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On the mechanism of photoinduced addition of acetonitrile to phosphonium–iodonium ylides

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Recently, a novel photochemical reaction of pseudocycloaddition of nitriles to mixed phosphonium–iodonium ylides 1 was found. Nitriles R_1CN give corresponding oxazoles (2) with a high yield, with PhI (3) being a leaving group. The mechanism of the photoinduced cycloaddition of acetonitrile to mixed phosphonium–iodonium ylide 1 was studied by steady-state and time-resolved methods with resolution from 10 ns to 20 μs. The formation of photolysis products, substituted oxazole 2, and phosphonium salt 4, occurs in parallel reactions. The primary photochemical processes for the formation of 2 and 4 are the heterolytic and homolytic $C–I^+Ph$ bond cleavage in the excited singlet state of 1, respectively. Three transient species with lifetimes on microsecond and millisecond time scales were observed. The mechanism of the formation of major and minor products of the photolysis was suggested. Addition of water to the reaction mixture in acetonitrile changes the ratio of the products in favor of the phosphonium salt formation. The effect of water was accounted for by the acid catalysis of the homolytic $C–I^+Ph$ bond cleavage and the acceleration of the salt formation. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: cycloaddition reaction; phosphonium–iodonium ylides; photolysis; reactive intermediates; time-resolved spectroscopy

INTRODUCTION

At present, intensive attention is being focused on photochemical processes for two reasons: (1) these reactions often give unusual and even exotic structures inaccessible by other means and (2) the development of time-resolved methods with spectrophotometric registration of transient species makes it possible to analyze the mechanism of photochemical processes on time scales from tens of femtoseconds to milliseconds.[1,2]

Our previous research on the chemistry of phosphonium–iodonium ylides of type **1** revealed several different pathways for the reactions of these compounds: (1) the attack by electrophiles in silylation and acetylation reactions, with the enolate group $=C–O^-$ of **1** being a nucleophile; (2) the nucleophilic substitution, with the Ph–I moiety playing the role of a leaving group, and (3) the Wittig reaction.[3–5]

The structure of mixed phosphonium–iodonium ylides of type **1** is described by resonance structures **1a–1d** (Scheme 1). On the basis of X-ray diffraction analysis and the ^1H, ^{13}C, and ^{31}P NMR data, it was established that **1d** is a major structure in a crystalline state and in a solution; the contribution of **1a** was also observed in the NMR spectra.[3,4]

Recently, we have described two novel photochemical reactions of ylides of type **1** in the presence of compounds with triple bond, which afford products of pseudocycloaddition. The reactions proceed in different modes depending on the character of the triple bond.[6–10] Nitriles R_1CN give corresponding oxazoles (**2**), with PhI (**3**) being a leaving group (Scheme 2),[6,7] while the reaction between phosphonium–iodonium ylides of type **1** and acetylenes gives λ^5-phosphinolines.[8–10]

The photochemical reaction of ylides **1** with nitriles has a general character and proceeds with both aliphatic and aromatic nitriles, with the oxazole yields ranging from 15% to 60% in dependence on R and R_1 and being the highest for R = Ph and R_1 = Me.[6]

This communication opens a series of papers on spectral and kinetic study of the photolysis of the mixed phosphonium–iodonium ylides in the presence of compounds with triple bond. Here, we present the results of examination of the photolysis of mixed ylide **1** (R = Ph) in acetonitrile by steady-state photolysis and pulse photolysis with time resolution ranging from 10 ns to 20 μs. This study allows us to suggest a feasible mechanism for the formation of the major and minor products.

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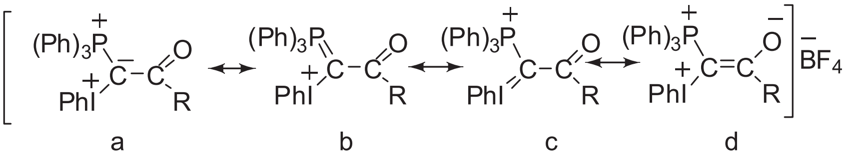
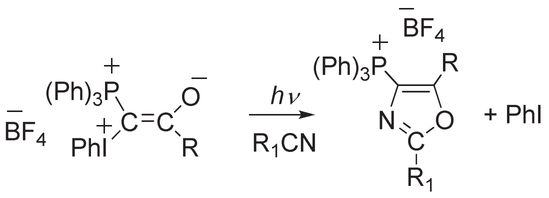


Scheme 1. Resonance structures of mixed phosphonium–iodonium ylides **1**



1 **2**

R = OMe, OEt, Ph; R_1 = Me, Et, Ph, NEt_2, C_5H_5N

Scheme 2. Formation of oxazole derivatives in the photolysis of ylide **1** in the presence of nitriles

EXPERIMENTAL

Materials

Ylide **1** and reaction products **2**, **4**, and **5** were synthesized according to the procedures described elsewhere.[4,6,7] Acetonitrile (BIOSOLVE (B.V., Valkenswaard, Netherlands), 99.95%) was dried according to the standard procedure.[11] Absorption spectra were recorded on a Shimadzu UV-3101 PC (Shimadzu Europa GmbH, Duisburg, Germany) spectrophotometer in quartz cells with a path length of 1 cm. ^{1}H NMR spectra were recorded on an Agilent 400-MR NMR spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA) in CD_3CN. Photochemical experiments were carried in the air atmosphere.

General procedure for the steady-state photolysis

The steady-state photolysis of a solution of ylide **1** in CH_3CN ($(1–10) \times 10^{-5}$ mol L^{-1}) was carried out under illumination by a high-pressure mercury lamp with the use of a glass filter with transmittance in the range of 280–400 nm or by a laser diode source ($\lambda = 365$ nm) in a quartz cell with an optical path length of 1 cm. The reaction course was followed on a Shimadzu UV-3101 PC spectrophotometer. The reaction quantum yield was measured with the use of ferrioxalate actinometer as described in [12].

General procedure for the laser flash photolysis

The kinetics of the reaction was monitored in real time utilizing the transient absorbance spectroscopy technique. A fully computerized spectrometer system (~7 ns response time) was described elsewhere.[13,14] Briefly, a pulsed Lambda Physic EMG 160MSC XeCl (Lambda Physik USA, Inc., Fort Lauderdale, FL, USA) excimer laser (308 nm, FWHM = 12 ns, ≤ 80 mJ/pulse/cm^2, 10 Hz) was used as an excitation source. The transient absorbance was probed at a right angle to the excitation laser beam along a 1 cm optical path by a 75 W pulsed xenon arc lamp in the range of 300–700 nm. The signal was recorded by a Tektronix TDS 5052 (Tektronix, Beaverton, OR, USA) oscilloscope.

General procedure for the conventional flash photolysis

The decay kinetics of the transient species was registered on a flash photolysis setup with time resolution of 20 μs and spectrophotometric registration of transient absorbance as described elsewhere.[1,15] Solutions of ylide **1** in CH_3CN ($5 \times 10^{-4}–10^{-3}$ mol L^{-1}) were irradiated in quartz cells with an optical path length of 20 cm by a pulse of a Xe lamp. The changes in the absorbance were monitored by a system consisting of a Xe lamp, a monochromator, a photomultiplier, and an oscilloscope based on a digital Bordo 211 array incorporated into a personal computer. To excite the long-wavelength absorption band of ylide **1**, a glass filter with transmittance in the range 280–400 nm was used. The registration of the transient absorbance was carried out in the wavelength range of 370–600 nm.

General procedure for data processing.

The experimental data on the decay of transient absorbance were processed by global kinetic analysis as described elsewhere[15] with the use of triexponential or biexponential kinetic equations (Eqn (1)) for the data of laser and conventional flash photolysis, respectively.

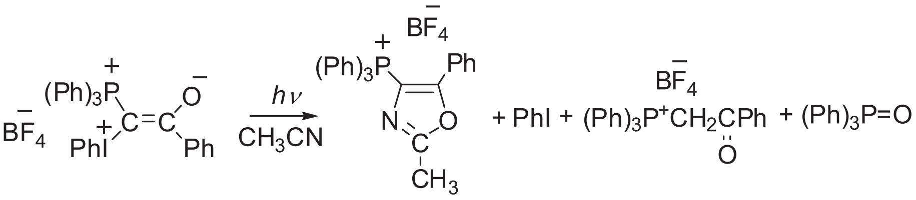
$$\Delta A = A_1\exp(-k_1t) + A_2\exp(-k_2t) + A_3\exp(-k_3t), \qquad (1)$$

RESULTS

Steady-state photolysis

Previously, oxazole **2** (60%) and iodobenzene **3** (100%) were identified as major products of the preparative-scale photolysis of ylide **1** ($[\mathbf{1}]_0$ ~0.1 mol L^{-1}) in CH_3CN. Under these conditions, we have additionally identified phosphonium salt **4** (30%) and triphenylphosphinoxide **5** (10%) as minor products (Scheme 3).[6,7]

In the study presented here we used significantly smaller concentrations for the steady-state photolysis of ylide **1** ($10^{-4}–10^{-5}$ mol L^{-1}), which are more convenient for following the reaction course by spectrophotometry. The quantum yield of the ylide consumption determined under irradiation of the solution by a light with



1 **2** **3** **4** **5**

Scheme 3. Principal scheme of the photolysis of **1** in CH_3CN

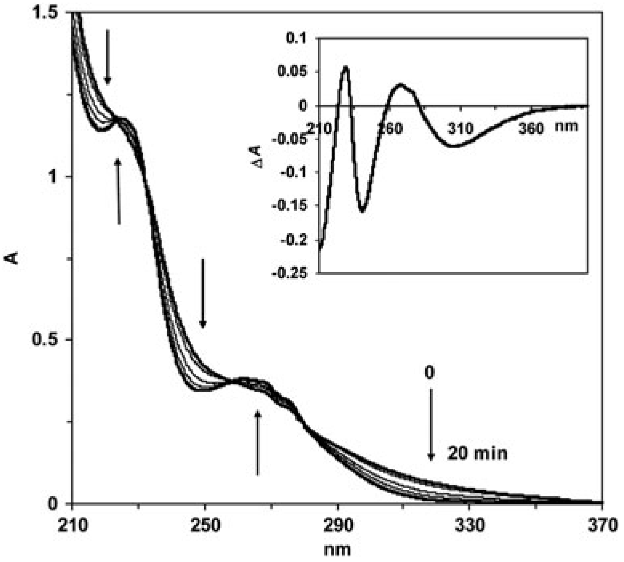


Figure 1. Evolution of the absorption spectrum of ylide **1** ($[\mathbf{1}]_0 = 3.3 \times 10^{-5}$ mol L^{-1}) in the course of the steady-state photolysis in CH_3CN; (inset) a difference between the initial and the final absorption spectra in the steady-state photolysis of **1** in CH_3CN

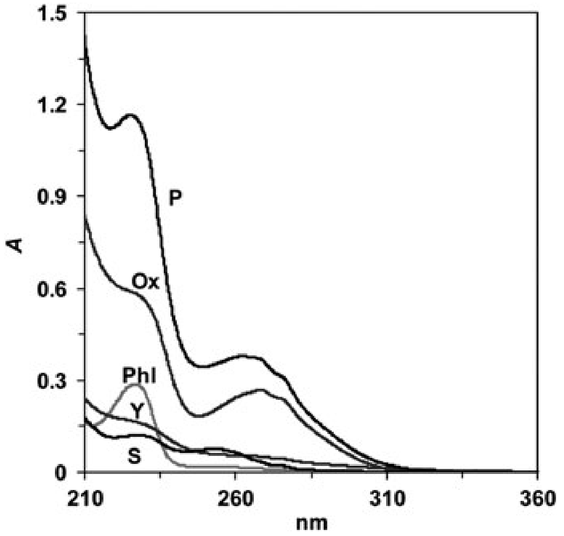


Figure 2. Absorption spectra of the sum of photolysis products (P) of ylide **1** ($[Y]_0 = 3.3 \times 10^{-5}$ mol L^{-1}): residual ylide (Y, 5×10^{-6} mol L^{-1}) and products of the photolysis: oxazole **2** (Ox, 2×10^{-5} mol L^{-1}), iodobenzene (PhI, 2.8×10^{-5} mol L^{-1}) and phosphonium salt **4** (S, 8×10^{-6} mol L^{-1})

$\lambda = 365$ nm is very high (0.5 ± 0.1). Isosbestic points in the UV spectra recorded in the course of the steady-state photolysis were observed (Fig. 1). This usually indicates the quantitative conversion of a starting compound into an only product. This is not the case for **1**, because more than one product is formed. The presence of isosbestic points, when several products are formed in the course of the steady-state photolysis, means that the ratio of the products does not change during the photolysis. This may take place, when oxazole, PhI, and phosphonium salt are formed in the same reaction at constant ratio or independently in parallel reactions. The former assumption is true for the pairs of products **2** + **3** and **3** + **4**, but seems improbable for **2** + **4**. This implies that oxazole **2** and phosphonium salt **4** are the products of parallel reactions.

The absorption spectrum of ylide **1** has no pronounced maxima: the absorbance increases gradually in the range from 400 to 210 nm, with weak vibrational structure at 280–250 nm and a shoulder at 223 nm (Fig. 1). The spectra does not depend on the ylide concentration in the concentration range used in this study (2.4×10^{-4}–0.8×10^{-6} mol L^{-1}) indicating either the absence of aggregation or strong complexation independent of the concentration. The absorption spectra of **1** in CH_3CN and CH_2Cl_2 differ only by extinction factors no more than by 10% (Fig. 1S(a)), rather than by the position of the vibrational bands that is clearly observed in the differential spectra $dA/d\lambda$ versus λ (Figure 1S(b)). At the same time, the spectrum of **1** in the solvent mixture CH_3CN–CH_2Cl_2 1 : 9 (*v*/*v*) coincides almost completely with the spectrum in CH_3CN indicating that more polar solvent forms a solvation shell around the polar ylide molecule.

The steady-state photolysis of ylide **1** (3.3×10^{-5} mol L^{-1} in acetonitrile) is completed in 20 min of irradiation. The product formation is accompanied by a decrease in the absorbance in the range of 385–284 nm and 260–235 nm (bleaching) (Fig. 1, inset) and appearance of two maxima at 260 and 225 nm. These maxima are defined by the absorbance of the sum of the photolysis products (Fig. 2): oxazole **2** (λ_{max} 268 nm), PhI **3** (a shoulder at 260 nm and λ_{max} 225 nm) and salt **4** (λ_{max} 252 and 227 nm). The absorption spectra of the photolysis products are given in Fig. 2 in the concentrations determined from the fitting of the final absorption spectrum by the sum of the spectra of the products and initial ylide (P = Ox + PhI + S + Y). The calculation shows that the conversion degree is 85%, and the photolysate contains residual ylide **1**. At this conversion degree, the reaction practically stops because of the fact that the absorbance of ylide **1** becomes significantly less than the absorbance of oxazole **2**, which is photostable. Under conditions of analytical steady-state photolysis, the ratio of oxazole **2** and phosphonium salt **4** is 2.5 : 1, which is higher than the ratio of these products found earlier in the preparative-scale photolysis (2 : 1).[6] The oxazole yield depends significantly on the purity of CH_3CN, especially on the water content in the solvent. The yield of oxazole relative to the photolyzed ylide decreases from 71% in dry CH_3CN to 46% in CH_3CN containing water (2.5 vol. %). Simultaneously the yield of **4** increases. It should be pointed out that the absorption spectrum of one of the minor products, triphenylphosphinoxide **5** identified in the preparative-scale photolysis, was not involved in the fitting procedure of the final absorption spectrum for two reasons: (1) the molar absorption coefficient for **5** throughout the whole spectral range is much lower than those for compounds **1–4**, therefore taking into account its low yield, the contribution of **5** into the final spectrum can be neglected; and (2) according to the literature data the formation of **5** occurs in secondary reactions of phosphonium salt photodecomposition to afford triphenylphosphine as primary product,[16] which being photolyzed in the presence of oxygen or water gives **5**.[17] In fact, slow degradation of **4** was observed under UV irradiation in CH_3CN.

The photolysis in deuterated acetonitrile (CD_3CN) affords phosphonium salt **4** with two deuterium atoms in the methylene group ($[(Ph)_3P^+CD_2CO(Ph)]BF_4^-$) and with a molecular weight higher by 2 Da (^{1}H NMR and MS spectra in Figs 2S–5S).

Pulse photolysis of ylide 1 in acetonitrile

The regularities in the formation and decay of active transient species in the photolysis of **1** were investigated by ns laser pulse photolysis (λ_{ex} 308 nm) and by conventional lamp flash photolysis ($280 < \lambda_{ex} < 380$ nm) with time resolution on μs time scale. The yield of short-lived transient species does not depend on the presence of oxygen in the system indicating that the primary photochemical processes in ylide **1** occur in the excited singlet state. The time-changes in the transient absorbance and in the absorption spectra during the photolysis of **1** in CH_3CN on ns time-scale (Fig. 3) show the fast decay of the transient absorbance from 40 to 130 ns with a characteristic time less than 30 ns, then in the time range from 130 ns to 2 μs, the spectrum of transient absorbance changes insignificantly. The transient species generated on the ns time-scale have a broad absorption spectrum from 350 to 600 nm with λ_{max} 390–420 nm and a steep growth of the absorbance at $\lambda \leq 330$ nm observed after a short (30 ns) bleaching at 300–330 nm. This distinguishes the results of the laser flash photolysis in CH_3CN and CH_2Cl_2. In CH_2Cl_2 the bleaching of the absorbance at $\lambda \leq 330$ nm is observed during the whole time of registration (Fig. 3, inset).

The decay of the transient absorbance at $\lambda > 350$ nm occurs over a relatively long time interval from 2 μs to 20 ms and is adequately described by a three-exponential function (Eqn (1)) (Fig. 4). This assumes the existence of three transient species A_1, A_2, and A_3 with the decay rate constants: $k_1 = 4 \times 10^4$, $k_2 = 2.3 \times 10^3$, and $k_3 = 173\,s^{-1}$ or lifetimes of these species (τ) being equal to 25 μs, 440 μs, and 5.8 ms for A_1, A_2, and A_3, respectively. Global kinetic analysis of the data obtained by the laser pulse photolysis demonstrates that transient species A_2 is not the product of A_1 conversion and A_3 is not formed from A_2. At the same time we cannot rule out that A_3 is the product of A_1 conversion.

The decay kinetics of transient absorbance obtained by conventional flash photolysis does not involve the fast component of the decay and is described with a biexponential function (Fig. 5). The absorption spectra for transient species A_2 (λ_{max} = 400 and 380 nm) and A_3 ($\lambda_{max} = 390$ nm) were calculated from the global analysis of the flash photolysis data (Fig. 5, inset). The rate constants obtained in the experiments with the lamp photoexcitation in dry CH_3CN ($k_2 = 2.0 \times 10^3$ and $k_3 = 200\,s^{-1}$) are close to those obtained by the ns laser pulse photolysis. The rate constant for the slow step (k_3) increases in the presence of water in CH_3CN and attains $360\,s^{-1}$ in CH_3CN containing 2.5 vol. % of water (Fig. 5), with the yield of A_2 decreasing by about 20% and the yield of A_3 correspondingly increasing.

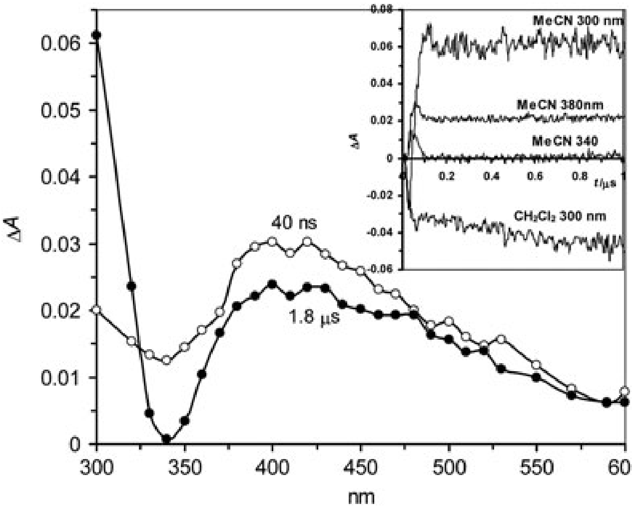


Figure 3. The spectrum of transient absorbance in the laser flash photolysis of **1** in CH_3CN at different registration times ($\lambda_{ex} = 308$ nm); (inset) kinetics of transient absorbance decay at different wavelengths in CH_3CN and CH_2Cl_2

DISCUSSION

The results of the steady-state experiments strongly indicate that oxazole **2** and phosphonium salt **4** are formed in parallel reactions, and the question is, at which step of the reaction the branching occurs. It should be pointed out that the photodecomposition of diaryliodonium salts was studied in detail because of their use as photoinitiators of cationic polymerization.[18–22] Two types of photodecomposition of the C–I$^+$Ph bond in diaryliodonium salts are known: (1) heterolytic cleavage as a result of electron transfer in the excited state with elimination of PhI and (2) homolytic cleavage with elimination of a PhI$^{+\bullet}$ radical cation.[18,19] The application of these two routes of the C–I$^+$Ph bond cleavage to the case of mixed ylide **1** is considered in Schemes 4 and 5, respectively. The first route results in the elimination of PhI in the excited singlet state of **1** with simultaneous formation of carbocationic species **6**, which gives oxazole **2** (Scheme 4). We consider two pathways of the oxazole formation: coupling with the CH_3CN molecule in the solvent cage to give either **2** or the formation of imine derivative **7**, which converts to **2** with rate constant k_2. The formation of **2** via concerted reaction in the solvent cage is supported by the data of the ns flash photolysis. In fact, the absorption spectra of all the final products formed in detectable amounts are shifted hypsochromically relative to the spectrum of the parent ylide **1**, with the absorption of **2**, **3**, and **4** starting from 320, 300, and 300 nm, respectively (Figure 2), and only oxazole **2** absorbs in the blue edge of the registration spectral window of the laser flash photolysis. This allows for the proposal that the bleaching followed with a fast increase in the absorbance observed at $\lambda_{reg} \leq 330$ nm in the laser flash photolysis at $t < 100$ ns (Figure 3) is the result of the PhI elimination and the formation of oxazole **2**. The absence of the positive absorbance in this spectral range in the photolysis of **1** in CH_2Cl_2 supports this proposal, because in CH_2Cl_2 salt **4** is the major product and oxazole cannot be formed. One more evidence of the preferential heterolytic C–I$^+$Ph bond scission in CH_3CN is the very low absorbance with $\lambda_{max} = 650$–670 nm characteristic of PhI$^{+\bullet}$ radical cation (τ ~ 500 ns), which is generated in the homolytic bond scission in the photolysis of diaryliodonium salts.[20–22] We cannot also rule out the possibility of the reaction between the excited ylide and CH_3CN molecules. If the pathway via formation of intermediate **7** takes place, then the spectrum A_2 (Fig. 5) belongs to **7**.

Three resonance structures can be considered for the species **6**: two carbocationic and one carbenic (Scheme 4). The cyclopropane derivative was not found upon irradiation of **1** in the presence of the carbene trap styrene[6] that infers that the carbocationic structures contribute mainly.

The possible reactions occurring upon homolytic C–I$^+$Ph bond photocleavage are shown in Scheme 5 and afford salt **4** as a final product. The mesomeric structures for the intermediates are given in Scheme 5. Salt **4** is a minor product

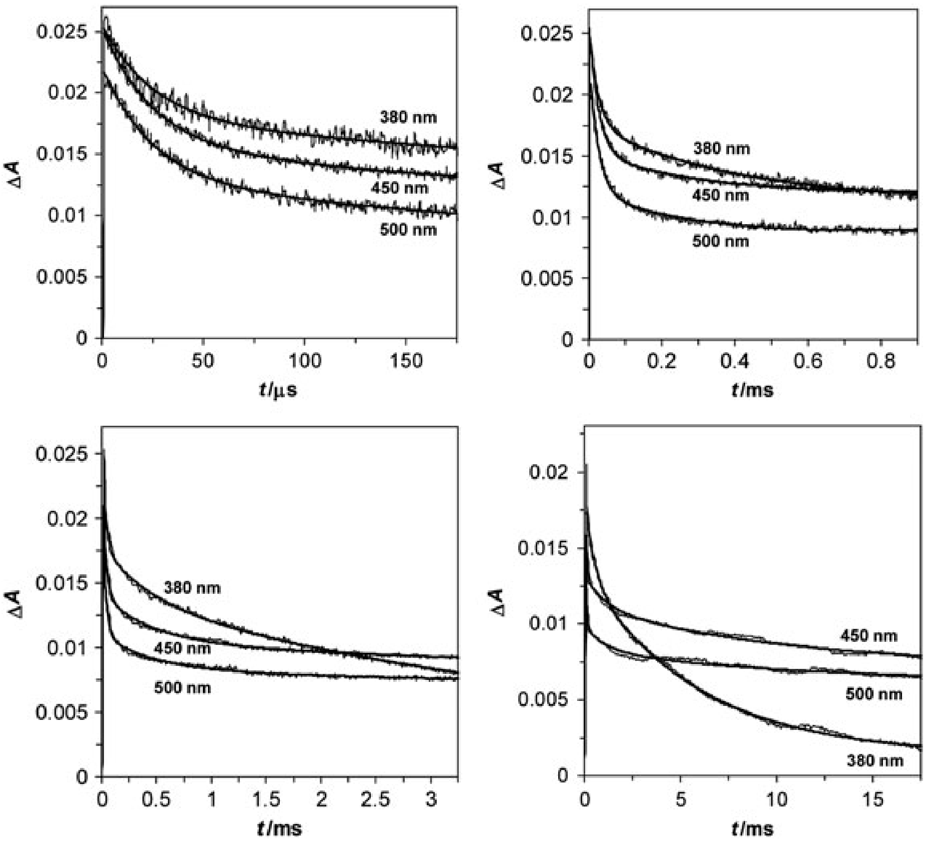


Figure 4. The decay kinetics of transient absorbance in the laser photolysis of **1** in CH_3CN ($\lambda_{ex} = 308$ nm) on various time scales; solid smooth lines represent results of the global kinetic analysis using Eqn (1)

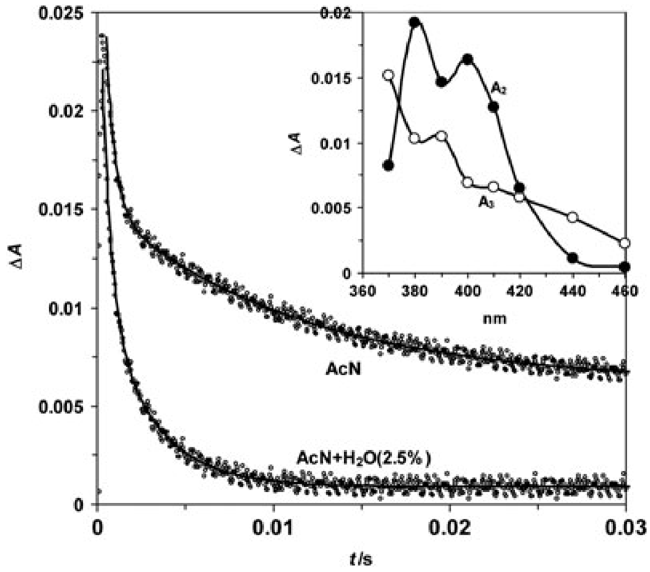
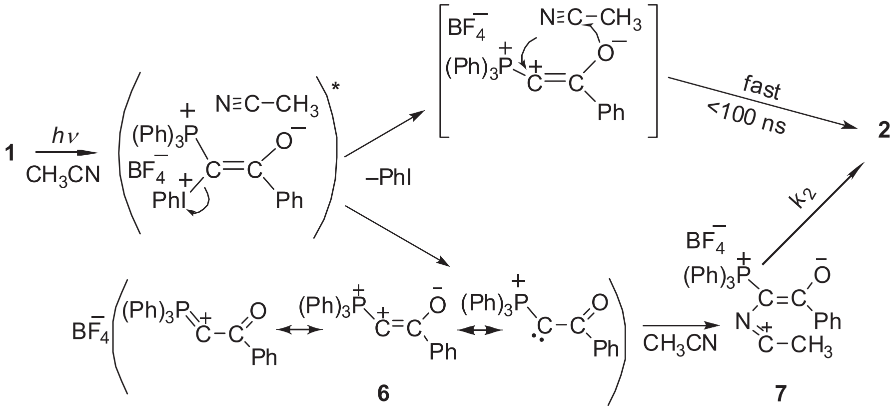


Figure 5. The decay of transient absorbance in the conventional flash photolysis of **1** in dry CH_3CN and in CH_3CN containing water (2.5 vol. %), $\lambda_{reg} = 380$ nm, experimental data (points) and results of the global kinetic analysis (solid lines); (inset) absorption spectra of transient species (A_2 and A_3) obtained from the global kinetic analysis

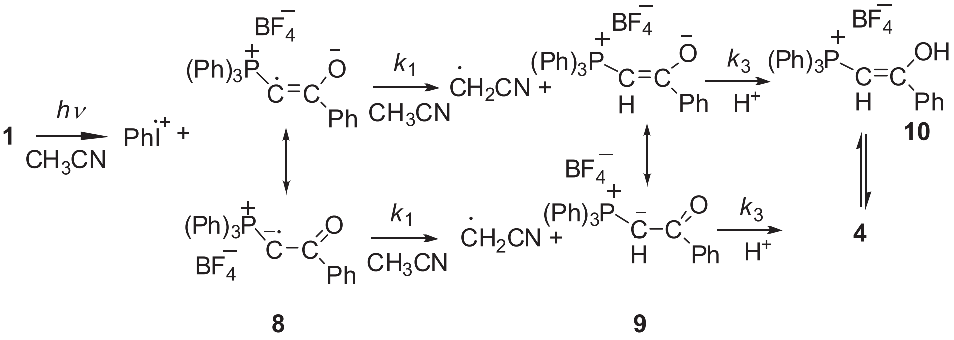
formed with a relatively high yield concurrently to the target oxazole **2**. The comparison of the salt structure with the structure of ylide **1** gives rise to a challenging question about a source of the two hydrogen atoms necessary for its formation. In other words, to explain the mechanism, it is necessary to answer the question about the origin of the two hydrogen atoms in this compound. In the given system, the methyl group of acetonitrile is the only potential source of the hydrogen atoms. To verify this, we carried out the preparative-scale photolysis of **1** in CD_3CN. The ^1H NMR and MS spectra of salt **4** synthesized in CH_3CN and CD_3CN show that the salt formed in CD_3CN does have two D atoms in the methylene group (Figs 2S–5S).

The formation of salt **4** as a result of the homolytic $C–I^+Ph$ bond cleavage suggests that the branching of the reaction occurs on the stage of the excited state photochemical reaction on the fs–ps time-scale, and the transient species A_1 and A_3 decaying with the rate constants k_1 and k_3 are **8** and **9** (Scheme 5). As was mentioned above, the concentration of $PhI^{+\cdot}$, the product of homolytic bond scission, is very small. Nevertheless, it seems to us that the formation of **4** in the reaction sequence given in Scheme 5 is very feasible. In this mechanism the two hydrogen atoms necessary for the salt formation are taken from CH_3CN: one in a form of the hydrogen atom detached from the CH_3CN molecule by radical **8** and the other in a form of the proton generated in the conversion of $PhI^{+\cdot}$ to PhI (Scheme 5).

The accepted mechanism for the transformations of $PhI^{+\cdot}$ in CH_3CN is given also in Scheme 5.[18–22] The formation of the $PhIH^+$ cation and the $C^{\cdot}H_2CN$ radical was postulated for diaryliodonium salts from the analysis of the photolysis products in CH_3CN, but it was shown that only the $PhI^{+\cdot}$ radical cation



Scheme 4. The mechanism of the formation of oxazole **2** in the photolysis of ylide **1** in CH_3CN



$$PhI^{\cdot +} + CH_3CN \longrightarrow Ph\overset{+}{I}H + \dot{C}H_2CN \longrightarrow PhI + H^+$$

Scheme 5. The mechanism of the formation of phosphonium salt **4** in the photolysis of ylide **1** in CH_3CN

had the absorption spectrum in the visible spectral range (600–700 nm).[20–22]

The increase in the yield of salt **4** upon addition of water indicates the participation of water molecules in the salt formation. We have shown that acids promote the decomposition of **1** in CH_2Cl_2, where **4** is the major product, probably, by protonation of ylide **1** facilitating the homolytic C–I^+Ph bond cleavage to give the $PhI^{\bullet +}$ radical cation and radical **8**. The study of this process is in progress. We propose that the effect of water added to CH_3CN is similar to the action of acid. The acceleration of the initiation reaction by water has to result in an increase in the yield of **8** and consequently of **4**. At the same time the observed increase in the rate constant k_3 is accounted for by an increase in the proton concentration. There is an uncertainty in the order of the reaction sequence in Scheme 5: either the first step is protonation or radical reaction. The increase in k_3 upon water addition strongly indicates that the protonation does occur in the second step.

CONCLUSIONS

The spectral and kinetic study of the photolysis of mixed phosphonium–iodonium ylide **1** in acetonitrile has demonstrated that the formation of the final products oxazole **2** and phosphonium salt **4** occurs in parallel processes. The primary photochemical process to give **2** is intramolecular electron transfer in the excited singlet state resulting in the heterolytic C–I^+Ph bond cleavage followed by in-cage fast coupling of the solvent with generated carbocationic species. The formation of salt **4** occurs as a result of the homolytic C–I^+Ph bond cleavage. The absorption spectra for the three transient species and the rate constants of their decay were estimated from the data of time-resolved experiments. The effect of residual water in acetonitrile on the ratio of the yields of the final products was accounted for by the acid catalysis of the decomposition of ylide **1** via the homolytic route with consequent participation of the proton in the formation **4**.

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