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Photochemical and thermal bromination of metal acetylacetonates by pyridinium bromochromate in acetic acid medium

S Abdul Samath*, N Raman, K Jeyasubramanian,
S Thambidurai & S K Ramalingam
School of Chemistry, Madurai Kamaraj University,
Madurai 625 021

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Photochemical and thermal brominations of metal β-diketonate complexes of Mn(II), Co(II), Cu(II), Zn(II), Cr(III), Mn(III), Fe(III), Co(III), Ce(IV), Th(IV) and UO_2(VI) by pyridinium bromochromate (PBC) in glacial acetic acid have been carried out. Under ambient conditions, the tris and tetrakis chelates underwent electrophilic γ-bromination whereas the bis-chelates decomposed yielding bromo complexes by nucleophilic addition of bromine. Under photo irradiation $\lambda = 254$ or $\lambda = 357$ nm except those of Cr(III), Ce(IV) and Th(IV) complexes which underwent electrophilic γ-substitution, all the other complexes decomposed forming bromo complexes.

Although in recent years, a number of photochemical studies of β-diketonate complexes have been published[1-8], none of these deal with the pseudoaromatic behaviour characteristic of metal β-diketonates. The present work reports the results of photochemical and thermal bromination of β-diketonates of many transition metals and a few inner transition metals in glacial acetic acid medium, using pyridinium bromochromate for these chelates.

Experimental

The metal acetylacetonates of Mn(II), Co(II), Cu(II), Zn(II), Cr(III), Mn(III), Fe(III), Co(III), Ce(IV), Th(IV) and UO_2(VI) and the reagent PBC[9] were prepared as reported[10a]. The brominated products obtained during thermal and photochemical reactions were identified by comparison with authentic bromo products prepared using reagents like $PyHBr_3$[11] NBS[10b,12] etc.

Bromination under thermal reaction condition

To a suspension of PBC (0.02/0.03/0.04 mol) in glacial acetic acid (20 ml) was added the β-diketonate chelate (0.01 mol) dissolved in acetic acid (20 ml). The reaction mixture was heated to boiling on a water bath with occasional stirring. Completion of the reaction could be judged from the green tinge of solution. The solid product obtained was filtered, washed with chloroform and dried *in vacuo*.

Bromination under continuous photolysis condition

The photoreaction between PBC and the metal β-diketonate was carried out in glacial acetic acid medium, in an immersion well photochemical reactor under irradiation at $\lambda = 254$ or $\lambda = 357$ nm. The composition of the solid reaction products obtained and the exposure time required are given in Table 1. Longer exposure time decomposed [Fe(acac)$_3$] to yield black pasty mass, which was found to be unworkable. In the case of Cr(III), Ce(IV) and Th(IV) complexes, the γ-substituted reaction product precipitated upon irradiation, while Mn(II), Co(II), Cu(II), Zn(II), Mn(III), Fe(III), Co(III) and UO_2(VI) complexes decomposed forming bromo complexes $(PyH)_2[MBr_4]$ and $(PyH)_2[UO_2Br_4]$. Ni(II) and Ti(IV) diketonates did not undergo bromination to any perceptible extent.

Results and discussion

A perusal of the composition of bromo products (Table 1) reveals that PBC is capable of yielding different bromo products under photochemical and thermal reaction conditions. They are (i) electrophilic γ-halogenated product – M(Br-acac)$_n$ and or (ii) nucleophilic bromo product – $(PyH)_2[MBr_4]$. It appears that the reagent yields Br^- or Br^+ species depending upon the nature of the substrate by Eqs. (1) and (2).

$$[CrO_3Br]^- + H^+ \rightarrow [HCrO_3]^+ + Br^- \quad \ldots(1)$$

$$\text{HOAC}$$

$$2Cr(VI) + 3Br^- \rightarrow 2Cr(III) + 3Br^+ \quad \ldots(2)$$

While Cr(III) chelate undergoes smooth γ-bromination both under thermal and photochemical conditions, Mn(III), Fe(III) and Co(III) chelates undergo such bromination thermally but not photochemically. The non-formation of electrophilic substituted products photolytically for the complexes 5-7 (Table 1), could possibly be attributed to the photoreduction of the metal ions in the chelates from 3^+ to 2^+ and the known lability of the bichelates under acidic conditions. The chelates on decomposition form bromo complexes by nucleophilic bromine addition.

Table 1 —Photochemical and thermal reaction products obtained on bromination of M(acac)$_n$ by PBC in glacial acetic acid medium

Substrate chelate	Reaction time (min)			Main products obtained by			
	Photochemical		Thermal (boiling condition)	Photochemical		Thermal	
	254 nm	357 nm		Electrophilic substitution	Nucleophilic substitution	Electrophilic substitution	Nucleophilic substitution
Ce(acac)$_4$	15	60	30	Ce(Br-acac)$_4$		Ce(Br-acac)$_4$	—
Th(acac)$_4$	15	60	60	Th(Br-acac)$_4$	—	Th(Br-acac)$_4$	—
Cr(acac)$_3$	15	30	60	Cr(Br-acac)$_3$		Cr(Br-acac)$_3$	—
Mn(acac)$_3$	30	180	120	—	[PyH]$_2$[MnBr$_4$]	Mn(Br-acac)$_3$	—
Fe(acac)$_3$	60	30	90	—	[PyH]$_2$[FeBr$_4$]	Fe(Br-acac)$_3^*$	—
Co(acac)$_3$	10	30	60	—	[PyH]$_2$[CoBr$_4$]	Co(Br-acac)$_3$	—
Mn(acac)$_2$	20	45	60	—	[PyH]$_2$[MnBr$_4$]	—	[PyH]$_2$[MnBr$_4$]
Co(acac)$_2$	10	30	60	—	[PyH]$_2$[CoBr$_4$]	—	[PyH]$_2$[CoBr$_4$]
Cu(acac)$_2$	5	10	instantaneous	—	[PyH]$_2$[CuBr$_4$]	—	[PyH]$_2$[CuBr$_4$]
Zn(acac)$_2$	15	30	30		[PyH]$_2$[ZnBr$_4$]	—	[PyH]$_2$[ZnBr$_4$]
UO$_2$(acac)$_2$	10	30	60	—	[PyH]$_2$[UO$_2$Br$_4$]	—	[PyH]$_2$[UO$_2$Br$_4$]

* Solid product was not thrown during the reaction. It was obtained after chloroform extraction and solvent removal. For the substrates (Mn, Co, Cu, Zn and UO$_2$), the nucleophilic solid reaction product was first formed and the filtrate then yielded the electrophilic product in the thermal condition.

The mechanism primarily involves a photo-induced dissociation of the ligand to give a free radical and is followed by proton abstraction[3]. Thereafter, Br$^-$ replaces the acetylacetone ligand in a stepwise manner to yield [PyH]$_2$[MBr$_4$]. That the tris-chelated chromium substrate does not yield a bis-chelate and a subsequent nuclophilic bromo product can be attributed to the exceptional photostability of Cr(III) ion.

For the bis-chelates under thermal condition, the decomposition appears to occur, following a direct ionic nucleophilic substitution by Br$^-$ of the chelate rings.

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