

Review Commentary

Fragmentation reactions of radical cations

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ABSTRACT: This paper summarizes most of the recent work by our group on the kinetic aspects of a variety of fragmentation reactions of radical cations involving the cleavage of C—H, O—H, C—C, and C—S bonds. In particular, the problems that have been addressed concern: (a) the carbon acidity/oxygen acidity dichotomy in the fragmentation of aryl- and thioarylalkanol radical cations; (b) the decarboxylation of aryl and thioarylacetic acid radical cations; (c) the structural factors influencing the rate of C—S bond cleavage in the radical cations of phenyl alkyl sulfides. The results presented and discussed have allowed us to recognize the important role played by the electron reorganization energy, associated with the intramolecular electron transfer from the scissile bond to the SOMO, with respect to the dynamics and mechanism of the fragmentation process in the radical cation. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: radical cations; fragmentation; oxidation; electron transfer; alkylaromatics; arylalkanol; aromatic sulfides

INTRODUCTION

One of the most important transformations in a radical cation is that involving the cleavage of a bond with formation of a cation and a radical (radical cation fragmentation). This process is much easier than in the neutral parent substrate due to the strong electron withdrawing effect of the positive charge. The bond more frequently involved is the one in the β position with respect to the center of positive charge (β -bond) as shown in Scheme 1.

Accordingly, this bond can efficiently overlap with the SOMO of the radical cation (Scheme 2, where Z is generally an aromatic moiety or a heteroatom, that is a species with a relatively low-ionization potential). However, as we will see, the cleavage of bonds in different positions is also possible. The C—H, C—C, C—S, and C—Si bonds are the ones most commonly involved in the fragmentation reactions of radical cations.^{1–5}

These reactions that imply an intramolecular electron transfer from the σ bond to be broken to the SOMO of the radical cation have been the object of intense research since long due to their mechanistic and technological aspects. The mechanistic aspects concern the dynamics of the cleavage, the need or not of a nucleophilic assistance, the stereochemistry, the connection between

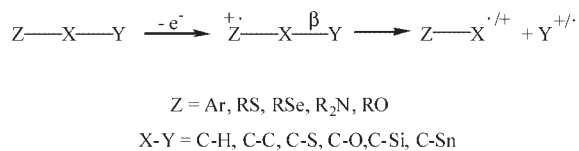
electron transfer and radical and acid base properties, the relative reactivity of the breakable bonds, and the possible role of these reactions in biological processes. The practical and technological aspects concern the organic synthesis,^{6,7} the initiation of free radical polymerization,⁸ and the enhancement in the efficiency of the photo-sensitization processes.⁹

We have been interested in this chemistry since long and a review of our previous work has been published few years ago.¹⁰ In the present paper we will describe our most recent results that, as the previous ones, came from pulse and γ -radiolysis (for reactions in water) and sensitized laser and steady state photolysis (for reactions in organic solvents) investigations. The principles of these well-known techniques are summarized in Scheme 3 (Sub = substrate, S = sensitizer).

FRAGMENTATIONS INVOLVING C—H BOND CLEAVAGE

Certainly, one of the most important fragmentation reactions of a radical cation is the one involving the cleavage of a C—H bond. In the gas phase, this cleavage leads to a hydrogen atom and a carbocation (homolytic cleavage, Scheme 4, path a), but the outcome drastically changes in solution where instead a carbon radical and a solvated proton are generally formed (heterolytic cleavage, Scheme 4, path b), the radical cation behaving as a carbon acid.⁵

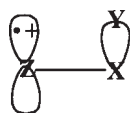
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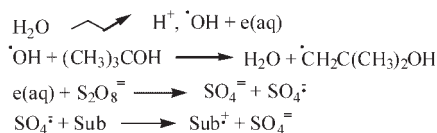
Scheme 1

One of the most studied cases of heterolytic cleavage in solution concerns the C—H bond cleavage of alkylaromatic radical cations (Scheme 4, Z = aryl). This process is very important for two main reasons. First, acidity/structure relationships can be dealt with into the theoretical framework of the carbon acidity. Second, this process represents the key step in the one electron transfer side-chain oxidation of alkylaromatics, a reaction of practical interest as it leads to aromatic aldehydes with high selectivity. As a consequence, much attention has been devoted so far to the practical and theoretical aspects of the kinetic and thermodynamic carbon acidity of alkylaromatic radical cations.^{11–13} In this paper, therefore, we will make only some brief considerations in this respect.

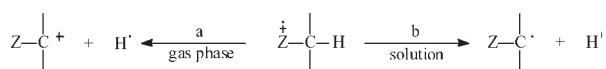
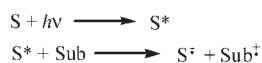
Generally, alkylaromatic radical cations are very strong carbon acids in solution. Accordingly, by a thermochemical cycle¹⁴ it is possible to calculate a pK_a value of –13.5 for toluene radical cation (**1**^{•+}) in MeCN. Of course, the pK_a value becomes less negative (acidity decreases) when electron-donating substituents that decrease the reduction potential of the radical cation are introduced in the ring. For example, 4-methoxytoluene radical cation (**2**^{•+}) is still a strong acid (pK_a = –4.3) but weaker than **1**^{•+}. For structurally related radical cations, kinetic acidity parallels thermodynamic acidity, as can be seen from the kinetic data for **1**^{•+} and **2**^{•+} in water (obtained by pulse radiolysis) reported in Figure 1.^{16,17} In the same figure, it can also be



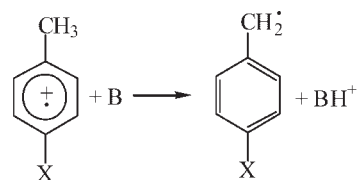
Scheme 2

Pulse and γ -radiolysis

Sensitized photolysis (laser and steady state)



Scheme 4



	$E_{\text{red}}(\text{vsSCE})$	$\text{p}K_{\text{a}}(\text{MeCN})$	$k_{\text{H}_2\text{O}}(\text{s}^{-1})$	$k_{\text{OH}^-}(\text{M}^{-1}\text{s}^{-1})$
X = H	2.39	-13.5	3×10^6	$> 10^8$
X = OCH ₃	1.71	-4.3	4×10^2	5.5×10^7

Figure 1. Relevant data for the deprotonation of toluene (**1**^{•+}) and 4-methoxytoluene (**2**^{•+}) radical cations. The kinetic data are in H₂O (text). The oxidation potentials are in MeCN²⁰

seen that the kinetic acidity is very sensitive to the strength of the base, increasing by about 5 powers of 10 as we move from H₂O to ⁻OH.¹⁸

However, the situation can change when the comparison concerns structurally unrelated systems. Thus, the deprotonation rate of thioanisole radical cation (**3**^{•+}) by ⁻OH in water²¹ is very close to that of **2**^{•+} in spite of the fact that the former is more than 7 pK_a units less acid than the second (Figure 2).

Probably, this is due to differences in the reorganization energy required for the intramolecular electron transfer that must accompany bond cleavage. **3**^{•+} should be a more localized radical cation than **2**^{•+}, having the SOMO mostly centered on sulfur. Thus, it is likely that a smaller extent of electron reorganization is necessary for the deprotonation of **3**^{•+} than for that of **2**^{•+}. Very interestingly, when a much weaker base (H₂O) is used, kinetic acidity turns out to be parallel to the thermodynamic acidity, the deprotonation rate constant being much higher with the stronger acid (**2**^{•+}), as reported in Figure 2.^{17,21} A possible explanation is that the role of electron reorganization is dominant with a strong base, whereas the thermodynamic factor becomes the most important one when the base is weaker. We will return on this point more in detail later on.

It is also important to remind that deprotonation of a radical cation is subject to stereoelectronic control as the C—H bond has to be aligned with the SOMO of the

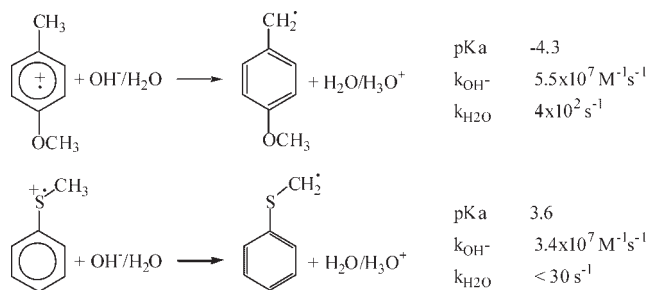
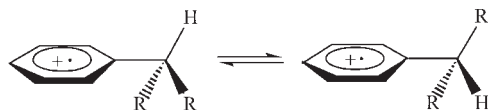


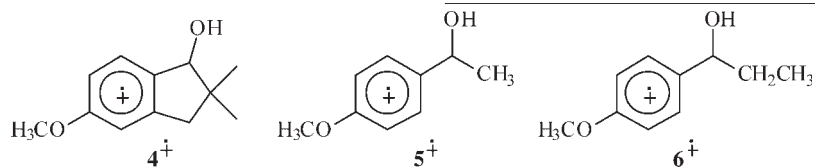
Figure 2. Kinetic and thermodynamic parameters for the deprotonation of 4-methoxytoluene (**2**^{•+}) and thioanisole (**3**^{•+}) radical cations. The kinetic data are in H₂O. The pK_a values¹⁴ are in MeCN. The oxidation potential of **3** in MeCN is taken as 1.47 V/SCE²²



Scheme 5

radical cation in the preferential conformation for C—H bond cleavage (Scheme 2, X=C, Y=H). When this conformation cannot be reached, the deprotonation rate is slowed down significantly. For the case of alkylaromatic radical cations, the preferred conformation for the cleavage is that with the C—H bond perpendicular to the plane of the aromatic ring (Scheme 5).

Considerable evidence in favor of the stereoelectronic effects is available in the literature.^{23–25} Additional information in this respect has been recently obtained through the study of the reactivity of 2,2-dimethyl-5-methoxyindan-1-ol radical cation ($4^{\cdot+}$), in acidic aqueous solution ($\text{pH} \leq 4$).²⁶

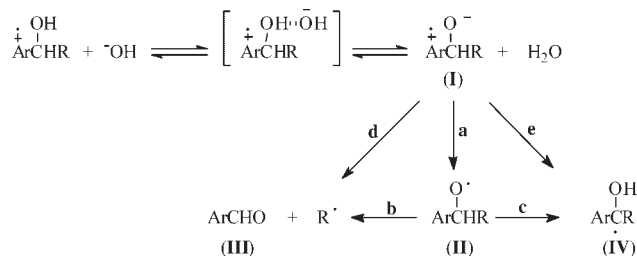


DFT calculations have shown that the most stable conformation for $4^{\cdot+}$ is that in which the scissile C—H bond is almost aligned with the π -system. Thus, $4^{\cdot+}$ undergoes C—H deprotonation as the exclusive reaction with $k = 4.6 \times 10^4 \text{ s}^{-1}$, a value that is significantly higher than those measured for the deprotonation of both 1-(4-methoxyphenyl)ethanol ($5^{\cdot+}$) and 1-(4-methoxyphenyl)propan-1-ol ($6^{\cdot+}$) radical cations under analogous experimental conditions ($k = 7.0 \times 10^3$ and $5.4 \times 10^3 \text{ s}^{-1}$, respectively).²⁷ With both $5^{\cdot+}$ and $6^{\cdot+}$, the most stable conformation is not the one most suitable for C—H bond cleavage and energy has to be spent to reach the alignment between the C—H bond and the π -system.

FRAGMENTATIONS INVOLVING O—H BOND CLEAVAGE

(a) 1-arylalkanol radical cations

An interesting development of our studies was the discovery that in aqueous solution radical cations from 4-methoxybenzyl alcohol ($7^{\cdot+}$) and derivatives undergo a pH-dependent mechanistic dichotomy. Whereas at $\text{pH} \leq 5$ the radical cations undergo direct C_α —H deprotonation behaving as *carbon acids*, in basic solution a diffusion-controlled deprotonation from the alcoholic α —OH group takes place and the radical cations behave as *oxygen acids*. On the basis of the results of several investigations, the mechanism described in Scheme 6



Scheme 6

(Ar = 4-MeOC₆H₄) has been proposed for the fragmentation initiated by α —OH deprotonation.²⁷

Deprotonation from the α —OH group of the radical cation leads to a radical zwitterion (**I**). By intramolecular electron transfer (IET) from the side-chain —O[−] to the aromatic π -system **I** forms an alkoxy radical (**II**, path a) which can undergo C—C β -scission (path b) leading to 4-methoxybenzaldehyde (**III**) and a radical R and/or

1,2-hydrogen shift (path c)²⁸ to give an α -hydroxy-4-methoxybenzyl radical (**IV**), depending on substrate structure.

The occurrence of path a was clearly demonstrated for 4-methoxycumylalcohol radical cation ($8^{\cdot+}$), a species where only C—C bond cleavage is possible.²⁹ However, it could not be excluded that with other substrates the radical zwitterion may undergo IET coupled with C—C bond cleavage (path d) or with 1,2-hydrogen shift (path e).

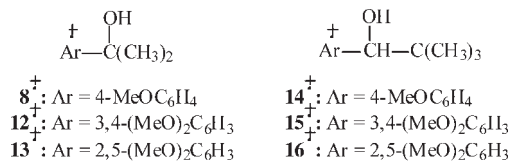
In order to get further information on this point it was deemed interesting to determine the influence of the radical cation stability. Thus, we extended our study to ring dimethoxylated and trimethoxylated 1-arylalkanol radical cations that form radical cations significantly more stable than those generated from 1-(4-methoxyphenyl)alkanol.³⁰

The [−]OH-induced decays of 3,4-dimethoxybenzyl alcohol ($9^{\cdot+}$) and 2,5-dimethoxybenzyl alcohol ($10^{\cdot+}$) radical cations occur with rate constants that are significantly higher than those measured for the corresponding methyl ethers, showing that also in this case the reaction is initiated by α —OH deprotonation. However, whereas with the 4-methoxybenzyl alcohol radical cation ($7^{\cdot+}$) the reaction was diffusion controlled, with both $9^{\cdot+}$ and $10^{\cdot+}$, lower rate constants were measured and significant kinetic deuterium isotope effects (between 3.2 and 3.7) were observed. These observations led to the suggestion that in these radical cations the energy barrier for the side-chain to ring IET in the corresponding radical zwitterions is probably higher as compared to that in $7^{\cdot+}$. Thus the IET might be coupled with the 1,2-H atom shift

directly leading to the carbon-centered radical (path e in Scheme 8) and no intermediate benzyloxy radical is formed.

Differently than the dimethoxylated systems 2,4,5-trimethoxybenzyl alcohol radical cation (**11**⁺) reacted with ⁻OH at the same rate as that of its methyl ether ($k \approx 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$), clearly suggesting that in this case there is no longer O—H deprotonation, but direct C—H deprotonation has taken over. Such a shift from oxygen to carbon acidity is probably due to the increased stabilization of the positive charge on the trimethoxylated aromatic ring that determines a further increase in the energy barrier for the IET in the radical zwitterion.

The effect of a second methoxy group in the aromatic ring has also been investigated in processes where O—H deprotonation appears to induce C—C bond cleavage. Thus, the reactivity of 3,4-dimethoxycumyl alcohol (**12**⁺), 2,5-dimethoxycumyl alcohol (**13**⁺), 1-(3,4-dimethoxyphenyl)-2,2-dimethylpropan-1-ol (**15**⁺), and 1-(2,5-dimethoxyphenyl)-2,2-dimethylpropan-1-ol (**16**⁺) radical cations in alkaline aqueous solution has been compared with that of the corresponding monomethoxylated (4-methoxycumyl alcohol (**8**⁺) and 1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol (**14**⁺)) radical cations.^{27,29}



Cleavage of the C—C bond was the exclusive fragmentation pathway in all cases leading to the corresponding acetophenones (from cumyl alcohols) or benzaldehydes (from 1-aryl-2,2-dimethylpropan-1-ols). The second order rate constants for ⁻OH-induced C—C fragmentation of radical cations **8**⁺ and **12**⁺–**16**⁺ are collected in Table 1.

It can be observed that the dimethoxylated cumyl alcohol radical cations **12**⁺ and **13**⁺ undergo C—C bond cleavage at a much lower rate (more than three orders of magnitude) than the monomethoxylated **8**⁺ (Table 1). Moreover, whereas the fragmentation of **8**⁺ involves, as already mentioned, the formation of an intermediate 4-

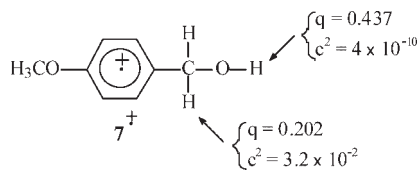
methoxycumyloxy radical, no evidence for the formation of an intermediate cumyloxy radical was instead obtained with **12**⁺ and **13**⁺. As very similar rates of β -cleavage have been measured for ring-substituted cumyloxy radicals,³¹ and very similar oxygen acidities can be assumed for **8**⁺, **12**⁺, and **13**⁺, it seems reasonable to suggest that the introduction of a second methoxy group on the aromatic ring induces a change in mechanism. The hypothesis is that the radical zwitterion, undergoes rate determining IET coupled with C—C bond cleavage, directly forming the carbonyl product (Scheme 6, path d). Through this concerted process, the energy of the transition state can be lowered by partial formation of a ring conjugated C=O double bond. If C—C bond cleavage has progressed to some extent in the transition state of the rate determining step, the observation that the radical cations undergoing C—*t*Bu cleavage are much more reactive than those undergoing C—Me cleavage might be rationalized on the basis of the much higher stability of the *tert*-butyl radical as compared to the methyl radical.³²

In summary, these results provide a quite complete mechanistic picture for the ⁻OH-induced fragmentation reactions of ring methoxylated 1-arylalkanol radical cations (Scheme 6). In these processes, a key role is played by the energy barrier for the side-chain to ring IET in the radical zwitterion intermediate (**I**). Such a barrier appears to determine the concerted or stepwise (via an alkoxy radical **II**) nature of the conversion of **I** into a carbonyl compound (**III**) or a carbon radical (**IV**). Accordingly, when the IET energy is relatively low (Ar = 4-MeOC₆H₄), conversion of **I** into **III** or **IV** occurs via **II** (path a), which then undergoes a 1,2-H shift and/or β -fragmentation (paths b and c, respectively). When Ar = 3,4- and 2,5-(MeO)₂C₆H₃, the IET energy is higher, and the reaction proceeds by IET concerted with bond breaking. Finally, when Ar = 2,4,5-(MeO)₃C₆H₂, the energy barrier for the IET becomes so high that carbon acidity (direct C—H deprotonation) takes over.

Another important discovery was that the carbon acidity/oxygen acidity mechanistic dichotomy also extends to the gas phase. This was shown by a FT-ICR study of the gas-phase deprotonation of the radical cations derived from benzyl alcohol and some derivatives by a variety of bases of different strength.³³ It was observed that with the relatively weak base cyclopropylmethylketone, C₆D₅CD₂OH⁺ undergoes predominantly deprotonation from the benzylic C—D bond, displaying *carbon acidity*, whereas with the stronger base 1,3-propanediamine deprotonation from the O—H group (*oxygen acidity*) is the major pathway. Moreover, experiments carried out on 4-MeOC₆H₄CD₂OH⁺ showed that this radical cation exhibits exclusive or predominant carbon acidity depending on base strength, clearly indicating that by increasing radical cation stability oxygen acidity decreases more than carbon acidity, as observed in solution.

Table 1. Second-order rate constants ($k_{-\text{OH}}$) for the ⁻OH-induced decay of ring methoxylated cumyl alcohol (**8**⁺, **12**⁺, **13**⁺) and 1-aryl-2,2-dimethyl-1-propanol (**14**⁺–**16**⁺) radical cations (ArR⁺), generated by pulse radiolysis of the parent substrates in aqueous solution, measured at $T = 25^\circ\text{C}$

Ar	$k_{-\text{OH}} (\text{M}^{-1} \text{s}^{-1})$	
	(R = CH(OH) <i>t</i> Bu)	(R = C(CH ₃) ₂ OH)
4-MeOC ₆ H ₄	(14 ⁺) 1.3×10^{10}	(8 ⁺) 1.2×10^{10}
3,4-(MeO) ₂ C ₆ H ₃	(15 ⁺) 8.3×10^9	(12 ⁺) 5.6×10^6
2,5-(MeO) ₂ C ₆ H ₃	(16 ⁺) 1.5×10^8	(13 ⁺) 1.6×10^5



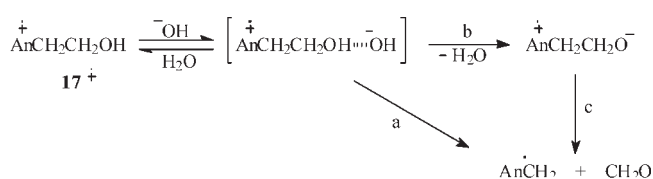
Scheme 7

To find some theoretical support to the carbon acidity/oxygen acidity dichotomy, DFT calculations (gas phase) at the UB3LYP/6-31G(d) level of theory were carried out for ring-monomethoxylated benzyl alcohol radical cations.³⁴ The results obtained indicate that the α -OH hydrogen atom of the radical cations bears a significantly greater amount of positive charge (q) than the benzylic ones whereas the reverse occurs when the square of the LUMO coefficient (c^2) are considered. This is illustrated in Scheme 7, for 7^+ .

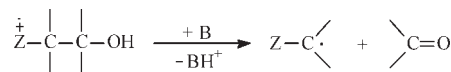
This observation can be interpreted on the basis of the frontier orbitals theory by suggesting that with the strong ^-OH base, the reaction is charge controlled and therefore the preferred site of attack by the base is the benzylic OH, the one with the highest charge. Conversely, with the weaker base H_2O , the reaction is governed by frontier orbital interactions and deprotonation occurs preferentially at the site bearing the largest spin density, that is, the benzylic hydrogens.

(b) 2-arylalkanol radical cations

An analogous pH-dependent carbon acidity/oxygen acidity mechanistic dichotomy has been also observed with ring-methoxylated 2-arylalkanol radical cations where the alcoholic OH group is β with respect to the positively charged aromatic ring.¹⁷ Accordingly, these radical cations undergo C—H bond cleavage at $pH \leq 5$, whereas in the presence of ^-OH , exclusive C—C bond cleavage occurs at a rate very close to the diffusion limit, which suggests a reaction initiated by deprotonation at the alcoholic group. As an example, 2-(4-methoxyphenyl) ethanol radical cation (17^+) undergoes C—H deprotonation in acid solution with $k = 5.2 \times 10^2 \text{ s}^{-1}$, but in alkaline solution C—C bond cleavage is the exclusive fragmentation pathway occurring with $k_{-OH} = 8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A mechanism similar to the one described in Scheme 6 for 1-arylalkanol was proposed. However, since it was possible to rule out the formation of an intermediate alkoxy radical, the mechanisms described in Scheme 8



Scheme 8



Scheme 9

(for 17^+) were suggested, where either C—C and O—H bond cleavage are concerted in the radical cation (step a) or an intermediate radical zwitterion is first formed that then undergoes C—C bond cleavage (steps b and c). In some respect, these pathways closely resemble those proposed for β -elimination reactions. Thus, occasionally the concerted mechanism may be indicated as E2 and the stepwise mechanism as E1cb.

To this category of fragmentations also belongs the OH-assisted C—C bond cleavage in 2-amino alcohol radical cations (Scheme 9 where Z is ArNR, ArNH, or R_2N), which has been the object of intensive investigations.^{35–37}

In this case, however, differently than with the 2-arylalkanol radical cations discussed above, the reactions were studied in MeCN as the solvent.

The reactions were base catalyzed (a quite high β Brønsted value of 0.62 was measured against a series of pyridine bases)^{36b} and exhibited a k_{OH}/k_{OD} kinetic isotope effect indicating that the cleavage of the OH group is part of the reaction coordinate. The proposed mechanism is practically the same as that shown in Scheme 8, with the pyridine base replacing ^-OH . A process where attack of the base is concerted with C—C bond cleavage was generally preferred. However, the possibility of a stepwise mechanism was also considered.

More recently, we have extended the study of this type of fragmentation to 2-arylsulfanyl alcohol radical cations in MeCN (Scheme 9, Z = ArS).³⁸ In many respects, the results are very similar to those obtained with 2-amino alcohol radical cations. However, an interesting and new observation was that the kinetic isotope effect, k_{OH}/k_{OD} , increases as the strength of the pyridine base increases, suggesting that O—H and C—C bond cleavage are concerted, but probably not synchronous and that the extent of O—H bond cleavage in the transition state increases as the base becomes stronger. A point can be reached where the mechanism shifts from concerted to stepwise and accordingly with the strong base 4-(dimethylamino)pyridine it was found that the fragmentation rate is independent of the stability of the radical cation. This indicates a stepwise process where the slow step is the formation of the zwitterion. Thus, a mechanistic shift from E2 to E1cb appears to occur by increasing the strength of the base.

Another notation worth of mentioning concerns the fact that, under identical conditions, 2-hydroxy arylsulfanyl radical cations undergo C—C bond cleavage at a significantly slower rate than that of structurally similar nitrogen radical cations (Scheme 9, Z = ArNH) with very similar C—C bond dissociation energies. The larger intrinsic reactivity of nitrogen radical cations with respect



Scheme 10

to that of the sulfide radical cation can be attributed to a more efficient overlap of the scissile C—C bond with the SOMO on nitrogen than with the SOMO on sulfur probably due to a better energy matching in the former case. In addition, the positive charge might be more localized on nitrogen in the aminium radical cation than on sulfur in the sulfide radical cation. This factor too might lead to a lower intrinsic barrier for fragmentation in the nitrogen than in the sulfur radical cation.

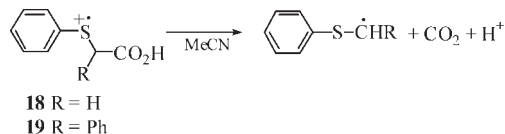
FRAGMENTATIONS INVOLVING CO₂ LOSS

The decarboxylation of carboxylic acid radical cations is another very interesting type of fragmentation. This process occurs when in the radical cation a carboxylate or carboxylic group is β with respect to the positive charge (Scheme 10).

These fragmentation reactions are generally very fast processes and have attracted considerable interest for their possible practical applications in the field of photoinitiation of free radical polymerization⁸ and for increasing the efficiency of silver halide photography.⁹ The latter application is of general interest as it involves the formation, by sensitized photolysis, of radical cations that by fragmentation can form a carbon radical capable to reduce a second molecule of sensitizer, thus doubling the efficiency of the photochemical process (two electron sensitization). It should be noted, however, that while decarboxylation appears very suitable in this respect,^{9,39} other fragmentations that can lead to the same carbon radical at a similar rate can be used as well. For example, aminosilane radical cations that can rapidly fragmentate by cleavage of the C—Si bond have also been considered for two-electron sensitization.⁴⁰

(a) Dynamics of the decarboxylation process

Among the more recent studies concerning the kinetic aspects of radical cation decarboxylations, very important are the detailed laser flash photolysis investigations of the decarboxylation of anilino carboxylate³⁵ and dicarboxylate³⁹ radical cations (Scheme 10, Z = ArNH, ArNAlk, R = H, CO₂⁻) in MeCN and aqueous MeCN. Interestingly, it appears that there are significant differences between mono and dicarboxylate radical cations. Thus, whereas with monocarboxylate radical cations the decarboxylation rate is almost insensitive to the stability of the formed carbon radical (similar rates were observed for R = H and R = Me, Scheme 10), with dicarboxylate radical cations the presence of an α -methyl group had a noticeable rate

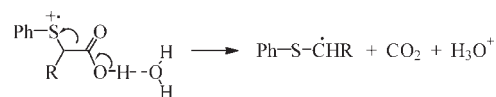


Scheme 11

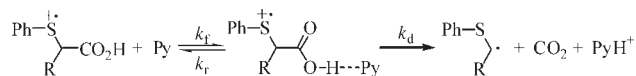
increasing effect. Conversely, the effect of solvent polarity seems less important with monocarboxylate than with dicarboxylate radical cations. Accordingly, with the former similar decarboxylation rates were observed in solvents ranging from EtOH to MeCN, whereas decarboxylation of the latter was very sensitive to the presence of H₂O, strongly decreasing with increasing the percent of H₂O in the solvent. In both cases, however, it was observed that the decarboxylation rate decreases with decreasing the oxidation potential of the substrate, a property also observed in the study of arylacetic acid radical cations by Bietti and Capone.⁴¹

Whereas the above studies have mostly looked at the decarboxylation of carboxylate radical cations (zwitterionic species), our group has recently devoted his attention to the decarboxylation of undissociated acid radical cations in dipolar aprotic solvents. The purpose was to get information on the role exerted by the presence of the proton in the decarboxylation process. Accordingly, in the decarboxylation of a carboxylic acid radical cation, the intramolecular electron transfer has to be accompanied by proton loss and a role of a base in this respect can be envisaged. We have studied, by laser and steady state photolysis, kinetics and products of the decarboxylation of radical cations of phenylthioacetic acids **18** and **19** in MeCN (Scheme 11).^{42,43}

The study has shown that the rates of decarboxylation of **18**⁺ and **19**⁺ are very similar, which means that the stability of the formed carbon radical is of little importance with respect to the decarboxylation rate. This finding is in line with previous observations for the decarboxylation of anilino carboxylate radical cations.³⁵ However, differently with what observed with dicarboxylate radical cations, the presence of 2–5% water in the solvent determines a significant increase in the decarboxylation rate. Moreover, when D₂O replaces H₂O the rate is lowered by a factor of 2. This suggests that the cleavage of the carboxylic OH is part of the reaction coordinate being concerted with the cleavage of the C—C bond (Scheme 12). The role of H₂O may be that of stabilizing the transition state by H-bonding or of acting as a base.⁴⁴ If, in the transition state, C—C bond cleavage lags behind O—H bond cleavage, the weak effect of the α -phenyl group on the decarboxylation rate is rationalized.



Scheme 12



Scheme 13

As expected, the decarboxylation rate was found to increase in the presence of pyridine. However, very interestingly, the effect of the base was not linear, but a plateau was reached at the higher base concentrations. This behavior suggests a mechanism where pyridine and the radical cation, in a fast and reversible step, form a complex that is the species actually undergoing decarboxylation (Scheme 13). Inside such a complex, the decarboxylation would involve a proton transfer coupled to an intramolecular electron transfer. This mechanism predicts a linear correlation between the reciprocal of k_{obs} (the observed rate of decarboxylation) and the reciprocal of the base concentration that is indeed observed (Fig. 3).

A further mechanistic insight is obtained by the important observation that the rate constant for the fragmentation of the complex, that can be evaluated from the plot in Figure 3 and the kinetic expression for the mechanism in Scheme 13, is practically the same for the two carboxylic acids and hence insensitive to the presence of the phenyl group. This additional information allows us to suggest that the slow step of the fragmentation of the H-bonded complex is probably the formation of the carboxyl radical, a step obviously not influenced by the presence of the phenyl group. Fast decarboxylation should follow (Scheme 14).

Interesting results were also obtained by the steady state photolysis study. Accordingly, the products were different for the two acids (Scheme 15), namely thioanisole (**3**) from $\mathbf{18}^{\cdot+}$ and 1,2-bis(phenylsulfanyl)-1,2-diphenylethane (**20**) from $\mathbf{19}^{\cdot+}$.

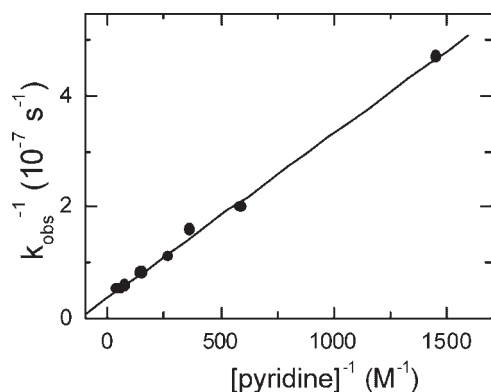
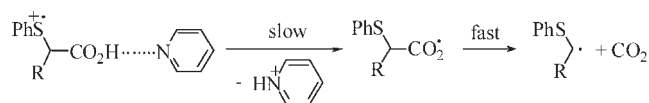
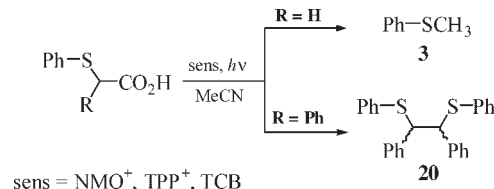


Figure 3. $1/k_{\text{obs}}$ versus $1/[\text{pyridine}]$ for the decay of $\mathbf{18}^{\cdot+}$ in MeCN



Scheme 14



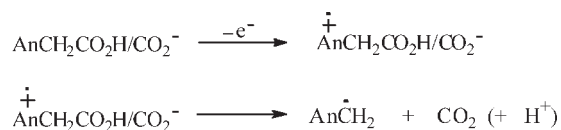
Scheme 15

Since these reactions, as seen before, involve the formation of a carbon radical, it is clear that the two carbon radicals formed, PhSCH_2^{\cdot} and $\text{PhSCH}(\text{Ph})^{\cdot}$ follow different paths: H or proton abstraction and dimerization, respectively. The formation of **3** from $\mathbf{18}^{\cdot+}$ is particularly intriguing, as it represents a case of a nonoxidative decarboxylation in an oxidative medium. On the basis of experiments in CD_3CN and $\text{CH}_3\text{CN-D}_2\text{O}$ it was ascertained that the hydrogen forming **3** comes from water. Since it was possible to exclude that the reduced form of the sensitizer (Scheme 3) reduces the carbon radical to a carbanion that then reacts with the residual water present in MeCN,⁴⁵ it is suggested that PhSCH_2^{\cdot} is protonated at carbon to form $\mathbf{3}^{\cdot+}$ that is then converted to **3** by the reduced form of the sensitizer. This hypothesis is supported by the fact that PhSCH_2^{\cdot} is a relatively strong carbon base ($\text{p}K_{\text{a}} = 3.6$), which might be protonated by the proton formed in the fragmentation process. Consistent with this is the observation that no **3** is formed when the reaction is run in the presence of small amounts of sodium carbonate. On the other hand, a $\text{p}K_{\text{a}}$ value of -4.5 can be calculated for $\text{PhSCH}(\text{Ph})^{\cdot}$, which therefore is a much less strong base than PhSCH_2^{\cdot} . Thus, protonation of $\text{PhSCH}(\text{Ph})^{\cdot}$ may not compete with dimerization.

(b) Role of radical cations in the oxidative decarboxylation of aryloethanoic acids

The decarboxylation of radical cations has attracted attention also because these species have been frequently suggested as intermediates in the oxidative decarboxylation of aromatic carboxylic acids. Thus, in the oxidation of 4-methoxyphenylethanoic acid (**21**), a mechanism has been proposed suggesting the formation of an intermediate radical cation $\mathbf{21}^{\cdot+}$ (or radical zwitterion) that undergoes rapid decarboxylation to give the corresponding benzyl radical as described in Scheme 16 ($\text{An} = 4\text{-MeOC}_6\text{H}_4$).⁴⁶

However, in a laser flash photolysis (LFP) study of the one-electron oxidation of 4-methoxy and



Scheme 16

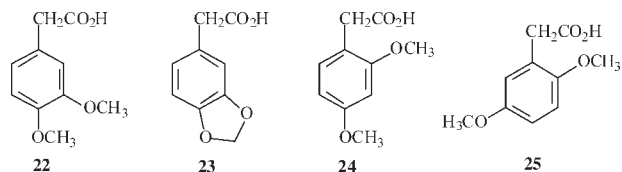
4-methylphenylethanoic acids in aqueous solution no direct evidence for the formation of an intermediate radical cation was obtained.⁴⁷ Only the formation of the 4-methoxy and 4-methylbenzyl radicals was observed. In the same study, it was also shown that the decarboxylation rate constants, measured following the formation of the corresponding benzyl radicals, increased by increasing pH, indicating that decarboxylation is faster when the carboxyl group is ionized.

We have recently carried out a kinetic study of the one-electron oxidation of 4-methoxyphenylethanoic acid (**21**) induced by Co(III)W.⁴⁸ The kinetic data were consistent with a rate determining electron transfer and it was also shown that ionization of the carboxylic group results in an almost 30-fold acceleration of the decarboxylation rate. It was proposed that under these conditions no aromatic radical cation intermediate is formed, but that the electron removal from the aromatic ring is concerted with an intramolecular side-chain to ring electron transfer. The 4-methoxyphenylacetoxyl radical is directly formed, which then undergoes rapid decarboxylation to give the 4-methoxybenzyl radical as described in Scheme 17. However, on the basis of the experimental data available, the possibility that decarboxylation is concerted with electron removal from the aromatic ring, bypassing 4-methoxyphenylacetoxyl radical formation, could not be excluded.

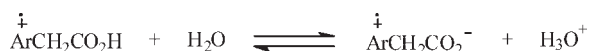


Scheme 17

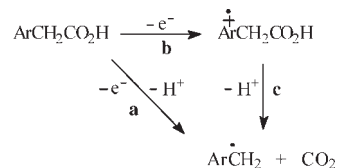
In order to obtain additional information on the role of aromatic radical cations in these oxidation processes, a product and time-resolved kinetic study at different pH values on the one-electron oxidation of the ring dimethoxylated phenylethanoic acids **22–25** was carried out.⁴¹



In this case, the formation of aromatic radical cations (or radical zwitterions depending on pH) was clearly observed by time-resolved spectroscopy, and $\text{p}K_a$ values for the corresponding acid-base equilibria (see below) were measured.



The radical cations undergo decarboxylation with first order rate constants (between $<10^2$ and $5.6 \times 10^4 \text{ s}^{-1}$) that decrease by increasing the radical cation stability, and are lower (between 10 and 40 times) for the acid radical



Scheme 18

cations than for the corresponding radical zwitterions. Clearly, the energy for the intramolecular side-chain to ring electron transfer required for decarboxylation increases the more the positive charge is stabilized in the aromatic ring. Moreover, in the acid radical cation additional energy is required as the process involves the transfer of a proton to the medium.

Taken together, the results presented above indicate that in the one-electron oxidation of arylethanoic acids in aqueous solution the reactivity is governed by the interplay between the electron removal from the aromatic ring and the intramolecular side-chain to ring electron transfer required for decarboxylation (Scheme 18).

With **21**, electron removal is relatively costly and is thus coupled with the intramolecular electron transfer (path a), and, no radical cation intermediate is formed. By increasing the ease of oxidation (as in **22–25**), electron removal becomes easier while the rate of intramolecular electron transfer decreases and a stepwise mechanism, proceeding through the formation of a radical cation (or radical zwitterion) followed by decarboxylation, occurs (paths b and c).

Interestingly, similar $\text{p}K_a$ values (between 3.34 and 3.67) were measured for the radical cations **22**⁺–**25**⁺, showing that the presence of an electron hole on the aromatic ring leads to an increase in acidity of almost one $\text{p}K_a$ unit as compared to the neutral acids. Very reasonably, this is due to the electron withdrawing effect exerted by the positively charged aromatic ring.

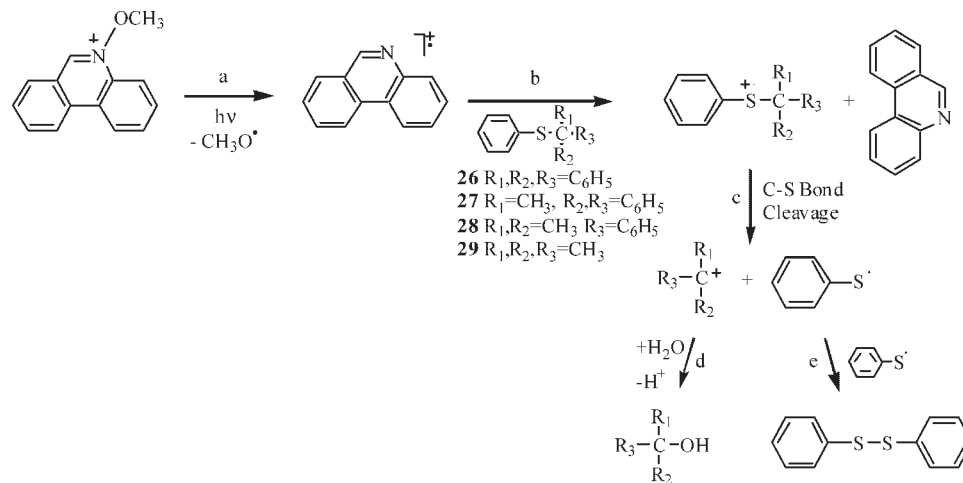
FRAGMENTATIONS INVOLVING C—S BOND CLEAVAGE

An interesting and peculiar aspect of sulfide radical cations is that in addition to the already described β fragmentations (e.g., Scheme 12), these species can also undergo the breaking of the C—S bond with formation of a sulfanyl radical and a carbocation (Scheme 19).

This process represents a peculiar type of $\text{S}_{\text{N}}1$ reaction where the leaving group is a radical. Moreover, the scissile bond is directly connected with the atom bearing most of the positive charge⁴⁹ and perhaps it seems more appropriate to consider this process as an α -fragmentation. The intramolecular electron transfer



Scheme 19



Scheme 20

accompanying the cleavage process might have therefore behaviors different than those of the β cleavage.

Many product studies have been concerned with this process,⁵⁰ but scanty information is available with respect to the quantitative aspects of its dynamic. The first determination of the rate of C—S bond cleavage was obtained several years ago in aqueous solution by a pulse radiolysis study of water soluble sulfides. Since an extension of this study turned out to be impractical in view of the generally low solubility of sulfides in H_2O , attempts were made to generate the radical cations by sensitized laser flash photolysis (Scheme 3) of aromatic sulfides in organic solvents. However, with the most common sensitizers (NMQ⁺, DCA, TCB etc.) the formed radical cations underwent back electron transfer in deaerated MeCN, or, in the presence of O_2 , reacted with O_2^- (generated by reaction of the reduced sensitizer with O_2), in both cases at rates faster than that of C—S bond cleavage.⁵¹ To overcome this problem we applied a method recently proposed by Dinnocenzo and Farid⁵² based on the very fast light-induced breaking of the N—O bond in *N*-methoxyphenanthridinium cation (MeOP⁺). This process leads to the methoxyl radical and the phenanthridinium radical cation (Scheme 20, path a). The latter species is a quite powerful oxidant (1.9 V vs. SCE) and in subsequent bimolecular reactions can form the radical cations of added donors (like aryl sulfides) with $E^\circ < 1.9$ V (vs. SCE) (Scheme 20, path b).⁵³

Indeed, by laser photolysis in MeCN of the *t*-alkyl sulfides **26–29** in the presence of MeOP⁺, formation of the corresponding sulfide radical cations was observed and with **26**⁺ and **27**⁺ also the formation of carbocations coming from C—S bond cleavage (Scheme 20, path c) was clearly detected.

The occurrence of C—S bond cleavage in the radical cation was also confirmed by steady state photolysis experiments that showed the formation of *t*-alkyl alcohols and diphenyl disulfide (Scheme 20, paths d and e). The first order rate constants of C—S bond breaking (k_f) are

reported in Table 2 together with the bond dissociation free energies (BDFEs) for the C—S bond in the radical cation (obtained by DFT calculations and classical thermochemical cycles).

A first observation is that the rates of C—S bond cleavage are not particularly fast, ranging from $6.6 \times 10^4 s^{-1}$ for **28**⁺ to $9.5 \times 10^6 s^{-1}$ for **26**⁺. With **29**⁺ the rate was so slow that only a higher limit can be given. A clear dependence of the fragmentation rate on the C—S bond dissociation free energies (BDFEs) in the radical cation can be noted and, accordingly, the rate of C—S bond cleavage increases by increasing the stability of the carbocation leaving group in the order $PhMe_2C^+ < Ph_2MeC^+ < Ph_3C^+$.⁵⁴ However, the influence of the BDFEs on the rate of fragmentation is rather low: for about 13 kcal/mol difference in BDFE the difference in ΔG^\ddagger is of only 2–3 kcal/mol. The probable reason is that the intrinsic barrier for the C—S bond cleavage reaction is not constant but changes along the series increasing as, in the leaving carbocation, the phenyl groups progressively replace the methyl groups (cumyl < diphenylmethyl < triphenylmethyl) and the fragmentation requires therefore more extensive electron reorganization. Since the intrinsic barriers appear to increase in an order opposite to that of the C—S

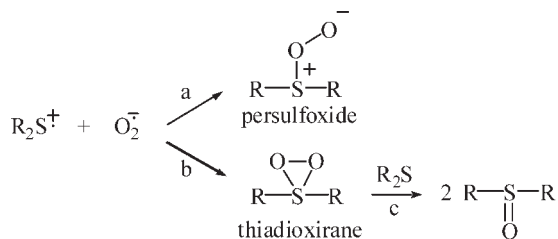
Table 2. C—S bond dissociation free energies, cleavage rate constants at 25°C and activation free energies for the C—S bond cleavage reactions of **26**⁺–**29**⁺ in deaerated MeCN

Radical cations	BDFE ^{a,b,c}	k_f ($10^5 s^{-1}$) ^c	ΔG^\ddagger ^{b,c}
26 ⁺	–12.3	95	8.2
27 ⁺	–2.2	2.0	10.1
28 ⁺	1.1	0.66	10.8
29 ⁺	10.7	<0.1	—

^a Free energy for the cleavage of the C—S bond in the cation radical.

^b kcal mol^{–1}.

^c at 298 K



Scheme 21

BDFEs, the thermodynamic contribution to the activation energy is in part compensated by the kinetic factor.

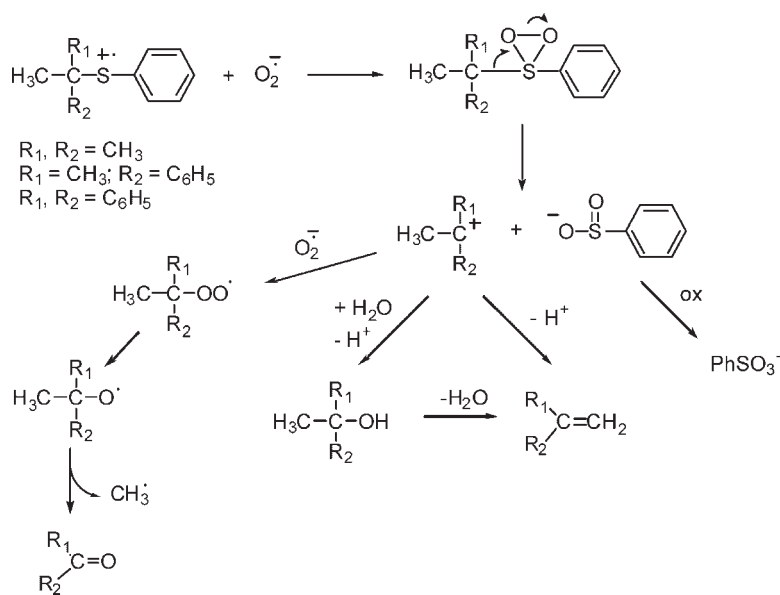
In the foregoing discussion, it was observed that the laser photolysis of sulfides, sensitized by common sensitizers like NMQ^+ , DCA, DCN etc., does not show any spectral evidence of C—S bond cleavage in the sulfide radical cation, both in the presence and in the absence of oxygen.⁵¹ However, whereas in deaerated MeCN this result was consistent with that of steady state photolysis experiments (formation of very small amounts of products), in the presence of oxygen, extensive formation of a complex mixture of products coming from C—S bond cleavage was observed. Since as already mentioned, in the presence of O_2 the sulfide radical cation can react with O_2^- , a reasonable proposal is that the C—S bond rupture does not take place in the radical cation itself, but very likely in the adduct formed by this reaction.

Attack at sulfur of sulfide radical cations by O_2^- has been suggested to be the key process in the sensitized photosulfoxidation of organic sulfides occurring by an electron transfer mechanism.^{55,56} In this process, either a persulfoxide (Scheme 21, path a) or a thiadioxirane (path b) can be formed, but the latter possibility has been recently supported by experiments and calculations.⁵⁷

In the sulfoxidation reaction, the thiadioxirane adduct generally reacts with another molecule of sulfide to form a sulfoxide (Scheme 21, path c). However, it is possible that with sterically congested sulfides, such a bimolecular reaction can become very difficult and the thiadioxirane may instead prefer to undergo C—S bond cleavage, presumably concerted with the opening of the three-member ring, leading to a quite stable tertiary carbocation and a phenyl sulfinate that can be converted to the observed fragmentation products as described in Scheme 22.

CONCLUDING REMARKS

The most recent work of our group concerned with fragmentations of radical cations has been reviewed. One of the objectives pursued in the last few years has been that of obtaining further information on the factors, which determine the oxygen acidity of benzyl alcohol radical cations and the competition between oxygen acidity and carbon acidity. An important result has been that the oxygen acidity can also be observed in the gas phase where it exhibits similar behaviors as those found in solution. The crucial role played in these fragmentations by the energy barrier for the intramolecular (from the scissile bond to the SOMO) electron transfer (IET) has also been clearly evidenced. Thus, carbon acidity appears favored by high-IET barriers even in the presence of strong bases. Moreover, when the systems exhibit only kinetic oxygen acidity, the IET barrier may determine the concerted or stepwise nature of the fragmentation. Interestingly, the energy barrier for IET is also important in the oxidative decarboxylation of arylacetic acids, a process which can involve a two step mechanism with the



Scheme 22

intermediacy of a radical cation. It has been found that such a possibility requires relatively high-IET barriers whereas, with low barriers, a single step mechanism is more likely. Another interesting result has been obtained in the study of the decarboxylation of phenylthioacetic acid radical cations in dipolar aprotic solvents where the rate-determining step seems to involve a proton transfer coupled to an intramolecular electron transfer. Finally, C—S bond cleavage reactions in sulfide radical cations have been investigated. The determination of structural effects on the rate of C—S bond breaking has shown the important role of the electron reorganization in the carbocation leaving group in this respect. Moreover, evidence has been obtained indicating that the C—S bond cleavage observed in the photosensitized electron transfer oxygenation of sulfides, probably does not take place in the radical cation but in the adduct formed by the reaction of the radical cation itself with O_2^- . Summing up, we think that the results presented and discussed in this article have contributed to improve our knowledge of the multifold aspects of the fragmentation reactions of radical cations. Of course, there are still several important questions that need to be addressed possibly by means of theoretical studies. A strong development of this area in the near future is highly desirable for a better interpretation of the experimental results and the design of new experiments.

Acknowledgements

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