Magnetic Measurements.—For the mononuclear complexes magnetic susceptibility measurements were made at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. Measurements of the variation of the magnetic susceptibility of $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ as a function of temperature between 106 and 316°K were made using a modification[15] of the apparatus described by Figgis and Nyholm.[16] Diamagnetic corrections for ligand and anions were calculated from Pascal's constants. The value of the molar susceptibility derived for ligand B is -161.3×10^{-6} cgsu.

Conductance Measurements.—Molar conductances were measured at 1000 cps and 25° using an Industrial Instruments Inc. Model RC-16B conductivity bridge and a cell having a constant of 1.469. Deionized water was used for preparing aqueous solutions, and nitromethane was dried over molecular sieves for at least 48 hr before use.

Electronic Spectra.—A Cary Model 14 recording spectrophotometer with 1-cm matched silica cells was used for all electronic spectral determinations.

Infrared Spectra.—These were measured over the range 4000–400 cm^{-1} using a Perkin-Elmer Model 337 grating spectrophotometer. Samples were prepared both in potassium bromide pellets and in Nujol mulls.

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged. The assistance of Mr. Philip Bryan during the early stages of this investigation is deeply appreciated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Photochemical Reactions of Cobalt(III) β-Ketoenolates in Organic Solvents[1]

BY NICOLAE FILIPESCU[2] AND HLA WAY

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Tris(acetylacetonato)cobalt(III), tris(benzoylacetonato)cobalt(III), and tris(dibenzoylmethanato)cobalt(III) have been photolyzed in different organic solvents. The complexed Co(III) ion is reduced photochemically to Co(II) with simultaneous oxidative fragmentation of one β-ketoenolate group. The reaction was partly reversible in the presence of oxygen. The quantum yields were found to be wavelength dependent and ranged from around 10^{-3} for excitation in the first d–d band to 0.6 in the ultraviolet region. A reaction mechanism consistent with the identified photoproducts is proposed.

An increasing number of papers have been published during the past 10 years on the photolysis of transition metal complexes in aqueous solutions.[3–5] However, very little is known about the photochemistry of transition metal chelates in nonpolar or less polar organic solvents. Presently we wish to report on the photochemical behavior of three cobalt(III) β-ketoenolates on exposure to near-ultraviolet irradiation in various organic solvents. A number of secondary reactions such as thermal and photoaquation or hydrolysis may be absent in nonpolar solvents, the role of which was expected to be less significant to the photochemical process than that of water.

The tris chelates of cobalt(III) with acetylacetone, $Co(acac)_3$, benzoylacetone, $Co(bzac)_3$, and dibenzoyl-

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(1) Taken in part from the dissertation submitted by H. W. to the Graduate School of The George Washington University in partial fulfillment for the degree of Doctor of Philosophy.

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methane, $Co(dbm)_3$, were selected because they are well characterized, chemically stable, and easy to prepare in high purity. The structural variations between these three typically inner complexes offer a gradual change in properties, such as energy of excited states associated with ligands, solubility, stability, and labeling of potential photoproducts, which may be correlated with the photochemical behavior. In addition, preliminary experiments have shown that all three chelates were sensitive to ultraviolet light but perfectly stable to thermal reactions in the photolysis conditions.

Experimental Section

Materials.—$Co(acac)_3$ was prepared from acetylacetone (Eastman), cobaltous carbonate, and hydrogen peroxide.[6] $Co(bzac)_3$ and $Co(dbm)_3$ were obtained from the respective β-diketones and sodium tricarbonatocobalt(III).[7,8] The chelates were purified by repeated recrystallization from appropriate solvents. Spectrograde solvents were used for irradiation experiments. Reagent grade chemicals were employed in the analytical work for product identification. The β-ketoenolates of Co(II) were prepared by known methods.[9]

Apparatus and Procedures.—A Hanovia 450-W arc source was used for all irradiations except for quantum yield measurements in which a 125-W medium-pressure Hg arc (PEK Laboratories) was used in conjunction with a high-intensity Bausch and Lomb monochromator. The irradiation wavelengths were selected by interposing appropriate glass and liquid filters between light source and sample cells or by the monochromator in actinometric measurements. Silica cells (1-cm^2) were used and absorption spectra were recorded on a Cary Model 15 spectrophotometer.

To follow the extent of chemical conversion and to detect eventual dark reactions, 1-cm path cells containing solutions of appropriate concentrations were irradiated for different periods and the changes in the uv–visible absorption spectra were monitored at different intervals. The cells used were provided with side reservoirs and constriction tubes. For irradiation in the absence of oxygen, the solutions were frozen in the side reservoir by immersion in liquid nitrogen, degassed by repeated freeze–pump–thaw cycles, and flame sealed under vacuum.

The ferric oxalate actinometer of Hatchard and Parker[10] was used to measure light intensities and photochemical quantum yields not only for irradiations in the near-uv region but at lower energy in the visible as well. Since the quantum efficiency of the actinometer drops to only about 0.01 at 590 mμ, the quantum yield values reported for irradiations at this wavelength are only informative. The use of this actinometer in the vicinity of 600 mμ is justified only by the even lower photosensitivity of cobalt(III) β-ketoenolates, as shown by control experiments in which optically thick solutions of the two samples were irradiated for long times. The reported quantum yield values are averages of three different runs. Co(III) → Co(II) photoconversion was determined spectrophotometrically from the decrease in absorbance at 590 mμ where only Co(III) absorbs. The variation of the light source with time was found to be within 5%.

For preparative-scale and product-isolation experiments, the 450-W Hanovia lamp was used in conjunction with the immersion-well photochemical reactor in which approximately 225 ml of sample solution surrounded the water-cooled light source.

Characterization of Products.—To identify the reaction products, the irradiated sample was first filtered (where precipitate was formed) and the filtrate was immediately tested by standard procedures for carbonyl, alcoholic OH, and carboxylic acid groups. The presence of carbonyl photoproducts was tested with 2,4-dinitrophenylhydrazine and *p*-nitrophenylhydrazine. For alcoholic hydroxyl groups, we used the acetyl chloride and xanthate procedures. Carboxylic acids were detected with sodium carbonate. Final characterization was done after comparison of melting points, ir absorption spectra, and glpc retention times of isolated products with those of authentic samples. The identification of photoproducts will be described below in detail for the irradiation of $Co(acac)_3$ in diethyl ether.

Following irradiation, the $Co(acac)_2$ precipitate was filtered off, washed with ether, and dried. The pink crystals were soluble in benzene. This solution gave an identical visible absorption spectrum with that of a known sample of $Co(acac)_2$ [λ_{max} 460 (sh), 490, and 540 (sh) mμ]. The solid photoproduct was also dissolved in concentrated hydrochloric acid with formation of a blue solution characteristic of the $CoCl_4^{2-}$ ion. The ir absorption matched that of an authentic sample of $Co(acac)_2$ which was purchased from Research Organic Chemicals and resublimed in our laboratory. The yellow crystals obtained by treating the ether filtrate with 2,4-dinitrophenylhydrazine were found to be contaminated with small amounts of Co(II) compound since it developed the characteristic blue color of $CoCl_4^{2-}$ in concentrated hydrochloric acid. To avoid this coprecipitation, the freshly photolyzed $Co(acac)_3$ solution was immediately distilled under vacuum at temperatures not exceeding 50°. Treatment of the distillate with 2,4-dinitrophenylhydrazine gave a yellow crystalline precipitate which melted sharply at 315–315.5°. Another portion of the distillate was mixed with *p*-nitrophenylhydrazine which led to the formation of needles, mp 230.5°. Based on these two melting points and the ir absorption spectrum of the dinitrophenylhydrazine, the parent carbonyl compound was identified to be biacetyl, $CH_3COCOCH_3$.

To check for the presence of other photoproducts, a small portion of the distillate was injected into an F & M Scientific 700 gas chromatograph. Except for three very small impurity peaks, the chromatogram showed only one other product, acetic acid. Its identity was established from comparison of retention time and ir spectrum of a collected sample with those of an authentic sample. The $Co(acac)_3 \rightarrow Co(acac)_2$ photoconversion can be carried out to completion as shown by the total disappearance of the blue-green color of $Co(acac)_3$. However, the amounts of the other organic photoproducts were found to vary greatly from one sample to another and to depend on the work-up time and exposure to air. Therefore, no meaningful quantitative correlation between the amount of starting material and ratio of photoproducts could be established.

Results

$Co(acac)_3$ in Diethyl Ether.—In degassed and sealed samples, the dark green original color disappeared on irradiation and was replaced by light pink color with simultaneous formation of a precipitate. Similar results were obtained in the Hanovia reactor under nitrogen atmosphere. However, when the pink reaction mixture was exposed to atmospheric oxygen, the dark green color was regenerated in part. The fluffy precipitate collected on filtration at the end of the reaction was identified to be $Co(acac)_2$ by comparing its ir and visible–uv absorption spectra with those of an authentic sample. Successive recordings of absorption spectra of degassed solutions in T cells at 10^{-3} *M* $Co(acac)_3$ at short irradiation intervals showed the presence of two isosbestic points at 478 and 532 mμ. These successive spectra could easily be reproduced with solutions prepared separately from $Co(acac)_3$ and $Co(acac)_2$ with a combined concentration of 10^{-3} *M*. The presence of the isosbestic points and the identity of spectra obtained from irradiated solutions and those from sep-

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TABLE I

PHOTOLYSIS QUANTUM YIELDS FOR β-KETOENOLATES OF COBALT(III) IN NONGASSED ETHER SOLUTIONS AT 25°

Compound	Concn × 10^3, M	Excitation wavelength, mμ	Light quanta absorbed, einstein	Mol reacted	Quantum yield
$Co(acac)_3$	5.58	265	5.2×10^{-7}	2.5×10^{-7}	0.49
	5.58	325	1.5×10^{-6}	2.0×10^{-7}	0.14
	5.58	590	5.6×10^{-5}	1.2×10^{-7}	$\sim 2 \times 10^{-3}$
$Co(bzac)_3$	9.10	260	4.3×10^{-7}	1.3×10^{-7}	0.31
	9.10	355	1.7×10^{-6}	1.8×10^{-7}	0.11
	9.10	595	4.2×10^{-5}	5.4×10^{-8}	$\sim 1.6 \times 10^{-3}$
$Co(dbm)_3$	6.60	285	3.2×10^{-7}	1.3×10^{-7}	0.40
	6.60	380	1.8×10^{-6}	1.9×10^{-7}	0.11
	6.60	598	4.2×10^{-5}	9.9×10^{-8}	$\sim 2 \times 10^{-3}$

TABLE II

PHOTOLYSIS QUANTUM YIELDS FOR β-KETOENOLATES OF COBALT(III) IN DEGASSED ETHER SOLUTIONS AT 25°

Compound	Concn × 10^3, M	Excitation wavelength, mμ	Light quanta absorbed, einstein	Mol reacted	Quantum yield
$Co(acac)_3$	3.72	265	5.5×10^{-7}	2.9×10^{-7}	0.52
	3.72	325	1.7×10^{-6}	2.9×10^{-7}	0.17
	3.72	590	4.2×10^{-5}	1.5×10^{-7}	$\sim 4 \times 10^{-3}$
$Co(bzac)_3$	8.10	260	4.4×10^{-7}	2.4×10^{-7}	0.55
	8.10	355	1.3×10^{-6}	2.4×10^{-7}	0.18
	8.10	595	4.2×10^{-5}	2.7×10^{-7}	$\sim 6 \times 10^{-3}$
$Co(dbm)_3$	5.40	285	3.5×10^{-7}	2.0×10^{-7}	0.57
	5.40	380	1.6×10^{-6}	1.8×10^{-7}	0.11
	5.40	598	1.6×10^{-5}	7.9×10^{-8}	$\sim 5 \times 10^{-3}$

arately prepared $Co(acac)_3$–$Co(acac)_2$ mixtures indicate that the only absorbing species in the 400–700-mμ region formed during photolysis is the divalent acetylacetonate.

The presence of biacetyl in the irradiated reaction mixture was established by comparison of the ir spectrum and melting point of the 2,4-dinitrophenylhydrazone with those of an authentic sample. Both acetyl chloride and xanthate tests proved the absence of alcoholic photoproducts. Acetic acid was identified in the filtrate as well as in the distillate of photolyzed solutions by comparison of the retention time on the gas chromatograph and from the sodium carbonate test.

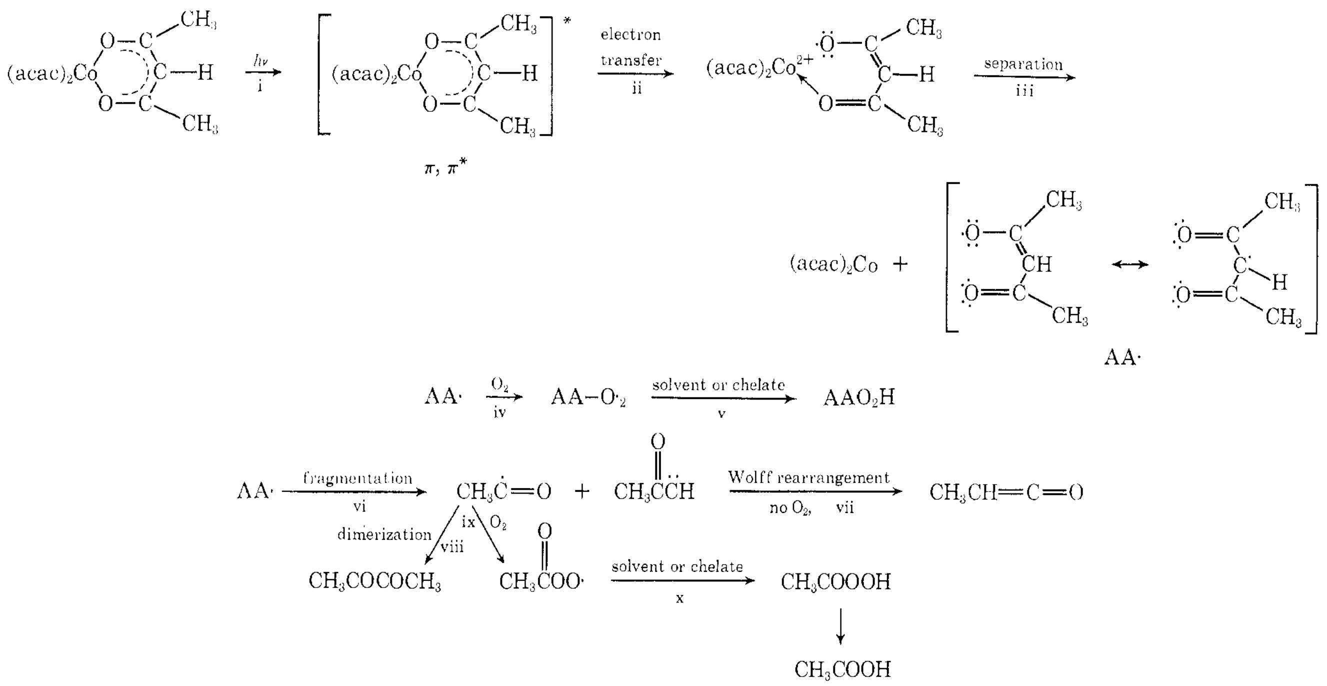
$Co(acac)_3$ in Other Solvents.—$Co(acac)_3$ was also photolyzed in the following solvents: methanol, benzene, dimethylformamide, dimethyl phosphite, tetrahydrofuran, dioxane, and pyridine. The results were similar to those described in detail for the experiments in diethyl ether. This suggests that the photoredox decomposition of $Co(acac)_3$ is essentially intramolecular and that the primary photoprocess does not involve reactions with solvent molecules.

With the exception of the dioxane and pyridine solutions, all of the others turned pink under irradiation consistent with the formation of $Co(acac)_2$. Precipitation of crystals as in ether, however, took place only in methanol solution. Again partial reversibility was observed when air was readmitted to the irradiated reaction mixture. In pyridine $Co(acac)_3$ solution turned orange-brown rather than pink during irradiation but the same coloration is obtained by dissolving pink $Co(acac)_2$ in pyridine. A similar $Co(acac)_2$–solvent adduct was formed in dioxane which was greenish yellow.

$Co(bzac)_3$ and $Co(dbm)_3$ in Ether and Benzene.—The procedures used for product isolation and identification were similar to those employed for $Co(acac)_3$. The green ether solutions of $Co(bzac)_3$ and $Co(dbm)_3$ turned orange-brown on irradiation and, as for $Co(acac)_3$, the absorption spectra of photolyzed solutions matched those of purposefully prepared mixed solutions containing $Co(bzac)_2$ and $Co(dbm)_2$, respectively. Partial reversibility was also observed on exposure to air. As for $Co(acac)_3$, however, the orange-brown color of freeze–pump–thaw degassed irradiated samples was stable indefinitely. The formation of $Co(bzac)_2$ and $Co(dbm)_2$ was verified not only from their absorption spectra but also from the characteristic blue color of the $CoCl_4^{2-}$ ion obtained on treatment of photolyzed solution with 3% sodium hydroxide and digestion of the precipitate in concentrated hydrochloric acid. The tris chelates do not react with 3% NaOH and only divalent cobalt forms $CoCl_4^{2-}$. Product analysis on photolyzed $Co(bzac)_3$ solutions revealed the presence of acetic acid and benzil in addition to $Co(bzac)_2$. The very fast reverse reaction $Co^{2+} \rightarrow Co^{3+}$ in the presence of air interfered with product identification in the case of $Co(dbm)_3$. In a thoroughly degassed sample, as mentioned above, the presence of $Co(dbm)_2$ was ascertained spectroscopically.

Photochemical Quantum Yields.—The quantum yield of the photodecomposition of the three tris(β-diketonato)cobalt(III) complexes in ether was determined actinometrically at the following excitation wavelengths: 590, 325, and 265 mμ for $Co(acac)_3$; 595, 355, and 260 mμ for $Co(bzac)_3$; 598, 380, and 285 mμ for $Co(dbm)_3$. These wavelengths coincide with the λ_{max} of the d–d absorption bands (at about 590 and 360 mμ) and the $\pi \rightarrow \pi^*$ transition in the ketoenolate ring (~270 mμ). The determinations were made using both degassed samples in flame-sealed cells and samples in which no effort was made to remove dissolved air in order to allow some evaluation of the reverse reaction.

SCHEME I



This evaluation, however, is only qualitative, since the content of dissolved oxygen may be different. The values obtained at room temperature in diethyl ether are given in Tables I and II. A 10% accuracy was estimated for the quantum yield values obtained on degassed samples from reproducibility. The extent of conversion was established spectrophotometrically from the decrease in the intensity of the characteristic absorption band in the visible region.

The photochemical reaction of Co(acac)$_3$ in diethyl ether can be summarized as

$$\mathrm{Co(CH_3COCHCOCH_3)_3} \xrightarrow[\text{ether}]{h\nu} \mathrm{Co(CH_3COCHCOCH_3)_2} + \mathrm{CH_3COCOCH_3} + \mathrm{CH_3COOH}$$

A few other minor photoproducts were detected in trace amounts by the gas chromatograph. However, their identification was not possible because of scarcity of available samples. The reaction mechanism outlined in Scheme I seems consistent with all observations.

Near-ultraviolet absorption of cobalt(III) β-ketoenolates is caused either by $\pi \rightarrow \pi^*$ transitions in the ligand[11,12] or by ligand-to-metal charge-transfer transitions.[13] Since both these types of transitions give characteristically intense bands ($\epsilon > 10^4$), any absorption due to the second d–d absorption ($\epsilon < 50$) in the near-ultraviolet region is negligible. The π,π^* excited state formed on photon absorption (step i) is probably followed by electron transfer to the Co(III) ion (step ii). It is conceivable that the π^* electron becomes localized in the empty e_g orbital on Co(III) which is certainly below lowest excited singlet and triplet π,π^* states. The lowest triplet of the acetylacetonate anion was determined from the phosphorescence spectrum of Gd(acac)$_3$ to be more than 20,000 cm^{-1} above the ground state[14] whereas the energy of the e_g state is around 17,000 cm^{-1}. Whether the electron transfer from the ligand to the Co(III) ion takes place before or after intersystem crossing cannot be determined.[15] The excited state in which a ligand π electron is localized on the chelated ion is probably obtained directly on charge-transfer absorption. Once the electron transfer has occurred, the acetylacetonate free radical (AA·) separates from the Co(II) ion. Since AA· is an unstable species, it will be expected either to react with oxygen as shown in steps iv and v to form a peroxide or to undergo fragmentation (step vi) into an acetyl radical and a ketocarbene. The carbene may undergo a Wolff rearrangement to methylketene whereas the acetyl free radical may dimerize to one of the identified products, biacetyl (step viii), or, in the presence of oxygen, may form the peracetate free radical (step ix). Hydrogen abstraction from the solvent or Co(acac)$_{2 \text{ or } 3}$ would lead to formation of acetic acid. The apparent reversibility Co(II) → Co(III) in the presence of oxygen is probably due to the action of AAO$_2$H and CH$_3$COOOH on Co(acac)$_2$. The regenerated Co(III) could, therefore, be (acac)$_2$Co(OOCCH$_3$)$_2^-$ and not Co(acac)$_3$. In samples in which oxygen has been removed before irradiation, the only photoproducts should be biacetyl, methylketene, and Co(acac)$_2$. However, when the cells are opened, the methylketene is expected to react with atmospheric oxygen to give peroxides which again transform Co(II) into Co(III). The instrumentality of the peroxy compounds in the reoxida-

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tion of Co(II) was postulated because the reaction observed with irradiated solutions exposed to air was considerably faster than that of pure Co(acac)$_2$ solutions under the same conditions. The pink color of pure Co(acac)$_2$ solutions, however, was rapidly changed to green by the addition of hydrogen peroxide.

The fact that benzil and acetic acid were detected along with Co(bzac)$_2$ in the photolysis of Co(bzac)$_3$ seems to agree with the mechanism suggested above for Co(acac)$_3$.

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The Formation of a Second Coordination Sphere for Tris(L-alaninato)cobalt(III) as Studied by Proton Magnetic Resonance

BY B. M. FUNG AND IRENE H. WANG

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The proton nmr spectra of the four isomers of tris(L-alaninato)cobalt(III) in D_2SO_4 and D_2O–D_2SO_4 solutions are reported. The change of the nmr spectra with temperature and solvent composition are explained by the solvation of the complexes. In D_2SO_4, the carboxyl group in the ligand has a strong interaction with the acid. When D_2O is first added to the solvent, the NH protons of the amino acid start to form hydrogen bonds with D_2O. Further increase of the D_2O content in the solvent leads to the departure of the acid molecules from the second coordination sphere. Increase of temperature tends to reduce the solvation of the complexes.

Introduction

It has been recently demonstrated that the formation of a second coordination sphere due to the solvation of a complex can be detected by nuclear magnetic resonance (nmr).[1] For cobalt(III) complexes with ethylenediamine, the formation of hydrogen bonding between the NH protons and basic solvents is reflected in the change of the NH proton signal.[1] Other ligands containing acidic protons are expected to behave similarly. On the other hand, if a ligand contains a proton-accepting site, it may form hydrogen bonding with acidic solvents. The interaction may be detectable under favorable conditions. For ligands with both proton-donating and proton-accepting sites, the interaction of the complex with solvents of varying acidity would be most interesting.

All α-substituted tris(L-amino acid) complexes of cobalt(III) have at least four isomers. Each of the geometrical (*cis* and *trans*) isomers can be separated into two optical ((+) and (−)) isomers. The geometrical isomers can be indentified by their absorption spectra[2–4] and the optical isomers have different rotational properties.[5–7] All four forms for several amino acids have been isolated.[5–7] Of those complexes, Co(L-ala)$_3$ are the least complicated ones. They have relatively simple structures, and the conformations of the chelate rings are probably fixed by the existence of the methyl groups. The NH_2 protons in the amino acid can act as proton donors, whereas the carboxyl group can behave as a proton acceptor. The formation of a second coordination sphere with both acids and bases is then expected for those complexes.

Although the proton nmr of *cis*-(−)-Co(L-ala)$_3$ and *trans*-(−)-Co(L-ala)$_3$ in D_2O have been reported,[7] the study did not emphasize the solvent–solute interaction. The present work describes the nmr study on the four isomers of Co(L-ala)$_3$ in solutions of D_2SO_4–D_2O mixtures. The results demonstrate that information on the second coordination sphere of the complexes with both D_2O and D_2SO_4 can be inferred from the results of proton magnetic resonance.

Experimental Section

The Co(L-ala)$_3$ complexes were prepared according to the method of Mori, *et al.*,[4] and separated by methods suggested by Denning and Piper.[7] The *cis*-(+) isomer was obtained from ligand exchange of hexaamminecobalt(III) chloride. In preparing the other three isomers, potassium tricarbonatocobaltate(III) was used as the starting material.[4] The less soluble *trans*-(+) complex separated out first; the more soluble *trans*-(−) and *cis*-(−) isomers contained in the remaining mother liquor were separated on an alumina column. D_2O and D_2SO_4 (99%) were purchased from Stopler Isotope Chemicals.

Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer. The signal of sulfuric acid was used as the external lock. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was added to the samples for measuring chemical shifts. However, it decomposed at elevated temperatures and in concentrated sulfuric acid and could not be used as an internal standard. Therefore in measuring the chemical shifts, we took the methyl peak of DSS in solutions of 1:1 D_2O–D_2SO_4 as 0.00 ppm and treated the methyl signals of the complexes as un-

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