New Insights into the Photodissociation of Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide

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Benzoylphosphine oxides are widely known as industrial photoinitiators in photochemical curing processes. In the recent past, their photochemistry and photophysics have been studied, for example by Laser Flash Photolysis[1], Time Resolved ESR[2] and Picosecond Pump Probe Spectroscopy[3]. These efforts suggested, for phosphine oxide radical starters of the type Ar-CO-PO-Ar_2 (where Ar = aromatic residue), C-P bond breakage taking place on a time scale of hundred picoseconds and being facilitated by an S_1-T_1 intersystem crossing. The time scale for the initial non-adiabatic transition remained, however, unresolved.

Here, we unravel the primary processes of the photoinitiator Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) in great detail, using femtosecond UV-pump IR-probe spectroscopy. All experiments were carried out in dichloromethane solutions, using pump pulses of 100 fs duration, centered at a wavelength of λ = 380 nm.

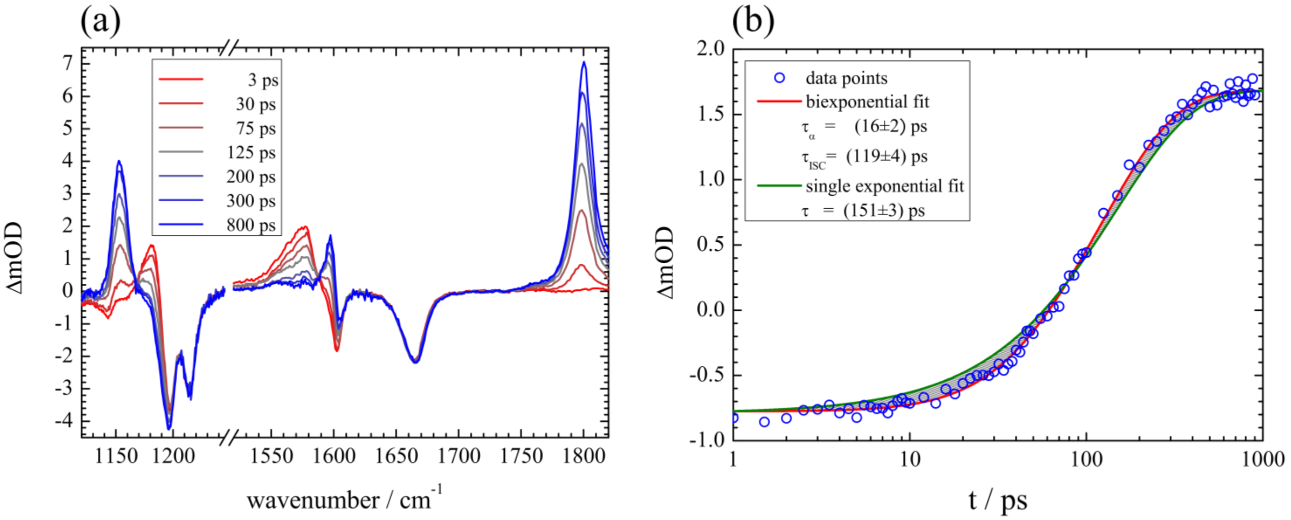

Figure 1 (a) Transient spectra recorded after excitation of the sample with λ = 380 nm light. (b) Kinetic trace for the absorption at 1597 cm^{-1} corresponding to the C=C-stretching vibration of the benzoyl radical. The area between the two fits has been marked to emphasize their deviation.

The obtained transient spectra are shown in Fig. 1 (a). The bleaching signals do not show any variation over time, meaning that there is no ground state recovery. Furthermore there are two transient absorptions at 1180 cm^{-1} (PO-stretching vibration) and 1570 cm^{-1} (CO-stretching vibration) of the S_1-excited state, which exhibit their maximum absorption directly after excitation and then decay over time. The two transient absorptions at 1597 cm^{-1} (C=C-stretching vibration) and at 1800 cm^{-1} (CO-stretching vibration) correspond to the generation of the benzoyl radical. The signal at 1150 cm^{-1} corresponds to the PO-stretching vibration of the emerging phosphinoyl radical. All transient absorptions of the radical species reach their maximal intensity after ~600 ps and then remain constant. It is remarkable that we were not able to observe any signal corresponding to the absorption of an excited triplet state (T_1), as might be expected after looking into the previous studies.[1-3]

In Fig. 1 (b) the kinetic trace for the transient absorption sited at 1597 cm^{-1} is shown. We found that the formation of the benzoyl radical occurs in a delayed fashion and cannot be fit to first order growth kinetics, as was assumed previously.[3] A careful analysis of the spectro-temporal evolution in the mid-infrared region yields accurate time constants of 120 ps for the initial S_1-T_1 intersystem crossing and 15 ps for the ensuing α-cleavage with radical pair formation, respectively. The time constant we extracted for the α-cleavage is about seven times faster than proposed in the prior studies which is why we were not able to observe the excited triplet state of TPO. This fast α-cleavage means that nearly every molecule, after reaching the excited triplet state, nearly instantly undergoes α-cleavage. Therefore the overall concentration of the T_1-state remains low during the whole reaction and is not detectable with our experimental setup.

Also it is notable, that we were able to identify the C=C-stretching mode of the benzoyl radical in liquid solution, which has been accomplished previously only in the gaseous phase or through complex cryogenic matrix isolation techniques.

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