

The photoinduced reaction of 2-iodothiophene in solutions of *n*-heptane, dichloromethane and methanol

O. S. Herrera^a, J. D. Nieto^b, A. C. Olleta^b and S. I. Lane^{b*}

The photoinduced reaction of 2-iodothiophene in *n*-heptane, dichloromethane and methanol was studied at room temperature from experiments carried out with degassed solutions. The photoproducts of the reaction were mainly thiophene and small amounts of iodine in all three solvents used. The concentration of 2-iodothiophene decreases throughout photolysis, following a first-order rate law and the pseudo-first-order rate constants were determined in the three solvents used. The photochemistry of the system was quantified determining the quantum yields of 2-iodothiophene consumption and thiophene formation in *n*-heptane solutions. The results show that under the experimental conditions of this research, products deriving only from the reaction of the thienyl radical were observed. To support the experimental results, calculations were performed of the ionization potential of the thienyl radical, electron affinity of the iodine atom and free energy of solvation of the corresponding iodide and carbocation in the different solvents used. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: 2-iodothiophene; chemical kinetics; photoinduced reaction; thienyl radical; thiophene

INTRODUCTION

The photoinduced reaction of organic halides, in particular iodides, has been widely studied, as well as the reactions involving the respective bromides and chlorides but to a lesser extent.^[1] Studies made by Kropp and co-workers^[2,3] and Taniguchi and co-workers^[4] have shown that alkyl and vinyl halides, particularly iodides, in polar solvents give products which are formed both from the radical obtained in the primary process and from the carbocation produced by electron transfer in the radical pair originally formed. However, there have been differences observed between the behaviour of organic iodides and bromides. In the case of bromides, photoproducts generally stem from the radical, whereas in the case of iodides it has been observed in numerous studies that an ionic intermediate is involved.

The hypotheses set out, which might justify the difference of bromide and iodide behaviour are the difference of reactivity of Br and I atoms as well as the great polarizability of iodine which might facilitate the electron transfer.^[5,6] Experiments performed in more viscous solvents have shown both in case of some organic iodides and bromides, an increase in obtaining products via the carbocation.^[6] This is due to the fact that the lifetime of the radical pair originally formed increases, thus allowing the electron transfer process in the radical pair to compete favourably with the H abstraction from the solvent.

In the photolysis of 1-bromo and 1-iodo-1-hexynes in polar and nonpolar solvents, only radical-derived products were obtained,^[7] contrary to the previously reported on alkyl and vinyl halides.^[2-4]

In all cases, an initial process leading to the homolytic cleavage of the carbon-halogen (C—X) bond with the formation of a pair, alkyl radical-halogen atom, is advocated.^[8] After this initial process, radical reaction products can be obtained; this process

competes with electron transfer in the radical pair within the solvent 'cage' thus producing the ion-pair and finally some characteristic products of the carbocation as intermediate. In many primary and secondary iodides, non-saturated products are obtained from a carbene.

Although in favourable cases it has been possible to recognize these steps directly from the products obtained, in other cases the results are ambiguous and have been interpreted both as ionic and radical steps by different groups of researchers.^[9] Results show that, in general, these steps compete and that the individual reactions that occur through ionic and radical pathways depend on the nature of the substrate and the solvent used.^[7] Therefore, it is interesting to study these reactions in order to assess the limitations and the determinant factors of the process.

The A-band dissociation dynamics of 2-iodothiophene was studied by Zhu and co-workers^[10] using resonance Raman measurements. They found that the dissociation of the molecule has multidimensional character, and simultaneously involves the

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stretching vibrational modes of the C=C, C—S—C and C—I bonds. They also carried out a UV-photolysis study of 2-iodothiophene by using the matrix isolation infrared method and the thienyl radical was not detected.

Our motivation to carry out research on the 2-iodothiophene photoinduced reaction in different solvents was the fact that the thienyl radical is a very important intermediate in the synthesis of bioactive compounds^[11–13] and is also a precursor of conductive polymers.^[14,15]

MATERIALS AND METHODS

Experimental

Materials and reagents

The solvents used were *n*-heptane (Mallinkrodt ChromAR) HPLC grade, dichloromethane (J.T.Baker) and spectroscopic grade methanol (J.T.Baker and Merck) without further purification.

The purity of the 2-iodothiophene (Aldrich) and of the reference compounds used, thiophene (Riedel de Haen), iodine (QUIMICOR, Droguería Córdoba S.A.) as bisublimated iodine and 1-iodoheptane (Aldrich) was controlled by GC-MS.

All the reagents used for measurements of quantum yields were commercially obtained: ferric alum (Fe(NH₄)(SO₄)₃·12H₂O) (J.T.Baker), potassium oxalate (K₂C₂O₄·H₂O) (Merck), *o*-phenanthroline (C₁₂H₈N₂·H₂O) (Aldrich), sodium acetate (NaC₂H₃O₂·3H₂O) (J.T. Baker), sodium fluoride (NaF) (Anebra) and sulphuric acid (H₂SO₄) (J.T.Baker) were used without further purification.

Irradiation process

Experiments were carried out under static photolysis conditions at room temperature (25 °C). A low-pressure mercury lamp was used as irradiation source (Cathodeon TUV 6 W). It was placed 6 cm away from the cell and a blackened screen was put in the beam trajectory in order to attenuate the radiation and thus obtain a lower conversion.

The 2-iodothiophene photolysis was performed degassing the solutions in a vacuum line in order to thoroughly eliminate O₂. The reaction cell used was a 1 cm-optical-path length quartz spectrophotometric cell, volume of 4 cm³ equipped with a glass ampoule, which allowed cooling of the solution down to liquid N₂ temperature. The cell was connected through a Teflon valve to a mercury and grease free high-vacuum system to degas the solution contained in the cell.

The initial concentration of 2-iodothiophene varied between 5.0 × 10⁻⁵ and 2.0 × 10⁻⁴ M, with the exception of the experiments performed in order to identify products in which higher concentrations of 2-iodothiophene, on the order of 10⁻²–10⁻³ M, were used.

Analytical procedures

The identification of the reaction photoproducts was made by means of a gas chromatograph coupled to a mass spectrometer (GC-MS) after carrying out preparatory photolysis experiments at high conversions (>50%) in order to obtain significant quantities of products for the analysis.

Mass spectra were obtained using the following spectrometers: Perkin Elmer QM 910 GC-MS equipped with a 30 m long SE-30 column of 0.32 mm internal diameter employing

helium as carrier gas with a flow of 1 cm³/min and Shimadzu QP 5050A equipped with a 30 m long HP5VX column with 0.25 μm of film, 0.25 mm internal diameter. Helium was also used as the carrier gas with a 1.2 cm³/min flow.

Thiophene and 2-iodothiophene concentrations were determined during photolysis by ratio-spectra first and second derivative UV-visible spectrophotometry using a Shimadzu UV-1601 spectrophotometer.

In all cases, samples of the pure components were used for comparison of the spectra as well as for the calibration curves.

Determination of quantum yields

The quantum yields of the reaction, defined as the number of molecules of thiophene formed and the number of molecules of 2-iodothiophene decomposed divided by the number of absorbed photons at 254 nm in the same period of time in *n*-heptane, were measured as described by Hatchard and Parker^[16] using potassium ferrioxalate as actinometer.

Methods used in calculations

To calculate the spectra derivatives, Origin 6.0 (Microcal software) was used.

Enthalpy changes in isodesmic reactions used for calculating the ionization potentials of the radicals, were calculated using density functional theory just as implemented in GAUSSIAN 98.^[17] Geometries were optimized using Becke's^[18] three-parameter hybrid functional with Lee–Yang–Parr's^[19] correlation functional known as B3LYP and considering in each particular case, whether it is an open-shell or a closed-shell system. LANL2DZ Extra Basis internal base set was used.

Solvation energies of the ions in the different solvents were calculated by means of the Self-Consistent Reaction Field method which is based on the Polarizable Continuum Model (SCRF = PCM).^[20]

RESULTS AND DISCUSSION

2-Iodothiophene in a solution of the solvents used (*n*-heptane, dichloromethane and methanol) presents an absorption band with a maximum at 244 nm.^[10] Photolysis of a 2-iodothiophene solution in those solvents at 254 nm produces changes in the absorption spectrum. The changes observed in degassed solutions are shown in Fig. 1. Most experiments, by triplicate, were performed at conversions of 2-iodothiophene lower than 50% in order to corroborate the reproducibility and repeatability of the results obtained.

Control experiments were carried out at room temperature and in the dark. Product formation did not occur under these conditions, even over periods twice or three times longer than regular irradiation times.

Analysis of the reaction products enabled the detection of thiophene (*m/z* = 84) as the main product of the reaction and small amounts of iodine (*m/z* = 254) in all solvents used. When the solvent used was *n*-heptane, iodoheptane was also identified, whereas iododichloromethane was obtained when dichloromethane was the solvent. These results show that under the experimental conditions of this work, products deriving only from the reaction of the thienyl radical were observed and the reaction occurs in several hydrogen-donor solvents. The reaction products

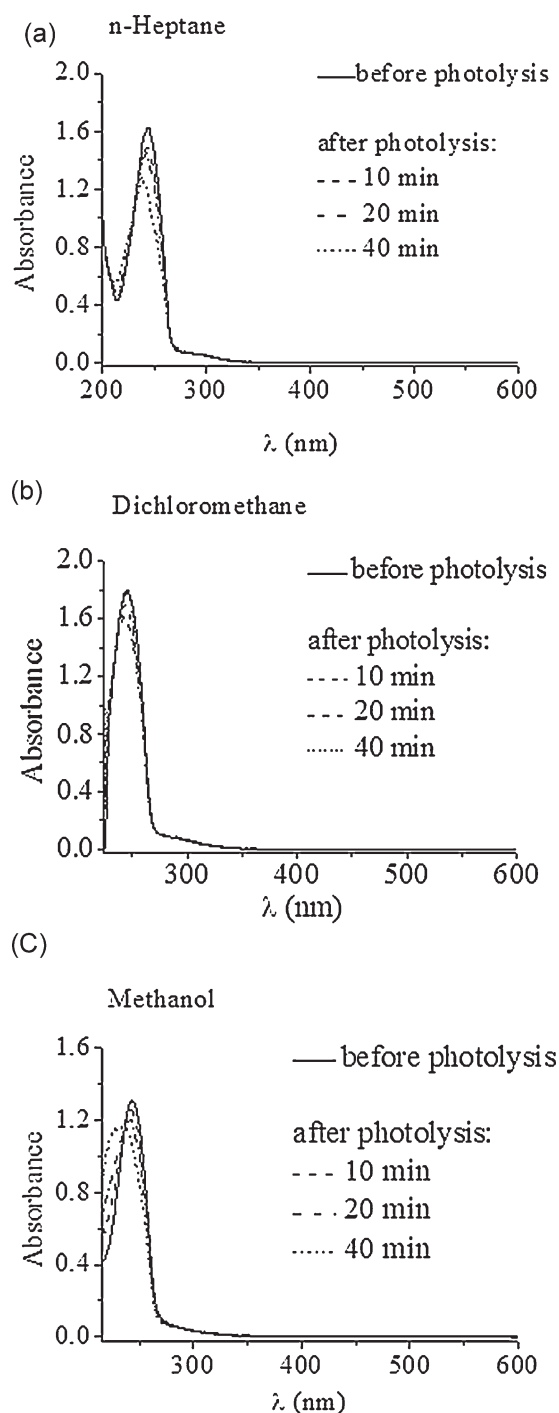


Figure 1. Absorption spectra of 2-iodothiophene degassed solutions 1.5×10^{-4} M: (a) *n*-heptane, (b) dichloromethane, (c) methanol

detected in the different solvents, the 2-iodothiophene solution concentration and photolysis time are shown in Table 1.

Considering the photoproducts identified by GC-MS, when irradiating the 2-iodothiophene solutions in the different solvents, the absorption changes observed in the spectra can be attributed to the increase in the concentration of thiophene ($\lambda_{\max} = 231.5$ nm in *n*-heptane, dichloromethane and methanol) and to the decrease of the concentration of 2-iodothiophene ($\lambda_{\max} = 244.0$ nm in *n*-heptane, dichloromethane and methanol).

When the initial concentration of 2-iodothiophene was lower than 2.0×10^{-4} M and the experiments were performed at conversion of 2-iodothiophene lower than 50%, an absence of the characteristic iodine absorption was observed in the spectra, indicating a production of iodine below the detection limit.

To determine the thiophene and 2-iodothiophene concentrations during photolysis, first and second derivative UV-visible spectrophotometry was used.^[21,22] After assessing several alternatives, spectra were recorded every 0.5 nm with the Shimadzu UV-1601 spectrophotometer. The following parameters for the resolution of the mixture were selected: concentration of the 2-iodothiophene (c_{ith}°) and thiophene (c_{th}°) standard solutions which were used as divisor, $\Delta\lambda$ to obtain the derivative, the number of experimental data used in the calculation, the smoothing function and the most adequate wavelength. Savitzky-Golay's^[23] smoothing method was used, which applies a local second order polynomial regression. The methodology and parameters selected for determining 2-iodothiophene and thiophene in each of the solvents are indicated in Table 2. Several thiophene and 2-iodothiophene solutions in the different solvents were prepared and resolved using first and second derivative UV-visible spectrophotometry, as described above and the results could be reproduced, in all cases, with less than 10% error.

In all the experiments carried out at less than 50% conversion, the concentrations determined applying this method enabled verification of the mass balance calculated as $c_{\text{ith},t} = c_{\text{ith},i} + c_{\text{th},t}$ with $c_{\text{ith},i}$ being the initial concentration of 2-iodothiophene, $c_{\text{ith},t}$ the concentration of 2-iodothiophene and $c_{\text{th},t}$ the concentration of thiophene after a certain irradiation time. The concentration of 2-iodothiophene and thiophene was determined after irradiating solutions of different concentrations of 2-iodothiophene in the different solvents to conversions always less than 50%. The solutions were thoroughly degassed prior to irradiation. Figures 2 and 3 show the concentration variation of thiophene and 2-iodothiophene, respectively, with the photolysis time for degassed solutions of different initial 2-iodothiophene concentrations in the different solvents. The curves shown in Fig. 3 were obtained considering a first-order decay in the concentration of 2-iodothiophene.

It was found that the concentration of 2-iodothiophene varies with photolysis time in the three different solvents, *n*-heptane, dichloromethane and methanol up to a conversion of 40% as: $c_{\text{ith},t} = c_{\text{ith},i} e^{-kt}$, where, $c_{\text{ith},t}$ is the concentration of 2-iodothiophene after photolysis time 't' and $c_{\text{ith},i}$ is the initial concentration of 2-iodothiophene. In order to verify that the reaction is pseudo-first-order, $\ln c_{\text{ith},t}$ was represented as a function of photolysis time in the different solvents. Results are shown in Fig. 4.

In all cases, a linear relationship, with a slope independent of the initial concentration of 2-iodothiophene is observed within the experimental error. The pseudo-first-order rate constants, which are shown in Table 3, were calculated from the slopes of the straight lines obtained. The pseudo-first-order rate constants determined, did not show a significant difference in the solvents studied, even in the most polar ones.

The quantum yields of thiophene production and of the 2-iodothiophene consumption were determined after irradiating solutions of 2-iodothiophene in *n*-heptane. Each of the determinations was done twice, previously checking that the results obtained were not affected by the increase of the 2-iodothiophene conversion and the results reported, correspond to the average of the results obtained. The

Table 1. Reaction products detected in the different solvents, 2-iodothiophene solution concentration and photolysis time

Solvent	Product	<i>m/z</i>	2-Iodothiophene concentration	Photolysis time
<i>n</i> -Heptane	Thiophene	84	1.5×10^{-2} M	6 h
	Iodoheptane	226		
	Iodine	254		
Dichloromethane	Thiophene	84	2.0×10^{-3} M	10 h
	Dichloriodomethane	210		
	Iodine	254		
Methanol	Thiophene	84	1.0×10^{-2} M	3 h
	Iodine	254		

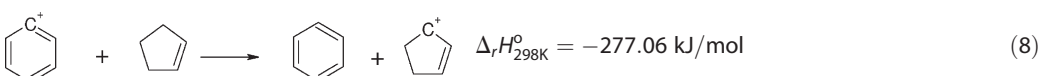
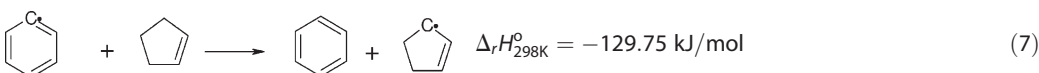
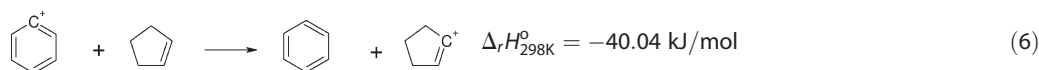
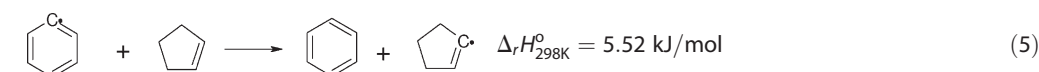
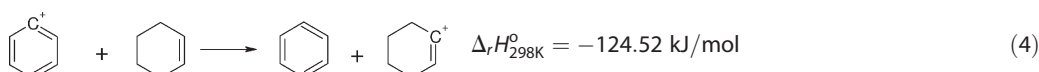
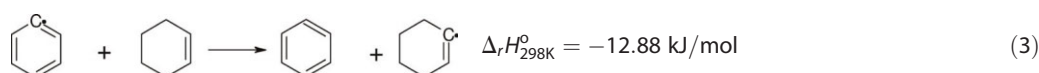
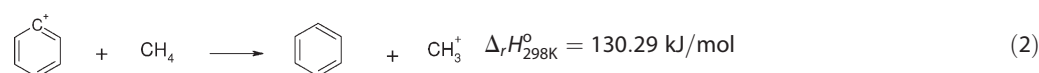
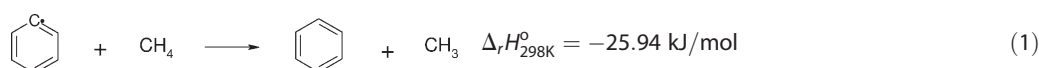
2-iodothiophene consumption and thiophene production quantum yields in *n*-heptane solutions were 0.31 ± 0.01 and 0.28 ± 0.01 , respectively.

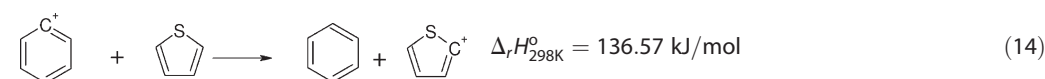
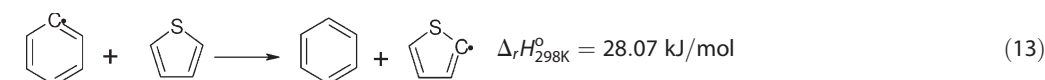
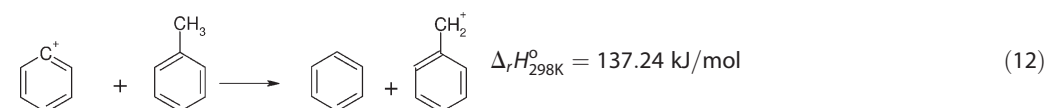
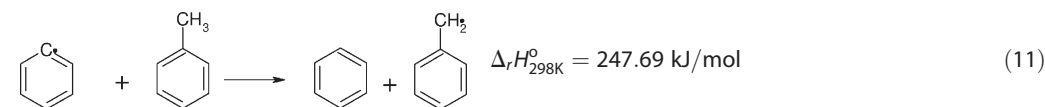
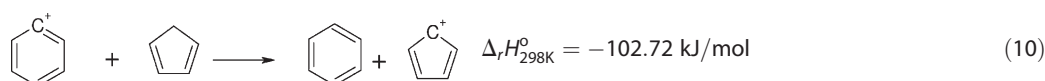
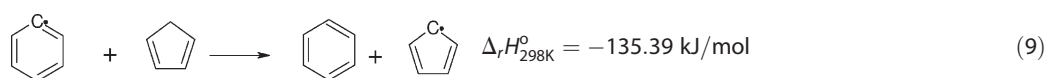
In order to validate the experimental results obtained in this work, calculations were performed to analyse the feasibility of electron transfer occurring in the radical generated, by the homolytic cleavage of the carbon–iodine bond (C–I) of 2-iodothiophene, in the different solvents used.

Although the electron donor–acceptor properties of a gas-phase molecule are determined by the ionization potential (IP) and the electron affinity (EA), these properties are not directly relevant in solution because the solvation of the ions is a factor of great importance. Calculations were made of the ionization potential of the thienyl radical, electron affinity of the iodine atom and free energy of solvation of the corresponding iodide and carbocation in *n*-heptane, dichloromethane and methanol solvents. In order to compare the results obtained and to verify

the methodology of the calculations, similar calculations for systems studied by other authors were carried out. For comparison purposes, an alkyl radical (CH₃·) and other non-saturated cyclic radicals were selected.

The ionization potentials of the radicals were calculated as the difference between the formation enthalpy of the carbocation and the corresponding radical. Several authors^[26,27] have proved the accuracy of calculating the formation enthalpies of molecules and radicals by a combination of computational methods for the calculation of isodesmic reaction enthalpies and experimental formation enthalpies of some of the species participating in the reaction. Thus, from the series of reactions indicated below (1–14) and the experimental value of the IP of the phenyl radical (802.63 kJ/mol),^[28] the IPs of the radicals appearing in Table 4 were determined. For comparison purposes the available experimental and estimated values of IP of some of the species were also included in Table 4.





The IP of the thienyl radical was calculated as follows:

IP (thienyl radical) = $\Delta_r H^\circ(\text{C}_4\text{H}_3\text{S}^+) - \Delta_r H^\circ(\text{thienyl radical}) = \text{IP}(\text{phenyl radical}) + \Delta_r H^\circ(14) - \Delta_r H^\circ(13)$.

The electronic affinity of the iodine atom (287.48 kJ/mol) was also calculated and compared with the experimental value (295.24 kJ/mol).^[33]

The electron donating and accepting properties of a species in solution can be assessed by knowing the oxidation and reduction electrochemical potentials, respectively. For most of the stable species of a certain medium, these values can be measured with conventional techniques, whereas for transient species, such as free radicals in solution, they cannot be determined by means of routine measurements because their lifetimes are very short. However, for some of these species it has been possible to determine free energies of solvation values from half-wave oxidation and reduction potentials in aprotic solvents. Wayner and co-workers^[34] measured half-wave potentials for the oxidation and reduction of several organic radicals in aprotic solvents and those values were used to calculate solvation free energies of the corresponding carbocations and carbanions.

Taking into account that the amount of experimental data of free energies of solvation is scarce and in order to verify the methodology used in this research, the free energy of solvation of

the benzyl cation in acetonitrile was calculated as the difference between the solvation free energies of the benzyl cation and the benzyl radical, yielding a value of -165.14 kJ/mol , which is in good agreement with the literature value -166.52 kJ/mol .^[34] Solvation free energies (ΔG_{solv}) of the corresponding carbocation and halide were calculated in *n*-heptane, dichloromethane and methanol solvents. Results obtained are shown in Table 5. The magnitude of the solvation free energies of the ions included in Table 5 suggests that they depend on the solvent used and not on the size of the ion. Hence, the ionization potentials of the radicals can be very useful in assessing the feasibility of formation of ionic pairs for a given radical pair in a certain solvent.

In Table 6, the difference between the IP of the radical and the EA of the gas-phase halogen is shown. In order to compare the results obtained with the system studied in this work, the results corresponding to the 1-cyclopentenyl and 1-cyclohexenyl radicals and the corresponding carbocations are included, since for the latter the photolysis products of the respective iodides were reported. Based on the results shown in Table 6, the feasibility of occurrence of the following process is discussed:

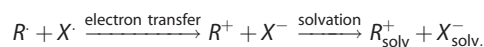


Table 2. Methodology and parameters selected for determining 2-iodothiophene and thiophene in different solvents

Methodology	2-Iodothiophene				Thiophene			
	Ratio-spectrum derivative UV-visible spectroscopy				Ratio-spectrum derivative UV-visible spectroscopy			
Solvent	Derivative order	$c_{\text{ith}}^\circ \times 10^5 \text{ (M)}$	$\Delta\lambda \text{ (nm)}$	$\lambda \text{ (nm)}$	Derivative order	$c_{\text{ith}}^\circ \times 10^5 \text{ (M)}$	$\Delta\lambda \text{ (nm)}$	$\lambda \text{ (nm)}$
<i>n</i> -Heptane	First	7.4	5	250	First	6.3	5	238.5
Dichloromethane	First	7.6	5	250	First	9.0	5	239
Methanol	Second	8.1	5	248.5	First	10.0	5	238.5

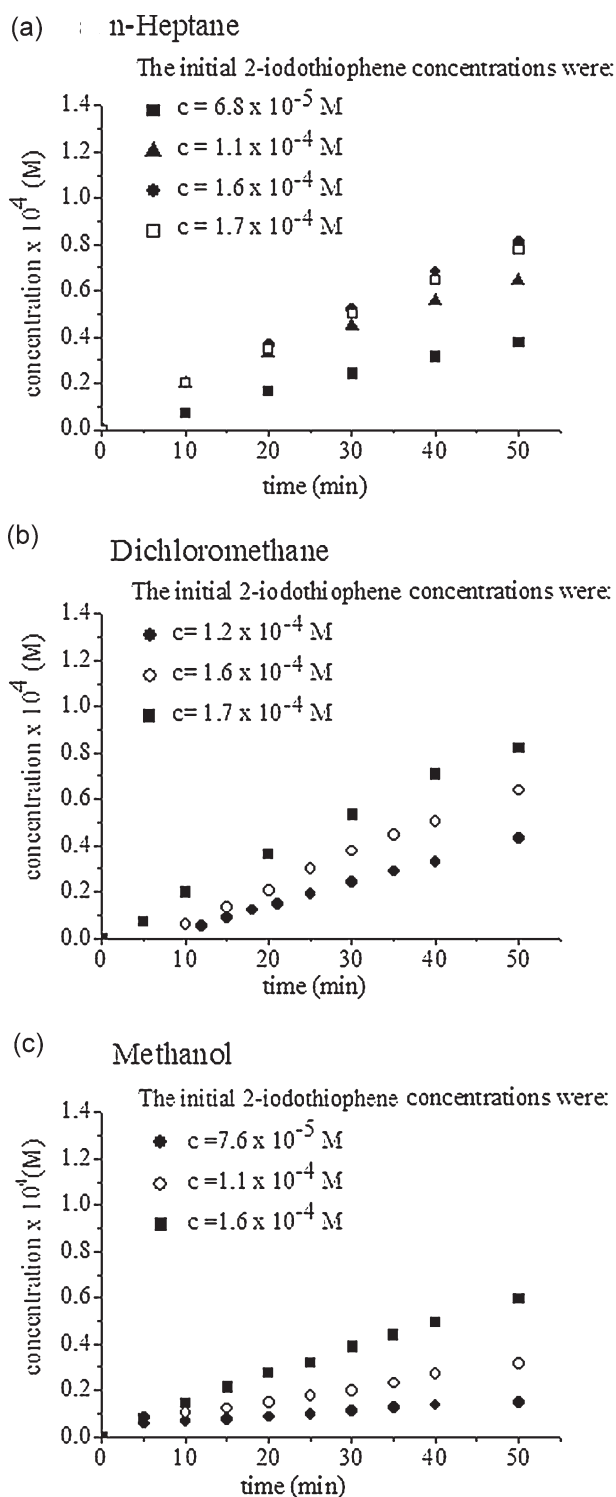


Figure 2. Variation of the concentration of thiophene with photolysis time for experiments carried out in degassed solutions of different initial 2-iodothiophene concentrations in: (a) *n*-heptane, (b) dichloromethane, (c) methanol

The first step requires an energy equal to the difference between the IP of the organic radical and the EA of the halogen atom. If systems with the same halogen atom (X·), but with different radical (R·) are compared, the larger the IP of R·, the more difficult it is for the process to take place. For the three radicals appearing

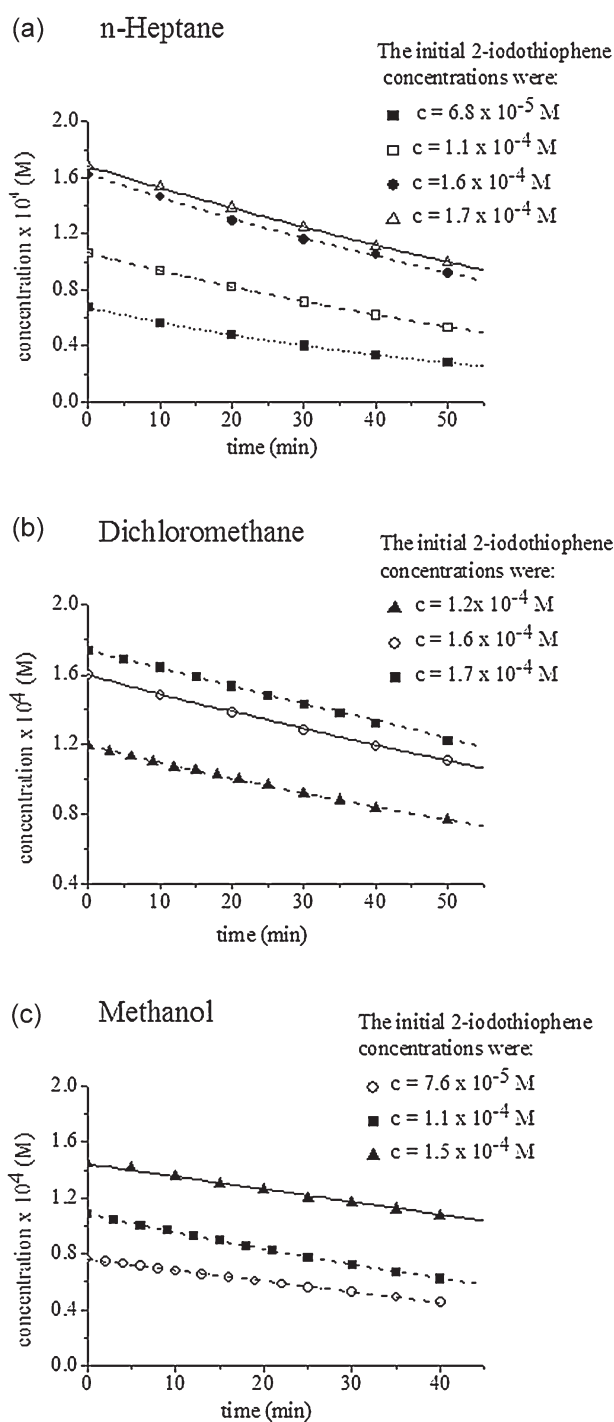


Figure 3. Variation of the concentration of 2-iodothiophene with photolysis time for experiments carried out in degassed solutions of different initial 2-iodothiophene concentrations in: (a) *n*-heptane, (b) dichloromethane, (c) methanol

in Table 6 the order of decreasing IP would be: thieryl radical > 1-cyclopentenyl radical > 1-cyclohexenyl radical.

That first step is generally very endothermic and does not occur if it is not accompanied by the stabilization by solvation of the ions formed. Only if the absolute value of the solvation free

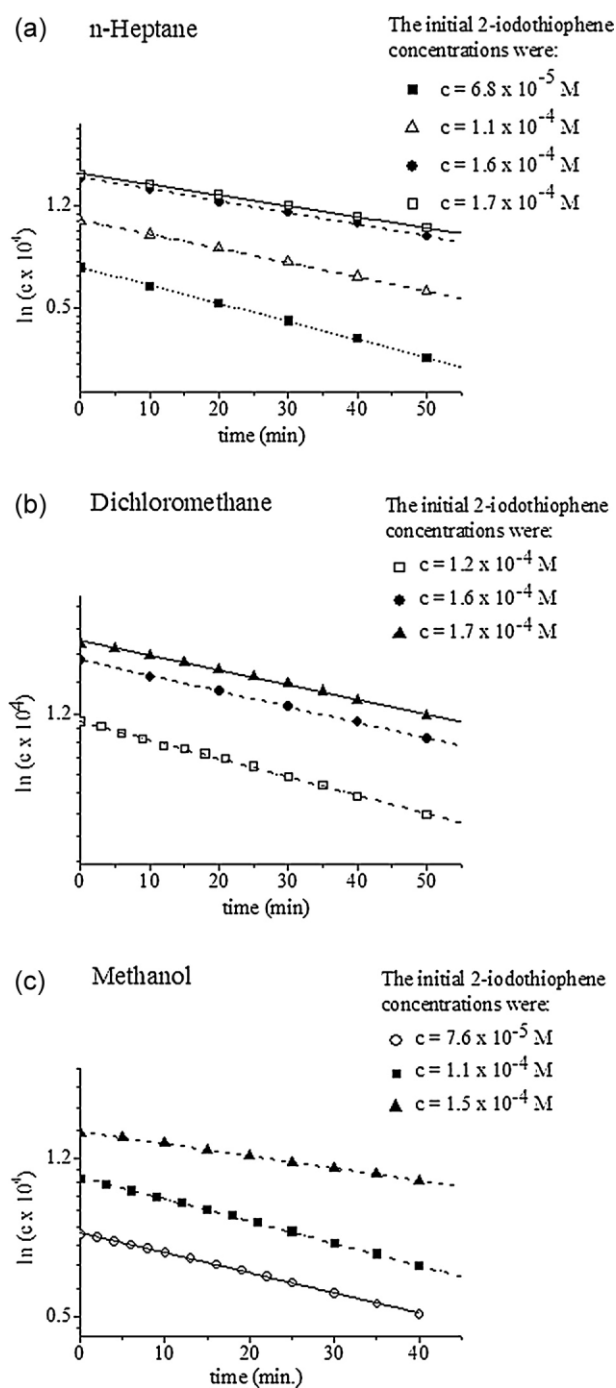


Figure 4. Variation of the \ln of the concentration of 2-iodothiophene with photolysis time for degassed solutions of different initial 2-iodothiophene concentrations in: (a) *n*-heptane, (b) dichloromethane, (c) methanol

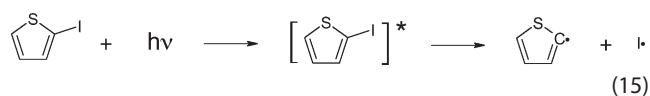
energy (ΔG_{solv}) of the ions which are formed, is larger than the difference between the IP of the radical and the EA of the halogen, will the process be thermodynamically favourable. From the observation of the values of ΔG_{solv} of the ions and the difference between the IP of the radical and the EA of the iodine atom, when *n*-heptane is the solvent, it is possible to observe that the process of formation of the carbocation and the iodide would not be thermodynamically favourable in any of the cases considered.

In the case of 1-iodocyclopentene, the process is thermodynamically possible in methanol and for 1-iodocyclohexene it would be, both in dichloromethane and in methanol. This is in agreement with the results obtained by Kropp and co-workers^[35] who have observed that the irradiation of 1-iodocyclohexene in a solution of methanol or dichloromethane at 40 °C leads mainly to the formation of products coming from nucleophilic substitution, together with smaller amounts of cyclohexene derived from the reaction via radicals.

In the irradiation of 1-iodocyclopentene in dichloromethane, only cyclopentene as photoproduct was detected at 40 °C, and at –25 °C ionic products were formed in dichloromethane and methanol.^[35] However, in the case of 2-iodothiophene, the process would not be thermodynamically feasible in any of the solvents considered, even in the most polar ones. As previously indicated, in the studies of 2-iodothiophene photolysis at 254 nm in solution of *n*-heptane, dichloromethane and methanol, carried out in this research, the only products observed were those coming from the reaction of the thienyl radical.

CONCLUSIONS

For the photoinduced reaction of 2-iodothiophene in the different solvents, the following steps are proposed as the most important:



In *n*-heptane

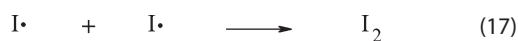
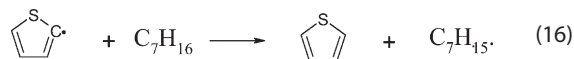




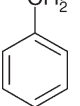



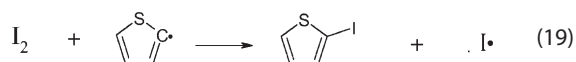
Table 3. Pseudo-first-order rate constants for the photoinduced reaction of 2-iodothiophene in degassed solutions of solvents of different polarity




Solvent	<i>n</i> -Heptane	Dichloromethane	Methanol
Relative permittivity (ϵ)	1.9246 ^[24] (at 20 °C)	9.08 ^[25] (at 20 °C)	32.63 ^[25] (at 25 °C)
k (s^{-1})	$(2.2 \pm 0.5) \times 10^{-4}$	$(1.3 \pm 0.4) \times 10^{-4}$	$(1.9 \pm 0.5) \times 10^{-4}$

Table 4. Ionization potentials calculated from isodesmic reaction enthalpies, using B3LYP/LANL2DZ ExtraBasis level of theory and the experimental value of the phenyl radical ionization potential. Data are included for comparison

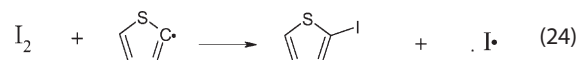
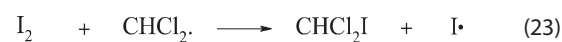
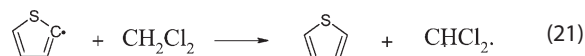
Radical	IP (kJ/mol)		
	Calculated	Experimental	Estimated
$\cdot\text{CH}_3$	958.97	949.77 ^[29]	
	691.11		727.48 ^{[30]a}
	757.30		845.17 ^{[7]b}
	655.42	673.62 ^[31]	
	835.42	811.72 ^[31]	
	692.28	694.67 ^[32]	
	911.23		

^a 2-Cyclohexenyl radical cited value.
^b Literature estimated value.

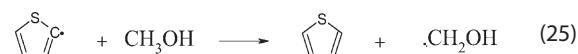
**Table 5.** Solvation free energies (ΔG_{solv}) of carbocations and iodide in *n*-heptane, dichloromethane and methanol solvents







Carbocation or halide	ΔG_{solv} (kJ/mol)		
	<i>n</i> -Heptane	Dichloromethane	Methanol
I^-	-126.48	-225.85	-276.31
CH_3^+	-137.28	-253.84	-326.31
	-109.96	-208.99	-255.31
	-106.40	-192.38	-230.20
	-104.14	-188.20	-223.59

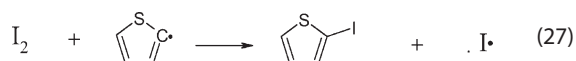
In dichloromethane



In methanol

**Table 6.** Sum of the solvation energies (ΔG_{solv}) of carbocations and of the halide in *n*-heptane, dichloromethane and methanol and the difference between the ionization potentials of the radicals and electronic affinity of the halogen atom ($\text{IP}(\text{R}\cdot) - \text{EA}(\text{X}\cdot)$).

Radical	IP (R·) – EA (I·) (kJ/mol)	Carbocation	ΔG_{solv} (R ⁺) + ΔG_{solv} (I ⁻) (kJ/mol)		
			<i>n</i> -Heptane	Dichloromethane	Methanol
	623.75		-236.44	-434.84	-531.62
	469.82		-232.88	-418.23	-506.51
	403.63		-230.62	-414.05	-499.9



The experimental and theoretical evidence which enables to propose this mechanism is:

- The formation of products coming only from the thienyl radical.
- The reaction takes place in several H-donating solvents.
- The high value of ionization potential of the thienyl radical when compared to other vinylic radicals (cyclopentenyl and cyclohexenyl).
- That the sum of the solvation free energy of the carbocation and the iodide is not larger than the difference between the ionization potential of the thienyl radical and the electron affinity of the iodine, making the generation of the carbocation and the iodide in the solvents used, thermodynamically unfavourable.
- No significant difference of the pseudo-first-order rate constant is observed when comparing the results obtained in solvents of different polarity.

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