Photoinduced Substitution Reactions in Halothiophene Derivatives. Steady State and Laser Flash Photolytic Studies

F. Elisei, L. Latterini, and G. G. Aloisi*

Dipartimento di Chimica, Università di Perugia, I-06123 Perugia, Italy

M. D'Auria

Dipartimento di Chimica, Università della Basilicata, I-85100 Potenza, Italy Received: September 7, 1994; In Final Form: November 28, 1994[®]

A photochemical and photophysical study by steady state and pulsed techniques of 5-bromo- and 5-iodo-2thiophenecarbaldehyde and 2-acetyl-5-iodothiophene in benzene is presented. The quantum yields for the direct and sensitized formation of the phenylthiophenes following the photocleavage of the carbon-halogen bond were determined in the 293-343 K temperature range. The transient species (triplets and free radicals) originated by laser excitation were investigated by laser flash photolysis; their spectral and kinetic properties and their formation quantum yields were determined at room temperature. The halogen atoms were detected through their interactions with the solvent to form benzene-X[•] complexes that were identified by absorption spectra and decay lifetimes. The characteristics of the triplets were also determined in methylcyclohexane/ 3-methylpentane (9:1, v/v) at 77 K. Phosphorescence measurements at low temperature gave the spectral and kinetic characteristics of the lowest triplet states of halothiophenes. Through the effect of the solvent polarity on the triplet energy (E_T), evidence was obtained of the n, π^* nature of the lowest triplet. Results obtained by steady state and pulsed techniques gave strong indication that the sensitized photosubstitution takes place through an upper triplet state (likely σ , σ^* in nature) localized on the carbon-halogen bond. A scheme showing the energies of the involved electronic states is presented. For the direct photoreaction the main route is probably the triplet again, although a singlet pathway cannot be excluded.

Introduction

The photochemical synthesis of phenyl derivatives of furanand thiophenecarbaldehydes and methylketones following the irradiation of the corresponding haloderivatives in benzene, studied in one of our laboratories, was reported to occur with high chemical yield.¹ This photoreaction was also used to synthesize other arylfurans and arylthiophenes² which are important intermediates in the synthesis of naturally occurring compounds.³

The photochemical behavior of aliphatic and aromatic halides,⁴⁻¹³ halothiophenes,¹⁴ and haloketones¹⁵⁻¹⁷ has been studied for a long time. Although it is well-known that photoexcitation of these compounds induces the cleavage of the carbon-halogen bond (C-X), the mechanism of the radical formation and, in particular, the excited states responsible for the dissociation have not been well established.

The picture for the alkyl halides, where the electronic excitation generates repulsive n,σ^* states leading to direct dissociation of the molecule (for methyl iodide an excited state lifetime of 0.07 ps was reported),⁷ is the most clear. Both singlets and triplets are repulsive states and are able to dissociate with high quantum yield; moreover for bromo- and iodoalkyl derivatives, due to the heavy atom effect, the lowest energy transition is predominantly ${}^{1}A_{1} \rightarrow {}^{3}Q_{0}$,¹¹ which gives rise to a dissociative triplet state.

Differently, in the aryl halides the electronic excitation involves the π system of the aromatic chromophore (π , π^* excited state) and then an intramolecular energy transfer process takes place before dissociation. The results of a study on photodissociation of aryl and arylalkyl halides by molecular beams^{6,7} showed that the lifetimes of their excited states are 1 order of magnitude longer than that of methyliodide. On the basis of this finding, the authors concluded that the initially excited electronic state (S_n , π,π^* in nature) should be stable with respect to dissociation. However, due to the heavy atom effect (especially in the presence of bromine and iodide), a crossing to a dissociative triplet can be facilitated. The repulsive triplet (that should be an upper state on the basis of the analysis of the fragment translational energy) is localized on the C-X bond and is σ,σ^* in nature.⁶

More recently Hilinski et al. presented novel experimental data on the photodissociation of 1- and 2-(halomethyl)naphthalenes obtained by picosecond emission and absorption spectroscopy in *n*-hexane at room temperature.¹² In agreement with the mechanism reported in ref 7, which is generally applicable to haloaromatics, they proposed that the main channel for the photocleavage of the C-X bond is the intersystem crossing (isc) from an upper singlet to an upper triplet. This can be, or crosses to, a dissociative σ,σ^* triplet state.¹² The authors also presented evidence that the lowest excited triplet state offers a less efficient path to the C-X fission than the upper one.

Moreover, Scaiano et al. clearly showed that laser excitation of the lowest triplet state of bromo derivatives of naphthalene and phenanthrene produces the C–Br bond cleavage, thus demonstrating the photoreactivity of an upper triplet.¹³

Direct evidence for the role of the triplet state in the photodissociation of iodonaphthalene came from experiments with triplet energy sensitizers.^{4,5} Interestingly, for the sensitized dissociation quantum yield a marked temperature effect has been observed⁵ as well as a dependence on the triplet energy of the sensitizer.⁴

To obtain a deeper insight into the mechanism of the

^{*} Author to whom correspondence should be addressed.

[®] Abstract published in Advance ACS Abstracts, March 1, 1995.

photocleavage of the C-X bond, a detailed photochemical and photophysical study on 5-bromo- and 5-iodo-2-thiophenecarbaldehyde and 2-acetyl-5-iodothiophene in benzene was undertaken by steady state and pulsed techniques.

$$\begin{array}{c} & \\ X & = Br; R = H \ (5-bromo \ -2-thiophenecarbaldehyde, BTCA) \\ X & = I; R = H \ (5-iodo \ -2-thiophenecarbaldehyde, ITCA) \\ & \\ H & X = I; R = CH_3 \ (2-acetyl \ -5-iodothiophene, AIT) \end{array}$$

The quantum yields for the direct and sensitized photoreaction at different temperatures, the spectroscopic and kinetic properties, and the formation quantum yields of the triplet states and of the radical species originated by the bond photocleavage were determined and discussed. Moreover, the triplet state was characterized in glassy matrix at 77 K by phosphorescence and $T_1 \rightarrow T_n$ absorption spectra.

Experimental Section

5-Bromothiophene-2-carbaldehyde (BTCA), 5-iodothiophene-2-carbaldehyde (ITCA), and 2-acetyl-5-iodothiophene (AIT) were the same as used in previous works.¹⁻³ Solvents (Carlo Erba RPE) were used as received or purified by standard methods.

All measurements were carried out at room temperature (296 \pm 2 K) in deaerated solutions (by purging with argon) unless otherwise indicated.

Absorption spectra were recorded by a Perkin-Elmer (Lambda 5) double-beam spectrophotometer, while phosphorescence spectra and lifetimes were measured in methylcyclohexane/3-methylpentane (MCH/3MP, 9:1, v/v) and ethanol (EtOH) matrices at 77 K with a Spex Fluorolog-2 spectrofluorometer equipped with a 1934D phosphorimeter.

The steady state irradiation of the halothiophenes under direct and sensitized conditions was performed by a high-pressure mercury lamp coupled with interference filters or by the excitation system of the Perkin-Elmer-MPF 66 spectrofluorimeter using ferrioxalate as an actinometer. The irradiation for the direct photoreaction was performed at 313 nm on deaerated benzene solutions and in total absorption of light. The photosensitized reaction was carried out irradiating at 340 nm (xanthen-9-one) or 360 nm (benzophenone and chrysene) correcting for the transmitted light; the photosensitizers were Baker products (Photosensitizers and Quencher Kit). The photoproducts, 5-phenyl derivatives of 2-thiophenecarbaldehyde and 2-acetylthiophene, were identified by using a gas chromatograph (capillary column) coupled with a mass spectrometer. The extinction coefficients of the phenyl derivatives were determined by combining the spectrophotometric technique with HPLC. The analysis with the latter was performed at the wavelength corresponding to the isosbestic point of the reagentproduct spectra (see Figure 1), where the ratio of the peak areas was equal to the ratio of concentrations. The quantum yields (estimated error $\pm 7\%$) for the direct or sensitized photoarylation (ϕ_{PA} and ϕ_{SPA} , respectively) were determined spectrophotometrically (halothiophene concentration ca. 10⁻⁴ M, except for xanthone-sensitized experiments in benzene, where a halothiophene concentration of ca. 10^{-3} M was used); in all experiments the conversion percentage was held below 10% to avoid internal filter effects. The ϕ_{SPA} values were determined by taking into account the efficiency of the energy transfer process as calculated by the quenching of the donor lifetime (quenching efficiency = $1 - \tau/\tau_0$, where τ_0 and τ are the lifetimes of the donor in the absence and in the presence of the acceptor, respectively).



Figure 1. Absorption spectra of BTCA in benzene before (1) and after (2–6) increasing steady state irradiation ($\lambda_{exc} = 313$ nm). Curve 6 corresponds to 100% of conversion.

 TABLE 1: Direct (ϕ_{PA}) and Sensitized (ϕ_{SPA})

 Photosubstitution Quantum Yields of BTCA, ITCA, and AIT

					$\phi_{ ext{SPA}}$	
compound	solvent	$\phi_{ ext{PA}}$	Т (К)	xanthen- 9-one	benzo- phenone	chrysene
BTCA	MCH	< 0.01	293			
	benzene	0.23	293	0.22	0.16	≤0.01
			308			0.02
			323			0.027
			328			0.04
		0.26	333			0.08
	MeCN	< 0.001	293			
ITCA	benzene	0.15	293	0.13	0.06	0.01
			309			0.02
			334			0.04
			338			0.05
			343			0.09
AIT	benzene	0.19	293	0.28	0.24	0.09
			303			0.11
			310			0.17
			325			0.16

Two excitation wavelengths, $\lambda_{\text{exc}} = 347$ nm from the second harmonic of a Ruby laser (J.K. Lasers) and $\lambda_{\text{exc}} = 308$ nm from a XeCl excimer laser (Lambda Physik), were used in the nanosecond laser flash photolysis experiments (laser energy < 10 mJ and pulse width ~ 20 ns). Other experimental details are given elsewhere.¹⁸ Absorption spectra were recorded by a point-to-point technique averaging at least 5 decay kinetics at each wavelength. Laser flash photolysis measurements were carried out in a flow-through cell to avoid sample degradation. $\tau_{\rm T}$ (the time at which the initial signal was reduced to 1/*e*) and $t_{1/2}$ (the time at which the initial signal was halved) are reported (estimated error ±15%) for the transients showing first-order and second-order kinetics, respectively.

Results

Steady State Experiments. Direct and Sensitized Photoarylation. Direct irradiation of BTCA, ITCA, and AIT in benzene gave the corresponding phenyl derivatives with similar quantum yields of around 20% (see Table 1). The changes in the absorption spectrum of BTCA upon irradiation at 313 nm are reported in Figure 1, as an example. The photoreaction is very clean, as demonstrated by the isosbestic point at 303 nm. The absorption appearing at 327 nm corresponds to that of 5-phenyl-2-thiophenecarbaldehyde. Analogous results were obtained by irradiation of ITCA and AIT.

In a previous paper,¹ chemical yields of 0.54, 0.94, and 0.79 for BTCA, ITCA, and AIT, respectively, were obtained irradiating halo derivatives in an immersion apparatus with a 500 W high-pressure unfiltered mercury lamp. These chemical yields are not directly related to the quantum yields because the number of quanta absorbed by the substrates was not measured. In the present experiments, using 313 nm, it was possible to follow the photoreaction up to the complete transformation of the halothiophenes in the phenyl derivatives, as shown by spectrophotometric and HPLC analyses. Only long-term irradiation with an unfiltered Hg lamp caused a slow decrease of the photoproduct absorbance. Methylcyclohexane (MCH) and acetonitrile (MeCN) solutions of halothiophenes did not show considerable absorbance changes after irradiation, indicating that in these solvents the photoreaction quantum yields are very low. These values were estimated to be less than 0.01 and 0.001 for BTCA in MCH and ITCA in MeCN, respectively.

The photoarylation was investigated in the presence of triplet energy ($E_{\rm T}$) donors: xanthen-9-one ($E_{\rm T} = 74 \text{ kcal mol}^{-1}$), benzophenone ($E_{\rm T} = 69$ kcal mol⁻¹), and chrysene ($E_{\rm T} = 57$ kcal mol⁻¹) were used as sensitizers. Since the optical density of the sensitizers was around 0.6 at $\lambda_{exc} = 347$ nm, where the absorption of the acceptor was negligible, the absorbed light was determined by taking into account the transmission of the solution. The ϕ_{SPA} values for the three halothiophenes are reported in Table 1. One can see that they are strongly dependent on the triplet energy of the donor; in particular ϕ_{SPA} increases with the increase of the sensitizer $E_{\rm T}$, being negligible for ITCA with chrysene and the highest (practically equal to the ϕ_{PA} value) for AIT with benzophenone. This behavior should reflect the different population of the reactive triplet (see the Discussion section). Similar dependence on E_{T} of the donor was reported by Wilkinson for the photosensitized decomposition of iodonaphthalene.4

Temperature Effect on the Sensitized Photoarylation. The results obtained at room temperature, in particular those for BTCA and ITCA which have the lowest ϕ_{SPA} values with chrysene as sensitizer, prompted us to investigate the temperature effect on the direct and sensitized photoarylation. For the two carbaldehydes, with chrysene, the ϕ_{SPA} values were very low (0.05 and 0.01, respectively) despite the efficient quenching of the sensitizer triplet by the halothiophenes observed by laser experiments (see below). The aim was to verify the existence and to understand the nature of a possible activated process. The ϕ_{SPA} values obtained in the 293-343 K range are reported in Table 1. In all cases the temperature effect indicates the presence of activated pathways in the sensitized photoreaction; in particular, at the highest temperature the ϕ_{SPA} for chrysene and AIT is comparable with the ϕ_{PA} value. In order to locate the activated process, it was also important to determine the temperature effect on the quenching rate constant. To check the temperature effect on the efficiency of the energy transfer (e.t.) process, measurements of the donor lifetime were performed at 293 and 337 K (by laser experiments) in the absence and in the presence of BTCA at comparable concentrations to the stationary state experiments. At the two temperatures small differences in k_q were found (~20% taking also into account the change of volume¹⁹ and hence of the quencher concentration); such differences are close to the experimental error, ±15%.

This indicates that the quenching rate constant does not depend noticeably on the temperature, despite the expected viscosity change. This can be due to the fact that the rate constant is not diffusion-controlled; moreover, since the $E_{\rm T}$ of

the donor is not far from the energy of the lowest acceptor triplet, the temperature can also facilitate the back energy transfer from this state.

Due to the small dependence of k_q on temperature in the determination of ϕ_{SPA} , it was assumed that the efficiency of energy transfer would be constant in the temperature range investigated. This assumption is justified by the huge temperature effect on the measured ϕ_{SPA} values.

The temperature effect on ϕ_{PA} , on the other hand, is moderate (see Table 1 for BTCA), increasing about 15% on going from 293 to 333 K.

Phosphorescence Properties. Emission spectra of BTCA, ITCA, and AIT were measured in MCH/3MP and EtOH at 77 K, while room temperature phosphorescence was not detected. Unstructured bands were observed, which were very similar for all the halothiophenes with the maximum ranging from 515 to 540 nm, depending on the solvent and on the compound. Their decay followed first-order kinetics, and the corresponding lifetimes for BTCA, ITCA, and AIT were less than 5 ms, which are, in these experimental conditions, typical lifetimes of $n \rightarrow \pi^*$ triplets. Phosphorescence spectra and related decays for AIT in MCH/3MP and EtOH are shown in Figure 2, as an example. From these spectra the triplet energies of the halothiophenes were obtained (Table 2). Since the emission was unstructured, the $E_{\rm T}$ reported in Table 2 is that corresponding to the maximum wavelength.

Laser Flash Photolysis Experiments. Direct and Sensitized Population of the Lowest Triplet State. The main transient absorption, centered around 370 nm, observed under direct excitation by 308 and 347 nm pulses of BTCA in MCH, benzene, and MeCN (see time-resolved spectra in Figure 3 and Table 3), was assigned to the lowest triplet state, T_1 . The attribution of this transient to the triplet is supported by the fact that (i) it was produced within the laser pulse by a monophotonic process (see inset of Figure 3), (ii) it decayed by first-order kinetics, (iii) it was sensitized by several triplet energy donors, e.g. xanthone, benzophenone, and chrysene (see Figure 4), (iv) its absorption spectrum is very close to that of the unique transient detected in MCH/3MP at 77 K (see Figure 5), where phosphorescence was also detected (Figure 2), and (v) it was quenched by oxygen with a rate constant (k_{ox}) close to the diffusional limit (Table 3). The remaining absorption below 400 nm, detected at room temperature (Figure 3), was attributed to the phenylthiophene photoproduct, taking also into account the effect of the ground state absorption at $\lambda < 325$ nm (see curve 1 of Figure 1).

Also, in the case of ITCA and AIT, the laser excitation in MCH, benzene, and MeCN produced an absorption that can be attributed mainly to the $T_1 \rightarrow T_n$ transition (see Figure 6 and the spectroscopic and kinetic properties in Table 3) on the basis of points (i), (iii), and (iv) already listed for BTCA. For the iodo derivatives, the $T_1 \rightarrow T_n$ spectra have absorption maxima around 430-440 nm, as shown by the measurements at low temperature (MCH/3MP matrix) shown in Figure 5. In fact, for these compounds at room temperature, the decay kinetics in this wavelength range are more complicated than for the triplet of BTCA due to the absorption, in the same wavelength range, of the heteroaromatic radicals produced by the fission of the C-I bond which decay with similar lifetimes (see below).

The energy transfer experiments concerning the thiophene derivatives were performed in acetonitrile by using benzophenone and xanthen-9-one as high-energy donors and chrysene as a low-energy one. The triplet states of the former donors were quenched with rate constants close to the diffusional limit, around 10^{10} M⁻¹ s⁻¹ ($k_{diff} = 2.7 \times 10^{10}$ M⁻¹ s⁻¹),²⁰ while the



Figure 2. Phosphorescence spectra of AIT in MCH/3MP (full line) and EtOH (dashed line) at 77 K ($\lambda_{exc} = 300$ nm). Inset: decay kinetics at λ_{max} recorded in MCH/3MP (1) and EtOH (2) at 77 K.

 TABLE 2: Phosphorescence Properties of BTCA, ITCA, and AIT in MCH/3MP and EtOH at 77 K

	MCH/3MP			EtOH		
compound	$\frac{\lambda_{max}}{(nm)}$	τ _P (ms)	$\frac{E_{\mathrm{T}}^{a}}{(\mathrm{kcal}\ \mathrm{mol}^{-1})}$	$\frac{\lambda_{max}}{(nm)}$	τ_{P} (ms)	$\frac{E_{\rm T}^a}{(\rm kcal\ mol^{-1})}$
BTCA ITCA	540 535	3.0 0.51	53 53.5	530 515	4.5 1.0	54 55.5
AIT	530	0.61	54	518	0.92	55.2

^{*a*} Estimated error $\pm 10\%$. Anyway, since T₁ of halothiophenes was sensitized by chrysene, $E_T \leq 57$ kcal mol⁻¹.

quenching rate constant decreased with the lowering of the donor triplet energy, being ca. $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the latter. The quenching of the donor triplets was accompanied by the appearance of the sensitized $T_1 \rightarrow T_n$ absorption, whose maximum was coincident with that obtained by direct irradiation. Time-resolved absorption spectra for the benzophenone-BTCA system are reported in Figure 4.

The extinction coefficient of triplet BTCA (ϵ_{T}) in benzene and acetonitrile was measured by energy transfer from triplet benzophenone (³B^{*}) at $\lambda_{exc} = 347$ nm (wavelength at which the ground state absorption of BTCA is very low (see curve 1 of Figure 1). For ${}^{3}B^{*}$, ϵ_{T} values at 520 nm of 7200 and 6500 M^{-1} cm⁻¹ in benzene and acetonitrile, respectively, were used.²¹ A comparison between the ΔA values at λ_{max} of optically matched solutions of BTCA in benzene and acetonitrile and benzophenone in acetonitrile allowed the triplet formation quantum yields (ϕ_T , Table 3) of BTCA in the two solvents to be obtained, using $\epsilon_{520}\phi_{\rm T} = 6500 \, {\rm M}^{-1} \, {\rm cm}^{-1}$ for benzophenone.²¹ The triplet quantum yields in benzene, measured with λ_{exc} of 347 and 308 nm, were practically the same, taking into account the experimental error. The triplet lifetimes changed slightly with the solvent, indicating that there is a small effect of the polarity of the medium on the decay rate constants of T_1 .

Radicals upon Direct Excitation of Halothiophenes. In addition to the triplet, the three halothiophenes showed another transient produced within the laser pulse.

The time-resolved spectra of AIT recorded in benzene are shown in Figure 6 (similar results were obtained by irradiating

ITCA). This short-lived nontriplet transient has a λ_{max} close to 500 nm, second-order decay kinetics, and a half-life of ca. 0.4 μ s (See Table 4 and Figures 6 and 7). This absorption was assigned to the complex between the iodine atom and the solvent (benzene-I) because its properties (spectrum and decay kinetics) were practically the same as those of the transient obtained by direct irradiation of I₂ in benzene ($\lambda_{exc} = 347$ nm) and also reported in refs 22-24, taking into account the ground state absorption spectra of I₂ and iodothiophenes. Furthermore, it can be noted that prolonged irradiation of iodothiophenes in benzene and in other solvents caused the solutions to become violet, the typical color of molecular iodine. The broad absorption band centered at 450 nm (Figure 6) was due to the $T_1 \rightarrow T_n$ absorption and partially to the $D_0 \rightarrow D_n$ transition of the thienyl-substituted radical, which decays, in benzene, with first-order kinetics and similar lifetimes (see Table 4 and Figure 7). In this solvent, in fact, the decay of these radicals is of pseudo-first-order because they react with the solvent. In MCH and MeCN the main decay pathway is the recombination, and therefore the kinetics become more complex.

In addition to the transient ascribed to T_1 , laser excitation of BTCA produced a broad absorption in the 400–600 nm range. This absorption, produced within the laser pulse, was substantial in benzene, while its intensity was lower in MeCN and MCH (Figure 3). The absorption around 550 nm in benzene was attributed to the benzene-Br[•] complex on the basis of (i) literature data^{17,24} and (ii) our results obtained by exciting Br_2 in benzene, which showed a transient centered at 550 nm that decayed by second-order kinetics ($t_{1/2} = 0.7 \ \mu s$). In fact, the kinetic analysis of BTCA transients in this solvent showed that the decay at 550 nm had the same characteristics. The nontriplet species absorbing in the 370-500 nm range is assigned to the thienyl-2-formaldehyde radical. A kinetic analysis of the thienyl radical was not possible, due to the very similar lifetime/halflives of the three transients $(T_1, benzene-Br^{\bullet}, and thienyl$ substituted radical) and to the overlap between the absorption of the thienyl radical with those of the triplet and of the complex at shorter and longer wavelengths, respectively.



Figure 3. Time-resolved absorption spectra of BTCA in benzene (a) and MeCN (b) recorded 0.2 (O), 0.9 (Δ), and 3 (\Box) μ s after the laser pulse ($\lambda_{exc} = 308 \text{ nm}$). Inset: effect of the laser dose on the change of absorbance recorded at 380 (O) and 500 (Δ) nm in benzene ($\lambda_{exc} = 308 \text{ nm}$).

 TABLE 3:
 Properties of the Lowest Triplet State of BTCA,

 ITCA, and AIT
 ITCA

compound	solvent	λ _{max} (nm)	τ _T (μs)	$k_{ox} (10^9 M^{-1} s^{-1})$	$\epsilon_{\mathrm{T}}[\lambda, \mathrm{nm}]^{a}$ (M ⁻¹ cm ⁻¹)	$\phi_{\mathrm{T}}{}^{b}$
BTCA	MCH	360	0.77	1.3		
	benzene	370	0.75	1.5	8000[370]	0.70
	MeCN	370	0.59	2.2	10 500 370	0.73
ITCA	MCH	430	1.8	2.3		
	benzene	450	1.7	2.6		
	MeCN	430-450 ^c	2.1			
AIT	MCH	440	1.2	2.2		
	benzene	450	0.78	1.6		
	MeCN	440	1.1	2.1		

^{*a*} These values were calculated taking into account the fraction of dissociative triplet (obtained by the ϕ_{SPA} value at room temperature) populated by energy transfer. Estimated error $\pm 15\%$. ^{*b*} Estimated error $\pm 15\%$. ^{*c*} Low signal.

Taking into account the transient measurements and the photochemical behavior in the three solvents, the nontriplet transients detected in MCH and MeCN (350-600 nm range) can be assigned to the thienyl-substituted radicals and to the complexes between the halogen atom and the starting thiophene derivatives. Since in these two solvents the quantum yield of the photoreaction is negligible (Table 1), the main decay pathway of such radicals is recombination, as shown by the second-order kinetics. However, contribution from the MeCN-X[•] complex (molecular iodine is reported to form with MeCN a more stable complex than with benzene)²⁵ cannot be excluded in this solvent. In MCH, on the basis of the results reported in ref 22, absorption due to the complex MCH-X[•] is expected to interfere at wavelengths shorter than 350 nm.

Extinction Coefficients of Benzene $-X^{\bullet}$ Radicals. The measurement of the formation quantum yields of X^{\bullet} in benzene needs



Figure 4. Time-resolved absorption spectra of a solution of benzophenone and BTCA in MeCN recorded 0.08 (\bigcirc), 0.32 (\triangle), and 1.5 (\square) μ s after the laser pulse ($\lambda_{exc} = 347$ nm).

the extinction coefficients of the complexes ($\epsilon_{\rm C}$) of these species with the solvent. For the benzene–I[•] complex we used the $\epsilon_{\rm C}$ value of 2450 M⁻¹ cm⁻¹ (mean value of the published data) that was reported by Bühler.²⁴ For the benzene–Br[•] complex anomalously high $\epsilon_{\rm C}$ values (23 700 and 11 000 M⁻¹ cm⁻¹) were reported by Scaiano and co-workers.^{13,17} These values are high with respect to that calculated²⁴ and to the experimental data of similar complexes of halogen atoms with aromatic molecules.^{22–24} As a matter of fact, a check of the data reported in Figure 3 of ref 17 with equations of ref 26 does not give 23 700 M⁻¹ cm⁻¹ but *ca*. 5500. Moreover, an experiment carried out



Figure 5. Normalized $T_1 \rightarrow T_n$ absorption spectra of BTCA (\triangle), ITCA (\Box), and AIT (\bigcirc) in MCH/3MP at 77 K ($\lambda_{exc} = 308$ nm).



Figure 6. Time-resolved absorption spectra of AIT in benzene recorded 0.2 (O), 0.9 (\triangle), and 3 (\Box) μ s after the laser pulse ($\lambda_{exc} = 308$ nm).

compound	solvent	λ_{\max}^{a} (nm)	$t_{1/2}$ (μ s)	$(10^9 \text{ M}^{-1} \text{ s}^{-1})$	$ \begin{array}{c} \epsilon[\lambda, nm] \\ (M^{-1} cm^{-1}) \end{array} $	$\phi_{\mathtt{R}}{}^{b}$
BTCA	MCH	~490	1.0	2.8		
	benzene	~460	0.7	2.0		
		550	1.0		2300[550] ^c	0.20
	MeCN	~ 500	1.2	2.1		
ITCA	MCH	490	2.9	1.5		
	benzene ^d	500	0.4	1.5	2450[500] ^e	0.20
	MeCN	500	2.0			
AIT	MCH	510	1.2	1.8		
	benzene ^d	500	0.4	1.5	2450[500] ^e	0.22
	MeCN	510	1.0			

^{*a*} Shoulder of the triplet absorption (see Figure 3). ^{*b*} Estimated error $\pm 20\%$. ^{*c*} Estimated error $\pm 15\%$. ^{*d*} The absorption of thienyl derivative radicals (detected at ~460 nm with BTCA) was strongly overlapped with the $T_1 \rightarrow T_n$ band. The two transients could not be resolved owing to their close first-order/pseudo-first-order decay kinetics. ^{*e*} From ref 24.

in our laboratory with bromoacetophenone and Aberchrome-540 as actinometer (same method used in ref 17) gave an ϵ_C of 7300 M⁻¹ cm⁻¹ for the benzene-Br[•] complex. However, despite the use of a flow-through cell, we noticed that there was an increase of ΔA during the experiment which influences the ϵ_C values. On the other hand, the reliability of this method is based on the assumption that the concentration of the benzene-Br[•] complex can be obtained from the photoproduct



Figure 7. Decay kinetics of AIT in benzene recorded at 440 (\bigcirc) and 510 (\triangle) nm. Inset: first-order (\bigcirc) and second-order (\triangle) best fits at 440 and 510 nm, respectively ($\lambda_{exc} = 308$ nm).

quantum yield.¹⁷ This is valid only if the radical recombination is a negligible process and the photoreaction is clean.

For these reasons the method described by Bossy and coworkers^{27a} to determine by pulse radiolysis the $\epsilon_{\rm C}$ value of the bromobenzene-Br[•] complex ($\epsilon_{\rm C} = 2800 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$ at 560 nm) was considered. Our laser flash photolysis experiments on the same system gave practically the same figure (2900 \pm 400 M⁻¹ cm⁻¹). This method allowed the $\epsilon_{\rm C}$ value to be obtained independently of any steady state quantum yield.

Upon laser irradiation of bromine in benzene at 347 nm, the absorption of the benzene–Br[•] complex at 550 nm was detected; ΔA and lifetime were measured. Addition of triphenylmethane (TPMH) caused a decrease in the lifetime of the complex (its ΔA value at zero time remained practically constant) and the formation of TPM[•] radical (λ_{max} ca. 513 nm in different solvents²⁷ and $\epsilon_{TMP^*} = 656 \text{ M}^{-1} \text{ cm}^{-1}$ at λ_{max} in benzene^{27b,c}).

The absorbance changes measured at λ_{max} of TMP[•] and benzene-Br[•], together with $\epsilon_{\text{TMP}^{\bullet}}$ allowed an ϵ_{C} of 2300 \pm 300 M⁻¹ cm⁻¹ at 550 nm to be determined, taking also into account the contribution of the complex at 516 nm (*ca.* 30%) and the fraction of the complex quenched by TMPH.

We are confident about the $\epsilon_{\rm C}$ value obtained in such a way because the efficiency of formation of TMP[•] was directly evaluated by the half-lives of the benzene-Br[•] complex, in the absence and in the presence of TMPH.

The $\epsilon_{\rm C}$ value allowed the quantum yield of the radical production ($\phi_{\rm R}$) upon irradiation of BTCA to be determined, assuming that all Br[•] atoms react with benzene. The corresponding $\phi_{\rm R}$ values in this solvent are reported in Table 4 together with those for iodo derivatives.

Discussion

The energy of the C-Br and C-I bonds in halobenzenes are reported to be 74.8 \pm 1.2 and 63.7 \pm 1.2 kcal mol⁻¹, respectively.²⁸ Assuming that in the halothiophene derivatives the bond energies have comparable values, the excitation energy to the lowest singlet is enough to dissociate the C-X bond (the excitation threshold in Figure 1 is around 325 nm, corresponding to 88 kcal mol⁻¹). On the other hand, the energy of the lowest triplet state, obtained by phosphorescence measurements, is only 53-54 kcal mol⁻¹ for the three thiophene derivatives (Table 2), and, hence, this state should not lead to dissociation. Moreover, the solvent effect on the phosphorescence maximum energy (see the blue shift of the emission spectrum on going from MCH/3MP to EtOH in Figure 2) indicates an n,π^* nature of the emitting triplet. This attribution suggests an excited state where the antibonding π density is placed between the carbon atoms, and, therefore, the photocleavage of the C-X bond is unlikely in this state. Similar conclusions were reported for π,π^* triplet¹² and π,π^* singlet⁷ states in haloaromatics.

On the other hand, the inefficiency of the lowest triplet to give dissociation is clearly demonstrated by the fact that the radicals (in particular the benzene-X* complex) are produced during the laser pulse; hence they could not have the detected triplet as precursor. The sensitization experiments are also in agreement with this conclusion; in fact, the triplet of chrysene sensitizer ($E_T = 57 \text{ kcal mol}^{-1}$) is efficiently quenched by BTCA and ITCA ($E_T \simeq 53 \text{ kcal mol}^{-1}$), $k_q \simeq 10^9 \text{ M}^{-1} \text{ s}^{-1}$, but ϕ_{SPA} is very low at room temperature and increases at higher temperature (Table 1), showing an activated process in the sensitization (see below).

The quantum yield for the production of the lowest (nonreactive) triplet of BTCA in acetonitrile and benzene is 0.70 and 0.73, respectively. This high value is in agreement with the presence of the heavy atoms sulfur and bromine and of the aldehydic group. The ϕ_T values were not measured for iodine derivatives due to the overlap between the triplet and radical absorptions in the 430 nm region (see Figure 6), but it seems to be unlikely that it is lower than that of BTCA. Therefore, the remaining 25-30% of photons can cause the photodissociation through a singlet or an upper triplet pathway. The lowest singlet, n,π^* or π,π^* in nature, should be ruled out for the distribution of antibonding π density (see before), while higher singlets $(\pi, \sigma^* \text{ or } n, \sigma^*)$ seem to be unimportant (although they cannot be excluded) because the reaction also takes place when irradiating on the absorption threshold. Hence, an upper triplet where the electron is in a σ^* orbital (n, σ^* , π , σ^* , or σ , σ^* state), mainly localized on the C-X bond, should be invoked as a precursor of dissociation. The energy of this triplet, which depends on the particular derivative, is not directly determinable, but it is possible to speculate on its value on the grounds of the experiments with the sensitizers. In the case of BTCA, the ϕ_{SPA} value obtained with chrysene, which was very low at 293 K, was about 8 times higher at 333 K, reaching about 30% of that obtained by direct excitation and with the high-energy sensitizers (Table 1). In the case of ITCA, it increases about 9 times, while for AIT it is only doubled. Since the quenching rate parameter (see the Results section) has only a 20% increase from 293 to 337 K, the effect of temperature observed on ϕ_{SPA} cannot be caused by the viscosity change (that in any case is too low to explain the huge increase observed for the quantum yield). On the other hand, the effect of temperature on the direct reaction, which includes contributions due to activated processes for the radical production and for the reaction of the thienyl derivative radicals with the solvent, is very low (Table 1). It is therefore reasonable to assume that the increase of reactivity in the sensitized reaction is due to an activated process of the energy transfer that can populate the upper triplet. With increasing temperature the pathway toward this state competes with that toward the lowest triplet in deactivating the triplet donor. Moreover, it is possible that the back energy transfer from the lowest triplet of the acceptor (53 kcal mol^{-1} for BTCA) increases, thus masking the effect of the decrease of viscosity. In this hypothesis, the position of the reactive triplet should be between 60 and 70 kcal mol⁻¹. The reactive triplet of ITCA, for which the trend of ϕ_{SPA} values with temperature is similar to that of BTCA, should be in the same range. For AIT, the temperature effect is moderate with respect to the previous



compounds; the ϕ_{SPA} value at 325 K is only doubled with respect to that at 293 K; here the upper triplet must be not much higher than 60 kcal mol⁻¹. The hypothesis that the activated process is a reaction channel of the lowest triplet state must be ruled out taking into account the very small temperature effect on ϕ_{PA} for BTCA, under direct excitation (Table 1). Under these conditions the lowest triplet is produced with $\phi_{\text{T}} \cong 0.7$, and hence the existence of an activated reactive pathway as in ref 5 would be shown by a large increase of ϕ_{PA} with the temperature. As a matter of fact, the ϕ_{PA} value of BTCA increases by about 15%, in the same temperature range of ϕ_{SPA} ; this increase can be explained with changes of viscosity of the solvent and changes in the rate constant for the reaction of the radical with benzene.

Scheme 1 summarizes the relative energy position of the excited states involved in the photochemical and photophysical behavior of halothiophene derivatives:

In the direct excitation, a photon of energy hv_{exc} promotes the halothiophene molecule from the ground state, S₀, to the first excited singlet, S₁, from which intersystem crossing (isc) to the lowest and to the upper triplet (T₁ and T_u, respectively) takes place. T₁ is phosphorescent at 77 K (quantum energy hv_P), while T_u is able to dissociate at room temperature. The energy of this state should be in the 60–70 kcal mol⁻¹ range, and hence its position in the scheme is only tentative. In the sensitized reaction exothermic (or almost exothermic) e.t. takes place with xanthen-9-one and benzophenone to both triplets, while with chrysene as donor e.t. is exothermic to the lowest unreactive triplet and endothermic to T_u.

The comparison of the photoarylation quantum yields with those for the production of the benzene-X[•] species gives indications of the reactivity of the radical produced by the laser excitation. If the experimental error is taken into account, the two series of data are not so different and in practice they indicate that the thienyl derivative radical (whose production quantum yield is equal to that of benzene-X[•]) reacts quickly with the solvent to form the corresponding phenylthiophenes. A partial recombination of the photolysis products before arylation can only be invoked for ITCA to explain a ϕ_{PA} smaller than ϕ_R (Tables 1 and 4).

The only evidence of the fate of the halogen atoms is that after repeated flashing of the iodine derivative solution a weak absorption of molecular iodine appeared. However, the nature of the photoproduct and the cleanness of the photoreaction indicate that X^{\bullet} reacts mainly with H[•] (formed through the reaction of thienyl radical with benzene) to give the corresponding hydrogen halide. For the same reasons, recombination between Th[•] radicals should be a very slow process. Scheme 2 shows a photoreaction scheme that omits the homogeneous

SCHEME 2



recombination of the radical atoms and of the Th[•] radicals, where ¹ThX is the ground state halothiophene.

Even if the mechanism has not been investigated for other systems, the photoarylation is a quite general reaction that was found to occur upon photolysis of several halo derivatives of aromatic and heteroaromatic compounds (five- and six-membered rings).²⁹ The halogen can be substituted by aryl groups coming from benzene, toluene, naphthalene, arylalkenes and arylalkynes, and heteroaromatics such as furan, thiophene, and their derivatives.²⁹

Acknowledgments. Financial support by the Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione (Rome) is gratefully acknowledged.

References and Notes

(1) Antonioletti, R.; D'Auria, M.; D'Onofrio, F.; Piancatelli, G.; Scettri, A. J. Chem. Soc., Perkin Trans. 1 1986, 1755.

(2) D'Auria, M. Gazz. Chim. Ital. 1989, 119, 419.

(3) D'Auria, M.; De Mico, A.; D'Onofrio, F.; Piancatelli, G. Gazz. Chim. Ital. **1989**, 119, 381. D'Auria, M.; De Mico, A.; D'Onofrio, F.; Piancatelli, G. J. Org. Chem. **1987**, 52, 5243. D'Auria, M.; De Mico, A.; D'Onofrio, F.; Piancatelli, G. J. Chem. Soc., Perkin Trans. **1987**, 1777.

(4) Wilkinson, F. J. Phys. Chem. 1962, 66, 2549.

(5) Levy, A.; Meyerstein, D.; Ottolenghi, M. J. Phys. Chem. 1973, 77, 3044.

(6) Freedman, A.; Yang, S. C.; Kawasaki, M.; Bersohn, R. J. Chem. Phys. 1980, 72, 1028.

(7) Dzvonik, M.; Yang, S.; Bersohn, R. J. Chem. Phys. 1974, 61, 4408.
(8) Scaiano, J. C.; Barra, M.; Calabrese, G.; Sinta, R. J. Chem. Soc., Chem. Commun. 1992, 1418.

(9) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. J. Am. Chem. Soc. 1993, 115, 8340.

(10) Hunter, T. M.; Leong, C. M. Chem. Phys. Lett. 1984, 104, 538.
(11) van Veen, G. N. A.; Baller, T.; De Vries, A. E.; van Veen, N. J. A. Chem. Phys. 1984, 87, 405. van Veen, G. N. A.; Baller, T.; De Vries, A.

E. Chem. Phys. 1985, 92, 59.
 (12) Hilinski, E. F.; Huppert, D.; Kelley, D. F.; Milton, S. V.; Rentzepis,
 P. M. J. Am. Chem. Soc. 1984, 106, 1951.

(13) Scaiano, J. C.; Arnold, B. R.; McGimpsey, W. G. J. Phys. Chem. 1994, 98, 5431.

(14) Kellogg, R. M.; Wynberg, H. J. Am. Chem. Soc. **1967**, 89, 3495. Bratt, J.; Iddon, B.; Mack, A. G.; Suschitzky, H.; Taylor, J. A.; Wakefield, B. J. J. Chem. Soc., Perkin Trans. 1 **1980**, 648. Párkányi, C. Bull. Soc. Chim. Belg. **1981**, 90, 599.

(15) Purohit, P. C.; Sonawane, H. R. Tetrahedron 1981, 37, 873.

 (16) Bergmark, W. R.; Barnes, C.; Clark, J.; Paparian, S.; Marynowski,
 S. J. Org. Chem. 1985, 50, 5612. Morrison, H.; de Cardenas, L. J. Org. Chem. 1987, 52, 2590.

(17) McGimpsey, W. G.; Scaiano, J. C. Can. J. Chem. 1988, 66, 1474.
(18) Aloisi, G. G.; Elisei, F.; Latterini, L. J. Chem. Soc., Faraday Trans.

1992, 88, 2139. Elisei, F.; Aloisi, G. G.; Mazzucato. U. J. Phys. Chem. **1990**, 94, 5818.

(19) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents. Physical Properties and Methods of Purification; Wiley: New York, 1986.

(20) Murov, S. L. In Handbook of Photochemistry; Dekker: New York, 1973.

(21) Carmichael, I.; Hug, G. L. J. Phys. Chem. Ref. Data 1986, 15, 1.

(22) Gover, T. A.; Porter, G. Proc. R. Soc., Ser. A 1961, 262, 476.

(23) Strong, R. L.; Rand, S. J.; Britt, J. A. J. Am. Chem. Soc. 1960, 82, 5053.

(24) Bühler, R. E. J. Phys. Chem. 1972, 76, 3220.

(25) See for example: Foster, R. Organic Charge-Transfer Complexes; Academic Press: London, 1969, and references therein.

(26) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. J. Am. Chem. Soc. 1988, 110, 511.

(27) (a) Bossy, J. M.; Bühler, R. E.; Ebert, M. J. Am. Chem. Soc. 1970,
92, 1099. (b) Taub, I. A.; Harter, D. A.; Sauer, M. C., Jr.; Dorfman, L. M.
J. Chem. Phys. 1964, 41, 979. (c) Bartl, J.; Steenken, S.; Mayr, H.;
McClelland, R. A. J. Am. Chem. Soc. 1990, 112, 6918. (d) Ziegler, K.;
Ewald, L. Ann. Chem. 1929, 473, 163.

(28) Weast, R. C. Handbook of Chemistry and Physics; CRC: Cleveland,
1972. Benson, S. W. Thermochemical Kinetics; Wiley: New York, 1968.
(29) See refs 1-3 and papers cited therein.

JP9424015