Photochemistry of Uranium(IV) 1,3-Diketonates in Organic Solvents

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Electronic spectra of tetrakis(acetylacetonato)- and tetrakis(dibenzoylmethanato)-uranium(IV) have been investigated. Irradiations at the wavelengths of the intraligand and ligand-to-metal charge-transfer transitions of these chelates cause reduction of U^{IV} to U^{III} as the primary photoprocess. A secondary thermal reaction in halogenocarbon solvents leads to reoxidation of U^{III} to U^{IV} and abstraction of halogen. Irradiation at the wavelengths of the *f–f* transitions in the presence of oxygen induces a photo-oxygenation reaction forming bis(1,3-diketonato)dioxouranium(VI) complexes.

ALTHOUGH there has been a recent surge of interest in the photochemistry of actinide compounds,[1,2] there are also many parts of this general field which have received little attention. Thus, while the photochemistry of uranium(VI) compounds has been extensively investigated,[2-5] very little is known about the photochemical behaviour of uranium(IV) compounds with the sole exception [6] of $[UCl_6]^{2-}$. Consequently, we have initiated a study of uranium(IV) complexes and in this research we focused our interest on $[U(1,3\text{-diketonate})_4]$ in organic solvents. Secondary reaction such as hydrolysis or thermal and photochemical aquation may be absent in organic solvents, the role of which in the photochemical process was expected to be less significant than that of water.

The complexes of uranium(IV) with 1,3-diketones are of considerable interest. They have been used in solvent-extraction procedures, and their volatility may be of use in fractional sublimation. Some features of this class of chelates that make photochemical studies of potential interest are: (*i*) the $[UL_4]$ (L = 1,3-diketonate) complexes are soluble in a wide range of solvents, enabling a critical assessment of the effect of solvent variation on the photochemical reaction; (*ii*) the rather complex spectra of $[UL_4]$ in the 10 000—40 000 cm^{-1} region allow various reaction schemes to be postulated, depending on the irradiating wavelength. In addition, certain 1,3-diketonate chelates of uranium(IV) exhibit quite high vapour pressures.[7] Thus, gas-phase photochemistry of such compounds may be feasible.

We find that the $[U(acac)_4]$ and $[U(dbm)_4]$ (acac = acetylacetonate; dbm = dibenzoylmethane anion) complexes exhibit a gradual change in properties, such as the energy of excited states associated with the ligands, solubility, and stability, which may be correlated with their photochemical behaviour.

EXPERIMENTAL

Materials.—Uranium tetrachloride was prepared as reported.[8] Thallium 1,3-diketonates were obtained from thallium(I) ethoxide and acetylacetone (Hacac) or dibenzoylmethane (Hdbm) respectively.[9] Acetonitrile, chloroform, dichloromethane, 1,2-dichloroethane, and hexane were purified by successive fractional distillations, under nitrogen, from $Li[AlH_4]$. All the operations were carried out in a dry-box filled with nitrogen, and dried over Na/K alloy.

Preparation of Compounds.—The uranium(IV) diketonates were prepared by addition of aqueous sodium hydroxide to an aqueous solution containing uranium(IV) chloride and the 1,3-diketone.[8] The products obtained in this way comprised a mixture of the desired products with uranium hydroxides, which was difficult to separate. A better method of preparing the pure compounds in good yield is that of the reaction of a thallium 1,3-diketonate with UCl_4 in anhydrous organic media.

$[U(acac)_4]$. Solid Tl(acac) (4 mmol) was added slowly under agitation to a solution of UCl_4 in tetrahydrofuran (thf) (4 mmol in 20 cm^3 of solvent). The mixture was stirred at room temperature for 4 h, then TlCl was filtered off. By addition of hexane to the green solution, a green solid was obtained which, after recrystallization from thf–hexane, analysed for $[U(acac)_4]$ {Found: C, 37.85; H, 4.45; U, 37.55. Calc. for $[U(acac)_4]$: C, 37.85; H, 4.45; U, 37.5%}.

The dibenzoylmethane complex was prepared similarly {Found: C, 63.75; H, 3.90; U, 21.1. Calc. for $[U(dbm)_4]$: C, 63.7; H, 3.90; U, 21.05%}.

The yields of $[UL_4]$ were quantitative. Infrared spectra of Nujol mulls: $[U(acac)_4]$ 1 578vs, 1 523vs, 545m, 395m, 235s; $[U(dbm)_4]$ 1 590s, 1 580w, 1 518s, 780m, 775s, 715vs, 685s, 550m, and 230s cm^{-1}. The general band pattern is characteristic of chelated transition-metal 1,3-diketonates.[10]

Apparatus.—Our customary procedure [11] was used for irradiation wavelengths of 254, 280, 313, 334, 404, and 433 nm. Irradiations with $\lambda > 500$ nm were carried out using a tungsten incandescent lamp (Philips Attralux Spot, 150 W) by means of a filter solution [12] of $[Fe(phen)_3][SO_4]$ (phen = 1,10-phenanthroline). Microsecond flash-photolyses were performed on an Applied Photophysics model KR-10 Flash-Kinetic spectrometer. Infrared and electronic spectra were recorded on Perkin-Elmer 577 and 323 recording spectrometers respectively, n.m.r. spectra on a Perkin-Elmer R.24.60 spectrometer.

Irradiations.—All samples were degassed by repeated freeze–pump–thaw cycles. Samples were usually prepared either in n.m.r. tubes or in 1 cm optical cuvettes, depending upon the analytical method chosen. All irradiations were carried out at 295 K. The course of a reaction was followed using either ^1H n.m.r. or electronic spectroscopy.

RESULTS

Electronic Spectra.—The electronic spectra from 5 000 to 40 000 cm^{-1} have been investigated in the following media: acetonitrile, dichloromethane, 1,2-dichloroethane, chloroform, and Nujol mulls at 295 K (Table 1 and Figures 1 and 2). Three groups of bands occur in each of the spectra. Only small deviations (5—10 cm^{-1}) in band maxima were observed among the solvents, including the solid-state spectrum.

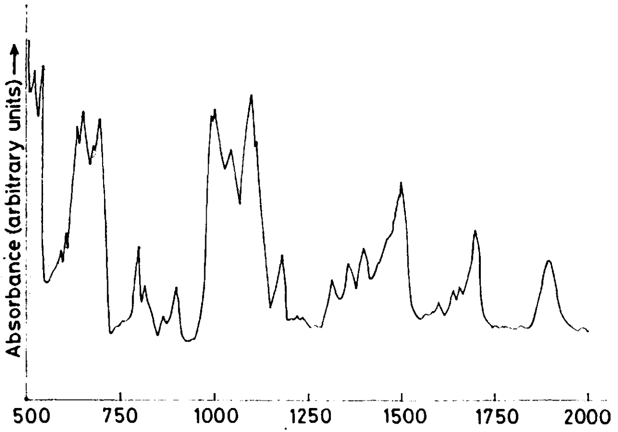


FIGURE 1 Electronic spectrum of solid [U(acac)$_4$] in Nujol mull at ambient temperature

Changes upon Photolysis. Photolysis of deaerated solutions of [U(acac)$_4$] with wavelengths of 254—450 nm results in absorption changes in the visible and near-i.r. region with isosbestic points at 625, 720, and 1 300 nm (Figure 3). A decrease in absorbance ($\lambda_{max.}$ 600, 655, 1 000, and 1 100 nm) was observed indicating induced reduction[4] of U^{IV}. Additionally, new absorption peaks were gradually formed at 550, 875, and 1 280 nm, which coincide with those established for U^{III} in various media.[13,14] A comparison of observed and calculated band positions for U^{III} is reported in Table 2.

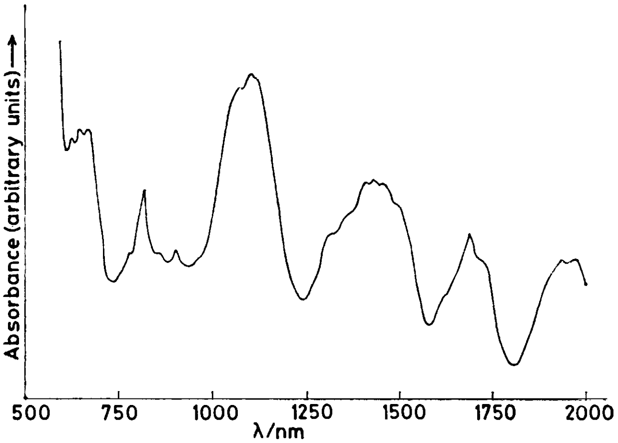


FIGURE 2 Electronic spectrum of solid [U(dbm)$_4$] in Nujol mull at ambient temperature

TABLE 1

Electronic absorption maxima * for [U(acac)$_4$] and [U(dbm)$_4$] in CH$_3$CN

[U(acac)$_4$]		[U(dbm)$_4$]	
$10^{-3}\,\tilde{\nu}$/cm^{-1}	log ε	$10^{-3}\,\tilde{\nu}$/cm^{-1}	log ε
38.5	4.61	39.30	4.50
(35.7)		(31.2)	
(32.4)		(30.3)	
28.5	3.16	29.1	4.9
22.2	2.21	27.7	4.74
20.08	2.05	21.2	2.99
(19.04)	1.40	20.0	2.67
(18.73)		18.86	2.33
16.00	1.35	18.1	1.98
14.41	1.34	15.7	1.95
(12.58)		12.34	1.09
11.11	1.58	9.52	1.60
10.02	1.34	9.09	1.67
9.22	1.35	(7.69)	
(8.39)		7.14	
(7.40)		5.88	(1.25)
6.71	1.31		

* Figures in parentheses indicate shoulders.

During the initial stages of photolysis the decrease in absorbance of U^{IV} at 655 nm obeyed zero-order kinetics, enabling calculation of an apparent quantum yield {based on the light absorbed by the [U(acac)$_4$] complex}. The rates of disappearance of U^{IV} and of formation of U^{III} were equal. Moreover, positions of the isosbestic points were almost constant. At the photostationary state (Figure 4), in the dark, the photoproduct underwent oxidation to U^{V}.

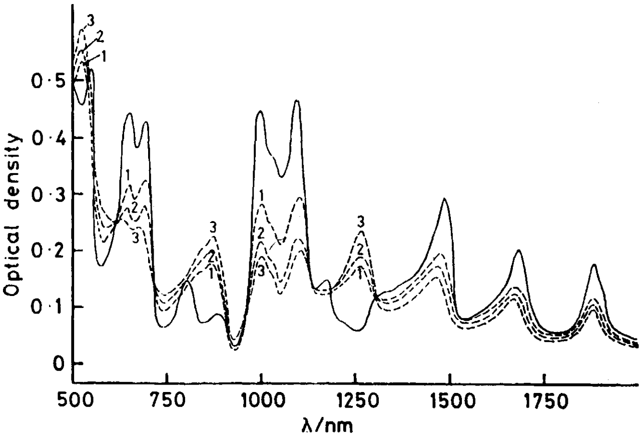


FIGURE 3 Electronic spectra of [U(acac)$_4$] (2.15 × 10^{-2} mol dm^{-3}) in dichloromethane before (——) and after photolysis (– – – –) (254 nm). Curves 1, 2, and 3 refer to irradiation for 10, 15, and 20 min

At the end of a prolonged photolysis (2 h) the solutions revealed the presence of Cl$^-$ ions, indicating an interaction of U^{III} with the solvent. Careful checking of blanks and samples revealed that Cl$^-$ ions are present only in the

TABLE 2

Comparison of observed and calculated band positions (cm^{-1}) for U^{III}

Obs. in solution [a]		
[U(acac)$_3$]	[U(dbm)$_3$]	Calc.[b]
19 083	18 868	18 800
		18 100
(17 241)	(16 949)	17 300
(16 393)	(16 260)	16 600
(14 285)	(13 986)	15 000
(12 195)	(12 048)	12 600
11 695	11 628	11 700
7 698	8 000	7 800
		4 100

[a] In CH$_3$CN. Figures in parentheses indicate shoulders. [b] Ref. 13.

photolysed solutions. Moreover, n.m.r. spectra of the photolysed solutions showed the presence of Hacac in addition to uranium(IV) products. A generally similar pattern of behaviour was given by [U(dbm)$_4$].

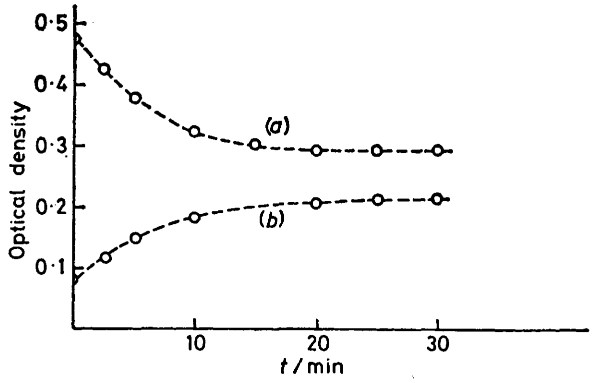


FIGURE 4 Change of absorption [λ 655 (*a*), 785 nm (*b*)] of a deaerated [U(acac)$_4$] solution (2.15×10^{-2} mol dm^{-3} in CH_2Cl_2) with irradiation time

Irradiations were also performed with light of equivalent energy to the *f–f* transitions. Whilst irradiation of degassed solutions of [U(acac)$_4$] and [U(dbm)$_4$] (5×10^{-2} mol dm^{-3}) in dichloromethane or acetonitrile with visible light ($\lambda > 500$ nm) caused no appreciable reaction, photolysis ($\lambda > 500$ nm) of aerated solutions generated new absorptions in the 400—500 nm region characteristic of $[UO_2]^{2+}$. After photolysis (2 h) the yellow solutions were evaporated and the crude residues were crystallized from ethanol–hexane to give [UO_2L_2] (L = diketonate), identified by comparison of their ^{1}H n.m.r. and i.r. spectra with those of an authentic sample.[7,15]

On admission of air to [UL_4] solutions in the dark an oxidation of $\mathrm{U^{IV}}$ to $\mathrm{U^{VI}}$ begins; however, the resulting yellow-brown solutions did not yield [UO_2L_2] but polymeric products. The n.m.r. reaction profile of [UL_4] in CD_2Cl_2 showed a fast broadening of the signals at τ 12.5 and 13.5, followed by slow appearance of signals due to Hacac and Hdbm.

Microsecond flash photolysis. Flash photolysis of [U(acac)$_4$] and [U(dbm)$_4$] in dichloromethane also produces new absorptions ($\lambda_{max.}$ 525 ± 5, 875 ± 10 nm) within 20 μs of the flash, indicating that $\mathrm{U^{III}}$ is a primary photoproduct.

N.M.R. Measurements.—Proton n.m.r. data of uranium(IV) chelates show the expected large chemical shifts due to paramagnetism[15] of $\mathrm{U^{IV}}$: [U(acac)$_4$] CH (τ 12.5), CH_3 (1.12); [U(dbm)$_4$] CH (13.40), H_o (2.40), H_m (5.70), and H_p (6.82). N.m.r. profiles of photoreactions in CD_2Cl_2 indicated that a gradual decrease in intensity of these resonances takes place simultaneously with the formation of the free ligands Hacac (τ 5.39) and Hdbm (τ 6.83). Under continuous photolysis the intensities of the signals of the free ligands increase until a steady state is reached, whereupon the integrated resonance of the co-ordinated methide almost matched those of [U(acac)$_3$] and [U(dbm)$_3$].

DISCUSSION

Three main types of electronic transition are observed in the spectra of [UL_4] (L = 1,3-diketonate) (Table 1). The first group in the 30 303—40 000 cm^{-1} region is caused by $\pi \rightarrow \pi^*$ transitions of the ligand. The energies of the transition in the diketonate are slightly lower than in the diketone and nearly identical to those observed for transition-metal chelates.[16] This can be considered an adequate justification for regarding the transition as being mainly of ligand character.

The second group of bands 22 220—30 303 cm^{-1} consists of the intense, quite broad, bands arising from ligand-to-metal charge-transfer transitions. The similar optical electronegativities[17] of acac$^-$ (2.7) and Cl$^-$ (3.0) suggest that the relative energies of the metal and acac$^-$ ligand orbitals are not likely to be altered by the replacement of Cl$^-$ with acac$^-$. Increasing the conjugation in the ligand by substitution of methyl by phenyl groups would be expected to diminish the $\pi \rightarrow \pi^*$ energy gap and thus to diminish the energies of the charge-transfer transitions. There is a drop in the energies of the electronic absorption bands on going from [U(acac)$_4$] to [U(dbm)$_4$] (Table 1).

Finally there are the relatively weak bands that stem from *f—f* transitions, 5 555—22 220 cm^{-1}. These transitions are rather complex because of a large number of states of the f^2 configuration is possible.[8] The complexity is further increased by the splitting of the states as a result of spin–orbit interaction. The general features of the spectra are similar to solid-state spectra (Figures 1 and 2) recorded for the square antiprismatic [U(acac)$_4$] and for dodecahedral [U(dbm)$_4$]. These geometries seem to be lost in solution as shown by ^{1}H n.m.r. data which indicate a less symmetrical structure.[15] However, the general similarities between the solid-state and solution spectra indicate only small changes in site symmetry.

Photochemical Reactions.—On flash photolysis of [UL_4] in dichloromethane, immediate and efficient bleaching of the *f—f* absorptions was observed. The spectral distribution of the bleaching is consistent with production of $\mathrm{U^{III}}$, but inconsistent with production of $\mathrm{U^{V}}$.[4,13] Exposure of degassed solutions of [U(acac)$_4$] to 254—450 nm radiation results in a photochemical reaction as indicated by the decrease in intensity of the uranium(IV) absorptions, and new absorption peaks are gradually formed in the near-i.r. region which coincide with those reported for $\mathrm{U^{III}}$. This process did not go to completion, and the $\mathrm{U^{III}}$ was reoxidized to $\mathrm{U^{IV}}$, a photochemical stationary state being obtained. The n.m.r. profile of the first stages of photoreaction indicated that a gradual decrease in intensity of the absorption due to co-ordinated acac$^-$ takes place simultaneously with formation of acetylacetone. At the stationary state, peak integration indicated that the primary photoproduct could be [U(acac)$_3$]. However, examination of the n.m.r. spectra obtained after prolonged photolysis revealed a number of secondary products. Product analysis of photolysed [U(acac)$_4$] solutions indicated the presence of Cl$^-$ ions and Hacac in addition to uranium(IV). The [U(acac)$_3$] complex is too readily oxidized to the quadrivalent state to sustain preparative work-up. Uranium(III) has such potent reducing properties that a halogen atom could be extracted from the solvent and reoxidation to $\mathrm{U^{IV}}$ occurs.[8] The same results were obtained in chloroform and in 1,2-dichloroethane.

The photochemical results indicate that π^* and ligand-to-metal charge-transfer (l.m.c.t.) states are chemically active with respect to reductive dissociation of [U(acac)$_4$]. The apparent quantum yield for the decomposition of [U(acac)$_4$] is approximately independent of wavelength from 254 to 450 nm and approximately constant (0.28) in all solvents used. Since reduction takes place, it is presumably a l.m.c.t. state that is efficiently populated by intersystem crossing from π^* levels.

The experimental results are consistent with a two-step mechanism in which [U(acac)$_3$] is formed in a primary photochemical process followed by a thermal reaction producing U$^{\text{IV}}$ and protonated acac [equations (1)—(4)].

$$[\mathrm{U(acac)_4}] \xrightarrow{h\nu} [\mathrm{U(acac)_4}]^* \quad (1)$$

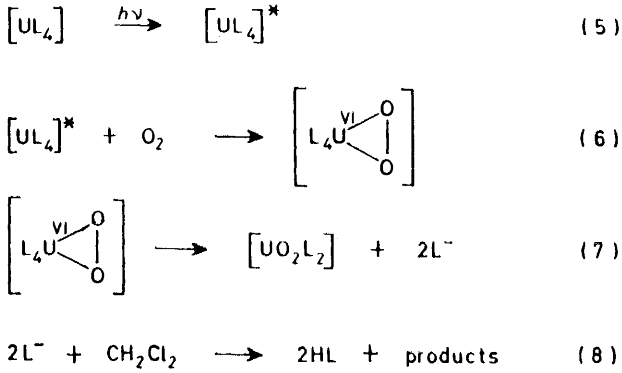
$$[\mathrm{U(acac)_4}]^* \longrightarrow [\mathrm{U(acac)_3}] + \mathrm{acac}^{\bullet} \quad (2)$$

$$[\mathrm{U(acac)_3}] + \mathrm{CH_2Cl_2} \longrightarrow [\mathrm{U(acac)_3}]^+ + \mathrm{Cl}^- + {}^{\bullet}\mathrm{CH_2Cl} \quad (3)$$

$$\mathrm{acac}^{\bullet} + \mathrm{CH_2Cl_2} \longrightarrow \mathrm{Hacac} + {}^{\bullet}\mathrm{CH_2Cl} \quad (4)$$

Formation of [U(acac)$_3$] as a distinct intermediate prior to reaction with solvent is supported by the n.m.r. spectral profile of photoreaction and by the negligible effect of solvent on the quantum yield.

Analysis of the electronic and n.m.r. spectra indicates that [U(dbm)$_4$] undergoes the same reductive dissociation involving intraligand and charge-transfer state excitation. In this case the very fast reaction U$^{\text{III}}$ $\longrightarrow$ U$^{\text{IV}}$ interfered with product identification and calculation of the quantum yield. Exposure of degassed solutions of [UL$_4$] (L = acac or dbm) to visible radiation ($\lambda = 500$ nm, *f-f* excitation) does not result in a photochemical reaction. However, when [UL$_4$] in$\mathrm{CH_2Cl_2}$ are photolysed in the presence of oxygen, the reaction mixtures become yellow and the compounds [UO$_2$L$_2$] are obtained. The other major products are the protonated ligands which were identified spectrally. Under the conditions of the photochemical preparation, [UO$_2$L$_2$] probably arises from an oxidative-addition reaction in which a molecule of oxygen adds to eight-co-ordinated [UL$_4$] complexes to give an unstable intermediate. The latter could be formulated as a peroxo-complex [18] of formally U$^{\text{VI}}$. If such a mechanism were operative then the peroxidic O–O bond breaking would be synchronous with release of the co-ordinated L to give [UO$_2$L$_2$]. N.m.r. profiles of photoreactions indicated that a partial release of the co-ordinated L takes place only in the slower second step. Thus a reasonable mechanism is as in equations (5)—(8). This tentative proposal, supported by the isolation of [UO$_2$L$_2$] and the appearance of HL, only in the slower second step of the photoreactions, is probably similar to that proposed for oxygenation of certain metal complexes.[18]



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