

Benzophenone-4-sulfonate: Triplet Absorption and Decay in Trifluoroacetic acid and Acetonitrile, and Energies of Ground State, Triplet and Radical Species

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Benzophenone-4-sulfonate (BPSS) has been studied by nanosecond laser-flash photolysis in trifluoroacetic acid (TFA) and acetonitrile. The BPSS triplet has absorption peaks at 530 nm in acetonitrile and at 510 nm and 630 nm in TFA. Energies have been calculated for the BPSS ground state, triplet, and anion, cation and neutral radicals. The decay kinetics of the BPSS triplet state was also studied.

Benzophenone has been a key test substance in the development of organic photochemistry over the past decades.^{1–3} In particular, it serves as an actinometric standard in flash photolysis, since the triplet yield and molar absorption coefficient in benzene solution have been carefully established.⁴ For work in aqueous solutions the more soluble sodium benzophenone-4-sulfonate (BPSS) is also expected to be useful. The change in medium introduces new factors in the photochemistry of the species.⁵

The triplet-state absorption spectra of benzophenone and benzophenone-4-carboxylic acid have been recorded earlier.^{4,6} The triplet-state absorption spectra maxima were ca. 535 nm for both compounds. The characteristic hydrogen atom abstraction reaction of $n-\pi^*$ triplets occurs when water is present.^{1,2,3,6,7} In the case of benzophenone-4-carboxylic acid triplet the first-order reaction constant k_1 has been determined as $(1.5–2.0) \times 10^5 \text{ s}^{-1}$, which corresponds to the triplet returning to the ground state.⁶ The second-order radical formation reaction coefficient k_2 was determined as $3.0 \times 10^7 \text{ mol dm}^{-3} \text{ s}^{-1}$.⁶

Of special interest is the possible interaction with trifluoroacetic acid (TFA), which may lead to cation radicals with many aromatic hydrocarbons but which does not occur in the ground state of benzophenone.⁸ The BPSS radical anion can be produced by alkali-metal reduction in high vacuum conditions and be detected by EPR spectroscopy. The BPSS radical cation cannot be detected in high vacuum samples prepared in TFA. For

many easily oxidizable aromatic hydrocarbons this method can be used to produce radical cations.⁹

Experimental

Chemicals. Dry acetonitrile (Fluka; 'Garantie' for UV Spectroscopy and Burdick and Jackson UV grade), trifluoroacetic acid (Merck; For Spectroscopy). BPSS was synthesized as described earlier.⁵

Sample preparation. Solutions of BPSS in acetonitrile or TFA ($10^{-3} \text{ mol dm}^{-3}$) were purged with argon to remove most of the oxygen.

Flash photolysis equipment. Flash photolysis was carried out using 347 nm excitation from a pulsed frequency-doubled ruby laser as described elsewhere.¹⁰ Samples were measured in $1 \times 1 \text{ cm}$ Pyrex cells fitted with Teflon closures.

Molar absorption coefficient. The molar absorption coefficient for BPSS triplet-state was estimated relative to the known molar absorption coefficient of the benzophenone triplet.⁴ Because benzophenone and BPSS triplets have absorption maxima at the same wavelength and can be measured under the same experimental conditions, it is possible to estimate the molar absorption coefficient of BPSS. It is assumed that both compounds yield the same amount of the corresponding triplet.

Kinetics calculations. The decay of the triplet state follows mixed first- and second-order kinetics as follows:

$$-\frac{dC}{dt} = k_1 C + k_2 C^2 \quad (1)$$

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where C is the triplet state concentration. The solution for eqn. (1) is

$$\frac{C}{C_0} = \frac{k_1}{(k_1 + k_2 C_0) \exp(k_1 t) - k_2 C_0} \quad (2)$$

where $C/C_0 = \Delta A/\Delta A_0$. ΔA is the absorbance at time t , C_0 is the triplet concentration at $t=0$ and ΔA_0 is the absorbance at $t=0$.

If some long-lived product is formed with absorption at the measurement wavelength then a correction must be made according to eqn. (3):

$$\Delta A^T = \frac{\Delta A - \Delta A_\infty}{1 - \frac{\Delta A_\infty}{\Delta A_0}} \quad (3)$$

where ΔA^T is the absorption of the triplet state and ΔA_∞ is the absorption at $t=\infty$. The corrected triplet-state decay curve was fitted to eqn. (2) by the least-squares method, as shown in eqn. (4):

$$\min_{k_1, k_2} \sum_{i=1}^N \left(y_i - \frac{k_1}{(k_1 + k_2 C_0) \exp(k_1 t_i) - k_2 C_0} \right)^2 \quad (4)$$

A conjugate gradient-based routine was used for minimization of eqn. (4) with k_1 and k_2 constrained to be non-negative. The maximum relative errors for data points were usually of the order of 5–10%. All the kinetics calculations were performed at 530 nm. The presented decay curves have been normalized to unity at $t=0$.

Computational methods. The initial Z -matrices were generated using the SYBYL program.¹¹ The optimum geometries were calculated using the Gaussian 92 program with UHF/3–21G level of theory without any geometry constraints.^{12–15} The optimized ground-state structure for BPSS was verified by its X-ray structure obtained from the Cambridge Structural Database System.¹⁶

Results and discussion

Absorption spectra. The BPSS ground state has absorption maxima at 258, 259 and 260 nm in acetonitrile, TFA and water, respectively. This means that the ground-state ketone group is not protonated in acidic solvents. The triplet state of BPSS in acetonitrile has an absorption maximum at 530 nm. In TFA it has two maxima at 510 and 630 nm (Fig. 1). There are few possible explanations for the shift in the absorption maximum (530 to 510 nm): protonation of the sulfonate group, hydrogen-bond formation between the ketone group oxygen and water or protonation of the ketone group. The time required for this is less than 1 ns since it happens during the flash. The maximum at 630 nm may be from the same transient as 510 nm peak because the lifetime is essentially the same as at 510 nm within the measurement accuracy. The absorption spectra obtained at $t=\infty$ have very similar shape in TFA as in acetonitrile containing small amounts of water.

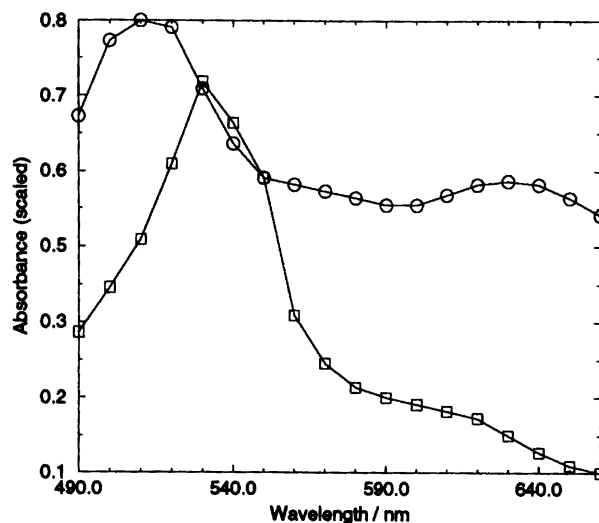


Fig. 1. Absorption spectra of the BPSS triplet state in acetonitrile (squares markers) and TFA (circles markers) at $t=0$.

Computational results. The fully UHF/3–21G optimized molecules were benzophenone-4-sulfonic acid, its excited triplet state, neutral radical ($>\dot{C}-OH$), radical anion and cation, as shown in Table 1. The relevant atom numbering is presented in Fig. 2. As seen from Table 1, the rough estimate for the energy difference between the singlet and triplet states is 92.4 kJ mol^{-1} . The calculated C–O bond length for the singlet BPSS corresponds to a standard double bond length between the carbon and oxygen. For the triplet state the C–O bond length increases to that of standard single carbon–oxygen bond. This is very close to the C–O bond length of the neutral radical of BPSS. The calculated energies of various states of BPSS roughly suggest that the neutral radical form ($>\dot{C}-OH$) has the lowest-lying energy and is therefore favoured instead of the radical cation and anion forms.

Table 1. UHF/3–21G calculated energies and C–O bond lengths of BPSS.

Charge	State	Energy/a.u.	r_{7-14}/nm
0	S ₀	–1188.472	0.1216
0	T	–1188.437	0.1400
0	D	–1188.552	0.1399 ^a
–1	D	–1188.487	0.1281
+1	D	–1188.169	–

^a The energy of one hydrogen atom was subtracted from the total energy.

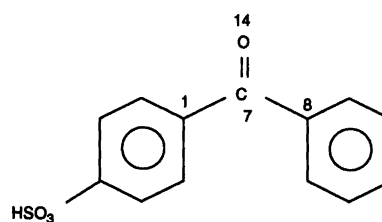


Fig. 2. Benzophenone-4-sulfonic acid atom numbering.

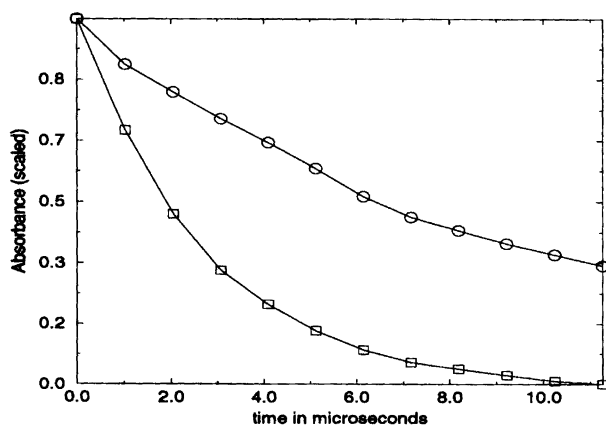


Fig. 3. Measured decay of the BPSS triplet state in dry acetonitrile (squares) and acetonitrile containing water (circles) at 530 nm.

This supports the neutral radical formation theory presented earlier for the benzophenone triplet.⁶

Kinetics. When the sample does not contain any water the ΔA transient sweep decreases to the zero level on the time-scale shown in Fig. 3 (squares). If water is added to the acetonitrile sample then the ΔA transient sweep decreases to the neutral radical level as seen in Fig. 3 (circles). When the neutral radical reaction occurs and it has an absorption at the measurement wavelength (530 nm) it must be taken into account in the rate-constant calculations using eqn. (3). The molar absorption coefficients for the BPSS triplet in both acetonitrile and TFA at 530 nm were estimated to be $5800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The average rate constants for the BPSS triplet in TFA are estimated as $k_1 = (3.3 \pm 0.5) \times 10^5 \text{ s}^{-1}$ and $k_2 = 3.7 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$. The value of k_2 is not very accurate. The rate-constants in dry acetonitrile are estimated as $k_1 = (4.2 \pm 0.5) \times 10^5 \text{ s}^{-1}$ and $k_2 = 0.0 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$, which corresponds to a first-order reaction. The values of k_1 are in the same order as reported earlier for benzophenone-4-carboxylic acid triplet.⁶

Reaction mechanism. In dry acetonitrile the only possible first-order reaction is the return of the BPSS triplet to the ground state. In TFA, which contains about 2% water, an additional reaction of hydrogen atom abstraction by the BPSS triplet occurs. Since k_2 is zero in

acetonitrile this must be the only second-order reaction in TFA, ruling out the reaction of two BPSS triplet molecules with each other. The hydrogen atom donor to the BPSS triplet may be water or TFA. At least water is capable of donating hydrogen atom to the BPSS triplet, as can be seen from the acetonitrile/water experiment.

The reactions of the BPSS triplet state are very much the same as benzophenone and benzophenone-4-carboxylic acid, as expected.

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