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Phototransformations of di-O-ethyl S,S-terephthaloyl dixanthate and terephthaloic bis(piperidinedithiocarbamic anhydride)[☆]

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Abstract

The phototransformations of di-O-ethyl S,S-terephthaloyl dixanthate (**3a**) and terephthaloic bis(piperidinethiocarbamic anhydride) (**3b**) were investigated by steady state and nanosecond laser flash photolysis. Irradiation of **3a** and **3b** in benzene resulted in the formation of terephthalic acid in good yields on work-up. The 308 nm laser pulse excitation of these substrates in benzene gave rise to transient species, identified as radical intermediates, produced via C(=O)–S bond scission. These decayed by second-order kinetics and were quenched by free radical quenchers, such as oxygen, 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxyl (HTEMPO). Based on these studies, a reasonable pathway has been suggested for the phototransformations of **3a** and **3b**.

Keywords: Phototransformation; S,S-Terephthaloyl dixanthate; Terephthaloic bis(piperidinedithiocarbamic anhydride)

1. Introduction

In an earlier publication, we reported the steady state and laser flash photolysis studies of certain representative aroyl xanthates and dithiocarbamic anhydrides [1]. These included S-*p*-chlorophenyl O-ethyl xanthate, unsymmetrical O-ethyl phthaloyl dixanthate, unsymmetrical phthaloic bispyrrolidine dithiocarbamic anhydride and a few related substrates. We observed that the aroyl xanthates and dithiocarbamic anhydrides underwent photofragmentation through their triplet states to yield different products depending on the nature of the starting substrates. In all cases, we observed that the primary chemical process involved the fragmentation of a C(=O)–S bond, followed by further reorganization. This type of fragmentation has been observed for most aryl and aroyl xanthates and carboxylic dithiocarbamic anhydrides subjected to photolysis [1–10].

In this study, we have examined the phototransformations of a representative dixanthate and a bis-(dithiocarbamic anhydride) to study the nature of the products formed and the reaction pathways. The substrates examined include di-O-ethyl S,S-terephthaloyl dixanthate (**3a**) and terephthaloic bis(piperidinedithiocarbamic anhydride) (**3b**). These were prepared in good yields (78%–81%) through the reaction of terephthaloyl chloride with potassium O-ethyl xanthate and sodium piperidine dithiocarbamate respectively.

The irradiation of a solution of **3a** in benzene at room temperature, followed by work-up involving treatment with water and extraction with organic solvents, resulted in the isolation of a 70% yield of terephthalic acid (**11**). In a blank run, in which the solution of **3a** was stirred for 24 h and worked up as in the earlier case, a nearly quantitative yield of the starting material was obtained indicating that terephthalic acid is formed essentially through a photoprocess. Similarly, the irradiation of **3b** in benzene for 45 min resulted in the isolation of a 66% yield of terephthalic acid (**11**). In addition, a 20% yield of cyclopentamethylene thiuram disulfide (**6b**) was isolated from this reaction.

This paper describes the details of the steady state photolysis and the results of the time-resolved study of the transient intermediates on nanosecond laser flash photolysis of **3a** and **3b**. Based on these studies, a

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reasonable mechanism has been proposed to explain the photochemical conversion of **3a** and **3b**.

2. Results

2.1. Steady state photolysis

Irradiation of 3a

A solution of **3a** (0.2 g, 0.53 mmol) in benzene (200 ml) was irradiated (Rayonet RPR 300 nm, light source) for 6 h at room temperature (approximately 300 K). Removal of the solvent under vacuum gave a product which, on treatment with water and extraction with benzene, gave 62 mg (70%) of terephthalic acid (**11**), melting point (m.p.) 300–301 °C (mixed m.p.).

In a blank run, a solution of **3a** (0.1 g, 0.26 mmol) in benzene (50 ml) was stirred for 24 h at room temperature (approximately 300 K) and worked up as in the earlier case to give 0.1 g (100%) of the unchanged starting material (**3a**), m.p. 119–120 °C (mixed m.p.).

In another blank run, a solution of **3a** (0.1 g, 0.26 mmol) in benzene (50 ml) was refluxed for 5 h and worked up as in the earlier case to give 0.09 g (90%) of unchanged **3a**, m.p. 119–120 °C (mixed m.p.).

Irradiation of 3b

A solution of **3b** (0.2 g, 0.44 mmol) in benzene (200 ml) was irradiated (125 W, medium pressure mercury lamp) for 45 min at 10 °C. Removal of the solvent under vacuum gave a product which, on treatment with water and extraction with methylene chloride, gave 30 mg (66%) of **11**, m.p. 300–301 °C (mixed m.p.). Removal of the solvent from the methylene chloride soluble fraction gave 28 mg (20%) of cyclopentamethylene thiuram disulfide (**6b**), m.p. 130–131 °C (mixed m.p.) [11].

In a blank run, a solution of **3b** (0.1 g, 0.22 mmol) in benzene (50 ml) was stirred for 24 h at room temperature (approximately 300 K). Removal of the solvent under vacuum and work-up as in the earlier case gave 80 mg (30%) of unchanged **3b**, m.p. 135–136 °C (mixed m.p.).

In a repeat run, a benzene solution of **3b** (0.1 g, 0.22 mmol in 50 ml) was refluxed for 6 h. Removal of the solvent under vacuum and fractional crystallization of the product gave a mixture of terephthalamide (**7b**) (40 mg, 60%), m.p. 205–206 °C (mixed m.p.) and recovered starting material (**3b**) (10 mg, 10%), m.p. 135–136 °C (mixed m.p.).

2.2. Laser flash photolysis studies

Di-O-ethyl S,S-terephthaloyl dixanthate (3a)

Excitation by 10 ns laser pulses of the 308 nm excimer laser of argon-degassed acetonitrile solutions of **3a** gave rise to transient absorptions as shown in Fig. 1. Curve A in Fig. 1 shows the absorptions of the transients formed within the laser pulse and is characterized by three distinct peaks at 360, 540 and 650 nm. The decay of these transients at the three different wavelengths is shown in the insets of Fig. 1. The transient absorbing around 650 nm decays by a second-order process ($2k/\epsilon = 7 \times 10^6$ cm s^{-1}) and is insensitive to oxygen. Stable free radicals, such as 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxyl (HTEMPO), which are capable of reacting with free radicals, quench this transient with rate constants of 1.8×10^9 and 1.3×10^9 M^{-1} s^{-1} respectively. Our earlier studies on S-*p*-chlorobenzoyl O-ethyl xanthate [1] have shown that the (ethoxythiocarbonyl)thiyl radical (**5a**) absorbs strongly at 650 nm and its spectral and quenching properties are similar to those of the 650 nm transient derived from **3a**. We therefore assign the 650 nm transient to the (ethoxythiocarbonyl)thiyl radical (**5a**), which can arise through the photoinduced C(=O)–S bond scission of **3a**.

The transient absorption spectrum obtained immediately after the laser pulse (Fig. 1, curve A) shows two other peaks at around 360 and 540 nm. The absorptions at 360 and 540 nm decay by a second-order process, yielding $2k/\epsilon$ values of 3.9×10^6 and 8.4×10^6 cm s^{-1} respectively. Since (as seen from Fig. 1, curve A) there is a difference of a factor of about two in the ϵ values at 360 and 540 nm, the second-order decay constants at these wavelengths are nearly identical. Both the 360 and 540 nm absorptions are efficiently quenched by oxygen ($k = 1 \times 10^9$ M^{-1} s^{-1}) and the free radical quenchers TEMPO ($k = (1.1\text{–}1.2) \times 10^9$ M^{-1} s^{-1}) and HTEMPO ($k = (1\text{–}1.4) \times 10^9$ M^{-1} s^{-1}). The similarity in the second-order decay rates, as well as the quenching behavior, suggests that the 360 and 540 nm absorptions are due

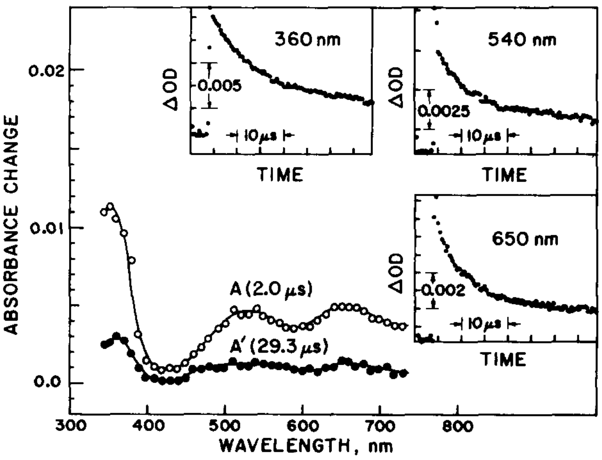


Fig. 1. Transient absorption spectra of **3a** following 308 nm laser pulse excitation in acetonitrile at 295 K. The insets show the kinetic traces of the decay of the transients at different wavelengths.

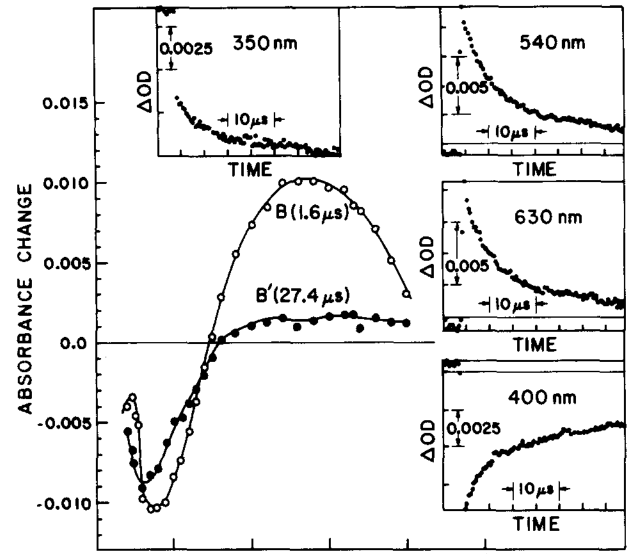


Fig. 2. Transient absorption spectra of **3b** following 308 nm laser pulse excitation in acetonitrile solution. The insets show the kinetic traces of the decay of the transients at different wavelengths.

to a single transient species. The C(=O)–S bond cleavage of **3a** will lead to the formation of the radical fragment **4a**, together with **5a**. Radical **4a** may be responsible for the absorption around the 350 and 540 nm regions. The behavior of this radical species is very similar to that of unsubstituted [12] and substituted [1] benzoyl radicals, reported earlier.

The quenching of the xanthone triplet ($E_T = 74$ kcal mol^{-1}) [13] by **3a** was studied by 308 nm excitation of xanthone in the presence of 0.05–0.5 mM of **3a** in benzene. The xanthone triplet was monitored at 650 nm, where it has a much stronger absorption than the radical formed from **3a**. The xanthone triplet is quenched efficiently by **3a** ($k_q = 1.4 \times 10^{10}$ M^{-1} s^{-1}). In the direct excitation studies of **3a**, no triplets were observed, and this could be due to the rapid deactivation of the triplets via bond cleavage to yield the radicals **4a** and **5a**. Earlier reports on the laser flash photolysis of S-*p*-chlorobenzoyl O-ethyl xanthate have shown that it undergoes photofragmentation through a triplet-mediated pathway [1].

Terephthaloic bis(piperidinedithiocarbamic anhydride) (3b)

The transient absorption spectrum of **3b**, obtained immediately after the 308 nm laser pulse excitation in acetonitrile solution, is shown in Fig. 2. The spectrum obtained 1.6 μs after the laser pulse (Fig. 2, curve B) shows a depletion at 390 nm and a broad peak around 590 nm. The spectrum of **5b** is expected to be very similar to that of **5a**. Although no clear peak is observed around 630 nm, the kinetic decay behavior at 630 nm is very similar to that of the 650 nm absorption transient derived from **3a**. It shows a second-order decay with a rate constant $2k/\epsilon = 4.1 \times 10^6$. Its decay rate is insensitive to oxygen, but sensitive to other free radical quenchers such as TEMPO ($k = 7 \times 10^8$ M^{-1} s^{-1}) and HTEMPO ($k = 7 \times 10^8$ M^{-1} s^{-1}). The transient absorption in the 630 nm region could be due to the thiyl radical **5b**, and the absence of a clear maximum around this region may be attributed to the merging of the transient absorption maxima of **4b** and **5b**. The absorption of **4b** may be slightly red shifted in comparison with **4a**.

The transient absorption around 360 nm for **3b** is very different from that of **3a**. There is a large depletion around 390 nm. Compound **3b** has an absorption spectrum in the ground state which extends to the visible region and the extinction coefficients at 350 and 400 nm are 6820 and 1820 M^{-1} cm^{-1} respectively, which are much higher than those of **3a** in these regions (see Section 4). Thus, even though the radicals may absorb in this region, due to the depletion of **3b** there will be a net depletion in absorption at these wavelengths.

Over longer time scales, the transient absorption shows further changes. The transient absorption taken 27.4 μs after the laser pulse is shown in Fig. 2 (curve B') and the decay traces are shown as insets. At 350 nm there is a further depletion, whereas at 400 nm a partial recovery is observed. Both of these processes follow second-order kinetics. At 540 nm, a second-order decay of the transient absorption is observed and the rate constants for transient decay are shown in Table 1. As can be seen in Table 1, the transient absorption in this region is efficiently quenched by free radical quenchers such as oxygen, TEMPO and HTEMPO.

The quenching of the xanthone triplet by **3b** was also studied. As with **3a**, an efficient quenching of the xanthone triplet was observed ($k_q = 2.1 \times 10^{10}$ M^{-1} s^{-1}).

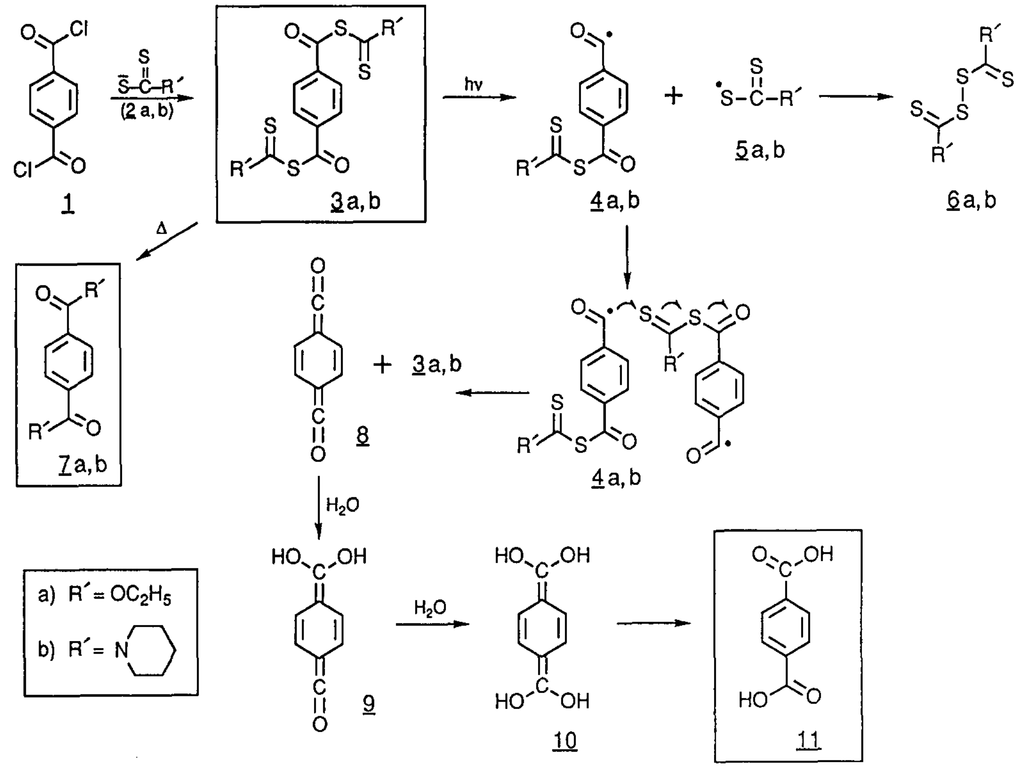
3. Discussion

The photofragmentation process of **3a** and **3b** leads to the formation of the corresponding aroyl radicals (**4a**, **4b**) and (thiocarbonyl)thiyl radicals (**5a**, **5b**). A probable route to the further transformation of these radicals is shown in Scheme 1. The transient decay rates at the different wavelengths of 360, 540 and 650 nm are nearly the same, allowing for the differences in ϵ. Since the absorption at 650 nm can be clearly assigned to radicals **5a** and **5b** by analogy with earlier studies [1], the similarity in rate constants at the different wavelengths suggests that the predominant pathway for the transient decay is via a radical recombination reaction to give back the starting materials **3a** and **3b**. The formation of the observed products may be attributed to a slow unimolecular competing reaction involving the fragmentation of **4a** and **4b** to form the bisketene intermediate **8** and radicals **5a** and **5b**. The

Table 1
Spectral and kinetic behavior of the photogenerated transients from **3a** and **3b** and the rate constants for the quenching of xanthone triplets by **3a** and **3b**

Substrate	$10^{10}\ k_qT$ ($M^{-1}\ s^{-1}$)[a]	Transient, λ_{max}[b] (nm)	$10^6\ 2k/\epsilon$[c] ($cm\ s^{-1}$)	$10^9\ k_q$ ($M^{-1}\ s^{-1}$)[c]			
				O_2	TEMPO	HTEMPO	Ferrocene
3a	1.4	360	3.9	1.0	1.2	1.0	
		540	8.4	1.0	1.1	1.4	0.2
		650	7.0	–	1.8	1.3	–
3b	2.1	350	6.2	0.3	1.3	1.1	–
		540	4.2	1.2	0.6	0.7	0.13
		630	4.1	–	0.7	0.7	

[a] Rate constant for the quenching of the xanthone triplet by the substrate, ±15%.
[b] ±10 nm.
[c] ±15%.



Scheme 1.

residual transient absorptions at longer time scales (Fig. 1, curve A′; Fig. 2, curve B′) decay very slowly. However, no distinct absorptions which could be attributed to the bisketene intermediate **8** were observed. The reaction of the bisketene **8** with water on work-up could lead to the water addition products **9** and **10**, and subsequent air oxidation of **10** would result in the formation of **11** as shown in Scheme 1.

No direct evidence was obtained from the laser flash photolysis studies for the formation of the triplet states of **3a** and **3b**. Earlier studies [1] on related compounds, such as aroyl xanthates and dithiocarbamic anhydrides, have shown clearly that the photodissociation to radical intermediates occurs via short-lived triplets, and it is probable that the photodissociation of **3a** and **3b** also occurs via triplets. The diffusion-rate-controlled quenching of xanthone triplets by **3a** and **3b** indicates efficient energy transfer from the xanthone triplets to the triplet states of **3a** and **3b**. However, the formation of free radical intermediates from **3a** and **3b** could not be followed in the triplet quenching studies due to the large differences in extinction coefficient between the xanthone triplet and the free radicals.

4. Experimental details

All melting points are uncorrected and were determined on a Büchi 580 melting apparatus. The IR spectra were recorded using a Perkin–Elmer model 882 IR spectrometer and the absorption spectra were recorded using a Hitachi 220 spectrophotometer. The nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-360 NMR spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Finnigan MAT model 8430 mass spectrometer or JEOL model JMS-AX505HA mass spectrometer.

Solvents for steady state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. TEMPO and HTEMPO from Aldrich, were used as received. Commercially available terephthaloyl chloride (**1**) was used after purification.

4.1. Starting materials

Potassium O-ethylxanthate (**2a**) [14], m.p. 185–186 °C, and sodium piperidine dithiocarbamate (**2b**), m.p. 169–170 °C, were prepared by reported procedures.

Preparation of di-O-ethyl S, S-terephthaloyl dixanthate (3a)

To a solution of **1** (2 g, 0.01 mol) in methylene chloride (30 ml), maintained at 0 °C, was added **2a** (3.2 g, 0.02 mol), with constant stirring, over a period of 1 h. The reaction mixture was treated with water and the organic layer was collected and dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave a yellow product, which was recrystallized from a mixture (1:1) of methylene chloride and petroleum ether to give 2.9 g (78%) of **3a**, m.p. 119–120 °C. Analysis: calculated for $C_{14}H_{14}O_4S_4$: C, 44.90%; H, 3.77%; S, 34.24%; found: C, 44.85%; H, 3.67%; S, 34.38%. IR (KBr): 1705 cm^{-1} (C=O), 1030 cm^{-1} (C=S). UV (CH_3CN): 260 nm (ϵ, 25 450), 284 (22 950), 396 (820). ^1H NMR ($CDCl_3$): δ 1.5 (t, 3H, CH_3), 4.6 (q, 2H, CH_2), 8.0 (s, 4H, aromatic). Mass (fast atom bombardment (FAB)) *m/e*: 375 (MH^+).

Preparation of terephthaloic bis(piperidinedithiocarbamic anhydride) (3b)

To a stirred suspension of **2b** (1.83 g, 0.01 mol), maintained at 0 °C, was added a solution of **1** (1 g, 0.005 mol) in methylene chloride (20 ml), over a period of 1 h. The reaction mixture was treated with water to remove any unchanged **2b** and the organic layer was dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave 1.8 g (81%) of **3b**, m.p. 135–136 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether. Analysis: calculated for $C_{20}H_{24}N_2O_2S_4$: C, 53.07%; H, 5.34%, N, 6.19%; S, 28.33%; found: C, 52.97%; H, 5.25%; N, 6.17%; S, 28.14%. IR (KBr): 1680 cm^{-1} (C=O), 1490 cm^{-1} (C=S). UV (CH_3CN): 254 nm (ϵ, 27 730), 284 (30 230), 350 (6820), 410 (1820). ^1H NMR ($CDCl_3$): δ 1.8 (broad m, 12H, CH_2), 4.3 (broad m, 8H, CH_2), 8.1 (m, 4H, aromatic). Mass (FAB) *m/e*: 453 (MH^+).

4.2. Laser flash photolysis

For laser flash photolysis, laser excitation was carried out at 308 nm (XeCl, Lambda Physik EMG 101 MCS excimer laser, 50 mJ, 10 ns). The details of the kinetic spectrophotometer and data collection system have been given previously [15,16]. Unless oxygen effects were to be studied, the solutions were deaerated by purging with pure argon.

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