Thermochimica Acta 398 (2003) 33–37

thermochimica acta

www.elsevier.com/locate/tca

Solvent effect in a two phenoxyl radical equilibrium

Marta E.J. Coronel*

Departamento de Química, Universidad Nacional de Mar del Plata, Funes 3350, 7600 Mar del Plata, Argentina

Received 29 March 2002; received in revised form 15 July 2002; accepted 15 July 2002

Abstract

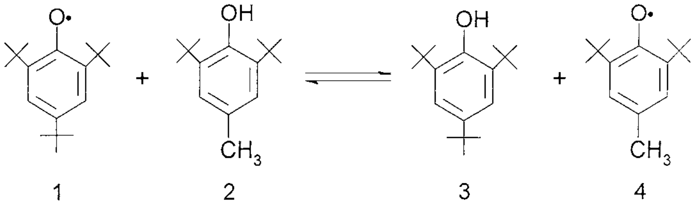
The equilibrium of the reaction: 2,4,6-tri-*tert*-butylphenoxyl radical (**1**) + 2,6-di-*tert*-butyl-4-methyl phenol (**2**) → 2,4,6-tri-*tert*-butylphenol (**3**) + 2,6-di-*tert*-butyl-4-methylphenoxyl radical (**4**) was studied from 243 to 298 K, for solutions 0.25 mol l^{-1} in phenols, in two groups of experiments. In the first group the equilibria were obtained in benzene–toluene (1:1) what yielded a second degree correlation in T^{-1}: $\ln K_{eq} = -23.31 + 1.3281 \times 10^4\,T^{-1} - 1.69038 \times 10^6\,T^{-2}$. In the second group the equilibria were performed in 0.25 mol l^{-1} 1,4-dioxane solution in benzene–toluene (1:1) which gave a linear correlation: $\ln K_{eq} = 0.949 + 5.278 \times 10^2\,T^{-1}$, from which $\Delta H_1 = 2.14 \pm 0.1$ and D_{sln} (O–H) $= 338.0 \pm 0.5$ kJ mol^{-1} in **2** were derived. The hydrogen bond of phenols to dioxane could explain the differences between the results found for the two sets of experiments.

Keywords: Phenoxyl radical; Hindered phenols; Bond dissociation enthalpy; Phenoxyl solvation; Solvent effect

1. Introduction

In a recent work released from this laboratory the electron paramagnetic resonance (EPR) study on $\ln K_{eq} = f(T^{-1})$ for the reaction 1 was reported in benzene–toluene (1:1), between 241 and 298 K. The function showed a parabolical dependence on T^{-1} with a maximum at 258 K [1]. The non-linear correlation could be attributed to the existence of hydrogen bonding of phenols to phenoxyl radicals in the lowest temperature zone under study.

In order to get an approach to the true nature of these results, a complementary set of measurements has been carried out. This new examination was followed by the same kind of experiments carried out with the addition of 0.25 mol l^{-1} 1,4-dioxane—an aprotic hydrogen bond acceptor (HBA)—to the samples [2].



(1)

2. Experimental

Reaction 1 was first performed in benzene–toluene (1:1) to obtain stable solutions over the temperature

---

* Fax: +54-223-475-3150.
E-mail address: mcoronel@mdp.edu.ar (M.E.J. Coronel).

0040-6031/03/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00394-5

range from 243 to 298 K. In the second set of experiments 0.25 mol l^{-1} 1,4-dioxane was present in the solvent. The phenols, **2** + **3**, amounted to 0.25 mol l^{-1} in all the samples.

The persistent radicals **1** and **4** were generated in EPR sampling tubes by addition 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 μl mixed solutions of phenols [3–6]. Samples, 120 μl in volume, were frozen and degassed by vacuum pumping up to 5 kPa to minimize differences of pressure in the experiments. The monitoring of the radicals in the equilibria was carried out in the thermostated cavity of a Bruker ER-200, X band EPR spectrometer, equipped with a B-VT variable temperature unit, where samples were allowed to thaw. EPR spectra were recorded after a 2 min delay and repeated at different periods of time after the first run to monitor the equilibrium constant during the slow decay of phenoxyl radicals.

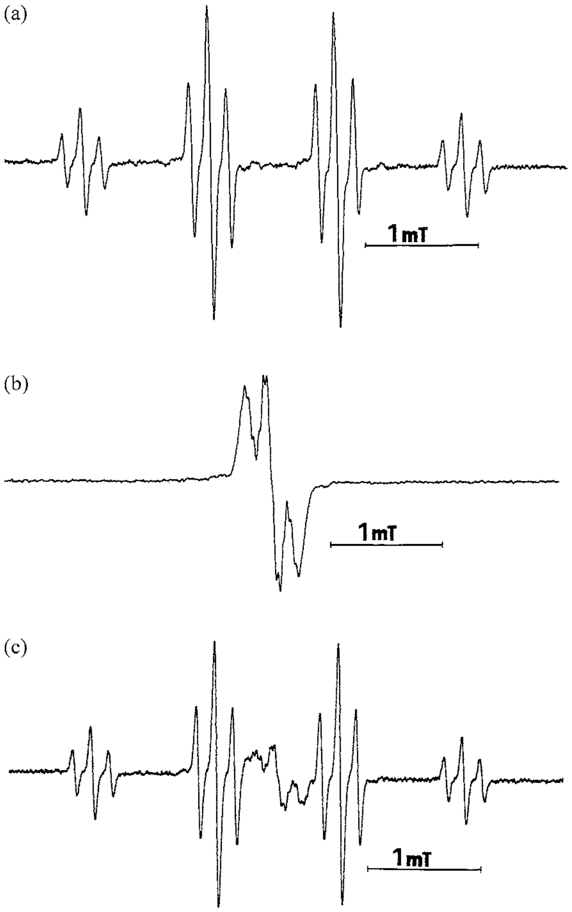


Fig. 1. (a) 2 × 10^{-5} mol l^{-1} **G** quenched with solution of benzene–toluene (1:1) 0.05 mol l^{-1} in **2**. (b) 3 × 10^{-7} mol l^{-1} **G** quenched with solution of benzene–toluene (1:1) 0.20 mol l^{-1} in **3**. (c) 2 × 10^{-5} mol l^{-1} **G** quenched with solution of benzene–toluene (1:1) 0.05 mol l^{-1} in **2** and 0.20 mol l^{-1} in **3**.

The concentration of each radical, **1** and **4**, was independently estimated by the area of non-overlapped lines [7]: the lowest field triplet of **4** and the central line in the triplet of **1** (Fig. 1a and b, respectively). The equilibrium constant $K_{eq} = [\mathbf{3}][\mathbf{4}]/[\mathbf{1}][\mathbf{2}]$ was straightforwardly calculated from the mol l^{-1} concentrations of phenols and phenoxyl radicals in the samples.

Phenols **2** and **3** (Aldrich) were crystallized from hexane and their purity was checked by TLC and nuclear magnetic resonance (NMR).

Proton NMR spectrum of phenol **2**—δ:1.50 (singlet, 18H, 2,6-di-*tert*-butyl); 2.34 (singlet, 3H, 4-methyl); 5.06 (singlet, 1H, aryl OH); 7.04 (singlet, 2H, two *m*-aryl H). Proton NMR spectrum of phenol **3**—δ:1.27 (singlet, 9H, 4-*tert*-butyl); 1.41 (singlet, 18H, 2,6-di-*tert*-butyl); 4.98 (singlet, 1H, aryl OH); 7.17 (singlet, 2H, two *m*-aryl H). NMR spectra (200 MHz, in deuterochloroform) 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.

3. Results and discussion

The persistence of radicals **1** and **4** 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 spectrum and is free from contributions of **4** (Fig. 1c). This allows the estimation of [**1**] independently of [**4**] by the complete quenching of **G** (10^{-7}–10^{-6} mol l^{-1}) in 0.2 mol l^{-1} solutions of **3**, which gives [**1**] since this radical is not involved in dimerization [8]. Phenoxy radical concentration [**4**] was calculated by measuring the area [7] of the lowest field triplet of this radical signal in the concentration given by its dimerization equilibrium at 295 K [9].

Table 1
Reaction performed in benzene–toluene (1:1)

T/K	$\ln K_{eq}$[a]	ΔG_1[a] (kJ mol^{-1})	ΔH_1[a] (kJ mol^{-1})	ΔS_1[a] (J mol^{-1} K^{-1})	N[b]
243	2.73 ± 0.02	−5.40 ± 0.11	5.25 ± 0.03	43.8 ± 0.1	8
248	2.78 ± 0.01	−5.73 ± 0.06	2.92 ± 0.02	34.9 ± 0.1	7
253	2.67 ± 0.03	−5.62 ± 0.17	0.77 ± 0.01	25.3 ± 0.2	4
258	2.82 ± 0.01	−6.05 ± 0.06	−1.48 ± 0.01	17.7 ± 0.1	10
263	2.76 ± 0.01	−6.04 ± 0.06	−3.55 ± 0.02	9.5 ± 0.1	10
268	2.70 ± 0.01	−6.02 ± 0.06	−5.54 ± 0.03	1.8 ± 0.1	10
273	2.69 ± 0.01	−6.11 ± 0.08	−7.46 ± 0.04	−0.5 ± 0.1	10
278	2.57 ± 0.01	−5.94 ± 0.03	−9.31 ± 0.05	−15.0 ± 0.1	10
283	2.47 ± 0.04	−5.81 ± 0.23	−11.10 ± 0.08	−18.7 ± 0.2	7
288	2.44 ± 0.04	−5.84 ± 0.02	−12.83 ± 0.07	−24.3 ± 0.1	10
293	2.38 ± 0.02	−5.80 ± 0.12	−14.49 ± 0.12	−29.7 ± 0.2	6
298	2.18 ± 0.04	−5.40 ± 0.02	−16.10 ± 0.12	−35.9 ± 0.1	7

[a] Mean ± S.E.

[b] Number of measurements.

Each sample was monitored during two half-life periods of the radicals (typically 450 s at 298 K) or over a 20 min period for the measurements below 263 K, so the constant value of K_{eq} was confirmed in the slow decay process described for **4** [8,9].

The results for the dioxane free samples are summarized in Table 1. A second degree polynomial fit in T^{-1} was found to be:

$$\ln K_{eq} = -23.31 + 1.3281 \times 10^4\, T^{-1} - 1.69038 \times 10^6\, T^{-2}$$

$R = 0.9426$, S.D. $= 0.51$ (Fig. 2). Its first derivative, $d \ln K_{eq}/d(T^{-1}) = -\Delta H_1/R$, was evaluated from 243 to 298 K (Table 1). Those data indicate the reaction is exothermic between 258 and 298 K, i.e. it releases heat to the surroundings. On the other hand, the reaction is endothermic below 258 K. This can be understood from the expression:

$$\Delta G = \Delta H - T\Delta S$$

arranged as

$$-\frac{\Delta G}{T} = \left(-\frac{\Delta H}{T}\right) + \Delta S$$

When the reaction is endothermic, $-\Delta H/T$ corresponds to a negative change in entropy of the surroundings and the formation of products is decreased [10]. That is, it has become apparent that there is a process with entropic cost which works at low temperature, a picture that agrees with some degree of hydrogen bonding of phenols to phenoxyl radicals. Foti et al. [11] have postulated the existence of encounters unproductive for the hydrogen transfer, namely hydrogen bonded complexes of radicals and phenols, involving the oxygen lone pairs of electrons in the radicals.

The results found for samples with addition of 0.25 mol l^{-1} 1,4-dioxane are presented in Table 2. For this set of experiments a linear fit in T^{-1} was found to be

$$\ln K_{eq} = 5.278 \times 10^2\, T^{-1} + 0.949$$

Table 2
Reaction performed in benzene–toluene (1:1) 0.25 mol l^{-1} in 1,4-dioxane

T/K	$\ln K_{eq}$[a]	ΔG_1[a] (kJ mol^{-1})	N[b]
243	3.10 ± 0.02	−6.26 ± 0.12	16
248	3.06 ± 0.02	−6.31 ± 0.12	12
253	3.06 ± 0.02	−6.44 ± 0.13	15
258	2.97 ± 0.03	−6.37 ± 0.19	12
263	3.09 ± 0.03	−6.76 ± 0.20	15
268	2.90 ± 0.03	−6.46 ± 0.19	15
273	2.79 ± 0.02	−6.33 ± 0.13	13
278	2.86 ± 0.02	−6.61 ± 0.13	12
283	2.82 ± 0.03	−6.64 ± 0.20	11
288	2.71 ± 0.05	−6.49 ± 0.33	10
293	2.78 ± 0.04	−6.77 ± 0.27	9
298	2.75 ± 0.04	−6.81 ± 0.28	9

[a] Mean ± S.E.

[b] Number of measurements.

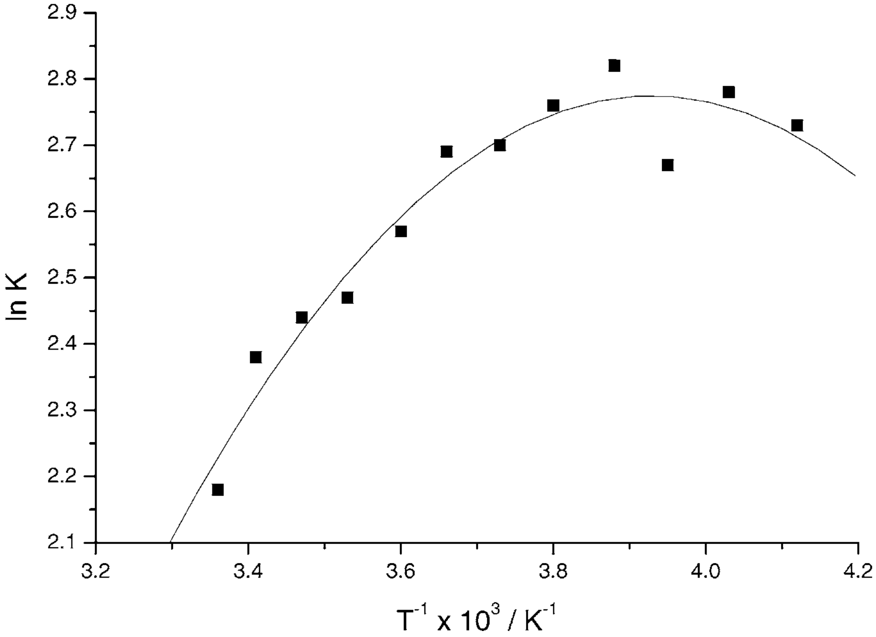


Fig. 2. Variation in $\ln K_{eq}$ with T^{-1} in benzene–toluene (1:1) in the range 243–298 K.

$R = 0.9163$, S.D. $= 0.06$, that yielded $\Delta H_1 = -2.14 \pm 0.10\,\text{kJ}\,\text{mol}^{-1}$ and $\Delta S_1 = 7.89 \pm 0.2\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$.

Barclay et al. [12] have showed that, despite the steric hindrance, phenol **2** can interact in some degree with acetone, another aprotic HBA. The linear Van't Hoff relationship, sustained over all the range of temperature, should indicate that phenoxyl radicals have been to a greater extent free from hydrogen bonding, presumably due to the interaction of phenols with dioxane. In this context it is possible to derive the homolytic bond dissociation enthalpy in **2**, related to that in **3**, which is 340.1 kJ mol^{-1} according to Mahoney et al. [13], by

$$\begin{aligned} D_{\text{sln}}\,(\text{OH})_2 &= D_{\text{sln}}\,(\text{OH})_3 + \Delta H_1 \\ &= (340.1 - 2.14)\,\text{kJ}\,\text{mol}^{-1} \\ &= 338.0\,\text{kJ}\,\text{mol}^{-1} \end{aligned}$$

4. Conclusion

It is possible that the severe steric hindrance of 2,6-di-*tert*-butylphenols does not prevent the hydrogen bond interaction with their derived phenoxyl radicals at low temperature. This could be the reason for the lost of linearity in $\ln K_{eq} = f(T^{-1})$ for dioxane-free samples. It appears conclusive that the presence of dioxane has allowed derivation of the homolytic bond dissociation value for 2,6-di-*tert*-butyl-4-methylphenol, relative to that for 2,4,6-tri-*tert*-butylphenol, possibly by interfering with the formation of hydrogen bond complexes between phenols and phenoxyl radicals.

Acknowledgements

The author thanks the Universidad Nacional de Mar del Plata for infrastructure and financial support.

References

[1] F.F. Pedeconi, M.E.J. Coronel, Anales Asoc. Quím. Argentina 88 (2000) 53.
[2] J.L.M. Abboud, R. Notario, Pure Appl. Chem. 71 (1999) 645.
[3] M.E.J. Coronel, A.J. Colussi, Int. J. Chem. Kinet. 20 (1988) 749.
[4] M.E.J. Coronel, A.J. Colussi, J. Chem. Soc., Perkin Trans. 2 (1994) 785.

[5] D.E. Paulon, M.E.J. Coronel, J. Chem. Soc., Perkin Trans. 2 (1998) 885.
[6] A. Watanabe, N. Noguchi, A. Fujisawa, T. Kodama, K. Tamura, O. Cynshi, E. Niki, J. Am. Chem. Soc. 122 (2000) 5438.
[7] J.E. Wertz, J.E. Bolton, Electron Spin Resonance. Elementary Theory and Practical Applications, McGraw-Hill, New York, 1972, Chapter 1, p. 33.
[8] M. Lucarini, G.F. Pedulli, M. Cipollone, J. Org. Chem. 59 (1994) 5063.
[9] R. Stebbins, F. Sicilio, Tetrahedron 26 (1970) 291.
[10] P.W. Atkins, Physical Chemistry, 6th ed., Oxford University Press, New York, 1998, Chapter 9, p. 225.
[11] M. Foti, K.U. Ingold, J. Lusztyk, J. Am. Chem. Soc. 116 (1994) 9440.
[12] L.R.C. Barclay, C.E. Edwards, M.R. Vinqvist, J. Am. Chem. Soc. 121 (1999) 6226.
[13] L.R. Mahoney, C. Ferris, M.A. Da Rooge, J. Am. Chem. Soc. 91 (1969) 3883.