ELSEVIER

Journal of Chromatography A, 917 (2001) 261–275

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Application of gas chromatography–tandem mass spectrometry to the analysis of inhibition of dimerisation of tributylphosphate under radiolysis
Identification of isomeric tributylphosphate-alkylbenzene inhibitor coupling products

C. Lamouroux[a,*], H. Virelizier[a], C. Moulin[a], C.K. Jankowski[a,b]

[a]*DCC/DPE/SPCP/Laboratoire d'Analyse et Synthèse Organique, CEA Saclay, BP2, 91191 Gif sur Yvette, France*
[b]*Université de Moncton, Moncton, N. B., E1A3E9, Canada*

Received 22 June 2000; received in revised form 21 February 2001; accepted 21 February 2001

Abstract

Tributylphosphate (TBP), solvent used as extractant for reprocessing spent nuclear fuel, can dimerise under radiolysis. This occurs by radical radical recombination, leading to 10 isomeric dimers (TBP–TBP). These species are complexation agents and are responsible of fission product retention in the organic phase that increases the solvent degradation. In order to limit their formation two free radical inhibitors (In), isopropyl and 1,4-diisopropylbenzenes, were used. These additives reduce by about 50% the concentration of TBP–TBP dimers but this reduction is not strictly followed by TBP regeneration as mixed coupling products from TBP and inhibitor are detected. By using GC–MS–MS and selectively deuterated compounds, the identification of these different isomers (TBP–In) has been realised. From these identifications and from the analysis of the proportion of the different isomers, the major primary TBP radical generated under radiolysis was determined.

Keywords: Dimerisation; Radiolysis; Tributylphosphate; Alkylbenzene

1. Introduction

In nuclear technology, tributylphosphate (TBP) is the most frequently used solvent in liquid–liquid extraction for fuel reprocessing. This extraction, known as the PUREX process (Plutonium Uranium Refining by Extraction) is still considered as the most convenient method to treat the spent fuel. TBP, exposed to acidic conditions but also to intense radiation (α, β, γ) produces various degradation compounds [1–4]. Some of them, like covalent TBP dimers (called TBP–TBP), considered as minor products, can accumulate in the solvent and are complexing agents in particular for cationic species of uranium and plutonium [5]. Therefore, they can lead to a diminution of the selectivity of

*Corresponding author.
E-mail address: clamouroux@cea.fr or jankowc@umoncton.ca (C. Lamouroux).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00674-4

the solvent and to the retention of cations in organic phase which increases the solvent degradation.

The TBP–TBP compounds are supposed to be formed from the dimerisation of two TBP radicals. From TBP, four distinct TBP radicals ($TBP^{\cdot}$) can be produced from α, β, γ and δ positions in the butyl chain. Thus, 16 diastereoisomeric compounds may be formed with 10 positional isomers. By GC–IC-MS analysis, 10 peaks are detected, and have been already depicted [1,2].

In order to control and limit the formation of these covalent dimers (TBP–TBP) under radiolysis, free radical inhibitors were used. These additives described as hydrogen-donating agents under radiolysis can reduce the $TBP^{\cdot}$ dimerisation.

One of the most popular inhibitor families is derived from alkylbenzenes such as isopropyl or 1,4-diisopropylbenzene which have at least one mobile hydrogen on the isopropyl group. For example, for isopropylbenzene, the bonding dissociation energy BDE $(C–H)_{iso}$ is evaluated as 79 kcal/mol. The homolytic cleavage of this C–H bond produces a benzylic tertiary radical stabilized by resonance.

The two inhibitors, isopropylbenzene and *p*-diisopropylbenzene, when added to TBP under radiolysis in small quantity (10% molar ratio), reduce seriously (by about 50%) the quantity of TBP–TBP dimers. However, the reduction of the TBP dimers does necessarily induce an equivalent concentration of regenerated TBP.

In fact, other couplings compounds are formed such as ''In–In'' by inhibitor dimerisation or ''TBP–In'' by recombination between $TBP^{\cdot}$ and inhibitor ($In^{\cdot}$) radicals. This latter category of isomeric compounds, although not desired, has been studied in order to precise the localisation of the primary radical formation site on TBP during radiolysis and by the same way to confirm the lability of the hydrogen in the isopropylic position in these alkylbenzenes molecules.

In this paper, we report on the identification of several isomeric compounds of the TBP–In family for two radical inhibitors, isopropyl and 1,4-diisopropylbenzene by using GC–MS with specifically deuterated products and we discuss the position of the primary TBP radical formed under radiolysis.

2. Experimental

2.1. Chemicals

TBP used came from Marsan (Monaco) with 99% purity.

2.2. Deuterium labeled TBP

These deuterated compounds were synthesised in our laboratory using standard $POCl_3$ esterification developed with the appropriate butanols-d_2 or d_3 in the presence of pyridine. The yield of compounds was respectively: 1,1,1′,1′,1″,1″-d_6 TBP ($TBPC_{\alpha}$-d_6) 31%, 2,2,2′,2′,2″,2″-d_6 TBP ($TBPC_{\beta}$-d_6) 38%, 3,3,3′,3′,3″,3″-d_6 TBP ($TBPC_{\gamma}$-d_6) 9% and 4,4,4,4′,4′,4′,4″,4″,4″-d_9 TBP ($TBPC_{\delta}$-d_9) 78%.

The bisdeuterated butanols were prepared by lithium aluminium deuteride ($LiAlD_4$) reduction of 2,2-$d_2$butyric acid (2,2-d_2 butanol), 3,3-$d_2$butanal (3,3-$d_2$butanol) or ethyl butyrate (1,1-$d_2$butanol). The 4,4,4-$d_3$butanol, was purchased from CDN Isotopes, Canada (Interchim, France). All alcohols and esters purified by distillation were characterised by MS analysis and NMR (^1H and ^{13}C).

NMR ^1H or ^{13}C analyses of the labeled TBP were performed in $CDCl_3$; the chemical shifts are expressed in δ (ppm) using TMS as internal standard. The multiplicity of signals are quoted as: t (triplet), d (doublet), s (singlet), q (quadruplet), m (multiplet).

	TBP deuterated	δ (ppm) $C\underline{H}_2$	δ (ppm) $C\underline{H}_2$	δ (ppm) $C\underline{H}_2$	δ (ppm) $C\underline{H}_3$
^1H-NMR	1,1-d_2 (C_{α})	/	1.59 (t)	1.35 (m)	0.89 (t)
^1H-NMR	2,2-d_2 (C_{β})	4.01 (d)	/	1.4 (q)	0.92 (t)
^1H-NMR	3,3-d_2 (C_{γ})	4.15 (m)	1.64 (m)	/	0.88 (s)
^1H-NMR	4,4,4-d_2 (C_{δ})	4.05 (t)	1.68 (m)	1.37 (t)	/

2.3. Deuterium labeled alkylbenzenes

Isopropylbenzene-d_0 and 1,4-diisopropylbenzene-d_0 were purchased from Aldrich Chemical Co. Inc. and isopropylbenzene-d_1 (Φ-CD $(CH_3)_2$), -d_6 (Φ-CH $(CD_3)_2$) and -d_7 (Φ-CD$(CD_3)_2$) were purchased from Eurisotop (France).

Diisopropylbenzene -α,α′-d_2 (^{1}H-NMR, δ (ppm), 1.41 (s), 7.31 (s)) was synthesised from 1,4-diacetylbenzene (Aldrich) via the Grignard reaction with methyl magnesium bromide (Aldrich) followed by reduction with trimethylsilyl deuteride (TMSD) of the resulting diol (97%). The later compound was synthesised from trimethylsilyl chloride and lithium aluminium deuteride [6] (35%). The overall yield of this reaction sequence was 40%.

2.4. Radiolysis conditions

Panoramic irradiation of samples was performed in the presence of air (22±2°C) using a ^{60}Co gamma radiation source. The dose rate of gamma radiation at 6.3 kGy/h (total absorbed dose about 10^6 Gy) simulated three years alteration of solvent in real life process. Pure TBP-d_0 (1 ml) was irradiated in a sealed test tube in the presence of 10% molar ratio of the two selectively labeled or non-labeled alkylbenzenes in two series of isopropyl or diisopropylbenzene. By the same way, selectively pure deuterated TBP (250 μl) was irradiated in the presence of 10% of isopropyl or 1,4-diisopropylbenzenes.

Irradiation of TBP with additives mixture generate respectively about 5×10^{-3} mol l^{-1} of TBP–In coupling products. Each sample is diluted at 1/100 with $CHCl_3$ before analysis by GC–MS.

2.5. Mass spectrometry conditions

Chemical ionization was used in order to observed the quasi-molecular ion, not observable with electronic impact ionization. So, electronic impact was used exclusively for the detection of the In–In dimerisation products, not protonated in chemical ionisation by ammonia. All the peaks in GC–MS correspond to radiolysis products except the peak at m/z 391 mentioned in the spectra which is attributed to a phthalate.

2.6. GC–IC-MS

All mass spectra were recorded by using a triple quadrupole tandem mass spectrometer (R30-10 Nermag, France) coupled to a gas chromatograph (Delsi, France) using a 25×0.25-mm I.D. CpSil 5 CB column, film thickness 0.25 μm, inserted directly into the ion source. Helium at 1.25 bar was used as carrier gas. The on-column injector was used in these experiments in order to avoid thermal degradation of isomers at the injection point. The temperature programming was the following: injection at 50°C with a heating rate of 15°C/min until 90°C, followed by 10°C/min until 200°C and 5°C/min until 290°C, hold for 10 min. The interface was heated at 290°C. The 2 μl sample, diluted 1/100 in $CHCl_3$, was injected. The electron energy used was 70 eV, the emission current 200 μA; the electron multiplier was maintained at 50 KV, source temperature was at 100°C. Chemical ionisation gas (ammonia) pressure in the source housing was at 10^{-1} Torr.

2.7. GC–IC-MS–MS

Collision activated decomposition (CAD) was performed using argon as collision gas at 3.10^{-2} Torr, with a collision offset of −22 eV.

3. Results and discussion

Study of mechanism of inhibition, quantification and identification of the coupling TBP–In compounds obtained during radiolysis of TBP with 10% In, selectively labeled, are presented here.

3.1. Radiolysis of TBP

The radiolysis of the butyl chain of TBP generates four different alkyl radicals, as can be seen from Fig. 1a, according to Eq. (1):

$$\text{TBP–H} \xrightarrow{(\gamma)} \text{TBP}^{\cdot} + \text{H}^{\cdot} \quad (1)$$

The recombination of these radicals can produce 10 positional isomers (24 isomeric enantiomers included) [2] Eq. (2):

$$\text{TBP}^{\cdot} + \text{TBP}^{\cdot} \xrightarrow{(\gamma)} \text{TBP–TBP} \quad (2)$$

Radical stabilization [7–9] depends in the first place on the hybridisation of the C$^{\cdot}$ involved. The

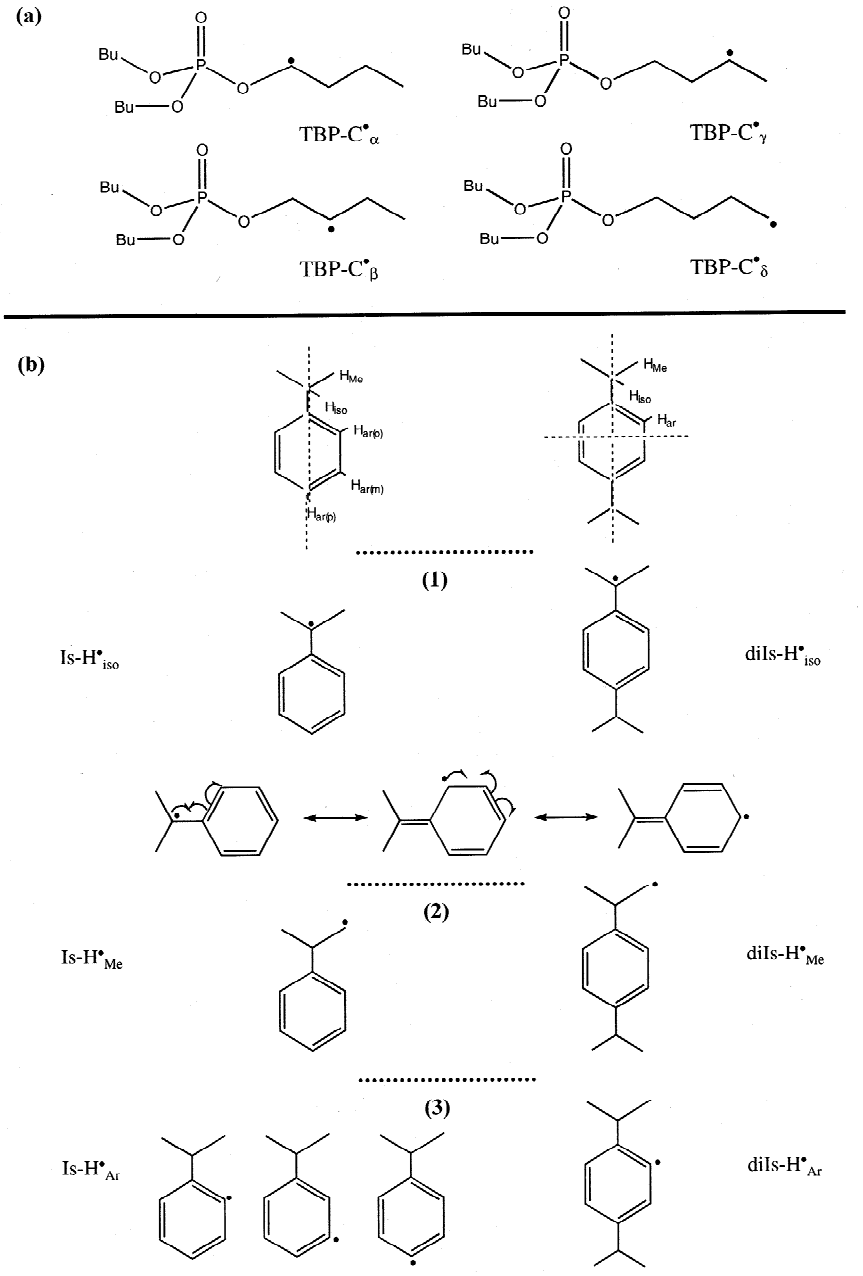

Fig. 1. Radicals formed under radiolysis: (a) from tributylphosphate (TBP); (b) from alkylbenzene–isopropylbenzene and 1,4-diisopropylbenzene.

hybridisation is the same for all four TBP radicals, thus the stability depends on the alkyl radical involved. TBP yields three secondary alkyl radicals (TBP–$C^{\cdot}_{\alpha}$, TBP–$C^{\cdot}_{\beta}$, TBP–$C^{\cdot}_{\gamma}$) and one primary alkyl radical TBP–$C^{\cdot}_{\delta}$ which is less stable than the three others (Fig. 1a). As reported from the electron spin resonance study (ESR) [8], the resonance effects (−R) or (+R) of the substituents are involved in

spin delocalization. From these three secondary radicals, TBP–$C^{\cdot}_{\alpha}$ should be the more stable because of the resonance effect from the ester oxygen non-bonding electron pairs.

All four TBP$^{\cdot}$ radicals are supposed to be formed under radiolysis, which is confirmed by the great number of isomers observed. We assumed that radicals formed did not rearrange but rather recombine rapidly with another radical in solution. The analysis of the ion profile at m/z 531, corresponding to the TBP covalent dimer formed by radical–radical recombination, showed the presence of 10 isomers having different abundance. So, the probability of formation of the TBP radicals TBP–$C^{\cdot}_{\alpha}$, TBP–$C^{\cdot}_{\beta}$, TBP–$C^{\cdot}_{\gamma}$, TBP–$C^{\cdot}_{\delta}$ under radiolysis is different. One can also considered also an equilibrium of TBP–$C^{\cdot}_{\alpha}$ and TBP–$C^{\cdot}_{\gamma}$ radicals by a rearrangement reaction but considering that radiolysis produced a large stationary concentration of radicals, such reactions can be disregarded. The comparison of the abundance of different TBP–TBP isomers did not allow a direct estimation of the ratio of radical formation on C_{α}, C_{β}, C_{γ}, C_{δ} because of the symmetric character of these recombination products. On the other hand, the abundance of the TBP–In coupling products seems to be diagnostic to the population ratio of each radical TBP$^{\cdot}$ released. It is necessary to point out that the TBP dimeric structure identification is essentially realised from deuterium labeling experiments, however the quantitative conclusions have been reached from non labeled experiments chosen as reference in every case. These experiments were made after verification of the reproducibility of results obtained in terms of abundance of different isomers under radiolysis from two radiolysis samples. The total repeatability (radiolysis and determination) was evaluated at 5%, which enabled us to discuss the variation of abundance for different isomers observed.

3.2. Radiolysis of alkylbenzene

Alkylbenzenes are considered as hydrogen donors under radiolysis by homolytic cleavage of a C–H bond as described in Eq. (3):

$$\text{In–H} \xrightarrow{(\gamma)} \text{In}^{\cdot} + \text{H}^{\cdot} \quad (3)$$

Under radiolysis, different radicals can be formed. The stability of these free radicals is related to the ability of the group directly attached to the radical to delocalise the unpaired electron. Therefore, three different radical categories are considered.

The first category concerns the formation of benzylic tertiary radical. It is easily obtained thanks to the low dissociation energy of the (C–H) bond in the isopropylic, (for isopropylbenzene about 79 kcal/mol). This benzylic tertiary radical is stabilised by resonance but still reacts easily with carbon radicals (Fig. 1b(1)).

The second category concerns the formation of a radical in methylic position which is not stabilised (Fig. 1b(2)).

The third category deals with the formation of radicals in aromatic positions. These neutral phenyl radicals are not much stabilised because they are σ radicals with small interactions with the perpendicular π system of the aromatic ring. Hence, phenyl radicals are less stable than alkyl radicals. In this case, one could also think that by irradiation an electron instead of a hydrogen atom is detached from the ring (Fig. 1b(3)).

The inhibitor dimerization, which started from the hydrogen abstraction under radiolysis, is possible according to Eq. (4) and is leading to twelve isomeric products for isopropylbenzene and only seven products for 1,4-diisopropylbenzene, as detected by GC–EI-MS thanks to the molecular ion at m/z 238 and m/z 322 respectively:

$$2\,\text{In}^{\cdot} \rightarrow \text{In–In} \quad (4)$$

3.3. Inhibition of TBP$^{\cdot}$ dimerisation

We have noticed that the radiolysis of TBP performed in the presence of alkylbenzenes leads to a diminution of TBP–TBP produced by reaction (2). Alkylbenzenes under radiolysis generate locally an important quantity of H$^{\cdot}$ by reaction (3), however, there is a competition between three radical recombination reactions for this H$^{\cdot}$ radical (5), (2) and (6). As a result, a reduction of about 50% of the total dimer formation is observed:

$$\text{TBP}^{\cdot} + \text{H}^{\cdot} \rightarrow \text{TBP–H} \quad (5)$$

$$\text{TBP}^{\cdot} + \text{In}^{\cdot} \rightarrow \text{TBP–In} \quad (6)$$

Coupling compounds resulting from reaction (6) characterised the inhibition mechanism involved. The recombination of these radicals, assuming the absence of radical rearrangements, enabled the prediction of a theoretical number of isomers as well as their assignment to specific chromatographic peaks shown in Fig. 2.

The competition between processes (5) and (6) for the radical $TBP^{\cdot}$ is obvious. However, the mobility of $H^{\cdot}$, the smallest and very labile radical and for these reasons very reactive, favours reaction (5) whereas reaction (6) implicating less reactive chemical species. Also, in solution, the addition of aromatic products protects the decomposition of TBP for instance via the ionisation transfer from TBP to the aromatic compounds [10,11].

The evaluation of the hydrogen mobility on the alkylbenzenes and differences in stability of radicals and hydrogen mobility on the TBP molecules can be evaluated by studying the isomeric coupling products obtained.

3.4. Methodology for identification of isomeric coupling products: cross coupling experiments

TBP is well protonated by ammonia during CI experiments, its proton affinity was evaluated to be 918 $kJ.mol^{-1}$. The TBP–In coupling products are also well detected by CI ammonia experiments. Diagnostic ions for the TBP and alkylbenzene radical coupling products are at m/z 385 and m/z 427 respectively for coupling with isopropylbenzene and diisopropylbenzene. The respective ion currents of these two ions are shown in Figs. 2a and 2b and marked from 1 to 14 for isopropylbenzene–TBP and 1′ to 13′ for diisopropylbenzene–TBP. Tandem mass spectrometry experiments have allowed to show that both ions, m/z 385 and m/z 427, are diagnostic of TBP–In coupling. The mass spectrometric fragmentation mechanisms of phosphate, phosphonate, and diphosphate have already been reported using an important number of techniques [12–19]. At low collision energy (22 eV), daughter spectra of the protonated molecular ion of TBP–alkylbenzene (m/z 385; m/z 427) obtained with ammonia show the most abundant fragments at m/z 211, 155 and 99 which are formed by three successive C–O bond cleavages by a sort of Mac Lafferty rearrangement characteristic of phosphate ester fragmentation. Although the C–O and P–O bonds represent the most fragile part of the molecule, C–C bond cleavages can also be achieved. Cleavages of the butyl chain are absent and only the C–C bond formation between one carbon of the TBP butyl chain and one carbon of the alkylbenzene is observed. Thus, fragments at m/z 119 (ϕ-$C^{\cdot+}(CH_3)_2$) and 217 can be respectively observed in MS–MS on MH^+ 385 and 427 as can be seen in Fig. 3. Therefore, the use of tandem mass spectrometry allows to verify that these ions are diagnostics to TBP–In products but the lack of specific fragments does not allow the discrimination and the identification of the positional isomers. For this reason the identification was undertaken by using selectively deuterated molecules.

The characterisation of all these isomers represents an important challenge. By combining GC–CI-MS and deuterium labeling experiments, the localisation of the C–C bond between $TBP^{\cdot}$ and $In^{\cdot}$ was investigated. The ionisation yields are supposed to be similar for a series of isomers because the pseudo-molecular ions (MH^+) are produced through exothermic reactions at the collision frequency. Moreover, with the small injected quantity and the sharp chromatographic peak shape, the peak surfaces can be related to the concentration in solution. For all these reasons, one should assume that for a series of isomeric compounds, the measurement of peak surface gives an accurate idea on the proportion of the different isomers in solution. Thus, the largest peak corresponds to the major radical formed under radiolysis. This relation was realised exclusively from the protio mixture in order to avoid deuterium isotope effect. Therefore, the approach was realised in two steps: (i) identification of all the isomers by using a selectively deuterated mixture, (ii) position of the preponderant radical involved with the protio mixture.

The attribution of the specific GC peaks (1 to 14) and (1′ to 13′) for two inhibitors could be reached by using a cross coupling experiments methodology. During the same irradiation period, three sets of experiments were realized simultaneously, (i) irradiation of the unlabeled inhibitor/TBP mixture, (ii) irradiation of the selectively labeled TBP/unlabeled inhibitor mixture, (iii) irradiation of unlabeled TBP/selectively labeled inhibitor mixture. The non-

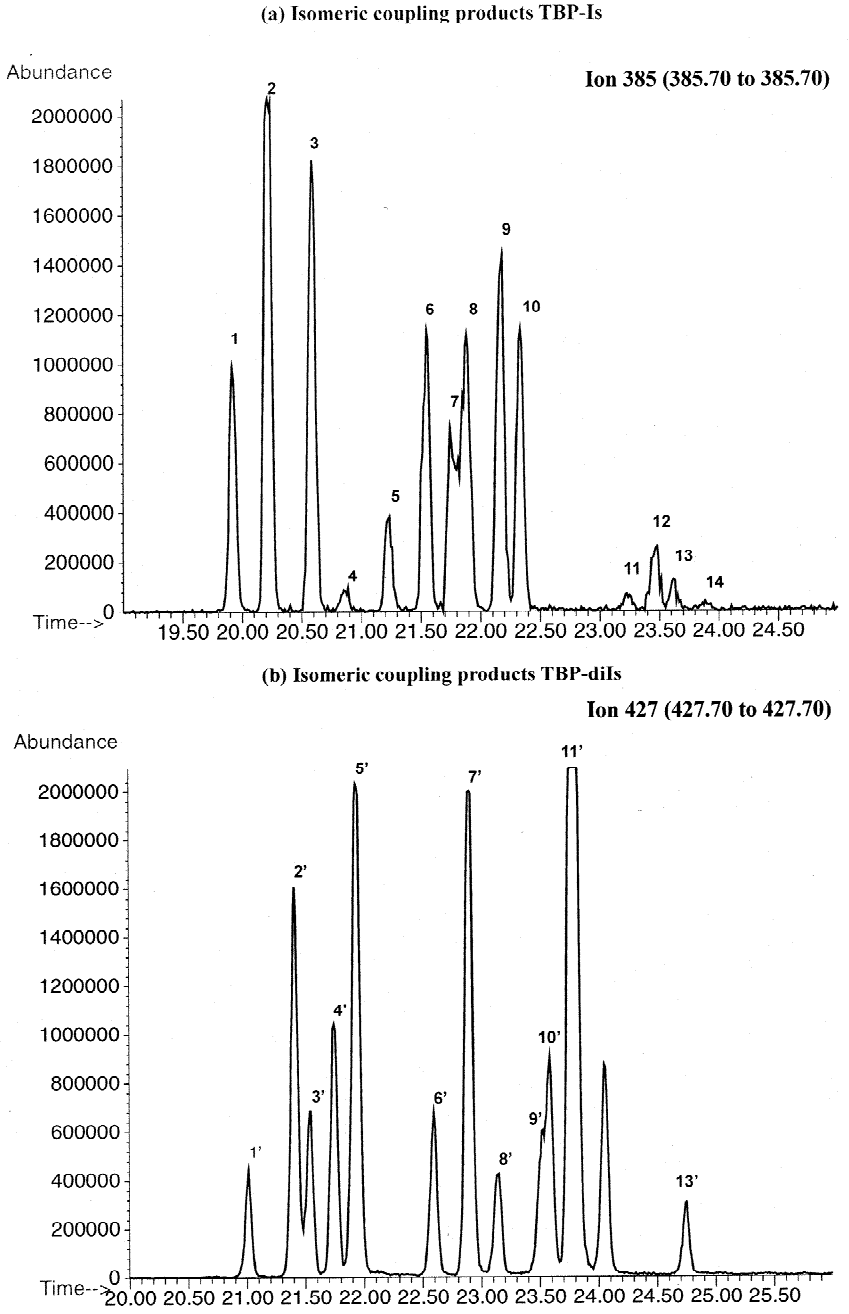

Fig. 2. Isomeric-coupling products separated by gas chromatography under NH_3-chemical ionization (GC/NH_3-CI-MS experiments, CPSil-5CB): (a) TBP–isopropylbenzene (MH^+, 385) isomers designed from 1 to 14; (b) TBP–1,4diisopropylbenzene (MH^+, 427) isomers designed from 1′ to 13′.

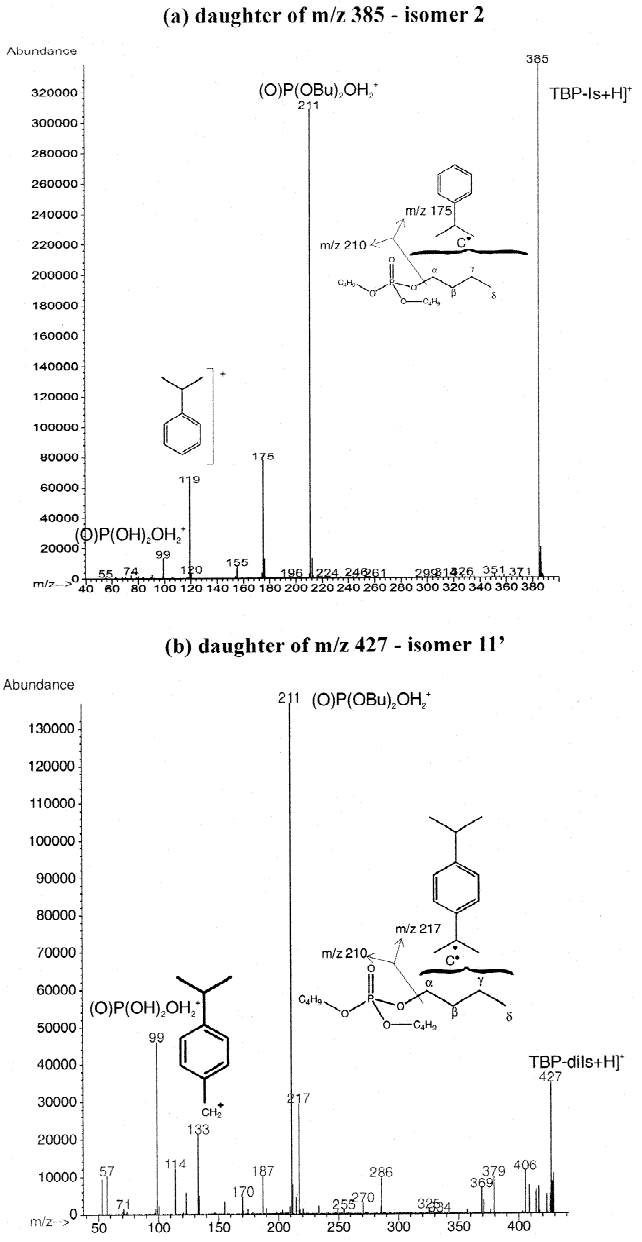

Fig. 3. Low energy collision induced dissociation spectra (E lab 22 eV); (a) MH^+, 385 formed by NH_3-chemical ionization from component 2 in Fig. 2; (b) MH^+, 427 formed by NH_3-chemical ionization from component 11′ in Fig. 2.

labeled mixture (i) is used as reference for quantitative measurements. The second one gives some evidence on the mobility of the different hydrogen atoms in the TBP molecule and therefore allows evaluation of the probability of each radical formation. Finally, the third one can give some evidence on the mobility of different hydrogen atoms in the inhibitor. The characterisation of the isomers was established by using four labeled TBP (three d_6 and one d_9) and three labeled isopropylbenzenes (d_1, d_6,

d_7) and one diisopropylbenzene (d_2). The analysis consisted in screening under CI/NH_3 GC–MS, MH^+ ion at m/z 385, 427 and by using the higher mass isomers obtained in separate experiments to determine the coupling localisation. The essential element of the identification was the abstraction of either H or D. The C–C bond formed between the TBP and the inhibitor can involve either two protonated or one protonated and one deuterated carbon. The sweeping of the GC with these masses leads to the identification of alkylphenyltributylphosphate isomers from these cross coupling experiments.

3.5. Cross coupling between selectively deuterated tbp and unlabeled alkylbenzene

The mass of the pseudo molecular ion expected for the different coupling products between selectively labeled TBP and inhibitors are shown in Table 1. The ionic current chromatogram of the mixture containing the unlabeled compounds was used, for both inhibitors tested, as the reference (Fig. 2a, 2b). The chromatogram for selectively deuterated experiments compared to the witness chromatogram allowed to attribute most of the peaks observed. Thus, the pseudo molecular mass ion resulting from coupling between a secondary radical of TBP (TBP–$C^{\cdot}_{\alpha}$, TBP–$C^{\cdot}_{\beta}$, TBP–$C^{\cdot}_{\gamma}$) with isopropylbenzene is 391 when the radical is formed by an H abstraction, and 390 when the radical is formed by a D abstraction. For a primary radical, the expected masses are m/z 394 for an H abstraction, and m/z 393 for a D abstraction. Thus, following this analysis, peaks 1, 2, 3 can be attributed to TBP–$C^{\cdot}_{\alpha}$, peaks 4,5,6,7 to TBP–$C^{\cdot}_{\beta}$and 11, 12, 13, 14 to TBP–$C^{\cdot}_{\delta}$ coupling. Consequently, remaining peaks 8, 9, 10 were attributed to TBP–$C^{\cdot}_{\gamma}$ isomers (Fig. 4). From the observation of the witness mixture based on the surface peak (Fig. 2a), it is possible to conclude that the preponderant radicals formed are respectively those coming from α and γ positions on the TBP butyl chain.

TBP–$C^{\cdot}_{\alpha}$ coupled with isopropylbenzene is the most abundant which is related to the stable character of the radical stabilised by resonance. The difference between TBP–$C^{\cdot}_{\beta}$ and TBP–$C^{\cdot}_{\gamma}$ radicals, respectively the second and third in abundance of recombination products, could be explained on the basis of better stabilisation of the radicals on C_{γ} (six-member ring) and on C_{β} (five-member ring). The stabilisation of such radicals [20–22] is possible in terms of Mac Lafferty like transition states and was already suggested both from spectral ESR studies and theoretical calculations.

The elution order for coupling products, related to the bonding between the inhibitor and TBP, follows the order α, β, γ, and δ. In this manner, it was possible to roughly assign four GC peak clusters to the four TBP radicals formed.

By the same method, identification of isomeric coupling products of TBP and diisopropylbenzene was undertaken. Peaks 2′, 3′, 4′, were assigned to the recombination with TBP–$C^{\cdot}_{\alpha}$ (Fig. 5a), the peaks at 1′, 6′, 7′, to TBP–$C^{\cdot}_{\beta}$ (Fig. 5b), finally peaks 5′,

Table 1
Pseudomolecular ion mass MH^+ expected in GC/MS experiments for bonding of TBP and alkylbenzene radicals under radiolysis: all protio (d_0); selectively deuterated TBP (d_n); selectively deuterated alkylbenzene Is (d_n)

In$^{\cdot}$	TPB$^{\cdot}$	TBP-d_0	(-H)	$TBPC_{\alpha}$-d_6 $TBPC_{\beta}$-d_6 $TBPC_{\gamma}$-d_6	(-D)	(-H)	$TBPC_{\delta}$-d_9	(-D)
Is-d_0		$MH^+=385$	$MH^+=391$		$MH^+=390$	$MH^+=394$		$MH^+=393$
Is-d_1	(-H)	$MH^+=386$						
	(-D)	$MH^+=385$						
Is-d_6	(-H)	$MH^+=391$						
	(-D)	$MH^+=390$						
Is-d_7	(-H)	$MH^+=392$						
	(-D)	$MH^+=391$						
diIs-d_0		$MH^+=427$	$MH^+=433$		$MH^+=42$	$MH^+=436$		$MH^+=435$
diIs-d_2	(-H)	$MH^+=429$						
	(-D)	$MH^+=428$						

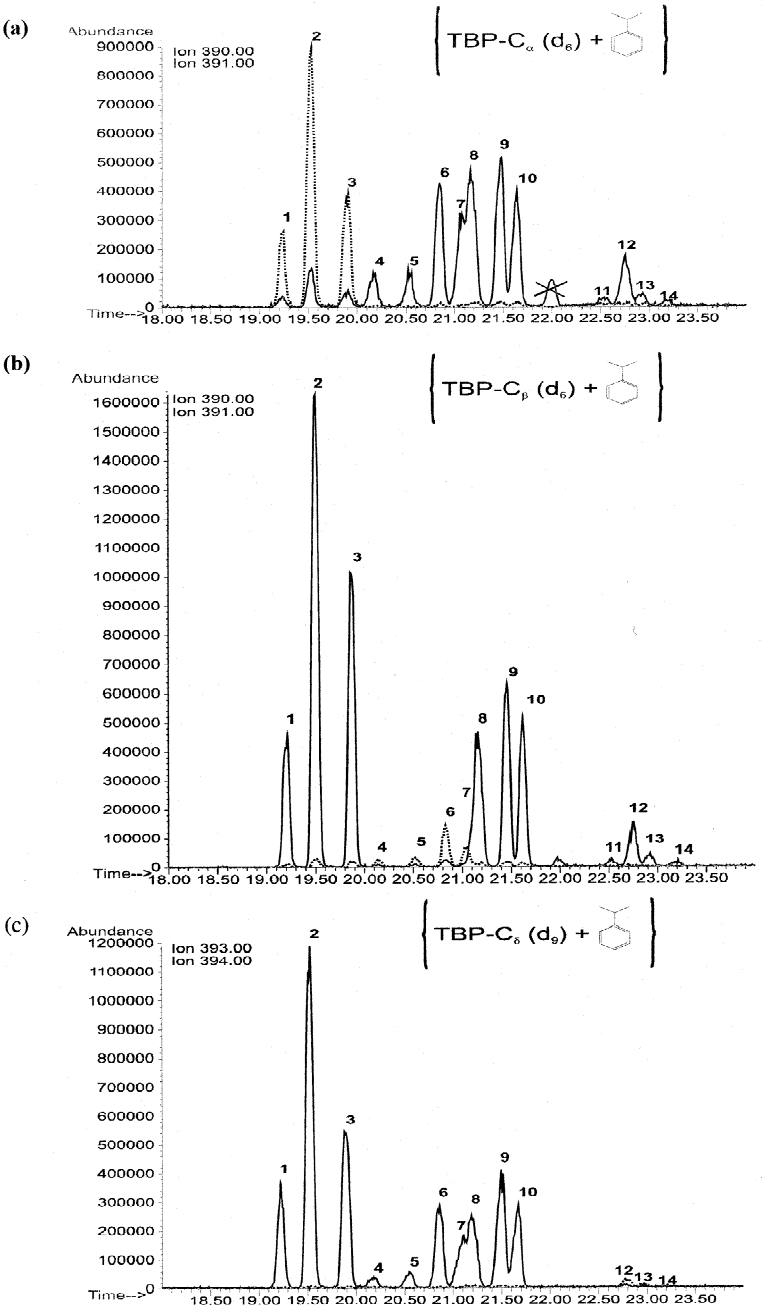

Fig. 4. Ionic current of selectively labeled coupling products; (a) TBP–C_{α}(-d_6)-Is(-d_0): (MH^+, 390 D abstraction); (MH^+, 391 H abstraction); (b) TBP–C_{β}(-d_6)-Is(-d_0): (MH^+, 390 D abstraction); (MH^+, 391 H abstraction); (c) TBP–C_{δ}(-d_9)-Is(-d_0): (MH^+, 393 D abstraction); (MH^+, 394 H abstraction).

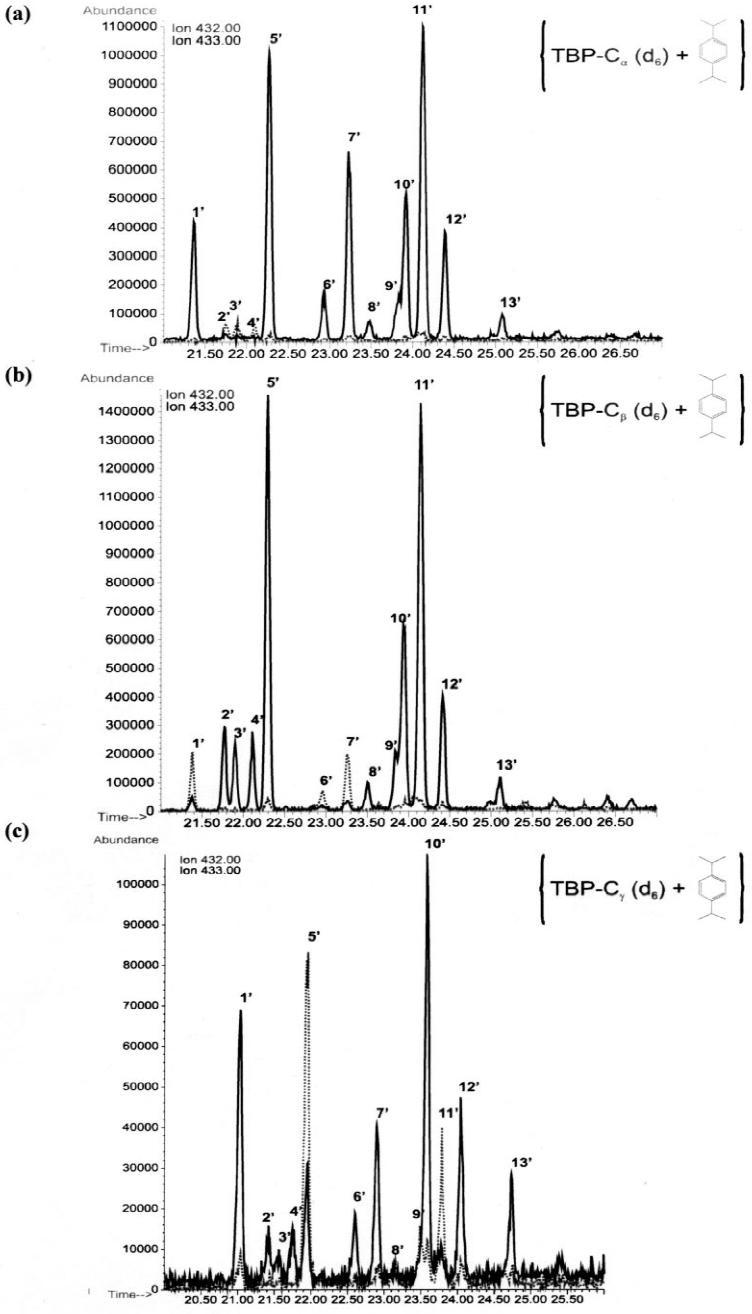

Fig. 5. Ionic current of selectively labeled coupling products; (a) TBP–C_{α}(-d_6)-diIs(-d_0): (MH^+, 432 D abstraction); (MH^+, 433 H abstraction); (b) TBP–C_{β}(-d_6)-diIs(-d_0): (MH^+, 432 D abstraction); (MH^+, 433 H abstraction); (c) TBP–C_{γ}(-d_6)-diIs(-d_0)(MH^+, 432 D abstraction); (MH^+, 433 H abstraction).

8′, 9′, 11′, to TBP–$C^{\cdot}_{\gamma}$ (Fig. 5c), and the last group of peaks 10′, 12′, 13′ to TBP–$C^{\cdot}_{\delta}$ (Fig. 5c).

In this group of compounds, the most abundant isomers were those for the C_{γ} position instead of the expected C_{α} isomers. Another factor affecting isomeric radical coupling to the inhibitor is here, the hindrance from the phosphate moiety, which is particularly important for coupling on C_{α} with an isopropyl group. These interactions are only of secondary importance for C_{β} and C_{γ}. This observation enabled us to choose between C_{β} and Cγ originated products with an unambiguous identification of these isomers.

3.6. Cross coupling between selectively deuterated alkylbenzene and unlabeled TBP: determination of the position of coupling to the inhibitor

The different recombination products detected and their molecular mass are summarised in Table 1. The ionic current chromatogram of all-protio products was used as a reference spectrum in this assignment (Fig. 2b). For isopropylbenzene (-d_6 and -d_7), the general shape of the chromatogram is different than for the protio profile. The difference in chromatographic profile and the retention time variation observed for coupling products bearing larger number of deuterium atoms is related to the possibility of D/H exchange on the inhibitor level. This phenomenon explains the variation of the shape of the chromatogram. Nevertheless, some peaks can be easily assigned. As can be seen from Fig. 6a, the pseudomolecular MH^+ 391 ions correspond to the recombination product with the loss of a D from the inhibitor which allows to locate the coupling both on isopropylic and methylic position while MH^+ 392 ions are characteristics to a recombination implicating the aromatic positions. The analysis of case (b) allows to discriminate peaks identifying methylic and isopropylic positions. Peaks 1, 3, are then assigned to coupling on the methylic position and peaks 2, 7, 9, 10, 12 on isopropylic position and the others to aromatic position. The exact determination of the aromatic carbons bearing the TBP radical position (o, m, p) are impossible without a specific deuteration of the aromatic ring which was considered outside the scope of this work.

For 1,4-diisopropylbenzene (d_2) Fig. 6c, the general shape of the chromatogram is similar to the protio one. It was possible then to assign peaks 2′, 3′, 4′, 6′, 7′, 8′, 9′, 11′, 12′ to a coupling with isopropyl while isomers 1′, 5′, 10′, 13′ were assigned to the coupling on the aromatic level assuming that there is practically no coupling via the C_{Me} position. For isopropylbenzene, peaks 5′ and 11′ are quite important and they correspond respectively to isopropyl and to aromatic position couplings.

4. Conclusion

Radical inhibitors such as alkylbenzene have been used in order to reduce the formation of TBP–TBP dimers during the radiolysis of TBP. In the presence of such hydrogen-donating agents, the concentration of the TBP–TBP is reduced by about 50%. However, this diminution is not strictly followed by a quantitative regeneration of TBP. In fact, some heterocoupling products such as TBP–In are detected. The mechanism envisaged consists of radical radical combination of $TBP^{\cdot}$, $In^{\cdot}$ and $H^{\cdot}$ during radiolysis. This constitutes a simplification because it does not take into account bimolecular reaction between TBP, In and their radicals. These reactions have been considered as minor in this study. Moreover, from TBP–In heterocoupling products, the possibility to deduce the major TBP radical formed under radiolysis has been shown. The analysis of the protio mixture allows to determine the most important isomers and by this way to deduce the preponderant TBP radical involved. Finally, the use of cross coupling experiments with selectively deuterium labeled compounds allowed to characterise the isomeric products resulting from $TBP^{\cdot}$ and $In^{\cdot}$ recombination under radiolysis. All identifications are summarised in Table 2. The most abundant isomers involve the C_{α} and C_{γ} position on TBP and both isopropyl and aromatic positions on the inhibitor.

For isopropylbenzene, peaks 1, 2, 3 are assigned to TBP–C_{α} –H_{iso} and peaks 9, 10 to TBP–C_{γ} –H_{iso} while peak 8 corresponds to TBP–C_{γ}–H_{ar} association. For diisopropylbenzene, coupling is favoured on γ compared to α carbon certainly due to steric effect. The most abundant isomers, corresponding to peaks 5′, 7′, 11′ are respectively identified as TBP–C_{α}–H_{ar}, TBP–C_{β}–H_{iso}, TBP–C_{γ} –H_{iso} but no

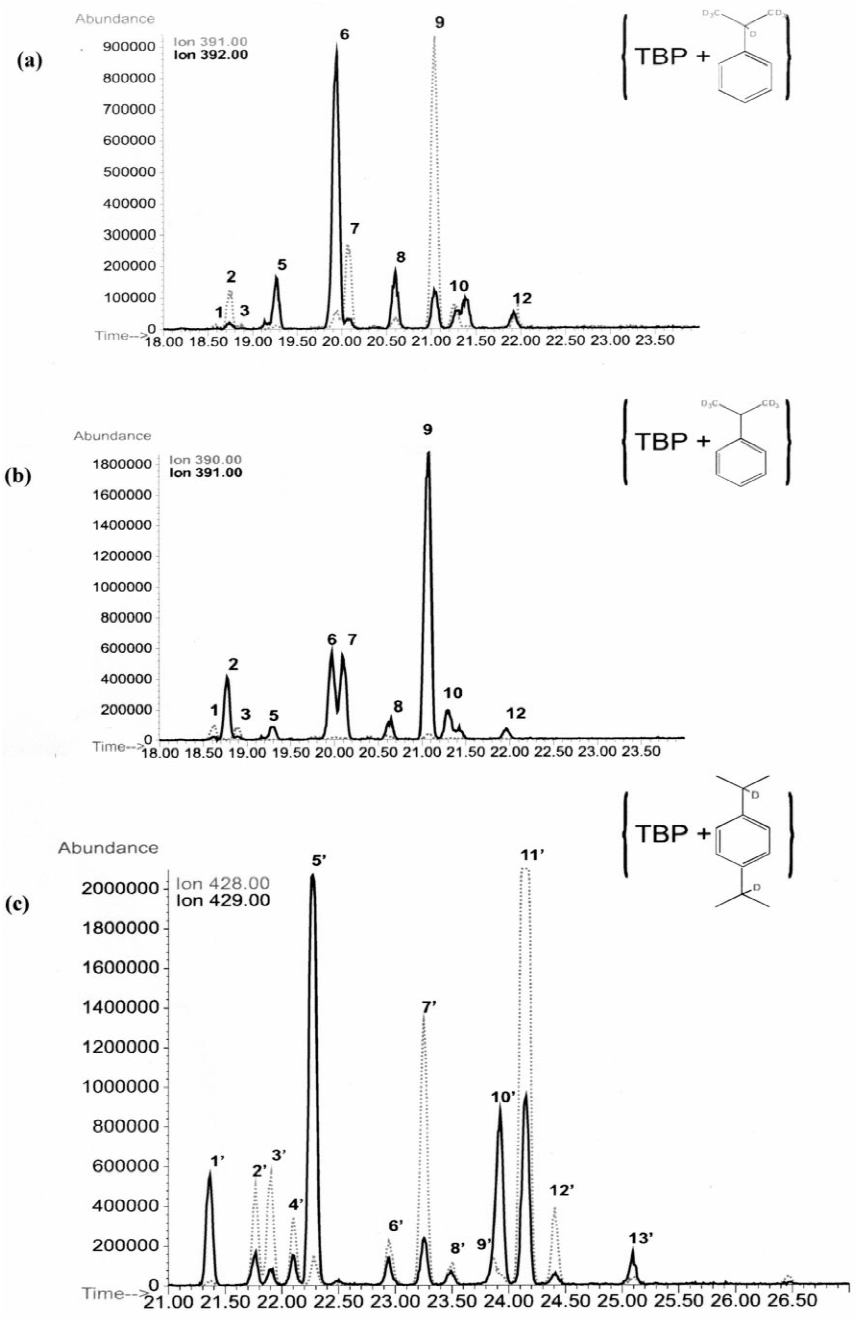

Fig. 6. Ionic current of selectively labeled coupling products; (a) TBP (-d_0)-Is(-d_7): (MH^+, 391 D abstraction); (MH^+, 392 H abstraction); (b) TBP (-d_0)-Is(-d_6): (MH^+, 390 D abstraction); (MH^+, 391 H abstraction); (c) TBP (-d_0)-diIs(-d_2): (MH^+, 428 D abstraction); (MH^+, 429 H abstraction).

Table 2
Identification of TBP-alkylbenzene coupling products related to the chromatographic (X) peaks shown in Fig. 2

TBP-Isopropylbenzene				
$TBP^{\cdot}$	$In^{\cdot}$	$H^{\cdot}_{iso}$	$H^{\cdot}_{Ar}$	$H^{\cdot}_{Me}$
$TBP–C^{\cdot}_{\alpha}$		2		1; 3
$TBP–C^{\cdot}_{\beta}$			5; 6	4
$TBP–C^{\cdot}_{\gamma}$		7; 9; 10	8	
$TBP–C^{\cdot}_{\delta}$			12	11; 13; 14
TBP-di-Isopropylbenzene				
$TBP^{\cdot}$	$In^{\cdot}$	$H^{\cdot}_{iso}$	$H^{\cdot}_{Ar}+H^{\cdot}_{Me}$	
$TBP–C^{\cdot}_{\alpha}$		2′; 3′;4′		
$TBP–C^{\cdot}_{\beta}$		6′; 7′	1′	
$TBP–C^{\cdot}_{\gamma}$		11′; 8′; 9′	5′	
$TBP–C^{\cdot}_{\delta}$		12′	10′; 13′	

couplings in α position are observed with the aromatic sites for both alkylbenzenes. Two factors can explain these results: (i) the steric hindrance effect; (ii) the proximity of the oxygen to the radical site.

Despite all these unambiguous identifications, some small peaks are difficult to assign. One possible explanation is the labeling level and the D/H exchange, quite uncontrolled under radiolysis, which is slightly stronger on activated carbons. Also, because of the quite important natural abundance isotopic peaks, the $^{13}C_{\alpha}$ signals could partially overshade those of $^{12}C_{\beta}$ isomers. Some of the peaks, because of the presence of chiral carbons, could also form two peaks.

The analysis of coupling products formed in solution via a simple technique such as GC–MS enabled to establish the ratio of different radicals formed. It is interesting to mention here that these results are similar to those obtained by ESR (Electron Spin Resonance) at low temperature in frozen matrices [20,21].

Localisation of the preferentially formed radicals has been realised by identifying these isomers. This methodology can probably be extended to define the preponderant radicals formed under radiolysis of other complex mixtures.

Acknowledgements

We would like to thank S. Banet, S. Robine and D. Lesage for their implication in the primary stages of this work, Ch. Dardonville and J. Boivin for the synthesis of some labeled molecules and professor J.C. Tabet for mass spectrometric advice.

References

[1] D. Lesage, H. Virelizier, C.K. Jankowski, Spectroscopy 13 (1997) 275.
[2] D. Lesage, H. Virelizier, C.K. Jankowski, Eur. Mass. Spectrom. (1998) 47.
[3] V.M. Adamov, V.I. Andreev, B.N. Belyaev, G.S. Markov, M.S. Polyakov, A.E. Ritari, A.Yu. Shil'nkov, Kerntechnik 3 (1990) 55.
[4] V.M. Adamov, V.I. Andreev, G.S. Markov, M.S. Polyakov, A.E. Ritari, A.Yu. Shil'nikov, Radiokhimiya 34 (1992) 189.
[5] C. Pozo, Applications de la chromatographie d'exclusion stérique à la séparation de produits de dégradation du solvant du retraitement des combustibles nucléaires, CEA Research Reprt CEA-R-5647 (1993).
[6] M. Brookhart, B.E. Grant, J. Am. Chem. Soc. 115 (1993) 2151.
[7] J. Kochi (Ed.), Free Radicals, A. Wiley, Interscience Publication, 312.
[8] J.M. Hay (Ed.), Reactive Free Radicals, Academic Press London (1974) 76.
[9] M. Lazar, J. Ryehly (Eds.), Free Radicals in Chemistry and Biology, CRC Press, Boca Raton (1989) 195.
[10] G.F. Egorov, A.P. Ilozhev, A.S. Nikiforov, V.S. Smelov, V.B. Shevchenko, V.S. Shidt, Atomnaya Energiya 47 (1979) 75.
[11] J. Canva, M. Pages, Radiochim. Acta. 4 (1965) 2.
[12] K. Barelko, M. Nowack, Nucleonika 31 (1986) 10.
[13] J. Quayle, Adv. in Mass Spectrum. (1959) 365.
[14] P.A. Cload, D.W. Hutchinson, Org. Mass. Spectrom. 18 (1983) 57.
[15] P.A. D'Agostino, L.R. Provost, Biomed. Environ. Mass Spectrum. 18 (1986) 57.

[16] P.A. D'Agostino, L.R. Provost, J. Chromatogr. 670 (1994) 127.
[17] S. Harden, A.P. Snyder, G.A. Eicemen, Org. Mass. Spectrom. 28 (1993) 585.
[18] J.C. Ingram, G.S. Groenwold, A.D. Appelhaus, D.A. Dahl, J.E. Delmore, Anal. Chem 68 (1996) 1309.
[19] G.S. Groenwold, J.C. Ingram, J.E. Delmore, A.D. Appelhaus, J. Am. Soc. Mass Spectrom. 6 (1995) 165.
[20] J. Kuruc, V.E. Zubarev, L.T. Bugarenko, F. Macasek, J. Radioanal. Nucl. Chem. Lett. 127 (1998) 37.
[21] A. Vashman, Yu.I. Savel'ev, Radiokhimiya 12 (1970) 12.
[22] V.P. Arkhipov, M.P. Votinov, V.N. Romanovskii, A.M. Seushiri, Khim. Vys. Energi 4 (1970) 362.