ELSEVIER

Spectrochimica Acta Part A 59 (2003) 135–138

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

High resolution electronic absorption spectra of anisole and phenoxyl radical

Fuat Bayrakçeken *, Selin Aktaş [1], Melek Toptan, Asli Ünlügedik

Department of Electronics Engineering, Yeditepe University, Kayışdağı, 81120 Istanbul, Turkey

Received 19 February 2002; received in revised form 22 March 2002; accepted 9 April 2002

Abstract

High resolution absorption spectra of anisole and phenoxyl radical has been recorded in the vapor phase at room temperature by flash photolysis technique, and subsequent reactions have been investigated by kinetic spectroscopy. It was possible to follow the kinetics of the radical's decay which occurred predominantly by bimolecular recombination. The concentration of the phenoxyl radical calculated from the concentration of diphenoxyl molecules formed in the reaction cell during the optical pumping. The absolute extinction coefficient of this radical was measured from the absorption band at 291 nm, and found to be $0.95 \times 10^{+4}$ mol^{-1} l cm^{-1}.

Keywords: Phenoxyl radical; Flash photolysis; UV-absorption; Extinction coefficient; Biomolecular decay

---

1. Introduction

Radicals can be prepared by either oxidation or reduction of aromatic compounds. Such transformations may be carried out by a variety of methods photolysis, radiolysis, chemical oxidation or reduction, pyrolysis, electrolysis, and electrical discharge. The first three methods are the most commonly used. Absorption of light by an aromatic molecule results in the formation of an unstable excited state. This excited state becomes deactivated by either a photophysical process or a photochemical process, dissociation into radicals or ionization. In most cases, although practically most of the energy is lost by a photophysical process, a definite action of exciting energy results in neutral radical or ion-radical formation. The photolytic method is often a good way of producing specific aromatic radicals as one can irradiate with light of energy capable of breaking only the required bond.

Phenolic compounds show antioxidant activity mainly by reacting with the free radicals, that are known to demage biomolecules. However, their

---

* Corresponding author. Tel.: +90-216-578-0000; fax: +90-216-578-0400

E-mail address: bayrakf@yeditepe.edu.tr (F. Bayrakçeken).

[1] Present address: Medical school, Istanbul University, Istanbul, Turkey.

1386-1425/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1386-1425(02)00143-9

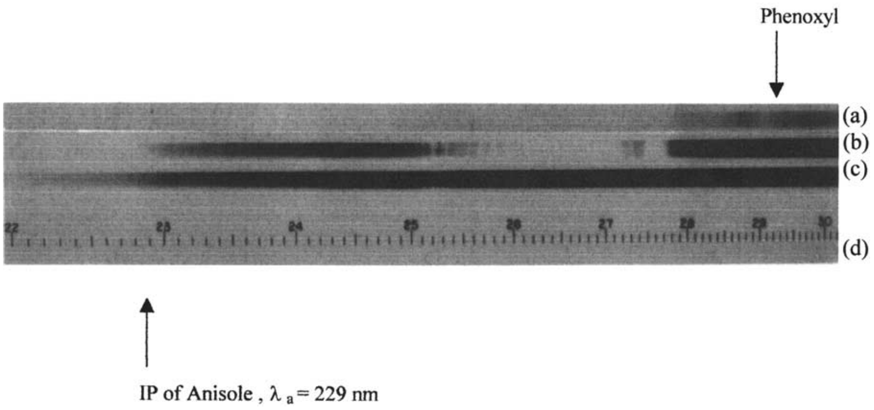

Fig. 1. (a) Transient absorption spectrum of phenoxyl radical, anisole (1 Torr) and nitrogen (500 Torr) in the vapor phase, $\lambda_a = 291$ nm; (b) absorption spectrum of anisole (1 Torr) and nitrogen (500 Torr), in the vapor phase; (c) absorption spectrum of empty cell; (d) wavelength scale (220–300 nm).

various competing reactions and the mechanism of action as antioxidants are still a matter of debate. In recent time, several natural phenols from plants like curcumin from turmeric and other plant derived phenols such as dehydrozingerone, eugenol and isoeugenol are found to show antioxidant behaviour. It possesses many structural similarities with curcumin and shows a wide range of pharmacological activities. Organic free radicals are generally short-lived, high reactive species, and the means of experimentally determining their structure and properties are, therefore, fairly limited.

The radicals are decaying rapidly by dimerisation, disproportionation or reaction with solvent. In such cases, special steps have to be taken in order to observe their absorptions [1–8].

The first satisfactory method of observing the spectra of aromatic radicals was by the flash photolysis technique of Porter [9], by this method momentarily high concentrations of radicals are produced photochemically by a short-duration high energy light flash. The transient radical absorption in then monitored in one of two ways: either by photographing over a wide wavelength range with a second lower-intensity light flash, triggered a few microseconds after the main flash, or at a single wavelength using a continuous monitoring light source and photoelectric detection.The former is the most useful for rapidly measuring complete absorption spectra [9,10].

2. Experimental

Flash photolysis apparatus: This employed two air filled photolysis lamps in series, with a flash duration of 2 μs, at a discharge energy of 845 J. Spectra were recorded on a Hilger medium quartz spectrograph, slitwidth 0.025 mm. The Ilford, HP-3 plates used were developed in Ilford PQ universal developer. Plate photometry: the spectra were photometered on a Joyce–Loeble double beam recording microdensitometer model MK1IB. Calibrated optical densities on the photographic plate were obtained with a seven step filter (Hilger, F-1273). Pressure measurements: low pressures of parent molecules (0.5 mTorr–3

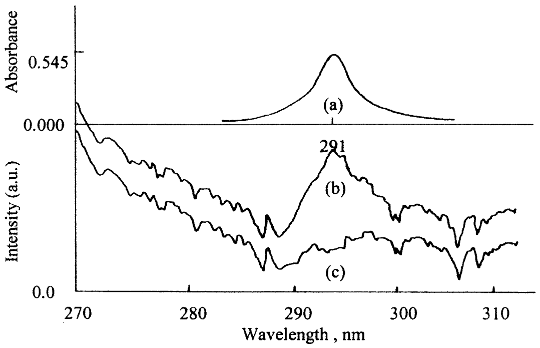

Fig. 2. (a) Background substracted absorption spectrum of the phenoxyl radical in the vapor phase; (b) microdensitometer trace of the phenoxyl radical in the vapor phase; (c) microdensitometer background trace.

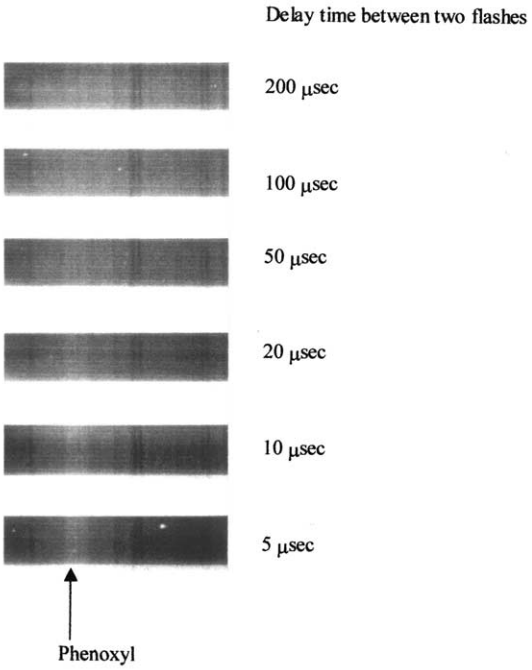

Fig. 3. Flash photolysis of anisole (1 and 500 Torr) showing the absorption spectrum of phenoxyl free radical and its decay, (flash energy = 1125 J).

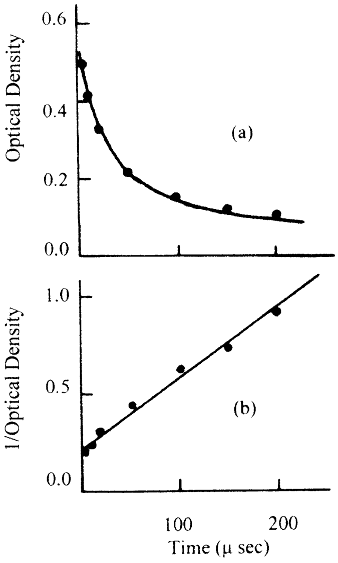

Fig. 4. (a) Decay of the phenoxyl radical at 291 nm; (b) second order plot for the decay of the phenoxyl radical at 291 nm.

Torr) were flashed after mixing with excess of nitrogen (at pressures up to 700 Torr), to maintain isothermal conditions. Pressures were measured with a McLoad gauge (up to 0.1 Torr), and above 50 Torr, with a mercury manometer. End product analysis: radical concentration was measured from the concentration by diphenoxyl molecule formed in the reaction cell during the photolysis flash. Face to face collision of two phenoxyl radicals produce diphenoxyl molecule which is in the steady state. Diphenoxyl molecule dissolved in ethyl alcohol, by using this solution, the concentration of diphenoxyl molecule measured by using Varian 3700/111 chromatography. Therefore, the concentration of the phenoxyl radical will be the twice of the concentration of the diphenoxyl molecule. The lifetime of the phenoxyl free radical was measured from the decay of the radical at 291 nm, which is the maximum location of the absorption band of the radical.

3. Results and discussion

Phenoxyl radical spectrum: radical was observed on flash photolysis of anisole and phenol. With phenol the radical absorption was just detected, due to the low vapor pressure at room temperature (i.e. phenol is in the solid form) but with anisole strong phenoxyl absorption spectra were obtioned. The free radical spectrum from the phenol is identical but the absorption bands of the radical spectra obtained by using phenol as a parent molecule do not appear clearly in photographic reproductions due to the low concentrations of the radicals formed during the vapor phase photolysis of phenol. Fig. 1, shows the high resolution absorption spectrum of the phenoxyl and anisole in the vapor phase at room temperature. Kinetics: a typical example of the decay of phenoxyl radical from anisole is shown in Figs. 3 and 4. The qualitative indications were that the bimolecular recombination of the phenoxyl radicals was an important reaction in the decay of the radical in experiments with both parent molecules. The lifetime of the radical is about 200 μs calculated from the decay parameters of Figs. 3 and 4. The primary photochemical processes (side chain fission) are as follows:

$$C_6H_5OH + h\gamma \ (UV) \rightarrow C_6H_5O^{\bullet} + H^{\bullet}$$

$$C_7H_8O + h\gamma \ (UV) \rightarrow C_6H_5O^{\bullet} + CH_3{}^{\bullet}$$

Fig. 2(a), shows the background substracted absorption spectrum of the phenoxyl radical in the vapor phase, (b) microdensitometer trace of the phenoxyl radical, and (c) microdensitometer background trace. Fig. 3, shows the typical absorption spectrum and decay of the phenoxyl radical in the vapor phase. Fig. 4(a) shows the decay of the phenoxyl radical at 291 nm, and (b) shows the second order plot for the decay of the phenoxyl radical at 291 nm (peak location). The decay of the phenoxyl radical in phenol system was rather faster than in anisole and second order plots were somewhat more erratic suggesting a possible contribution from the recombination of phenoxyl radicals with $CH_3{}^{\bullet}$, From Fig. 1, the ionization potential of anisole is found to be 5.4 eV ($\lambda = 229$ nm).The continuous absorption starts at 229 nm for anisole.

$$C_6H_5O^{\bullet} + C_6H_5O^{\bullet} \rightarrow C_6H_5O : OH_5C_6 \ \text{(Diphenoxyl)}$$

Face-to-face collision of two radicals, produce diphenoxyl molecule in the steady-state, therefore, we can calculate the concentration of phenoxyl radical by using the concentration of diphenoxyl molecules formed in the reaction cell. By using Lambert–Beer Law we also calculated the extinction coefficient at 291 nm.

The rate constant for the disappearance of phenoxyl free radical was: $k = 3.65 \times 10^4$ absorbance $\times$ s^{-1} for anisole.

A more detailed investigation of these and similar systems would be facilitated by an apparatus with which the ambient temperature could be varied, and with a more sensitive analytical technique. This would make possible the extention of the method to analogous compounds with lower pressure, phenol in particular, and probably result in a more complete kinetic analysis.

References

[1] K.I. Priyadarsini, T.P.A. Devasagayam, M.N.A. Rao, Rad. Phys. Chem. 54 (1999) 551–558 (and the references therein).

[2] C. Adamo, R. Subra, A. diMatteo, V. Barone, J. Chem. Phys. 109 (23) (1998) 10244–10254.

[3] L. Wojnarovits, A. Kovacs, G. Foldiak, Rad. Phys. Chem. 50 (4) (1997) 377–379.

[4] D. Shukla, N.P. Schepp, N. Mathivanan, L.J. Johnston, Can. J. Chem. 75 (1997) 1820–1829.

[5] T.N. Das, J. Phys. Chem. 105 (24) (2001) 5954–5959.

[6] T. Maki, Y. Araki, Y. Ishida, O. Onomura, Y. Matsummura, J. Am. Chem.Soc. 123 (14) (2001) 3371–3372.

[7] G.N. R. Tripathi, J. Phys. Chem A 102 (13) (1998) 2388–2397.

[8] F. Bayrakçeken, Chem. Phys. Lett. 74 (2) (1980) 298–300.

[9] F. Bayrakçeken, J.E. Nicholas, J. Chem. Soc. B 691 (1970).

[10] F. Bayrakceken, METU-J Pure Appl. Sci. 9 (1) (1976) 51–61.