Alkyl Substituted Phenoxyl Decay in a Hydrogen Transfer Equilibrium

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ABSTRACT: The kinetics of radical decay in the equilibrium: 2,4,6-*tri-tert*-butylphenoxyl radical **1** + 2,6-di-*tert*-butyl-4-methylphenol **2** = 2,4,6-tri-*tert*-butylphenol **3** + 2,6-di-*tert*-butyl-4-methylphenoxyl radical **4** was studied at 298 and 273 K by means of EPR spectroscopy. At 298 K second order prevails, whereas at 273 K the best fit was order 3/2. The extinction of **4** takes place in two steps: dimerization followed by disproportionation of the dimer, but the stable radical **1** enters in crossed dimerization with **4** to yield nonradical products. The mechanism ensures a constant [**4**]/[**1**] ratio along the decay. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 37: 1–4, 2005

INTRODUCTION

In the course of measuring the equilibrium constant for the reaction (1), the concentration of the phenoxyl radicals 1 and 4 was measured by electron paramagnetic resonance (EPR) spectroscopy [1,2]. Now, reaction (1) has been studied at 273 and 298 K for the purpose of investigating the kinetics of 1 and 4 phenoxyl radical decay in the equilibrium.



The isolated radical **1** is stable. Otherwise, **4** is involved in dimerization followed by disproportionation

of the dimer to give a quinone methide (Q) and 2 [3,4]. In the equilibrium of reaction (1) both radical decay keeping constant the proportion [4]/[1] = 1.3 was observed.

Reaction (1) will be indicated

$$1 + 2 = 3 + 4 \tag{2}$$

and the dimerizaton of 4 gives

$$\mathbf{4} + \mathbf{4} = \mathbf{4}_2 \tag{3}$$

followed by disproportionation:

$$\mathbf{4}_2 \to \mathbf{Q} + \mathbf{2} \tag{4}$$

where $\mathbf{4}_2$ being the dimer of radical $\mathbf{4}$.

In the presence of 4, 1 undergoes crossed dimerization and disproportionation of the reaction product 4_{-1} :

$$4 + 1 = 4_1$$
 (5)

$$4_1 \to Q + 3 \tag{6}$$

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EXPERIMENTAL

Reaction (1) was carried out in benzene-toluene (1:1). The persistent radicals 1 and 4 were generated in the EPR sampling tubes by addition of 20 µl of 1.2×10^{-4} M benzene-toluene (1:1) solution of galvinoxyl radical (G; 2,6-di-tert-butyl- α -(3,5-di-tert-butyl-4-oxohexa-2,5-dien-1-ylidene)-p-tolyloxy free radical; Aldrich) to 100 μ l mixed solutions of phenols 3 and 2 in the same solvent mixture. Samples $(120 \ \mu l)$ were frozen and degassed by vacuum pumping. The monitoring of the equilibrium was accomplished in the thermostated cavity of a Bruker ER-200 X-band EPR spectrometer, equipped with a B-VT 1000 variable temperature unit, where samples were let thaw. EPR spectra were recorded after 1 min delay and the records were repeated at constant intervals for one or two half-life periods of time.

Phenols 2 and 3 were purchased from Aldrich and their purity was checked by TLC and ¹H-NMR. NMR spectra (200 MHz, CDCl₃) were recorded on a Bruker AC-200 NMR spectrometer at the spectroscopy service unit UMYMFOR (Conicet- FCEN, University of Buenos Aires).

All the solvents (Merck, analytical grade) were dried over potassium carbonate and distilled before use.

RESULTS AND DISCUSSION

The persistence of the radicals **4** (Fig. 1a) and **1** (Fig. 1b) makes it possible to monitor them by continuous wave EPR. The central line in the signal of **1** is about the center field of the records and it is free from contributions of **4** [5] (Fig. 1c). This allows the measurement of **[1]** independently of **[4]** by the complete quenching of G $(10^{-7}-10^{-6} \text{ M})$ in 0.2 M solutions of **3**, which gives **[1]**. On the other hand, **[4]** was calculated by measuring the peak to peak amplitude of the fifth line (from left to right, Fig. 1c) in the first derivative spectra taken from the concentration given by its dimerization equilibrium at 296 K [5–7].

At 298 K, the decay of **4** approaches second-order kinetics that agrees with the theoretical derivation:

$$-d[4]/dt = 2[4]^{2}[k_{3}k_{4}/(k_{-3}+k_{4})]$$
(7)

that followed by integration yields

$$1/[\mathbf{4}] = [2k_3k_4t/(k_{-3}+k_4)] + (1/[\mathbf{4}]_0)$$
(8)

Here, $[4]_0$ represents the molar concentration of 4 immediately after mixing the reactants, i.e. after the very



Figure 1 EPR first derivative spectrum of (a) 4, (b) 1, and (c) 1 + 4 in the equilibrium of reaction (1) at 273 K.

fast equilibration of 1 and 4 in reaction (1) has taken place, but before the much slower decay of dimer 4_2 has occurred to any extent.

The least-square fit affords

$$2k_3k_4/(k_{-3}+k_4) = 7347.68(R=0.9979)$$
(9)

Taking into account the previously reported values for k_3 , 4.5×10^7 M⁻¹ s⁻¹ [8], and $K_3 = k_3/k_{-3} =$ 3.7×10^5 M⁻¹ [6], k_4 was found to be 9.96×10^{-3} s⁻¹ and $k_{-3} = 122$ s⁻¹. Thus, the decay of **4** approaches second-order kinetics because $k_{-3} \gg k_4$ despite the disproportionation of the dimer is a unimolecular reaction. The decline of **4** in the presence of **1** in the equilibrium (1) also follows second-order kinetics (Fig. 2). A set of reactions has been designed involving the parallel dimerization of **4** and the crossed dimerization of **1** and **4**, both followed by disproportionation, as represented in Eqs. (3)–(6). That group of equations, including Eq. (2), that accounts for the full reaction mechanism was solved using a noncommercial numerical



Figure 2 Second-order decay of radical 4 in the equilibrium of reaction (1) at 298 K, R = 0.9988.

integration program specially developed for this purpose (Table I). Equations (3) and (5) might imply rate constants k_3 and k_5 of similar order, but the equilibrium of Eq. (5) should approach a half the value of that of Eq. (3). The molecule 4_2 is a head-to-tail dimer [4]; it involves the attachment of the oxygen (head) of 4 on the C₄ (tail) of another radical 4. But position C₄ is much more hindered in 1; therefore, 1 must bind its oxygen to the C₄ of 4, that is, it has only one half of the chances to react with 4.

On the other hand, the rate of formation of 4_2 should become diminished in the presence of 1 because of that competition. Thus, both 4_2 and 4_1 formation must be considered variables in the overall scheme of equations to be solved.

Reaction (1) is considered to be diffusion controlled [6,9], and the rate constant k_1 was calculated by means of the Smoluchowsky–Einstein–Stokes equation [10]

$$k_{\rm AB} = (2/3)(RT/\eta)[2 + (r_{\rm A}/r_{\rm B}) + (r_{\rm B}/r_{\rm A})]$$

where $r_A \cong r_B$ are the hydrodynamical radii of the molecules that encounter each other. The reactions depicted by Eqs. (3)–(6), when studied at 273 K, show a change in the order of decay into 3/2 (Fig. 3). This behaviour, which is not uncommon in the kinetics of



Figure 3 Order 3/2 decay of radical 4 in the equilibrium of reaction (1) at 273 K, R = 0.9986.

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Reaction	Rate Constant
$1+2 \rightarrow 3+4$	$1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$\mathbf{3+4} \rightarrow \mathbf{1+2}$	$1.0 \times 10^{10} \mathrm{~M^{-1}~s^{-1}}$
$4 + 4 \rightarrow 4_2$	$4.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$4_2 \rightarrow 4 + 4$	122 s^{-1}
$4_2 \rightarrow \mathbf{Q} + 2$	$7.8 \times 10^{-3} \text{ s}^{-1}$
$4+1 \rightarrow 4_1$	$2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$4_1 \rightarrow 4+1$	150 s^{-1}
$4_1 \rightarrow Q+3$	$7.8 \times 10^{-3} \text{ s}^{-1}$

Table IRate Constants for Differential Equations forthe Full Reaction Mechanism at 298 K

free radical reactions, has been examined previously [11,12]. The full scheme and the rate constants for the kinetics at 298 K are presented in Table I.

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