

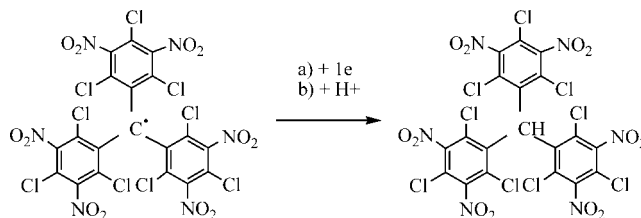
Oxidant Activity of Tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl Radical with Catechol and Pyrogallol. Mechanistic Considerations

Anna Carreras,[†] Isaac Esparbé,[‡] Enric Brillas,[‡] Jordi Rius,[§] Josep Lluís Torres,[†] and Luis Julià^{*,†}

Departament de Química Biològica i Modelització Molecular, Institut de Química Avançada de Catalunya (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain, Departament de Química Física, Universitat de Barcelona, Martí Franquès 1-11, 08028 Barcelona, Spain, and Institut de Ciència de Materials (CSIC), Campus de la U.A.B., 08193 Bellaterra, Spain

ljbmoh@cid.csic.es

Received November 18, 2008

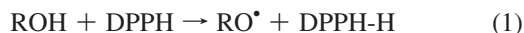


The reducing activity of simple polyphenols (PhOH), catechol and pyrogallol, is tested in different solvents in front of tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl (HNTTM) radical, a stable organic free radical of the TTM series. HNTTM radical is very active in electron-transfer reactions to give a very stable anion. The standard potential for the reduction of HNTTM radical by cyclic voltammetry in different solvents is $E^\circ = 0.60 \pm 5$ V vs SCE. In hydroxylic solvents, the electron transfer is a very rapid process and the electron-donating species is the ionized PhO^- , whereas in nonpolar solvents, it is suggested that the electron transfer is facilitated by the formation of an intermediate complex between HNTTM and PhOH.

Introduction

Polyphenols show a remarkable ability to be involved in many oxidation–reduction reactions in chemistry and biology. Many of them are constituents of natural antioxidant extracts whose significant role is associated with the ability to scavenge reactive oxygen species. Among the different methods designed to measure the activity of the antioxidants,¹ stable radicals leading to color changes upon reaction with them have received great attention. The hydrazyl radical DPPH is a commercially available stable radical that has been widely used to test the antioxidant properties of natural and synthetic polyphenols.^{1,2} In nonpolar and aprotic solvents, it is extensively accepted that the activity of DPPH is evaluated by its capacity to abstract

hydrogen atoms of the antioxidants, and the ability of these compounds to release hydrogen atoms depends mainly on the stability of the generated radicals.³ This is a free-radical reaction in which a hydrogen atom is transferred from the hydroxyl group, in the case of polyphenols as antioxidants, to the nitrogen of DPPH (reaction 1). Sometimes, the number of reduced DPPH molecules per polyphenol molecule corresponds to the number of available hydroxyl groups. However, for the majority of polyphenols tested, the mechanism is more complex.⁴



More recently, a new mechanism associated with a proton-coupled electron transfer (PCET) process has been proposed for the reduction of free radicals with phenols.^{5,6} This mecha-

[†] Institut de Química Avançada de Catalunya.

[‡] Universitat de Barcelona.

[§] Institut de Ciència de Materials.

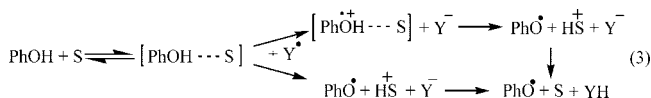
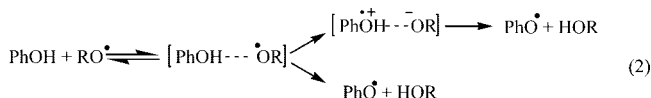
(1) Huang, D.; Ou, B.; Prior, R. L. *J. Agric. Food Chem.* **2005**, *53*, 1841–1856, and references therein.

(2) Blois, M. S. *Nature* **1958**, *181*, 1199–1200. Brand-Williams, W.; Cuvelier, M. E.; Berset, C. *Lebensm.-Wiss.-Technol.* **1995**, *28*, 25. Sanchez-Moreno, C.; Larrauri, J. A.; Saura-Calixto, F. *J. Sci. Food Agric.* **1998**, *76*, 270–276. Goupy, P.; Hugues, M.; Boivin, P.; Amiot, M. J. *J. Sci. Food Agric.* **1999**, *79*, 1625–1634.

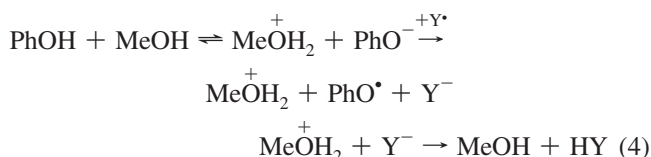
(3) A clear example of the hydrogen atom donating ability of antioxidants in front of alkyl, alkoxy, and peroxy radicals is: Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Valginigli, L.; Gimes, D.; Tordo, P. *J. Am. Chem. Soc.* **1999**, *121*, 11546–11553.

(4) Dangles, O.; Fargeix, G.; Dufour, C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1387–1395. (a) Dangles, O.; Fargeix, G.; Dufour, C. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1653–1663.

nism involves an intermediate hydrogen-bonding complex either between the phenol and the radical (an oxygen-centered radical) (reaction 2) or between the phenol and the solvent (a hydrogen bond accepting solvent) (reaction 3) that gives phenoxyl radical by electron-transfer reaction followed by or concerted with proton transfer.



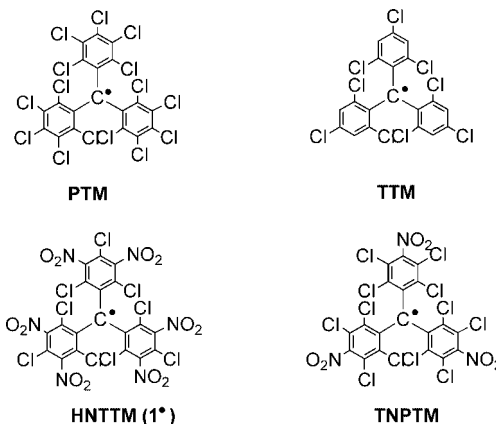
However, polyphenols are partially ionized losing a proton to give the corresponding anions in ionizable solvents, i.e., solvents able to accept protons such as methanol. In these cases, it has been suggested that the reaction of polyphenols with radicals consists of a fast electron-transfer process from the phenoxide anion to radical (reaction 4).⁷



The studies to measure the antioxidant activity of polyphenols using DPPH as a persistent free-radical sensor do not provide clear information of the mechanism involved, and both mechanisms, hydrogen abstraction and electron transfer, have been proposed as alternative reduction paths. We have been engaged for a long time with stable organic radicals of the tris(2,4,6-trichlorophenyl)methyl (TTM)⁸ and perchlorotriphenylmethyl (PTM)⁹ series. These free radicals are very persistent species, both in solid or in solution, due to the presence of the very bulky polychlorophenyl substituents around the trivalent carbon atom. As a general rule, they cannot abstract hydrogen atoms from H-donating compounds because the reactant species have a great steric hindrance to yield effective molecular collisions. However, they are very active species in electron-transfer processes reacting with electron-donating and/or electron-accepting substrates to give stable anions and/or cations,

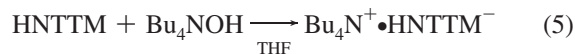
respectively. In fact, many of them behave as electrochemical amphoteric species, being reduced in the cathode and oxidized in the anode in quasireversible processes. These characteristic physicochemical properties of the free radicals of the TTM and PTM series provide a supporting base to use them to test the antioxidant power of polyphenols by electron-transfer reactions. In this context, we have reported the synthesis of tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl (HNTTM) radical with strong electron-acceptor properties (standard potential $E^\circ = 0.55$ V vs NaCl-saturated calomel electrode (SCE) in $\text{CHCl}_3/\text{MeOH}$ (2:1), by cyclic voltammetry) and the study of the reducing activity of some flavan-3-ols with HNTTM.¹⁰ More recently, we have reported the synthesis of a new radical of the PTM series, tris(2,3,5,6-tetrachloro-4-nitrophenyl)methyl (TNPTM) radical ($E^\circ = 0.20$ V vs SCE in $\text{CHCl}_3/\text{MeOH}$ (2:1), by cyclic voltammetry) as a new sensor to distinguish selectively the antioxidant power of catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene). This stable radical is able to accept an electron from pyrogallol and not from catechol.¹¹

The strong oxidant power of HNTTM radical presumably involves a reduced species of a great stability. Now we report the chemical generation and characterization of this species, the corresponding triphenylcarbanion HNTTM⁻, isolated as the tetrabutylammonium salt, and the oxidant activity of HNTTM radical in front of two simple polyphenols, catechol and pyrogallol, as essential components of the molecular structure of many natural antioxidants such as flavonoids. From the results obtained in these last experiments, we suggest some mechanistic considerations about the species responsible of the electron transfers involved in these reactions.



Results and Discussion

The reaction of HNTTM radical with an aqueous solution of tetrabutylammonium hydroxide (TBAH) in THF yielded a strong blue solution of the salt **2**.



The one-electron reducing power of the hydroxide ion in polar solvents other than water, such as DMSO, HMPT, and THF

(5) Mayer, J. M.; Hrovat, D. A.; Thomas, J. L.; Borden, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 11142–11147. Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363–390.

(6) Galian, R. E.; Litwinienko, G.; Pérez-Prieto, J.; Ingold, K. U. *J. Am. Chem. Soc.* **2007**, *129*, 9280–9281. Litwinienko, G.; Ingold, K. U. *Acc. Chem. Res.* **2007**, *40*, 222–230.

(7) (a) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2003**, *68*, 3433–3438. (b) Foti, M. C.; Daquino, C.; Geraci, C. *J. Org. Chem.* **2004**, *69*, 2309–2314. (c) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2004**, *69*, 5888–5896. (d) Foti, M. C.; Daquino, C.; Geraci, C. *J. Org. Chem.* **2004**, *69*, 2309–2314. (e) Musialik, M.; Litwinienko, G. *Org. Lett.* **2005**, *7*, 4951–4954. (f) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2005**, *70*, 8982–8990. (g) Daquino, C.; Foti, M. C. *Tetrahedron* **2006**, *62*, 1536–1547.

(8) Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravittles, C.; Olivella, S.; Brichfeus, J. *J. Phys. Chem.* **1987**, *91*, 5608–5616. (b) Carilla, J.; Fajará, L.; Juliá, L.; Riera, J.; Viadel, L. *Tetrahedron Lett.* **1994**, *35*, 6529–6532. (c) Teruel, L.; Viadel, L.; Carilla, J.; Fajará, L.; Brillas, E.; Sañé, J.; Rius, J.; Juliá, L. *J. Org. Chem.* **1996**, *61*, 6063–6066. (d) Carilla, J.; Fajará, L.; Juliá, L.; Sañé, J.; Rius, J. *Tetrahedron* **1996**, *52*, 7013–7024. (e) Gamero, V.; Velasco, D.; Brillas, E.; Juliá, L. *Tetrahedron Lett.* **2006**, *47*, 2305–2309.

(9) Ballester, M.; Riera, J.; Castañer, J.; Badia, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215–2225. (b) Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380–387, and references cited therein.

(10) (a) Torres, J. L.; Varela, B.; Brillas, E.; Juliá, L. *Chem. Commun.* **2003**, *74*, 75. (b) Jiménez, A.; Selga, A.; Torres, J. L.; Juliá, L. *Org. Lett.* **2004**, *6*, 4583–4586.

(11) Torres, J. L.; Carreras, A.; Jiménez, A.; Brillas, E.; Torrelles, X.; Rius, J.; Juliá, L. *J. Org. Chem.* **2007**, *72*, 3750–3756.

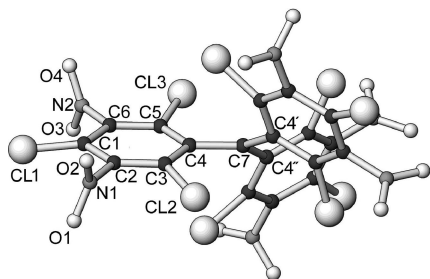


FIGURE 1. Perspective view of the anion of the salt **2** with atom numbering. To indicate the presence of a 3-fold symmetry axis in the molecule, the symmetry-related atoms of C4 have been labeled as C4' and C4''.

has been reported in the literature.^{12,13} This one-electron donation character of the hydroxide anion is assisted by the presence of powerful electron-acceptor substrates. Some perchlorinated aromatic substrates, such as perchlorinated triphenylmethyl radicals with enhanced electron affinity, have been very suitable substrates for this kind of electron-transfer reactions. Salt **2** is very stable in solid and in solution at room temperature, and it has been fully characterized. The absorption spectrum in chloroform solution shows a typical and broadband at $\lambda(\epsilon) = 499$ nm ($26700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The thermal stability has been measured by thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis, and it is stable at temperatures up to 273 °C. Salt **2** yields small dark violet needles by slow evaporation of a saturated solution in methanol. The molecular and crystal structure of **2** was solved from an X-ray powder diffraction pattern measured on a conventional laboratory equipment (Cu $K\alpha_{1,2}$ radiation) (see the Supporting Information for experimental, structure solution and refinement, and Figures S1–S4). The perspective view of the anion of salt **2** with the atom numbering is shown in Figure 1.

Due to the limited resolution of the powder data (minimum d spacing ≈ 1.43 Å), final bond distances are largely influenced by the target values introduced in the restraints. Consequently, the most reliable and useful information supplied by the refinement are the torsion angles and the dihedral angles between mean planes describing the overall geometry of the molecule (Table 1 as well as the crystal packing of the compound. Twist angles of phenyl rings around the plane defined by the sp^2 C7 and C4, C4', C4'' (51°) are very similar to the corresponding angles in the molecular structure of TNPTM radical.¹¹ Similarly, NO_2 planes are forced out of the phenyl planes (80°) due to the presence of *o*-chlorine atoms.

The stability of the reduced species, carbanions, derived from radicals of the TTM series is determined by the reversible reduction potential of the corresponding radical. At the same time, the reduction potential is predominantly related to the effects of the substituents in the phenyl rings, although the extent of localization of the charge density in the phenyl rings is

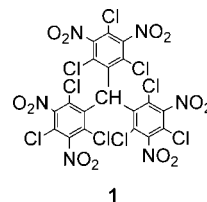
TABLE 1. Angles (deg) between Planes^a of the Molecular Structure of HNTTM Radical

A–D	A–B	A–C	A–A'	A–A''
51(1)	79(1)	80(1)	76.5(10)	67.4(10)

^a Planes are defined as follows: A (C1 to C7, N1 N2), B (C2, N1, O2, O3), C (C6, N2, O3, O4), D (C4, C4', C4'', C7), A' (C1' to C7', N1' N2') and A'' (C1'' to C7'', N1'' N2'').

partially inhibited by the twist angles around the central carbon atom. HNTTM radical exhibits a quasireversible reduction process in cyclic voltammetry with a standard potential ($E^\circ = 0.58$ V vs SCE) in CH_2Cl_2 solution, attributed to the addition of one electron to the trivalent carbon atom.^{10a} This positive and large value, compared with that of the TTM radical ($E^\circ = -0.66$ V vs SCE) is a consequence of the strong electron acceptor properties of the six *m*-nitro groups in the phenyl rings. The nitro group has traditionally been considered as a strong electron-withdrawing group, with a mode of action both inductive and through resonance. In the particular case of HNTTM radical, the nitro groups act by inductive effect. In fact, the E° value for the HNTTM radical is the highest value found into the radicals of the TTM series.)

The reactivity of simple polyphenols such as catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene) with stable radical **1**[•] was measured on the bench from equimolecular solutions of both reactants in solvents of different polarity such as benzene and CHCl_3 and in a polar solvent with hydroxylic hydrogen atoms such as a mixture of $\text{CHCl}_3/\text{MeOH}$ (2:1). The experiments with concentrations of the reactants (~ 0.1 M) much higher than those of the analytical tests were made during short (4 h) and long (47 h) times to assess and characterize all the HNTTM-containing products of the reaction in each trial. To measure reaction rates and stoichiometric factors of these redox processes, obviously any coupling reaction between HNTTM radical and any radical species derived from the decomposition of polyphenols must be discarded. These experiments were carried out as shown in the Supporting Information, and the reactivity results obtained are collected in Table 2. All of them were very clean and simple processes yielding the diamagnetic species **1** as the result of the reduction of **1**[•]. In some of the tested experiments, the compounds reacted very slowly or did not react at all, being recovered part of the species **1**[•].



1

From an analysis of Table 2, it follows that **1**[•] reacts very slowly with catechol in benzene and CHCl_3 but gently in $\text{CHCl}_3/\text{MeOH}$ (2:1). On the other hand, **1**[•] reacts smoothly with pyrogallol in benzene and CHCl_3 , although the reaction proceeds very fast in $\text{CHCl}_3/\text{MeOH}$ (2:1). The different results obtained in these experiments depended both on the electron-donating strength of the polyphenols and on the nature of the solvent employed. Thus, the reaction rates of **1**[•] with catechol and with pyrogallol either in benzene, CHCl_3 or in $\text{CHCl}_3/\text{MeOH}$ (2:1) are in accordance with their different anodic peak potentials in

(12) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109–6114.

(13) Ballester, M. *Pure Appl. Chem.* **1967**, *15*, 123–151. Ballester, M.; Riera, J.; Castañer, J.; Badia, C.; Monso, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215–2225. Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A.; Pujadas, J. *J. Org. Chem.* **1982**, *47*, 259–264. Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498–4505. Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J. *J. Org. Chem.* **1984**, *49*, 2884–2887. Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J.; Armet, O.; Onrubia, C.; Rio, J. A. *J. Org. Chem.* **1984**, *49*, 770–778. Roberts, J. L.; Sugimoto, H., Jr.; Barrette, W. C.; Sawyer, D. T., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 4556–4557. Ballester, M.; Pascual, I. *J. Org. Chem.* **1991**, *56*, 841–844. Lu, Y.; Liu, J.; Diffie, G.; Liu, D.; Liu, B. *Tetrahedron Lett.* **2006**, *47*, 4597–4599.

TABLE 2. Reactivity of Catechol and Pyrogallol with $1^{\bullet}$ in Benzene, CHCl_3 , and $\text{CHCl}_3/\text{MeOH}$ (2:1) (Equimolecular Solutions)^a

solvent	time (h)	reagent			
		Catechol $1^{\bullet}$ (%) ^b		Pyrogallol $1^{\bullet}$ (%) ^b	
benzene	4	92	8	76	24
	47	71	29	51	49
CHCl_3	4	96	4	75	25
	47	73	27	50	50
$\text{CHCl}_3/\text{MeOH}$ (2:1)	4	34	66	<5	>95
	47	11	89	0	100

^a Initial concentration of polyphenol and HNTTM radical, 0.12 M.^b Recovered radical.**TABLE 3.** Cyclic Voltammetry Parameters for the Oxidation of Catechol and Pyrogallol and for the Reduction of Radical $1^{\bullet}$

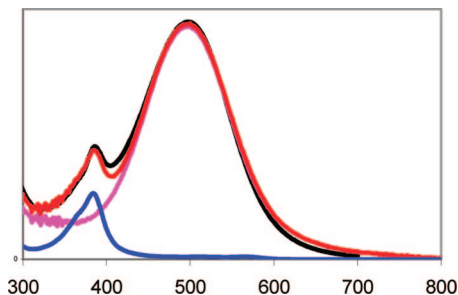
solvent	catechol E_p^a/V^a	pyrogallol E_p^a/V^a	radical $1^{\bullet}$ E°/V^a (E_c°/V^a) ^a
benzene	1.64	— ^b	0.65 (0.48)
CHCl_3	1.27	1.15	0.58 (0.50)
$\text{CHCl}_3/\text{MeOH}$ (2:1)	1.00	0.82	0.55 (0.46)

^a Anodic peak potential (E_p^a), standard potential (E°) and cathodic peak potential (E_c°) for the substrate (10^{-3} M) with 0.4 M tetrahexylammonium hexafluorophosphate in benzene and 0.1 M tetrabutylammonium perchlorate in CHCl_3 or $\text{CHCl}_3/\text{MeOH}$ (2:1), on Pt at scan rates of 50 mV s⁻¹ and 25.0 °C. ^b Not determined by partial adsorption of the substrate on Pt.

cyclic voltammetry¹⁴ ($E_p^a[\text{pyrogallol}] < E_p^a[\text{catechol}]$) (Table 3; Figures S5–S7, Supporting Information). So, the reactivity of $1^{\bullet}$ with pyrogallol is greater than with catechol and it follows the order $\text{CHCl}_3/\text{MeOH}$ (2:1) $\gg$ $\text{CHCl}_3 \sim$ benzene. The dramatic increase in $\text{CHCl}_3/\text{MeOH}$ (2:1) may be due to the partial ionization of the phenol to phenolate ion in hydroxylic solvents, as it has been accepted by other authors.⁷ In this case, the anodic peak potential of the phenolate ion is much lower than that of phenol.¹¹

All these reactions lead to the stable charged species 1^- by electron transfer from the polyphenol and, finally, to the diamagnetic triphenylmethane **1** by abstraction of a hydrogen ion. The presence of the charged species 1^- has been confirmed by electronic spectroscopy. Thus, electronic spectra of the products present in the course of the reaction between $1^{\bullet}$ and pyrogallol in $\text{CHCl}_3/\text{MeOH}$ (2:1) and in benzene are shown in Figures 2 and 3, respectively. In Figures 2 and 3 (right), the lowest-energy band intensities for the products resulting after a few minutes of mixing of both reactants, $1^{\bullet}$ and pyrogallol, are displayed together with a simulation of the spectra of single species $1^{\bullet}$ and 1^- in the same solvents. The simulated spectra were obtained by a linear combination of the spectra of $1^{\bullet}$ and 1^- showing that both species are present in solution in $\sim 19\%$ and $\sim 81\%$ in $\text{CHCl}_3/\text{MeOH}$ and in $\sim 99\%$ and $\sim 1\%$ in benzene, respectively. Figure 3 (left) displays the evolution of the absorption band of a more concentrated solution of $1^{\bullet}$ and pyrogallol, clearly observing the presence of the small absorption band of 1^- immersed into the very large band of $1^{\bullet}$.

To determine the kinetic parameters of the reactions of catechol and pyrogallol with radical $1^{\bullet}$, these processes were

**FIGURE 2.** Absorption spectra of $1^{\bullet}$ (blue), 1^- (purple) ($\lambda = 494$ nm), and $1^{\bullet}$ + pyrogallol in $\text{CHCl}_3/\text{MeOH}$ (2:1) after a few minutes of reaction (black) and a simulation of the black spectrum by a combination of $1^{\bullet}$ and 1^- (red).

carried out in $\text{CHCl}_3/\text{MeOH}$ (2:1) and benzene as solvents and monitored by electronic spectroscopy, recording the decay of the maximum absorbance of $1^{\bullet}$ ($\lambda_{\text{max}} = 384$ and 387 nm in benzene and $\text{CHCl}_3/\text{MeOH}$ (2:1), respectively) as a consequence of the electron addition to give anion 1^- . The experiments were effected with a $1^{\bullet}$ /polyphenol molar ratio of $\sim 5:1$ and an initial concentration of $1^{\bullet}$ of 54 μM . The reactions were completed when the absorptivities in the electronic spectra remained practically constants. The n -values of the stoichiometry of polyphenols were calculated using eq 6

$$n = \frac{A_0 - A_f}{\epsilon \cdot c} \quad (6)$$

where A_0 and A_f are the initial and final absorbances of the radical $1^{\bullet}$, respectively, c is the initial concentration of the antioxidant, and ϵ is the molar absorptivity of the radical.

The n values for the reactions of $1^{\bullet}$ with catechol and pyrogallol in $\text{CHCl}_3/\text{MeOH}$ (2:1) and $1^{\bullet}$ with pyrogallol in benzene are given in Table 4. While catechol reduces two molecules of radical per molecule, pyrogallol reduces up to three molecules of radical per molecule. Two steps of the decay of the absorbance of radical $1^{\bullet}$, one fast and one slow, with the antioxidant, catechol, or pyrogallol, in $\text{CHCl}_3/\text{MeOH}$ and only one slow decay step with pyrogallol in benzene can be distinguished in the course of the reducing processes. Calculated second-order rate constants (k_1) for the first fast step of the reactions in $\text{CHCl}_3/\text{MeOH}$ and for the only slow step in benzene are shown in Table 4.

Reactions of catechol and pyrogallol with radical $1^{\bullet}$ in $\text{CHCl}_3/\text{MeOH}$ (2:1) and pyrogallol with $1^{\bullet}$ in benzene could be evaluated after a moderate time (5.5 h) because they are practically completed and the number of electrons transferred per molecule of polyphenol were approximately 3 for pyrogallol and 2 for catechol. The rate constant values were estimated by using a simple kinetic model reported by Dangles et al.¹⁵ and are shown in Table 4 (Graphics of the kinetics of the reactions are displayed in the Supporting Information; see Figures S8–S10).

Experiments of catechol with radical $1^{\bullet}$ in benzene were also distinguished by only one very slow step. The number of electrons transferred from catechol to $1^{\bullet}$ after a long reaction time (13 h) corresponds to approximately one electron per

(14) Cyclic voltammograms for the oxidation of catechol and pyrogallol solutions (1 mM) in CHCl_3 and $\text{CHCl}_3/\text{MeOH}$ 2:1 (v/v) with tetrabutylammonium perchlorate (0.1 M) on Pt at 25 °C and in benzene with tetrahexylammonium hexafluorophosphate (0.3 M) on Pt at 25 °C were recorded. It was not possible to assign an anodic peak potential for the oxidation of pyrogallol in benzene due to the strong adsorption of the oxidized species in the electrode.

(15) Goupy, P.; Dufour, C.; Loonis, M.; Dangles, O. *J. Agric. Food Chem.* **2003**, *51*, 615–622.

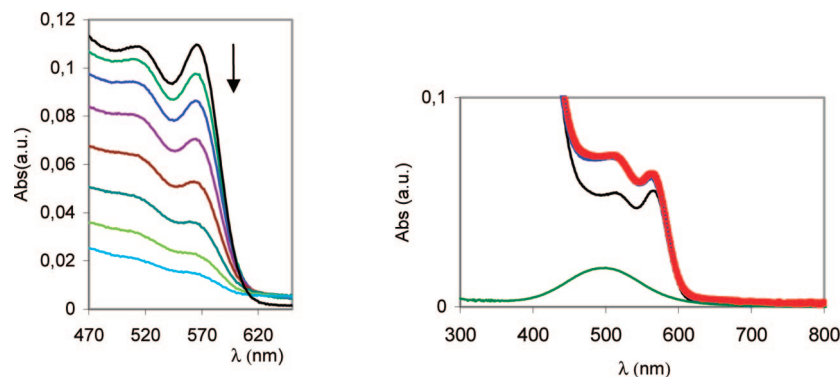


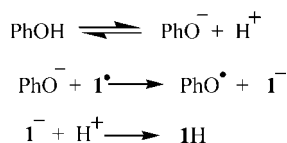
FIGURE 3. Left: Evolution of the lowest energy band intensity of a solution of $1^\bullet$ (120.2 μM) and pyrogallol (1.63 mM) in dry benzene at different times (first band in black, $1^\bullet$ in benzene; intervals of 10 min). Right: Lowest energy band in the absorption spectra of $1^\bullet$ (black), $1^{\bullet-}$ (green) (λ , 499 nm), theoretical combination: $1^\bullet + 1^{\bullet-}$ (red), and $1^\bullet$ (54.0 μM) + pyrogallol (10.6 μM) in dry benzene after 3 min of reaction (blue).

TABLE 4. Observed Rate Constants and Stoichiometric Factors for the Reactions^a of Radical $1^\bullet$ with Catechol and Pyrogallol in $\text{CHCl}_3/\text{MeOH}$ (2:1) and with Pyrogallol in Dry Benzene

	solvent	$1^\bullet$:polyphenol molar ratio ^b	k_1 ($\text{M}^{-1} \text{s}^{-1}$)	n^c
catechol	$\text{CHCl}_3/\text{MeOH}$ (2:1)	5.1	1123 ± 95	1.9
pyrogallol	$\text{CHCl}_3/\text{MeOH}$ (2:1)	4.6	5115 ± 82	3.1
pyrogallol	benzene	5.1	14.5 ± 0.4	3.0

^a Time of reaction, 5.5 h. ^b Initial concentrations of radical $1^\bullet$, 54 ± 2 μM . ^c Number of electrons transferred per molecule of polyphenol.

SCHEME 1

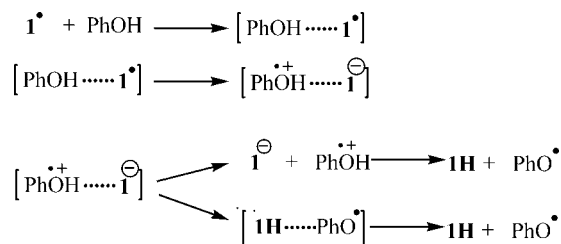


molecule of catechol, and values of the rate constant in the initial steps of these processes as low as $k_1 = 0.6 \text{ M}^{-1} \text{s}^{-1}$ were estimated.¹⁶

The rather fast reactions of catechol and pyrogallol with radical $1^\bullet$ in $\text{CHCl}_3/\text{MeOH}$ (2:1) are due, as mentioned above, to the fact that polyphenols are partially ionized to charged species PhO^- in this medium and these species can be more easily oxidized ($E_p^a = 0.25 \text{ V}$ vs SCE for catechol and $E_p^a = 0.06 \text{ V}$ vs SCE for pyrogallol in $\text{CHCl}_3/\text{MeOH}$ (2:1) in the presence of an excess of tetrabutylammonium hydroxide)¹¹ than the corresponding molecular species PhOH (see Table 3). Judging from the anodic peak potentials of catechol and pyrogallol, and the cathodic peak potential of $1^\bullet$ (see Table 3), both reactions should be exoergonic. The electron-deficient radical $1^\bullet$ reacts very fast by electron transfer reaction with the generally low concentration of PhO^- present in equilibrium with PhOH . Thus, the sequential proton loss–electron transfer (SPLET) mechanism, first reported by Litwinienko^{7a} and Foti,^{7b} occurs in these processes as described in Scheme 1.

The reaction of radical $1^\bullet$ with pyrogallol in benzene deserves especial mention. Benzene is a nonionizable solvent with a very low dielectric constant and it shows weak interactions with charged and polar species. However, the reaction of pyrogallol with radical $1^\bullet$, although slow as shown by the low value of the rate constant (Table 4), takes place through the generation of

SCHEME 2



the corresponding 1^- (see Figure 3). Now, if we pay attention to the onset potential values for pyrogallol and radical $1^\bullet$ in benzene from their corresponding cyclic voltammograms, i.e., when the electron transfer on Pt begins to take place, we obtain $E_{\text{onset}}^a \sim 1.1 \text{ V}$ for the oxidation of the former and $E_{\text{onset}}^c \sim 0.75 \text{ V}$ for the reduction of the latter, the electron-transfer reaction between pyrogallol and $1^\bullet$ should be endoergonic. To overcome this difficulty, it is reasonable to envisage the formation of a complex intermediate between both species. The strength of interactions between the phenol and the radical $1^\bullet$ can seriously affect the electrochemistry of both reactants providing an efficient intermolecular electron transfer from the pyrogallol. This intermediate may be constituted by hydrogen-bonding between the nitro oxygen atoms of the radical and the hydroxyl hydrogen atoms of the polyphenol, increasing the electron density on the phenolic oxygen and making it easier to be oxidized (Scheme 2).

This sequence of steps explains favorably the detection of the reduced species 1^- by electronic spectroscopy. Thus, once the electron is transferred into the complex, this rapidly dissociates leading to the free ions. Anion 1^- has been clearly detected by spectroscopy before the protonation of $1^{\bullet-}$ takes place. However, it is not discounted at all that the protonation of 1^- might take place in part into the complex as the acidity of the phenol significantly increases after one-electron oxidation to the radical cation.

In conclusion, the reactions between radical $1^\bullet$ and pyrogallol (PhOH) in different solvents occur by electron-transfer reaction to the SOMO of $1^\bullet$ to give the charged 1^- , which is consecutively protonated to 1H . In hydroxylic solvents, the electron transfer is a very rapid process and the electron-donating species is the ionized PhO^- , whereas in nonpolar and nonhydroxylic solvents, the electron transfer is facilitated by assuming an intermediate complex between $1^\bullet$ and PhOH . An additional experimental proof against the hydrogen atom abstraction mechanism of this last process is that TTM radical does not

(16) Values of k_1 were estimated proceeding with the Dangles' kinetic model. Now, the A_T value in eq 8 corresponds to the visible absorbance ($\lambda = 384 \text{ nm}$) of the radical $1^\bullet$ after 13 h when the reaction is not finished.

react at all with pyrogallol in benzene, although TTM and HNTTM have similar stability due to the steric hindrance provided by the six chlorine atoms around the trivalent carbon. The difference between both radicals resides in their electrochemical properties, HNTTM radical being much more oxidant ($E^\circ = 0.58$ V vs SCE) than TTM radical ($E^\circ = -0.66$ V vs SCE).¹¹

Experimental Section

Synthesis of Tetrabutylammonium Tris(2,4,6-trichloro-3,5-dinitrophenyl)methide (2). To a stirred solution of tris(2,4,6-trichloro-3,5-dinitrophenyl)methane (**1**) (269 mg; 0.3 mmol) in THF (15 mL) at rt was added an aqueous solution of tetrabutylammonium hydroxide (TBAH) (1.5 M) (26 μ L; 0.4 mmol), and the mixture was left in argon for a period of time (6 h). The precipitate (253 mg) was filtrated off, washed with water, and dried under reduced pressure to give salt **2** (253 mg; 73%): IR (KBr) 2973 (w), 2929 (w), 2871 (w), 1553 (s), 1465 (w), 1358 (m), 1222 (w), 945 (w), 833 (w), 784 (w), 735 (w), 677 (w), 638 (w) cm. Anal. Calcd for $C_{35}H_{36}Cl_9N_7O_{12}$: C, 39.4; H, 3.4; N, 9.2; Cl, 29.9. Found: C, 39.7; H, 3.6; N, 8.8; Cl, 29.2.

Reactions of Radical 1' with Polyphenols. Equimolecular solutions of tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl (**1'**) radical (50 mg) and catechol (6.7 mg) or pyrogallol (7.6 mg) in three different solvents (50 mL), $CHCl_3$, $CHCl_3/MeOH$ (2:1), and dry C_6H_6 , were stirred (47 h) at rt in the dark and in an inert atmosphere (Ar). The solutions were treated with water, and the organic fractions, dried over sodium sulfate, were evaporated off to yield a solid identified as a mixture of radical **1'** and methane **1** by IR and UV–vis spectra. The course of the reactions was monitored by UV–vis spectroscopy after 4 and 47 h of reaction.

Kinetic Measurements. An estimation of the kinetics of reactions of radical **1'** with catechol and pyrogallol in $CHCl_3/MeOH$ (2:1) and dry C_6H_6 at rt were performed. Procedure: To 3 mL of a freshly prepared solution (60 μ M) of **1'** in the solvent, placed in

the spectrometer cell, was added a freshly prepared solution (90.8 μ M) (390 μ L) of the polyphenol in the same solvent. The UV–vis spectra were recorded at different time intervals.

All of the procedures were carried out with an excess of radical. The rate constant of the electron transfer from phenol to HNTTM radical was estimated with a simple and general kinetic model reported by Dangles et al.¹⁵ making no hypothesis about the mechanism of polyphenol degradation, and only the fast steps of the reactions in $CHCl_3/MeOH$ were subjected to a kinetic analysis. Hence, in eqs 7 and 8, the digit 3 represents the number of moles of HNTTM radical that 1 mol of pyrogallol is capable to reduce, A_0 is the initial absorbance of the radical **1'** in the UV–visible spectra, A_f is the absorbance at the end of the fast step in the reactions in $CHCl_3/MeOH$ and at the end of the single step in the reaction in benzene, and c is the initial concentration of pyrogallol.

$$-d[TNPTM]/dt = k \cdot 3 \cdot [\text{pyrogallol}][TNPTM] \\ = k_1 [\text{pyrogallol}][TNPTM] \quad (7)$$

$$\ln \frac{1 - A_f/A}{1 - A_f/A_0} = -\frac{k_1 c}{A_0/A_f - 1} t \quad (8)$$

Acknowledgment. Financial support for this research from the MCT (Spain) through project AGL2006-12210-C03-02/ALI is gratefully acknowledged.

Supporting Information Available: Synthesis and X-ray powder diffraction study (experimental, structure solution, and refinement) of salt **2**; final atomic coordinates and observed and calculated X-ray diffraction patterns. Graphics for kinetics of HNTTM with pyrogallol and catechol. Cyclic voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO802559X