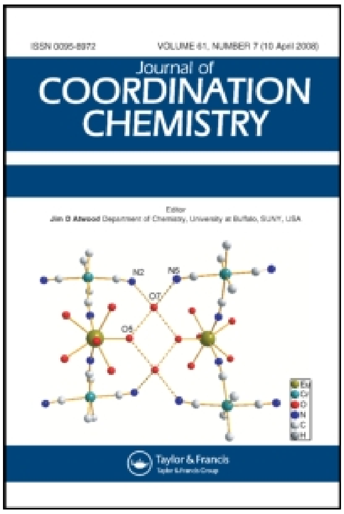

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DESTRUCTIVE PHOTOOXIDATION OF TRIS(DIBENZOYLMETHANATO)IRON(III)

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The photolysis of the benzene solution of tris(dibenzoylmethanato)iron(III) in the presence of oxygen gives basic ferric salt of diphenyltartaric acid, benzoic acid, and phenyl bezoate as the main reaction products, with phenylglyoxylic acid as the intermediate.

INTRODUCTION

In connection with our photochemical studies of metal chelates, it seemed of interest to investigate the photochemical behavior of tris(dibenzoylmethanato)iron(III) (I), $Fe(DBM)_3$, in the presence of oxygen.

Only a few experimental studies on the oxidation of metal chelates have been published in the literature. Johnson[1] studied the oxidation of metal chelates of some β-diketones by air oxygen. The oxidation of bis(acetylacetonato)iron(II) yielded acetic and pyruvic acid as the main reaction products. The identified products of the oxidation of bis(dipivaloylmethanato)nickel(II) in toluene or chlorobenzene were nickel(II) pivalate and pivalic acid whereas no oxidation was observed in cyclohexane or nitrobenzene solutions.[1] Main reaction products in the destructive autooxidation of tris(acetylacetonato)iron(III) with pure oxygen at atmospheric pressure and 100° in diphenyl oxide[2–5] were carbon dioxide, water, biacetyl, acetic acid, acetylacetone, mesityl oxide, and an amorphous residue containing iron, with the approximate molecular formula $C_7H_8FeO_{4.85}$. The rate of a similar oxidation of $Fe(DBM)_3$ was more than seven times as great as that for the acetylacetone complex.[2]

Hsu[6] studied the photolysis of some iron(III) chelates in the absence of oxygen. Solutions of the chelates in toluene, xylene, or mesitylene were irradiated in degassed, sealed Pyrex tubes with a 450 W Hanovia high-pressure mercury lamp. In photolyses of $Fe(DBM)_3$, tris(dipivaloylmethanato)iron(III), and tris(acetylacetonato)iron(III), Hsu failed to isolate any defined compounds. Some of his experiments were performed in the presence of benzophenone as the photosensitizer[6] (cf. ref.[7]).

EXPERIMENTAL

All melting points were determined on a Fisher-Johns hot-stage apparatus and are uncorrected. Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, California. The ultraviolet spectra were recorded on a Cary 11M spectrophotometer and the infrared spectra were measured on a Perkin-Elmer 257 instrument.

All irradiations were carried out in a Hanovia immersion-well type photochemical reactor with Hanovia high-pressure mercury lamps (250 or 450 W). In all irradiation experiments, the course of the oxidation of $Fe(DBM)_3$ was followed spectrophotometrically at 405 and 465 nm. Also, the composition of the reaction mixture and of chromatographic fractions was analyzed by thin-layer chromatography on silica gel Chromagram sheets with acetone as the solvent.

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Benzene (Mallinckrodt, Analytic Reagent Grade) was used in photooxidation reactions without further purification. Benzophenone (Calbiochem) was recrystallized from a benzene-ligroin mixture and had m.p. 49°.

Tris(dibenzoylmethanato)iron(III)

Tris(dibenzoylmethanato)iron(III), $Fe(DBM)_3$, was prepared from dibenzoylmethane and ferric chloride.[8-11] The product was twice recrystallized from a benzene-ligroin mixture. Dark red crystals, m.p. 275–276° (lit.[11] m.p. 275°); ultraviolet spectrum (in benzene), λ_{max}, nm (log ϵ): 326 (4.70), 407 (4.11), ~465 (3.56) [lit.[12,13] λ_{max}, nm 320, 410 (log ϵ 4.23) (in butyl acetate), cf. also ref.[14]].

Photooxidation of Fe(DBM)₃

A 5 x 10^{-3} *M* solution of $Fe(DBM)_3$ in benzene [0.273 g $Fe(DBM)_3$ in 75 ml benzene] was irradiated with a 450 W mercury lamp using a Pyrex glass immersion well. The irradiation was continued for 4 days and a stream of oxygen was bubbled through the irradiated mixture. The reaction mixture was then evaporated to dryness, the solid residue was dissolved in a small amount of benzene, the undissolved portion (0.045 g) was washed with benzene and ligroin (b.p. 60–70°), and dried under reduced pressure giving a brown substance, insoluble in most common solvents, soluble in dimethyl sulfoxide and very poorly soluble in acetone and benzene. The compound does not melt below 320° and contains trivalent iron (Prussian blue test). The ultraviolet spectrum (in acetone) has no characteristic or pronounced maxima (flat continuous absorption to 500 nm); the infrared spectrum (in dimethyl sulfoxide), $\tilde{\nu}_{max}$, cm^{-1}: 1550, 1275. The compound has been assigned the structure of basic ferric salt of diphenyltartaric acid.[15] *Anal.* Calcd for $C_{16}H_{13}FeO_7$: C, 51.50; H, 3.51; Fe, 14.97. Found: C, 51.53; H, 3.66; Fe, 14.66.

The benzene solution after the removal of the ferric salt was chromatographed on a silica gel column (1.8 x 20 cm) with ligroin, ligroin-benzene, benzene, and benzene-acetone as the solvents. The following main fractions were obtained.

(i) An unidentified, yellowish semi-solid substance (0.030 g, with ligroin), soluble in ligroin, sparingly soluble in methanol; the ultraviolet spectrum (in methanol), λ_{max}, nm: 237, 245.

(ii) Phenyl benzoate (0.060 g, with 1:1 ligroin-benzene), white crystals, m.p. 67° (from aqueous ethanol), no depression of the m.p. with authentic phenyl benzoate, m.p. 68°, synthesized from phenol and benzoyl chloride. Ultraviolet spectrum (in methanol), λ_{max}, nm (log ϵ): 231.5 (4.26), 265 sh (3.33), 273 sh (3.22), 280 (3.02) [lit.[16-19] λ_{max}, nm (log ϵ): 232 (4.21), 265 sh (3.3), 274 sh (3.30) (in ethanol); 282 (3.04) (in isoctane); cf. also ref.[20]]. *Anal.* Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.31; H, 5.22. The eutectic m.p. of the isolated phenyl benzoate with *trans*-azobenzene was 43° (lit. [21] m.p. 43°).

(iii) Benzoic acid (0.087 g, with benzene and benzene-acetone), white needles, m.p. 120–121° (sublimed at 100° and crystallized from ligroin-benzene), mixed m.p. with authentic sample 121–122°; the ultraviolet spectrum (in methanol) λ_{max}, nm (log ϵ): 227 (4.1), 266 sh (2.9), 273 (3.0), 280 (2.9) [lit.[22] λ_{max}, nm (log ϵ): 228–229 (4.16), 266 sh (2.84), 273 (2.95), 280–281 (2.86) (in ethanol)].

The total weight of isolated compounds was 0.222 g (81.5% of the $Fe(DBM)_3$ weight introduced into the reaction).

Photooxidation of Fe(DBM)₃ in the Presence of Benzophenone

A benzene solution 5 x 10^{-3} *M* in $Fe(DBM)_3$ and 10^{-3} *M* in benzophenone [0.273 g $Fe(DBM)_3$, 0.014 g benzophenone, 75 ml benzene] was irradiated in a quartz apparatus with a 250 W mercury lamp for 7 days and a stream of oxygen was bubbled through the reaction mixture. The formed brown precipitate was filtered off and the solution was irradiated for an additional 6 days in a Pyrex glass apparatus. The brown insoluble precipitate was combined with the first portion, the filtrate was evaporated, and the residue was chromatographed on silica gel. The work-up performed in the same manner as above gave the following main fractions.

(i) Basic ferric salt of diphenyltartaric acid (0.032 g), brown amorphous powder, insoluble in most common solvents, does not melt below 320°. *Anal.* Calcd. for $C_{16}H_{13}FeO_7$: C, 51.50; H, 3.51; Fe, 14.97. Found: C, 51.95; H, 3.72; Fe, 14.04.

(ii) Phenylglyoxylic acid (traces, with ligroin), m.p. 64.5–65° (from aqueous methanol) (lit.[23] m.p. 64–66°); ultraviolet spectrum (in methanol), λ_{max}, nm: 232, 265 sh, 273 sh, 281 sh [lit.[24,25] λ_{max}, nm (log ϵ): 262.5 (3.98) (in water)].

(iii) Benzoic acid (0.070 g, with ligroin-benzene), m.p. 120–121° (from ligroin-benzene, then sublimed at 100°), mixed m.p. with authentic sample 121–

122°; the ultraviolet spectrum in agreement with lit.[22]

In other runs with irradiation performed in Pyrex glass apparatus with Pyrex glass immersion well, analogous results were obtained. No benzophenone was recovered from the reaction mixture.

Attempted Photooxidation of Fe(DBM)$_3$ without Irradiation (Dark Reaction)

A stream of oxygen was bubbled through a benzene solution 5×10^{-3} *M* in Fe(DBM)$_3$ [0.273 g Fe(DBM)$_3$ in 75 ml benzene] for 14 days, the volume of the solution being kept constant by adding the solvent whenever necessary. No destruction of the complex occurred within this period of time.

RESULTS AND DISCUSSION

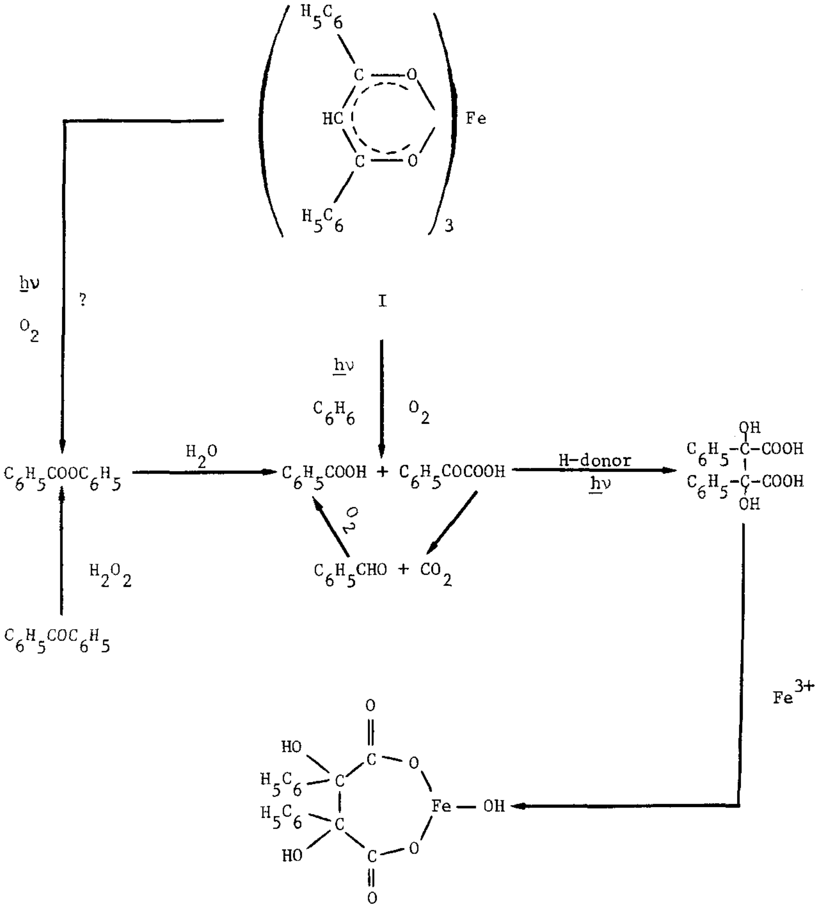
The present paper reports the results of the destructive photooxidation of Fe(DBM)$_3$ in benzene solution both in the absence and in the presence of benzophenone ($\tilde{\nu}_T = 24.6$ kcm^{-1}, i.e., $E_T =$ 69.7 kcal/mole[26]). The irradiation of benzene solutions of Fe(DBM)$_3$ with a high-pressure Hanovia mercury lamp in the presence of oxygen was carried out both in quartz and Pyrex glass apparatus.

The main iron-containing reaction product isolated in the photooxidation of Fe(DBM)$_3$ is an amorphous ferric salt which has been assigned the structure of basic ferric salt of diphenyltartaric (*s*-dihydroxydiphenylsuccinic) acid (II). Further identified products were benzoic acid and phenyl benzoate. In photooxidations carried out in the presence of benzophenone, the above ferric salt was obtained and further identified products were benzoic and phenylglyoxylic acid. No attempt was made to identify gaseous products formed in the photooxidation. Under the reaction conditions used in the experiments, benzophenone underwent oxidative photolysis and was not recovered from the reaction mixture.

In its simplest form, triplet energy transfer requires that the triplet energy of the donor be 3 kcal/mole or more greater than the triplet energy of the acceptor.[27] The respective energy of Fe(DBM)$_3$ is not known, however, one can assume that the condition mentioned above would be met with benzophenone used as the donor under certain conditions. Under the conditions employed in the present work, Fe(DBM)$_3$ was absorbing an appreciable portion of light and thus the photosensitizing effect of benzophenone in the photooxidation, if any, must have been quite small. The photooxidation in the presence of benzophenone was carried out only because Hsu used benzophenone in several photolysis experiments carried out in deaerated solutions.[6] While benzene seemed to be the only suitable solvent in which our photochemical oxidations could have been performed, it is appropriate to note that benzene itself absorbs strongly at energies higher than 34 kcm^{-1} and that irradiations in quartz can cause photoreactions of benzene, especially in the presence of oxygen. It is quite possible that benzene used as the solvent in the photooxidation of Fe(DBM)$_3$ could act as a photosensitizer.

We have reported the electronic absorption spectrum of Fe(DBM)$_3$ elsewhere.[14] No identification of the nature of electronic absorption bands of Fe(DBM)$_3$ was attempted, however. The electronic absorption spectra of transition metal chelates are, in general, quite complex, especially in the ultraviolet region, and the interpretation of the spectrum of Fe(DBM)$_3$ would require a complete molecular orbital treatment.

Fe(DBM)$_3$ attacked by oxygen (or the sensitizer-oxygen complex[28,29]) gives phenylglyoxylic acid and benzoic acid as the oxidation products, in agreement with the course of non-photochemical oxidations of similar chelates.[1] In our treatment of the reaction, we consider the singlet oxygen mechanism, however, a kinetically equivalent sensitizer-oxygen complex mechanism would be possible as well. Phenylglyoxylic acid is known to be highly sensitive towards ultraviolet irradiation, the main photolysis products being benzaldehyde and carbon dioxide.[24] It is also known that the irradiation of phenylglyoxylic acid in the presence of hydrogen donors (e.g., 2-propanol) gives diphenyltartaric acid.[15] Thus, it can be assumed that phenylglyoxylic acid formed by oxidation of Fe(DBM)$_3$ is partly transformed into diphenyltartaric acid which then gives the corresponding ferric salt, insoluble and thus stable under irradiation conditions. Another portion of phenylglyoxylic acid is photolyzed to carbon dioxide and benzaldehyde which is further oxidized to benzoic acid. Another possible reaction leading to the formation of benzoic acid is the hydrolysis of phenyl benzoate. The formation of phenyl benzoate itself can be explained by Baeyer-Villiger oxidation of benzophenone with hydrogen peroxide probably present in the reaction mixture (at least in small amounts).[30-32] The formation of phenyl benzoate in the absence of benzophenone is much more difficult to explain. Whereas phenol has been reported as one of the products of irradiation of



Scheme I

benzene with the 313 nm wavelength in the presence of water,[33] the formation of phenyl benzoate cannot be explained by esterification of benzoic acid by phenol. This reaction is not possible under the conditions employed in the present work. $Fe(DBM)_3$ can also be considered as a potential source of phenyl benzoate. The results obtained in the irradiations are summarized in Scheme I.

Non-irradiated benzene solutions of $Fe(DBM)_3$ are remarkably stable towards oxidation and do not undergo any noticeable change after two weeks in oxygen atmosphere.

It seems worth mentioning that the destructive photooxidation of tris(dipivaloylmethanato)iron(III) carried out under conditions analogous to those described in the present study yielded the corresponding ferric salt in the form of a brownish-yellow precipitate and pivalic acid, along with other reaction products.[34]

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