

A Photochemical and Electrochemical Investigation on the System Br_2 —Toluene in Acetonitrile

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The photochemical behaviour of the bromine/toluene system in acetonitrile was studied by voltammetric and spectrophotometric techniques. By irradiating at 257 nm we observed a transition from a hypothetically assumed initial ternary complex (toluene · acetonitrile · bromine) of undefined structure to a complex with a voltammetric behaviour similar to that of the Br_3^- ion.

(Keywords: Bromine—toluene interaction; Charge transfer complexes; Electrochemical bromination; Photochemistry)

Eine photochemische und elektrochemische Untersuchung des Systems Br_2 —Toluol in Acetonitril

Das photochemische Verhalten des Brom/Toluol-Systems in Acetonitril wurde mittels voltammetrischer und spektrophotometrischer Methoden untersucht. Bei der Bestrahlung bei 257 nm wurde ein Übergang eines hypothetischen, in der Struktur nicht genau definierten, Komplexes (Toluol · Acetonitril · Brom) beobachtet, der ein dem Br_3^- -Ion ähnliches voltammetrisches Verhalten zeigt.

Introduction

In a previous electrochemical study¹ dealing with the anodic bromination in acetonitrile (ACN), a photochemical step carrying to voltammetrically detectable complexes between bromine and some aromatic hydrocarbons has been documented. By oxidation on the anodic wave of these complexes, bromo-derivatives of the aromatics were obtained.

In this paper we report on the reactions occurring in the system Br_2 —toluene in ACN by irradiating in the region around 257 nm, were

we observed some perturbations of the Br_2 spectrum in *ACN* by adding toluene. Additionally the knowledge on the nature of the previously mentioned oxidizable complexes is improved.

For this study electrochemical techniques coupled with spectrophotometric measurements were used. Electrochemical methods are particularly suitable for the study of the strong ionic complexes frequently present in polar solvents²⁻⁴.

Experimental

Products

Analytical grade products were used. The solvent (*ACN*) was purified by double distillation over P_2O_5 and stored under N_2 atmosphere.

Apparatus and Methods

The electrochemical experiments were done with an AMEL "Electrochemolab" instrument. The working electrodes were a platinum microelectrode for the voltammetric measurements and a platinum net for the electrolytic experiments. All the potentials were measured against a saturated calomel electrode (S.C.E.) used as reference.

The irradiations were carried out by using a middle pressure mercury lamp coupled with a 257 nm interferential filter (Balzers). The light intensity, measured by a ferrioxalate actinometer, was $4.7 \cdot 10^{15}$ photons/s.

The photochemical-electrochemical experiments were performed in a quartz electrolytic cell, thermostated at 295 K. For UV measurements a Perkin-Elmer 555 spectrophotometer was used. The gaschromatographic measurements were carried out by using a C. Erba "Fractovap" with 2 m WEAS (ethylene glycole succinate) C. Erba column; the carrier (N_2) flux was $10 \text{ cm}^3 \text{ min}^{-1}$.

Results and Discussion

In Fig. 1 *a, b, c*, the absorption spectra of Br_2 (1 *a*), toluene (1 *b*) and Br_2 -toluene (1 *c*) in *ACN* are reported. Fig. 1 *d* shows the difference spectrum obtained by subtracting the sum of the optical densities of spectra 1 *a* and 1 *b* from the optical density of the spectrum 1 *c*. We did not find—under our experimental conditions (Fig. 1 *c*)—an absorption band at 300 nm, where an absorption maximum of the outer complex between Br_2 and toluene was observed in CCl_4 (301 nm, $\epsilon = 5980 \text{ M}^{-1} \text{ cm}^{-1}$)⁵. However, Fig. 1 *d* shows a perturbation in the 230–270 nm region, in our opinion due to the interaction of toluene with a CT complex between Br_2 and *ACN*^{3,6,7}.

The addition of NaClO_4 (supporting electrolyte in the electrochemical measurements) to the Br_2 solution in *ACN* causes a fast increase of the 270 nm band ($\epsilon = 29000$). The addition of toluene to this solution gives the same spectral changes shown by the system without NaClO_4 .

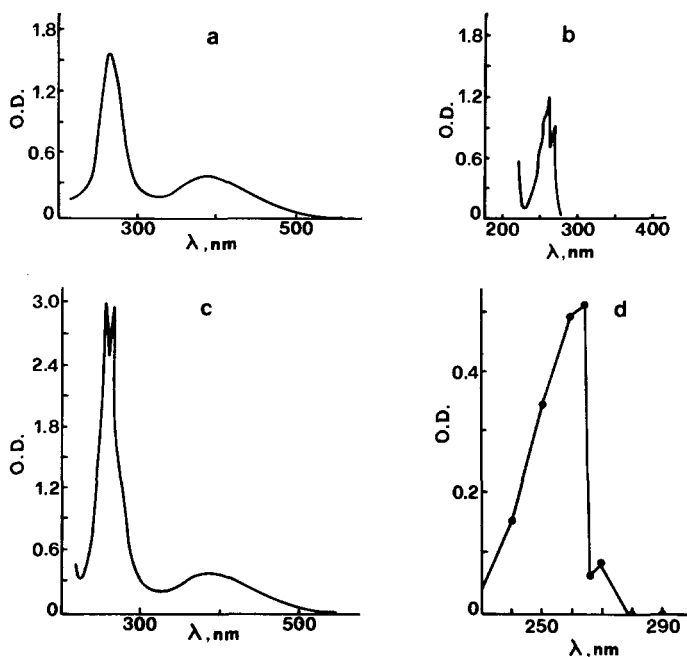


Fig. 1. *a* Absorption spectrum of $5.4 \cdot 10^{-3} M$ Br₂ in ACN. *b* Absorption spectrum of $2.6 \cdot 10^{-3} M$ toluene in ACN. *c* Absorption spectrum of a solution of $5.4 \cdot 10^{-3} M$ Br₂ and $2.6 \cdot 10^{-3} M$ toluene in ACN. *d* Spectrum obtained by subtracting (at various wavelengths) the sum of the optical densities of the spectra *a*) and *b*) from the optical density of the spectrum *c*)

No changes with the time of voltammetric and spectrophotometric patterns were detected in solutions kept in the dark, containing $5 \cdot 10^{-4}$ – $5 \cdot 10^{-3} M$ Br₂, $0.4 M$ NaClO₄ and toluene 5 to 100 times more concentrated than Br₂. Both voltammetric and optical changes were recorded in the same systems when irradiated at 257 nm. The voltammetric measurements (Fig. 2) show a decrease—until an almost complete disappearance—of the first cathodic wave (reduction of Br₂ to Br₃⁻¹), and the growing of a new anodic wave at a potential close to that of the Br₃⁻ oxidation wave¹. In Fig. 3 the limiting current of the first Br₂ cathodic wave and of the anodic wave for an experiment with $4.1 \cdot 10^{-3} M$ Br₂ and $0.43 M$ toluene is plotted vs. the irradiation time. The irradiations were interrupted when the height of the first cathodic wave was negligible*.

* We have also observed that, when the irradiation was continued after the disappearance of the first cathodic wave, a parallel very slow decrease both of the anodic and of the remaining cathodic wave took place.

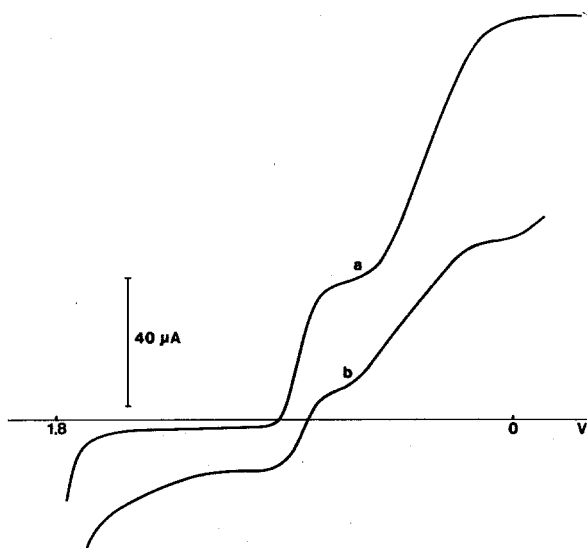


Fig. 2. Voltammetric behaviour of a solution of $4.1 \cdot 10^{-3} M$ Br_2 , $0.43 M$ toluene, and $0.4 M$ $NaClO_4$ in ACN ; *a* initial; *b* after 2 hours irradiation at $257 nm$

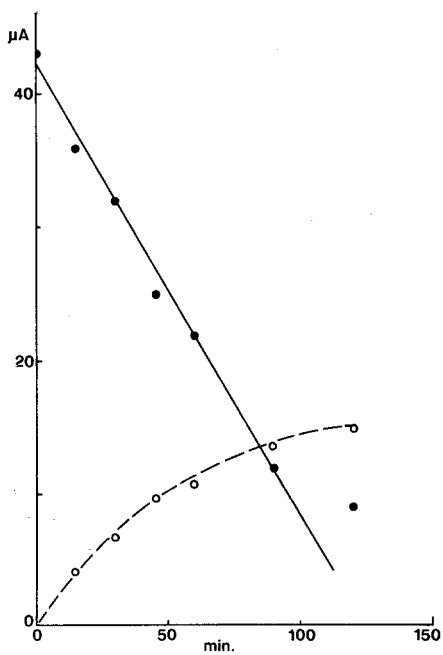


Fig. 3. Plots of the limiting current of the first Br_2 cathodic wave vs. irradiation time, ●; and of the limiting current of the anodic wave vs. irradiation time, ○. $[Br_2] = 3.1 \cdot 10^{-3} M$, $[toluene] = 0.43 M$ and $[NaClO_4] = 0.4 M$ in ACN ; $\lambda_{irr.} = 257 nm$

Table 1. Ratios between the limiting current of the voltammetric waves of the Br_2 /toluene system in *ACN* before and after irradiation. $[\text{Br}_2] = 4 \cdot 10^{-3} M$
 $[\text{toluene}] = 4.3 \cdot 10^{-1} M$

$i_{1c(0)}/i_{2c(0)}$	$i_{2c(t)}/i_{a(t)}$	$(i_{1c(0)} + i_{2c(0)})/i_{2c(t)}$
0.54	2.17	2.15

$i_{1c(0)}$ = limiting current of the first bromine cathodic wave before the irradiation

$i_{2c(0)}$ = limiting current of the second bromine cathodic wave before the irradiation

$i_{1c(t)}$ = limiting current of the first bromine cathodic wave after 2 h irradiation

$i_{2c(t)}$ = limiting current of the second cathodic wave after 2 h irradiation

$i_{a(t)}$ = limiting current of the anodic wave after 2 h irradiation

In Table 1 the ratios between the voltammetric limiting currents before and after irradiation are reported.

Parallel to the voltammetric measurements of the irradiated samples spectrophotometric measurements were done. In the latter case the unirradiated solution kept in the dark was used as reference. During the same irradiation time in which the previously described voltammetric changes occur, an absorption band ($\lambda_{\text{max}} = 268 \text{ nm}$) appeared and then decreased keeping its shape unchanged in the time (Fig. 4).

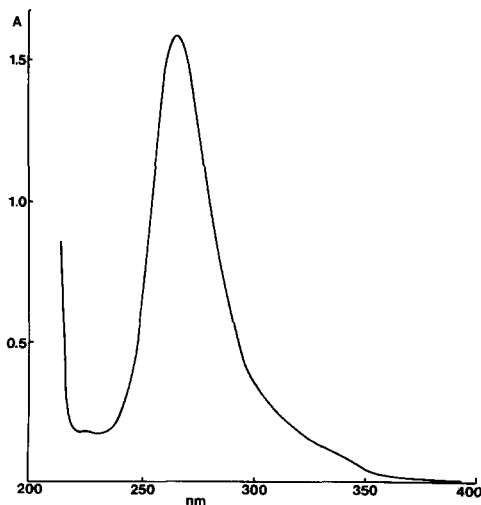
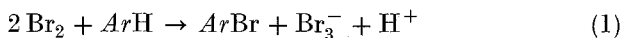


Fig. 4. Absorbance spectrum obtained after 50 min irradiation at 257 nm from a solution of $5.6 \cdot 10^{-4} M$, Br_2 $3.1 \cdot 10^{-3} M$ toluene and $0.4 M$ NaClO_4 in *ACN*, with the same unirradiated solution as reference

After the irradiation the solutions were analyzed by gas-chromatography and then electrolyzed at the potential of the resulting anodic wave (+ 1.1 V). After the electrolysis the solutions were again tested by gas-chromatography and by voltammetry. In Table 2 the analytical results of a typical experiment are reported. From the gas-chromatographic results it can be concluded that during the irradiation only one part of initial Br_2 reacts with toluene yielding bromotoluenes and Br_3^- , according to equ. (1)



Br_3^- , possessing a high stability constant in ACN ⁸, is formed by the reaction of Br^- with Br_2 .

The electrolysis on the anodic wave (after irradiation) results in a significant formation of bromotoluenes (almost twice the amount present before the electrolysis) and in a partial regeneration of Br_2 (detected by voltammetry). The results of the voltammetric experiments (Fig. 2, Table 1), suggest (leaving other measurements out of consideration) the hypothesis that the irradiation leads to the direct photochemical production of bromotoluenes and Br_3^- . In fact, the experimental values of the ratios $i_{2c(t)}/i_{a(t)}$ and $[i_{1c(o)} + i_{2c(o)}]/i_{2c(t)}$, (Table 1), are in agreement with the theoretical values for this process (2 and 2.4 respectively) obtained by taking into account the number of electrons involved in the oxidation and reduction of Br_3^- , and the diffusion coefficients of Br_3^- and Br_2 ⁹. Furthermore, the λ_{max} of the absorption band which appears during irradiation (Fig. 3) agrees with the formation of Br_3^- ¹⁰.

However, the comparison between the voltammetric and spectrophotometric results demonstrates that the anodic wave and the spectrophotometric band cannot be ascribed only to Br_3^- . In fact, the anodic wave is still increasing when the absorbance in the region of 270 nm is already decreasing; furthermore, at the end of the irradiation the absorption of the hypothetically assumed Br_3^- at 268 nm is only 40% of the value expected from the height of the anodic wave; this calculation was done by assuming $\epsilon_{\text{Br}_3^-} = 40\,000 \text{ M}^{-1} \text{ cm}^{-1}$ (as measured in our experimental conditions*) and $D_{\text{Br}_3^-} = 1.9 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, where $D_{\text{Br}_3^-}$ is the diffusion coefficient of Br_3^- anodic wave⁹.

Another important consideration arises from the examination of the amount of the toluene bromo-derivatives produced at the end of the irradiation. From this it appears evident that the whole bromine disappearance cannot be due to formation of toluene bromo-

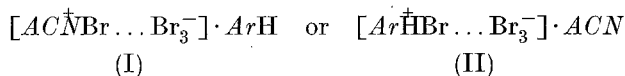
* In Ref. ¹⁰ a value of $55\,000 \text{ M}^{-1} \text{ cm}^{-1}$ was found for the Br_3^- absorption band ($\lambda_{\text{max}} = 269 \text{ nm}$) under condition not too different from the present ones.

derivatives. Alternatively, taking into account the results of the electrolysis at +1.1 V on the irradiated solution as well (Table 2), it appears more probable that (by irradiation) in addition to some amount of Br_3^- an oxidizable intermediate is formed¹ which (by electrolysis) gives rise to bromotoluenes. The stoichiometry of the formation of this intermediate from Br_2 and toluene must be the same as that of the Br_3^- formation by process (I) as can be seen from the experimental ratio: $[\dot{i}_{1c(0)} + \dot{i}_{2c(0)}]/\dot{i}_{a(t)}$ reported in Table 2.

Table 2. Analytical results before and after the electrolysis on the anodic wave (+1.1 V) obtained by 1.25 h irradiation, for a system $2.7 \cdot 10^{-3} M \text{ Br}_2$, $3.0 \cdot 10^{-1} M$ toluene in ACN (supporting electrolyte NaClO_4 0.4 M)

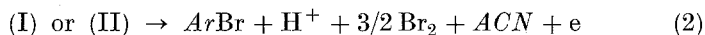
$\dot{i}_{2c(t)}/\dot{i}_{a(t)}$	2.1
$[\dot{i}_{1c(0)} + \dot{i}_{2c(0)}]/\dot{i}_{a(t)}$	2.7
Amounts of toluene monobromo-derivatives detected after the irradiation (M)	chain substituted $6.1 \cdot 10^{-4}$ ring substituted $3.4 \cdot 10^{-5}$
Time of the electrolysis at +1.1 V (s)	240
Faradays consumed in the electrolysis per initial Br_2 mole	0.46
Amounts of toluene monobromo-derivatives detected after the electrolysis (M)	chain substituted $1.1 \cdot 10^{-3}$ ring substituted $8.6 \cdot 10^{-5}$
% Br_2 restored by electrolysis at +1.1 V vs. initial Br_2 amount	60

From the above considerations the electroactive intermediate could have the following alternative formulas:



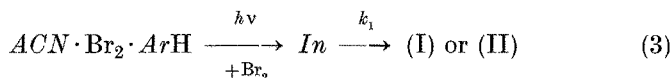
where ArH or, respectively, ACN could be bound to the remaining part of the complex by electrostatic forces. Owing to the low reactivity of the complex, we think that (I) is the more probable formula.

The overall electrodic process inherent to the complex (I) or (II) may therefore follow equ. (2):

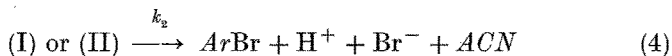


The *Faradays* per mole of initial Bromine implied in this process and the amounts of toluene bromo-derivatives and Br_2 detected in the electrolyzed solutions agree with this hypothesis, taking into account the amount of toluene bromo-derivatives and of Br_3^- present before the electrolysis.

In Fig. 3, where the voltammetric changes of the system Br_2 —toluene in *ACN* are reported vs. the irradiation time, it appears that (while the decrease of the Br_2 concentration follows a zero order kinetics) the increase of the anodic wave, as well due to the electroactive intermediate, shows a different kinetic behaviour. This experimental result and the trend of the absorbance at 268 nm confirm the complexity of the system but could indicate the presence of a further intermediate “*In*” (not voltammetrically detected) between the hypothetical initial CT complex ($\text{ACN} \cdot \text{Br}_2 \cdot \text{ArH}$) and the electro-active intermediate (I) or (II). The step between “*In*” and (I) or (II) should not be a photochemical one:



From (I) or (II) the toluene bromo-derivatives can be obtained both electrochemically by reaction (2) and, more slowly, by the following reaction (4):



Reaction (4) is able to explain how the bromo-derivatives of toluene can be produced only by irradiation, in accordance with the overall reaction (1).

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