Laser Flash Photolysis Study of Dialkylphenacylsulfonium Salts

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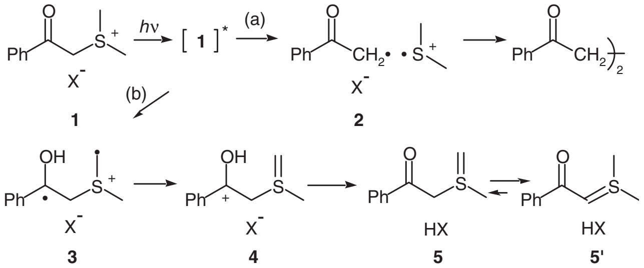
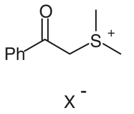
Laser flash photolysis of the title compound in degassed acetonitrile at room temperature revealed the presence of transient species showing the absorption at 480 nm, regardless of the structure of the precursors. The transient bands are assigned to phenacyl radical presumably formed as a result of the carbon-sulfur bond rather than 1,4-biradicals or cationic species proposed to be formed as a result of Norrish Type II process.

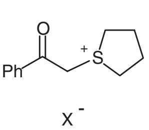
The photoinduced cationic polymerization systems are currently employed in a variety of industrial applications including adhesives, nonstick release coatings, abrasion resistant coatings for plastics, and so on.[1] Key to the development of this technology was the discovery of highly efficient cationic photoinitiators. Dialkylphenacylsulfonium salts (DPSs, **1**) are excellent photoinitiators for the cationic polymerization of reactive monomers such as multifunctional epoxides and vinyl ethers.[2] However, initial photochemical processes of **1** have been studied only by traditional product analysis method and the prevailing mechanisms seem to be controversial. Thus, early studies by Laird[3] and Maycock[4] proposed a cleavage of the phenacyl–sulfur bond, path (a), since products derived from phenacyl radical (**2**) were detected along with dialkyl sulfide. More recently, Crivello proposed a mechanism initiated by hydrogen abstraction by a typical Norrish Type II process, followed by internal electron transfer generating the cation **4** and subsequent proton transfer, path (b).[2] The proposal was mainly based on the observation that **1** was rather stable under irradiation but underwent H–D scrambling when irradiated in acetone-d_6. Thus, in path (b), ylides **5** (and **5′**) were the final product, which regenerated **1** by the reaction with protic acids, HX.



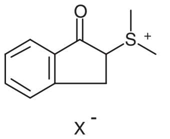
In spite of the importance of the initiators, it is rather surprising to note here that no spectroscopic studies have been made. In order to improve the sensitivity of the initiators, it is important to reveal the initial process of this photochemical process. Thus, laser flash photolysis (LFP) study of DPS was made in solution at room temperature. We chose four DPSs (**1a** to **1d**),[5] where ketone and sulfonium parts are located in either cyclic or acyclic systems.



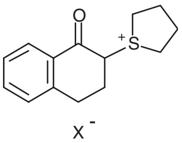
1a



1b



1c



1d

$X^- = C_4F_9SO_3^-$

LFP[6] of **1a** in a degassed acetonitrile solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl laser produced a broad absorption band with apparent maximum at 480 nm, which appeared 10 µs after excitation and disappeared within 2 ms (Figure 1a). The decay was analyzed by curve-fitting method in terms of the combination of first and second order kinetics, where 90% of the decay followed second order mode. The rate constants estimated at two different absorption bands are very similar (Table 1), indicating single transient specie is involved in the absorption bands. LFP of **1b**, having the same ketone part but with cyclic sulfonium ions moiety gave essentially the same transient absorption band which also decayed in a similar manner (Table 1).

LFP of cyclic ketone analogues, **1c** and **1d**, gave a similar but slightly shifted transient band with increased intensity (Figure 1b) as compared to those observed in LFP of acyclic ketone counterparts, **1a** and **1b**. This is probably because of larger molecular extinction coefficient of cyclic ketones at 308 nm as opposed to that of acyclic ones.[7] The decay modes were found to be similar with that observed in LFP of acyclic ones, although the first order rate constants were slightly larger in the cyclic ketones than the acyclic ones.

The observation suggested that very similar intermediates were generated during LFP of **1** regardless of the structure of ketone and sulfonium parts, although apparent maximum and decay rates are slightly dependent on the structure.

LFP studies of a series of alkyl(aryl) ketones undergoing Type II H abstraction reaction have been extensively carried out and the transient 1,4-diradicals have been well characterized.[8] Those diradicals showed a rather featureless spectrum with a maximum below 300 nm tailing up to 440 nm and decayed in hundred ns orders at the longest. For instance, LFP of valerophenone generated the corresponding 1,4-biradical, which showed the featureless band from 300 tailing to 400 nm with lifetimes of 9 and 70 ns in acetonitrile.[9] These characteristics are not seen in the transient bands observed in LFP of **1**.

Benzyl cations have been also generated by LFP of proper precursors and reported to have absorption maximum at 300 to 350 nm and decayed in µs orders.[10] For instance, phenethyl cation showed a strong absorption band at 315 nm with a very weak band at 430 nm.[10b] The transient band observed in LFP of **1** seems thus too long to assign it to the corresponding cations. Ylides (**5′**), proposed to be formed as a final product in Crivello's mechanism, are usually stable compounds but may decay in the

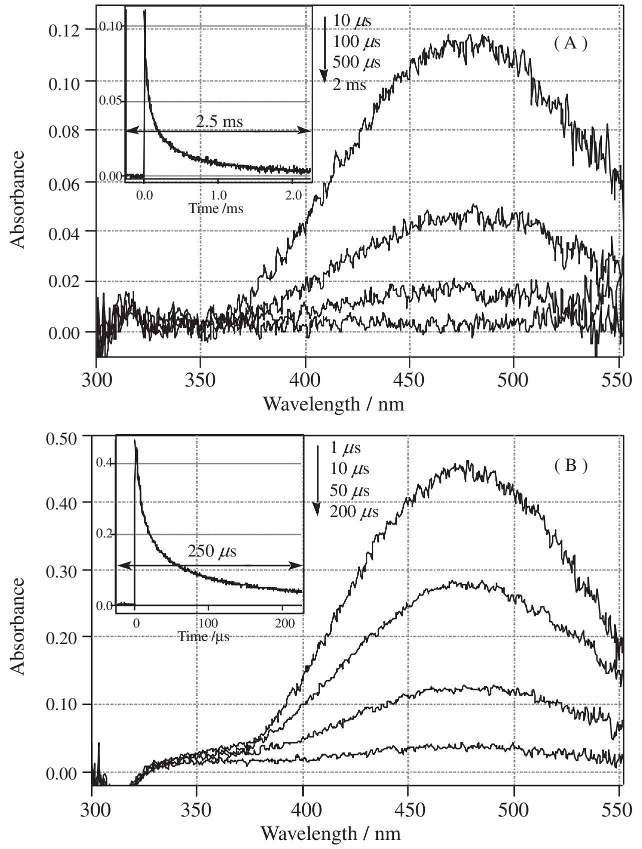


Figure 1. Transient absorption obtained by LFP of **1a** (A) and **1c** (B) in a degassed acetonitrile.

Table 1. Spectroscopic and kinetic data obtained in LFP of **1**[a]

DPS	$\lambda_{\max}$/nm	Decay Rates		
		k/s^{-1}	$2k'/\varepsilon\ell/\mathrm{s}^{-1}$	(λ/nm)[b]
1a	475	1.2×10^3	3.0×10^5	(450)
		1.1×10^3	2.2×10^5	(490)
1b	475	9.4×10^2	2.7×10^5	(450)
		9.3×10^2	1.8×10^5	(490)
1c	475	6.1×10^3	2.7×10^5	(470)
1d	480	4.3×10^3	3.5×10^5	(470)

[a] In degassed acetonitrile at room temperature.

[b] The wavelength at which the decay was monitored.

presence of acid generated under irradiation. However, the ylide is shown to have absorption maximum at 297 nm.[11]

All those possible intermediates in Crivello's scheme are unlikely to coincide with the observed transient band. Moreover, if all of DPSs (**1**) decompose by Type II mechanism, nature of the transient species must vary depending on the structure of the precursors.

On the other hand, phenacyl radical (**2**) was generated by the reaction of electron with phenacyl bromide in 2-methyltetrahydrofuran at 77 K and was reported to have a broad band with a maximum at 455 nm.[12] Although the absorption maximum of transient bands observed in LFP of **1** is somewhat longer than 455 nm, the matching of the spectral features is most reasonable among other possible species. The generation of essentially the same transient band from two different precursors with the same ketone moiety, **1a** and **1b**, and second order kinetic mode of the species as main decay pathway are in good agreement with the C–S bond cleavage mechanism. This assignment is indeed supported by the finding that the transient band from **1a** is quenched by 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) with the rate constant of $1.4 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Analysis of the spent solution showed the presence of phenacyl radical–TEMPO adduct (40%)[13] along with acetophenone.

Thus, the present study revealed that Norrish Type II H abstraction process is not a likely pathway undergone by the excited state of **1**, at least to an extent detectable by LFP, and that the photo-cleavage of C–S bond is more likely process.

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5 All the DPSs, **1a**,[4] **1b**,[2b] **1c**,[2e] and **1d**[4] were prepared according to the reported procedures.

6 For details of our LFP equipments, see; H. Tomioka, T. Watanabe, M. Hattori, N. Nomura, and K. Hirai, *J. Am. Chem. Soc.*, **124**, 474 (2002).

7 The molecular extinction coefficients of **1a**–**1d** at 308 nm in acetonitrile are 1.84×10^2, 2.97×10^2, 1.54×10^3, and 1.51×10^3, respectively.

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