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High resolution electronic absorption spectra of aniline, anilino and silicon dioxide

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Abstract

High resolution electronic absorption spectra of aniline and anilino free radical have 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 anilino radical's decay which occurred predominantly by bimolecular recombination. Decay parameters of anilino free radical were measured from the absorption bands.

Keywords: Aniline; Anilino; Flash photolysis; Silicon dioxide; Bimolecular 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, flash 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 free 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. The lifetime of most aromatic radicals is of the order of milliseconds in solution and microseconds in the gas or vapor phase, and high speed time resolution studies have to be made for them. Aromatic radicals are of growing significance in environmental chemistry due to their toxic nature and their suspected carcinogenic properties. Their use in the manufacturing of dyes, cosmetics, medicines and rubber increases the possibility of release into the environment with the risk being exacerbated further by the fact that some aromatic amines can

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be released from the degradation of pesticides. Therefore there is a clear need for a suitable sensing strategy to be designed. Aniline and its derivatives have been widely used for a variety of applications from photochemistry to medicine as antibacterial, anticancer, herbicidal, and fungicidal agents.

The radicals produced being trapped in inert rigid media and thus prevented from reacting. The matrices most commonly used were mixtures of ethanol, isopentane, and ether (EPA), and methyl cyclohexane and isopentane (MP). By flash photolytic method momentarily high concentrations of radicals were produced photo-chemically with a short-duration, high energy light flash. A quite simple way of differentiating between radical and triplet state absorptions occuring in flash photolysis and laser flash photolysis is to compare the spectra observed in the presence and absence of air. Since the rate of quenching triplet states by paramagnetic oxygen is so fast, therefore no triplet state absorption is seen in the presence of air, where as both radical and triplet state absorptions are seen in the absence of air. This method depends on the fact that in general, aromatic radicals react rather slowly with oxygen but it is only suitable when the presence of air does not interfere with photolytic formation of triplet states and radicals. The usual small shifts in going from gas–liquid–solid phases occur for aromatic radicals, for example, the wavelength maximum of the anilino free radical in the vapor phase, liquid paraffin and methyl-pentane glass (77 K) are: 300.8, 300.7 and 308.8 nm, respectively. Our apparatus has a high light output with short flash duration time which enabled kinetic as well as spectroscopic investigations to be carried out for the short lived, (i.e. microseconds), free radicals. 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 [1–10]. Phenolic compounds can also pose serious problems in environmental solutions and are major interferents in the direct electrochemical detection of aniline. This is primarily due to the formation of polimeric species on the electrode surface upon oxidation of the phenolic compound [11,12].

Microwave studies of the gas phase and X-ray diffraction of the solid state have shown the nitrogen environment in aniline to be non-planar. In fact, the nitrogen is out of the plane of the phenyl ring and the nitrogen itself is pyramidal. The structure has been difficult to reproduce theoretically, but the energy barriers to internal motional processes are in close agreement with the experimentally measured values. The rotation and inversion barriers for aniline have been measured experimentally to be 23 and 6 kJ/mol, respectively [13,14].

2. Experimental

2.1. Flash photolysis apparatus

This employed two air or argon 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.

2.2. Plate photometry

The spectra were photometered 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 pressures of parent molecules (0.5 mTorr–3 Torr) were flashed after mixing with excess of oxygen free 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. Face to face collision of two anilino radicals produce dianilino molecule which is in the steady state.

The lifetime of the anilino free radical was measured from the decay of the radical at 300.8 nm, which is the maximum location of the absorption band of the radical.

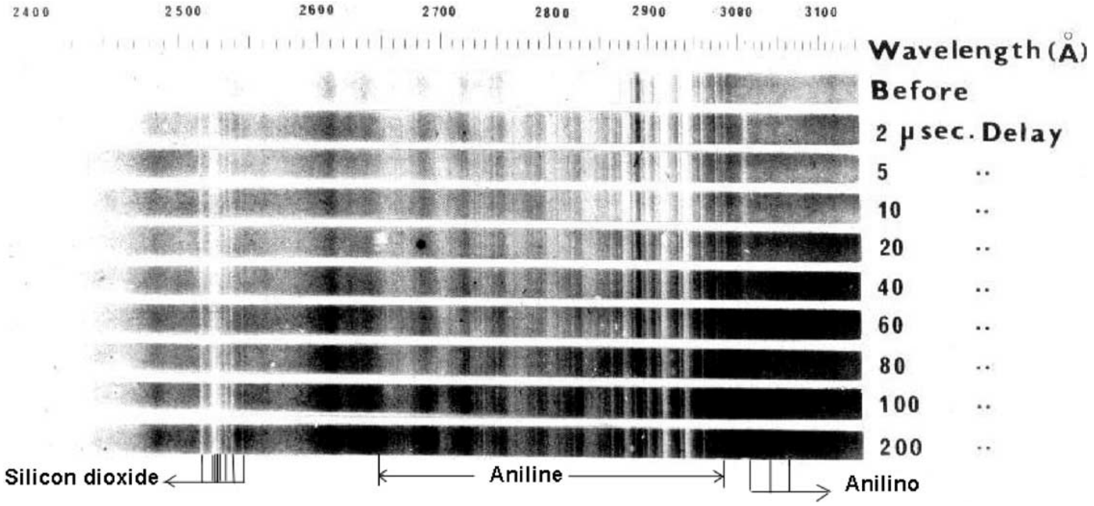

Fig. 1. Flash photolysis of aniline, (7.9×10^{-2} Torr) and N_2 (500 Torr), showing the absorption spectrum of aniline, anilino free radical and its decay in the vapor phase. Photolysis energy = 720 J.

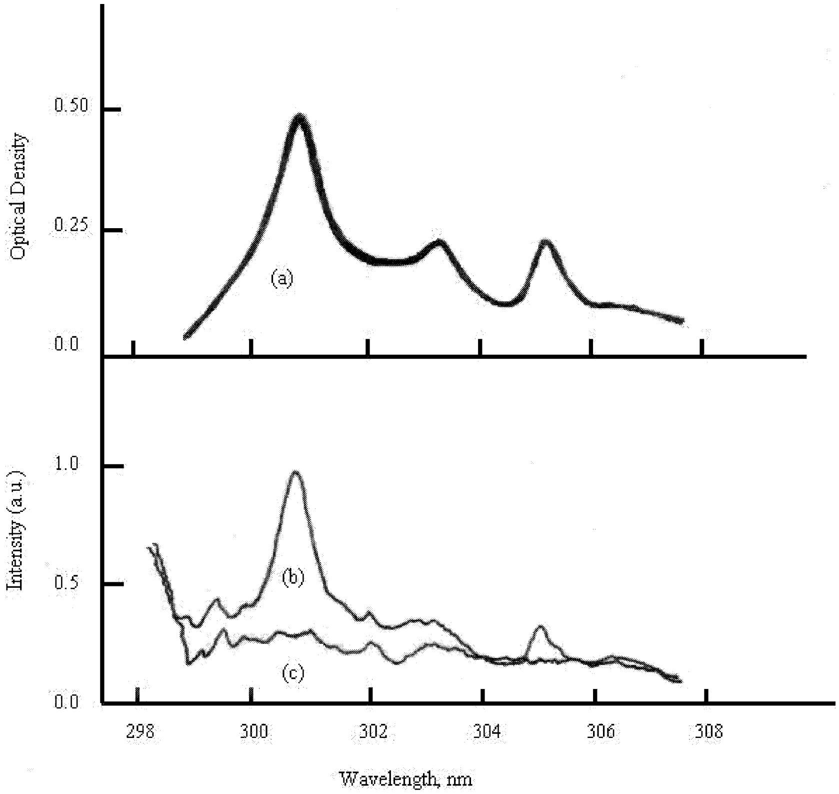

Fig. 2. (a) Background substracted absorption spectrum of the anilino radical in the vapor phase; (b) microdensitometer trace of the anilino radical in the vapor phase; (c) microdensitometer background trace.

3. Results and discussion

In this paper, the high resolution electronic absorption spectra of aniline, anilino radical and its decay by time is recorded photographically in the vapor phase at room temperature. The windows of the reaction cell were spectroscopically pure silicon dioxide therefore high resolution absorption spectrum of silicon dioxide is also recorded in the ultraviolet region. The flash photolysis of aniline vapor at 25 °C and at 0.79 μm mercury pressure in the presence of oxygen free nitrogen 500 mm mercury resulted in the appearance of a strong band at 300.8 nm and two weak bands at 303 and 305 nm. Weak bands were rather diffuse and their relative intensities was lower than the main band at 300.8 nm. Fig. 1 shows the high resolution absorption spectra of aniline, anilino free radical in the vapor phase at room temperature and high resolution absorption spectra of silicon dioxide in the solid state. Fig. 1 illustrates the complete decay of anilino free radical. The first strip written ‘before’ was recorded by using only the spectral flash alone. Before these were recorded by using photolysis flash and spectral flash with delay times from 2 to 200 μs, immediately after the photolysis flash within 1 μs experimental error. The calibration of the spectrograph was checked with a mercury light source. Second order decay was observed for anilino radical and the rate constant was found to be 81 000 × 1/optical density × 1/s. Fig. 2(a) illustrates the background substracted absorption spectrum of the anilino radical in the vapor phase; (b) microdensitometer trace of the anilino radical; (c) microdensitometer background trace (microdensitometer trace of the empty cell). Fig. 3(a) illustrates the decay of the anilino radical at 300.8 nm; and (b) second order plot for the decay of the anilino radical at 300.8 nm. The appearance and decay of the transient at 300.8 nm were similar to that in the benzyl radical at 305.3 nm [15].

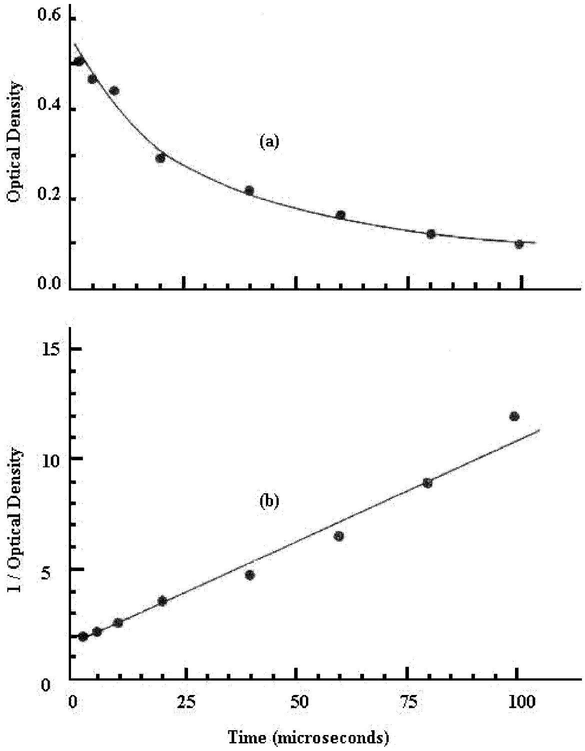

Fig. 3. (a) Decay of the anilino radical at 300.8 nm; (b) second order plot for the decay of the anilino radical at 300.8 nm.

The transitions are due to the excitation of valence electrons therefore there is no likelihood of another band occuring at wavelengths longer than 780 nm, but there is always a possibility that other absorptions may occur in the vacuum ultraviolet. Our flash photolysis apparatus does not permit us to do any investigation at wavelengths shorter than 210 nm. Therefore the absorption spectrum of the radical searched in the 210–780 nm region. The lifetime of the anilino free radical is about 100 μs. The primary photochemical process (side chain fission) is as follows:

$$C_6H_5NH_2 + \text{UV-photons} \rightarrow C_6H_5NH^\bullet + H^\bullet$$

The rate constant for the recombination of anilino has been presented in terms of its extinction coefficient at 300.8 nm in the vapor phase. Unfortunately, the extinction coefficient was unknown and end-product analysis was undertaken by the method of gas chromatography in an attempt to measure this quantity and the corresponding rate constant in absolute units. The aniline vapor in the reaction cell in different pressures was flashed, (energy of the flash lamp was 1125 J/pulse), a hundred times in the presence of a large excess of oxygen free nitrogen. The photoproduct was dissolved in an appropriate solvent and most of the solvent was then evaporated in order to concentrate the photoproduct for gas chromatographic measurements. No significant change in the absorption was observed in the aniline spectrum itself, therefore rate of the decay was given in terms of 1/optical density × 1/s, instead of absolute units. In view of these uncertainities it would be most interesting to extend these measurements by use of more sensitive gas chromatographic equipment in order that the vital product analysis should not be so close to the limits of detectability.

References

[1] F. Bayrakçeken, S. Aktaş, M. Toptan, A. Ünlügedik, Spectrochim. Acta Part A 59 (2003) 135.

[2] E.H. Seymour, N.S. Lawrence, E.L. Beckett, J. Davis, Talanta 57 (2002) 233.

[3] H.E. Birkett, J.C. Cherryman, A.M. Chippendale, P. Hazendonk, R.K. Harris, J. Mol. Struct. 602–603 (2002) 59.

[4] L.T. Bozic, Vibr. Spectrosc. 28 (2002) 235.

[5] A.N. Taha, N. True, J. Phys. Chem. A 104 (2000) 2985.

[6] N.G. Vasiilev, V.S. Dimitrov, J. Mol. Struct. 522 (2000) 37.

[7] G.L. Estiu, J. Mol. Struct. (Theochem.) 401 (1997) 157.

[8] R. Nakagaki, I. Aoyama, K. Chimizu, M. Akagi, J. Phys. Org. Chem. 6 (1993) 261.

[9] K. Sawada, T. Kanda, Y. Naganuma, T. Suzuki, J. Chem. Soc. Dalton Trans. (1992) 2955.

[10] F. Bayrakçeken, M. J. Pure Appl. Sci. 5 (2) (1972) 177.

[11] J.C. Merriman, D.H.J. Anthony, J.A. Kraft, R.J. Wilkinson, Chemosphere 23 (1991) 1605.

[12] T. Berjerano, C. Forgacs, E. Gileadi, J. Electroanal. Chem. 27 (1970) 469.

[13] D.G. Lister, J.K. Tyler, J. Chem. Soc. Chem. Comm. (1996) 152.

[14] M. Fukuyo, K. Hirotsu, T. Higuchi, Acta Crystallogr. B 38 (1982) 640.

[15] F. Bayrakçeken, Chem. Phys. Lett. 74 (2) (1980) 298.