Bond cleavage in the excited state of acyl phosphene oxides
Insight on the role of conformation by model calculations: a concept

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Dedicated to Lord George Porter on the occasion of his 80thbirthday

Abstract

Rotation profiles along the C(O)–P(O) bond of model system **1** were calculated for the S_0, S_1 and T_1 state on the B3LYP/6-31G* and RCIS/6-31+G* level of theory. Moreover, the cleavage of the bond was followed in the T_1 state. The computations reveal that the efficiency of the α cleavage reaction may depend on the different rotation barriers of the molecule in the electronic states attained during the photochemical pathway. It can be anticipated that specific solvation which may influence the conformational mobility and the lifetimes in the S_1 and T_1 states is likely to play a important role for solvent effects. © 2001 Published by Elsevier Science B.V.

1. Introduction

Chemical reactions proceeding via radical pathways can be found in a wide variety of reactivity patterns, e.g. (stereoselective) syntheses, in enzymatic reactions, or in radical polymerizations. In many cases, free-radical processes are induced by a bond leavage (α-cleavage, Norrish Type I reaction) [20] that can be accomplished either by a thermal reaction or by photolysis. Light-induced reactions proceed in two domains, i.e. either cleavage occurs in an excited singlet state or, after excitation and intersystem crossing, the bond is broken in the triplet state. It has been reported that such reactions indicate solvent or environmental effects [1,2,4,14,19]. In particular, photochemical α-cleavage reactions of ketones and their derivatives have been studied to a large extent [5,6,9,15,17,21]. Investigations by EPR spectroscopy [11] imply that several conformations are populated in the triplet state of diphenylacetone. This can be rationalized by at least three arguments: (1) several conformers populated in the ground state are excited yielding a broad range of excited-state conformations; (2) the spread of conformers occurs either during the photochemical pathway in the excited singlet or (3) conformational changes occur in the excited triplet state before the bond is cleaved. It is an open and interesting question whether conformational dynamics are responsible for the efficiency of the α-cleavage so that

computations of the type reported herein can provide some insight to this important issue. For the internal rotation of molecular moieties, the time scales for intersystem crossing and for the α-cleavage reaction are compatible (Fig. 1), i.e. rotations of molecular moieties are possible during the excitation of the molecule in the excited singlet (S_1) and triplet (T_1) states.

To obtain insight into the conformational effects on photochemical α-cleavage type I reactions, we have computed rotational profiles in the ground (S_0) and excited states (S_1, T_1) of a model system by appropriate methods.

2. Results and discussion

Acylphosphine oxides (**A**) have been utilized in industrial applications as photoinitiators for radical polymerizations. The photochemical reaction pathways of acylphosphine oxides of type **A** (Scheme 1) are well established [3,5,6,8,9,15,17,18,24], and therefore are ideal candidates for model computation. After irradiation and intersystem crossing, the (O)P–C(O) (α) bond is cleaved in the triplet state (Scheme 1).

In order to obtain results within reasonable CPU times, model system **1** was chosen for computational investigation. This molecule consists of a benzoyl moiety with methyl groups replacing the usual aromatic or alkyl substituents on the phosphorus atom. This is an acceptable model
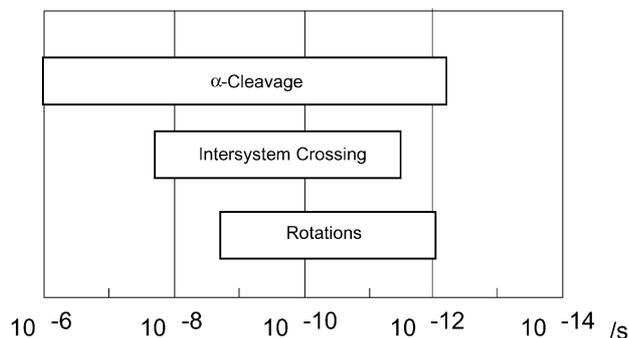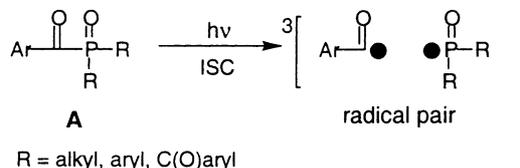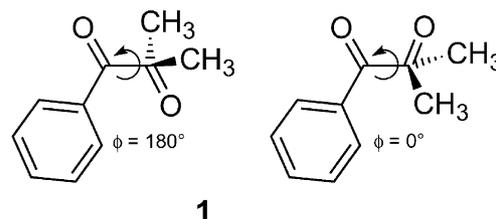
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Fig. 1. Time scales for α-cleavage, intersystem crossing, and rotations (according to [20,23]).

Scheme 1.

Scheme 2.

for acylphosphine oxide photoinitiators (**A**), because it is well established experimentally that different substituents at the P atom do not substantially alter the cleavage of the (O)C–P(O) bond. We have calculated rotation profiles along the P(O)–C(O) bond in the singlet ground state (S_0), excited singlet state (S_1), and the triplet state (T_1) of **1** using density functional theory and configuration interaction (CI-singles) methods. Moreover, we follow the cleavage of the Ph(O)C–P(O)Me$_2$ bond in the triplet state.

The rotation was begun at an angle $\phi = 0°$, where the carbonyl and the phosphinoyl O atoms are arranged in a s-*cis* fashion and being coplanar with the π plane of the phenyl substituent (Scheme 2). Consequently, the angle $\phi = 180°$ is represented by an s-*trans* conformation of the
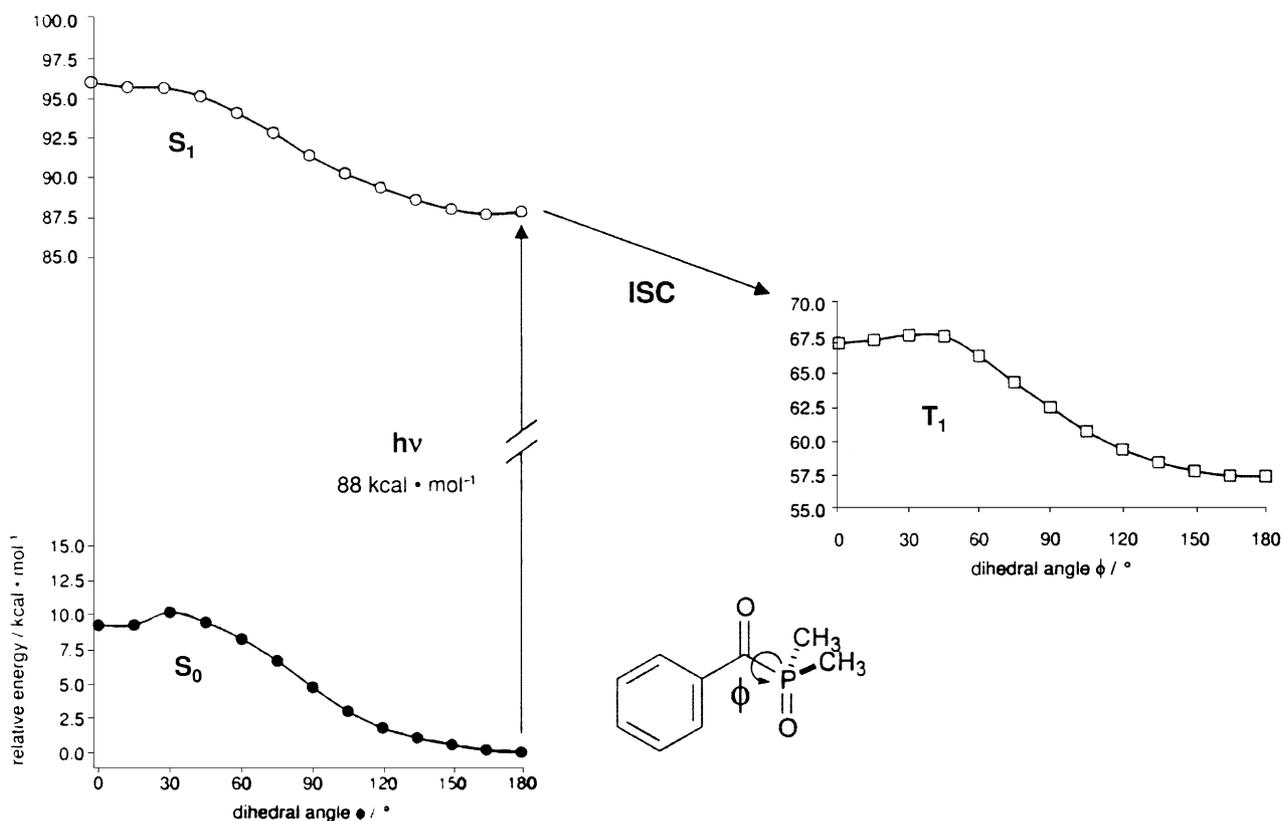

Fig. 2. The photochemical pathway upon excitation of **1** and the rotation profiles around ϕ in the S_0 (B3LYP/6-31$^+$G∗), S_1 (RCIS/6-31$^+$G∗), and the T_1 (UB3LYP/6-31$^+$G∗) states. The energy gap between S_1 and S_0 was estimated with the T_1 state as the reference. The $T_1 - S_0$ energy difference was determined by UB3LYP/6-31$^+$G∗, whereas the $S_1 - T_1$ gap was computed by RCIS/6-31$^+$G∗. These two values were added to give the numbers shown in the figure.
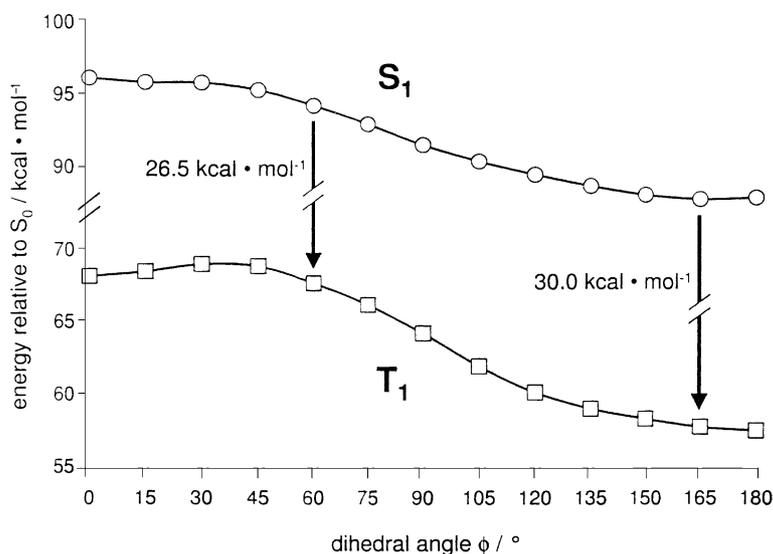
Fig. 3. Comparison of the rotation profiles around the (O)C–P(O) bond in the S_1 and T_1 states according to RCIS/6-31$^+$G* calculations.

O atoms. Twelve different conformations (15° steps) were computed and the rotation profiles of the ground state S_0 and the excited singlet (S_1) and triplet state (T_1) are displayed in Fig. 2. Whereas the profiles for the S_0 and the T_1 state indicate very similar shapes with almost identical (relative) energies for related conformers, the intermediate S_1 state shows a definitely flatter rotation profile. This is clarified in Fig. 3 where the S_1, and the T_1 state are compared. The energies were calculated using RCIS/6-31$^+$G* [12,13] because the S_1 state is not accessible by B3LYP/6-31$^+$G* (for T_1 both procedures give fully compatible results). Although arrangements close to the s-*trans* conformation are favorable for **1** in all states, there is no doubt that the lowest rotation barrier exists for S_1. Once the S_1 state is reached, the rotation along the (O)C–P(O) bond in phosphinoxide **1**

is facilitated, and assuming even a short lifetime of this excited state, several conformations are likely to be populated. If vertical transitions are assumed (bold arrows in Fig. 3), various "hot" conformations of the T_1 state are attained. Depending on the lifetime of T_1 such high-energy geometries are likely to be present during the α-cleavage reaction.

Is the α-cleavage in the triplet state really dependent on the conformations? An activation barrier in the range of ca. 6 kcal mol^{-1} exists for α-cleavage reactions [20], which has been substantiated by quantum mechanical calculations on formaldehyde [22] and acetone [16]. For two angles ϕ (60 and 180°) the energy profile for the elongation of the P(O)–C(O) is displayed in Fig. 4. Starting at the energy minimum of the T_1 state ($\phi = 180°$) and following the minimum energy path on the hypersurface, an activation barrier

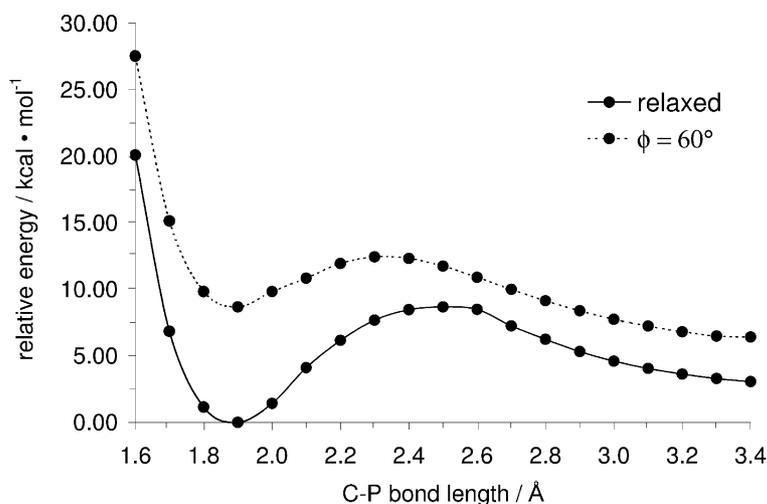Fig. 4. Activation barriers for the cleavage of the P(O)–C(O) bond (UB3LYP/6-31G*). The bold line represents the cleavage reaction on the minimum hypersurface, whereas the dashed line represents a geometry fixed at $\phi = 60°$.
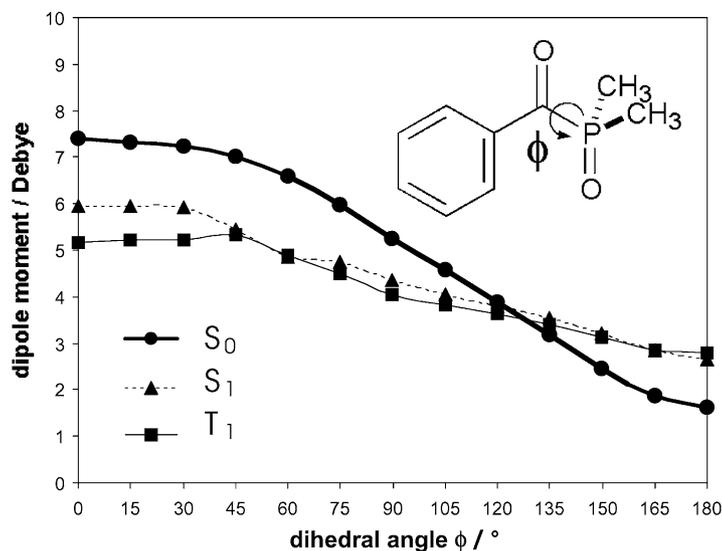
Fig. 5. Dipole moment of **1** in the S_0 (B3LYP/6-31$^+$G∗), S_1 (RCIS/6-31$^+$G∗), and T_1 (B3LYP/6-31$^+$G∗) states.

of ca. 8 kcal mol^{-1} is calculated for the bond scission. However, using a higher-energy conformation ($\phi = 60°$) without relaxing the angle ϕ for each step, the activation energy is considerably lowered to 4 kcal mol^{-1} (Fig. 4). Thus, not only is the distribution of different conformations present in the T_1 state, but also the corresponding activation barrier determines the efficiency of the bond cleavage.

The changes of the dipole moment of **1** within the three considered states are rather similar with smaller variations in the excited states (Fig. 5). This renders the reorientation of solvent molecules unlikely and, therefore, a direct dependence of the cleavage reaction from solvent polarity is not straightforward.

In several investigations it has been shown that the $n \rightarrow \pi*$ character of the T_1 state is shifted towards $\pi \rightarrow \pi*$ when phenyl substituents adopt a non-planar arrangement relative to the C–C–C plane of the ketone moiety [10] or by *p*-thioalkyl and *p*-dimethylamino substitution of the phenyl ring [7]. This substantially alters the efficiency of the bond cleavage. According to the B3LYP/6-31G∗ calculations utilized for the determination of the barrier for the α-cleavage, the T_1 state of our model system is dominated by an $n \rightarrow \pi*$ character independent of ϕ.

3. Conclusion

Summing up, this preliminary study points to the following concepts. Rationalization of reactions proceeding via triplet states can be attained by comparison of the molecular geometry in the excited singlet S_1 and the T_1 states. The lifetimes of these electronic states and the rate of intersystem crossing are of predominant importance for the efficiency of the bond cleavage. These interval times determine whether the molecule is able to relax to the minimum

energy or if a "hot" state is attained which has an activation barrier for the cleavage reaction lower than a relaxed state. In light of these findings a main contribution of the solvent would either be a slowing down of internal rotations by specific solvation or the modulation of excited-singlet or triplet state lifetimes. This behavior is compatible with the time scales of rotational motion, intersystem crossing and the kinetics of Norrish-type reactions [23]. It also becomes evident that the application of solvent polarity scales for the interpretation of solvent effects in bond cleavage reactions should consider conformational factors.

Further experimental and theoretical work is under way to test the above conceptual hypotheses.

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