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EXTINCTION COEFFICIENTS FOR THE PHENOXYL RADICAL

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ABSTRACT

The absorption spectrum of the phenoxyl radical has been recorded in the gas phase at room temperature, and subsequent reactions have been investigated by kinetic spectroscopy and gas liquid chromatography. The extinction coefficient of this radical was measured from the absorption band at 292 nm.

INTRODUCTION

Aromatic 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, electrical discharge, etc. 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, e.g. fluorescence or phosphorescence, or a photochemical process, e.g. dissociation into radicals or ionisation. In most cases, although practically all the energy is lost by a photophysical process, a definite fraction of exciting energy result in neutral radical or ion radical formation. For example, photolysis of toluene results in the photoejection in low quantum yield of a hydrogen atom, and the consequent formation of a benzyl radical $\varnothing$ CH_2 (Bayrakçeken, 1970). 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.

The first satisfactory method of observing the spectra of aromatic radicals in solution was the flash photolytic technique of (Porter, 1950). By this method momentarily high concentrations of radicals are produced photochemically by a short duration, high energy light flash. The transient radical absorption is 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, the latter being used in the main for following the reactions of radicals. In recent years the flash photolysis technique (Bayrakçeken, 1976), has been used to study aromatic radicals, the methods been similar to flash photolysis except that short high energy electron pulses are used instead of light flashes. The electron pulses used (0.2-2 microsecond duration) are shorter by a factor of ten than light flashes giving comparable radical concentrations, and therefore, shorter-lived species may be observed.

The absorption spectra of the isoelectronic radicals: benzyl, anilino (Bayrakçeken, 1970, 1972) and phenoxyl each consists of two distinct systems, a sharp band near 300 nm., and another transition in the region 400-500 nm., of varying relative intensities for the different radicals. The presence of a weak transition in the visible and a strong one in the near ultraviolet spectrum of benzyl was pedicted by the molecular orbital calculations of (Dewar, Longuet-Higgins and Pople 1955). Benzyl is an odd alternant hydrocarbon radical with seven electrons.

The wavelength shifts that are observed are not very significant, in view of the different band widths and shapes and the consequently different separations between the maximum and the origin. Because of the relationship of the spectra of phenoxyl and anilino to that of benzyl, both the 300 nm. and 400 nm. bands of all three radicals: $\varnothing O\cdot$, $\varnothing NH\cdot$ and $\varnothing CH_2$, are $\pi\rightarrow\pi^*$. There have been several recent theoretical discussions of the energy levels of the benzyl radical (Mori et al, 1961, Baudet et al, 1963).

EXPERIMENTAL

Flash photolysis apparatus: This employed two air filled photolysis lamps in series, with a flash duration (1 /e) of 2 microseconds., at a discharge energy of 845 J. Spectra were recorded on a Hilger medium quartz spectrograph, slitwith 0.025 mm. The Ulford HP3 plates used were developed in Ilford PQ universal developer. Plate photometry: The spectra were photometred on a Joyce-Loeble double beam recording microdensitometer model MKIIB. Calibrated optical densities on the photographic plate were obtained with a seven step filter (Hilger, F-1273).

Pressure measurements: Low presures of parent molecules (0.5 milli torr to 3 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), a spiral gauge (0.1-50 torr), and above 50 torr, with a mercury manometer.

End product analysis: Radical concentration is measured by Varian 3700 / 111 chromatography.

RESULTS AND DISCUSSIONS

Phenoxyl radical spectrum: Radical was observed on flash photolysis of anisole and phenol. With phenol the radical was just detected, but with anisole strong phenoxyl absorption spectra were obtained. The radical spectrum from the phenol is idendical 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 concentrati ons of the radicals formed during the gas phase photolysis of phenol (Bayrakçeken, 1976). Kinetics: A typical example of the decay of phenoxyl radical from anisol is shown in figure 1. The qualitative indications are that the bimolecular recombination of phenoxyl radicals is an important reaction in the decay of the radical in experiments with both parent molecules. At the total presures employed in this work the process is not termolecular involving either the parent molecule or the nitrogen present in excess. This is in accord with results for other radicals with many degrees of freedom available for the distribution of energy released on bond formation, such as simple aliphatic radicals for which the kinetic data have been reviewed by (Benson, 1960). The contribution of other reactions such as recombination with halogens cannot be quantitatively assessed. The lifetime of the radical is about 200 microseconds. The primary photochemical processes (side chain fission) are follows:

$$C_6H_5OH + (UV) \rightarrow C_6H_5O\cdot + H\cdot$$

$$C_7H_8O + (UV) \rightarrow C_6H_5O\cdot + CH_3\cdot$$

Figure two shows the typical kinetic plots for 1 / absorbance versus time for phenoxyl radical at 292 nm. The decay of the phenoxyl radical in phenol systems 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 hydrogen atoms.

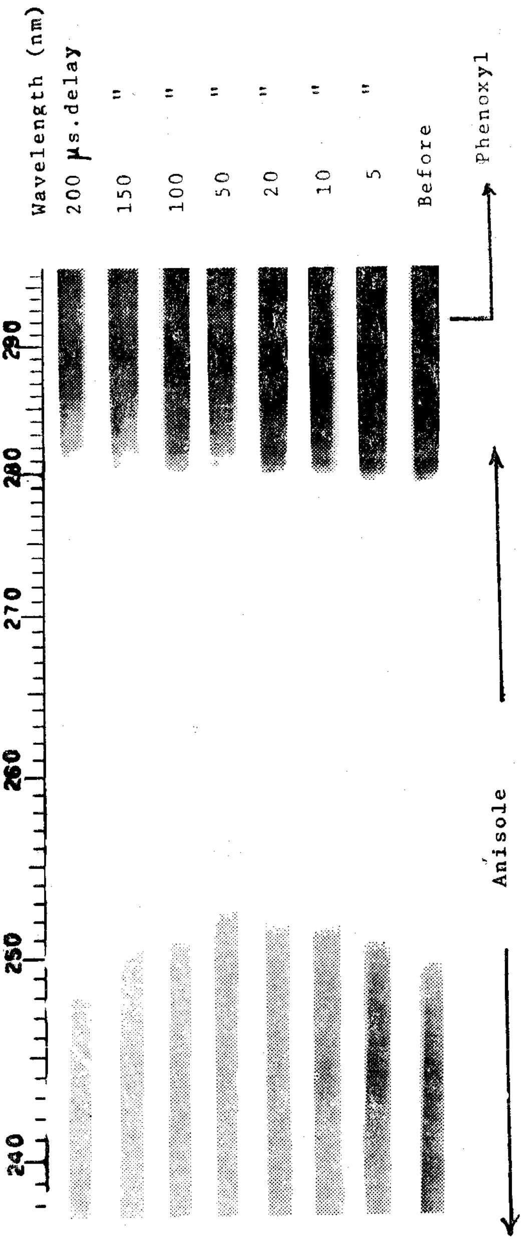

Fig. 1 Flash photolysis of Anisole (1 torr) and Argon (500 torr) showing the spectrum of the phenoxyl radical and its decay. Flash energy = 1125 J.

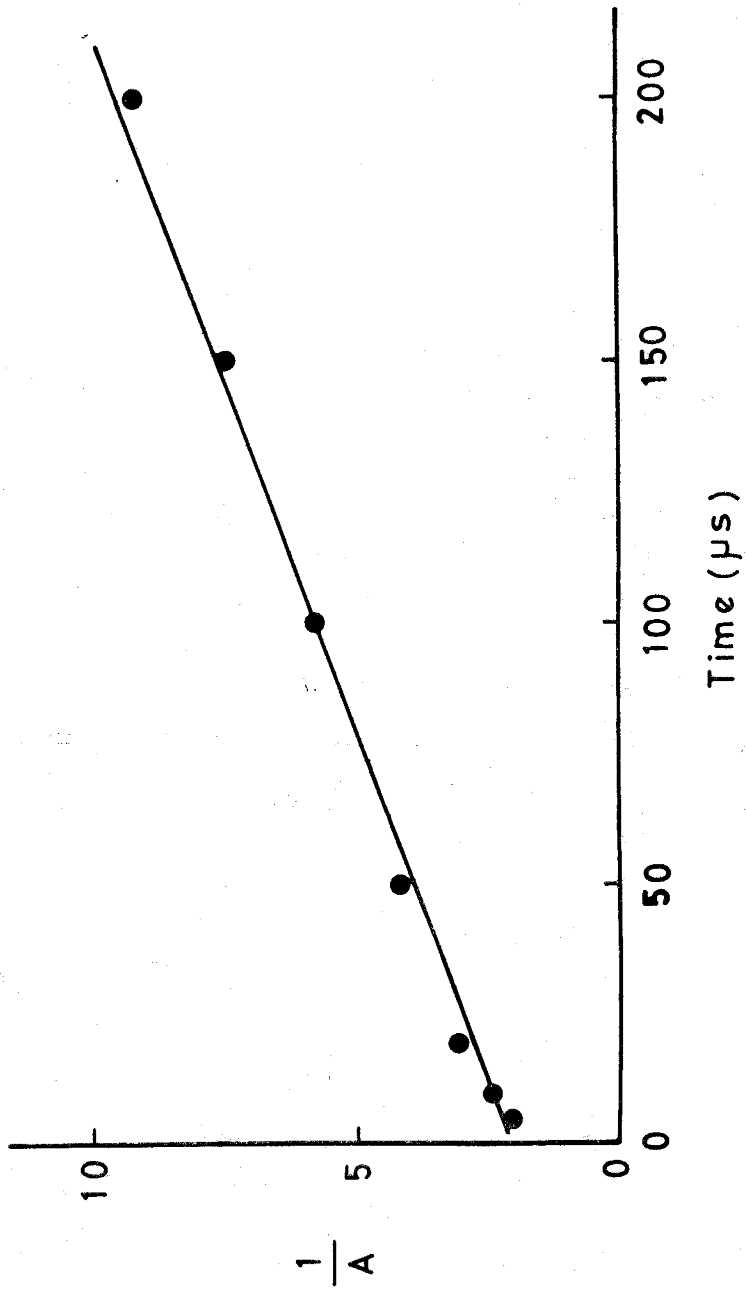

Fig. 2 Second order plot for the decay of the phenoxyl radical measured at 292 nm.

TABLE 1

Compound	k ($10^4 . A^{-1} . s^{-1}$	Wavelength (nm.)	Ex. Coeff. ($10^4 . Mol^{-1} . l . cm^{-1}$)
Anisole	3.65	292	0.95

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