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NITROBENZENE RADICAL ANION

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Several conflicting reports have appeared in the literature concerning the electronic spectra of nitrobenzene radical anion.[1-5] Kemula and Sioda[1] produced nitrobenzene radical anion (N^{-}) electrochemically in DMF with $NaNO_3$ as supporting electrolyte and found $N^{\dot{-}}$ to be brown in colour with a λ_{max} at 435 and 465 mμ. Nagakura and coworkers[2] found that the brown solution of $N^{\dot{-}}$ produced by potassium reduction in DME turned purple with time and showed five bands at 292, 325, 370, 420 and 568 mμ besides a charge transfer band at ~ 800 mμ. Kastening[3] has reported that the electrochemically produced $N^{\dot{-}}$ shows five bands in the region 390-450 mμ in aqueous solution. Recent reports,[4,6] however, indicate that $N^{\dot{-}}$ shows only one band around 464 mμ both in DMF solution and in the solid state.

In view of these conflicting reports, we have undertaken a study of the chemistry and spectroscopy of $N^{\dot{-}}$. We find that the reduction of nitrobenzene by alkali metals gives rise to several products, and the spectrum of N^{-} can be satisfactorily explained on the basis of these products.

We find that the brown solution of $N^{\dot{-}}$ formed by lithium reduction in ether solvents is not stable even in an inert atmosphere and changes its color to purple and later to red or dark brown, on keeping. Corresponding changes in the spectrum were also observed. Thus, a solution of nitrobenzene in THF, immediately on treatment with lithium, absorbs at 440 mμ; new bands appear at 295, 340 and 383 mμ, after about 30-40 minutes, whereas, after about 60-90 minutes, newer bands appear in the 420-710 mμ region, in addition to a band at 760 mμ. Of these several bands, some resembled those of nitrosobenzene (NO), whereas, few corresponded to those of azobenzene and its radical and dianions.[6] It was felt therefore, necessary to examine the chemical species formed by the alkali metal reduction of nitrobenzene.

Treatment of nitrobenzene with Li in THF gives a number of products, which include azobenzene (55%), small amounts of o-anilinoazobenzene m.p. 56°; λ_{max} 287 (log ϵ, 4.48), 522 (4.35) and 457 mμ (4.03) , o,o'-dianilinoazobenzene m.p. 158° (d); λ_{max} 288 (log ϵ, 4.51), 525 (4.02) and 504 mμ (4.13), an unidentified isomer of dianilinoazobenzene m.p. 120° (d); λ_{max} 290 (log ϵ, 4.51), 525 (4.19) and 472 mμ (3.63) and a few unidentified high molecular weight species, also showing characteristic absorption bands in the regions 285-295, 520-590 and 445-540 mμ. The identities of anilinoazobenzenes were confirmed by elemental analyses and mass spectra. It is possible that azobenzene is formed through the intermediates nitrosobenzene and azoxybenzene in the lithium reduction of nitrobenzene, whereas, the anilinoazobenzenes may arise through nitrene intermediates. In support of this view, lithium reduction of nitrosobenzene in THF gives azobenzene (55%) and similar products as in the reduction of nitrobenzene. Azoxybenzene (AOB) with lithium in THF gave a quantitative yield of azobenzene.

We have examined the electronic spectra of the radical anions of NO, AOB, o-anilinoazobenzene (ANB) and o,o'-dianilinoazobenzene (DAB) in order to explain the complexities in the spectrum of $N^{\dot{-}}$. The bands of $NO^{\dot{-}}$ (538 and 406 mμ) decreased in intensity with time giving rise to several newer bands in the 550-600 mμ region. The λ_{max} values of $AB^{\dot{-}}$ are known to be at 315, 420 and 605 mμ and that of azobenzene dianion ($AB^{=}$) at 579 mμ.[6] $AOB^{\dot{-}}$ shows a band at ~ 580 mμ which soon disappears giving rise to the characteristic bands of AB and $AB^{\dot{-}}$. $AAB^{\dot{-}}$ shows a band at 535 mμ, while $DAB^{\dot{-}}$ gives rise to bands at 508, 658 and 687 mμ. $AAB^{=}$ (λ_{max} 527 m) produced by reduction with excess lithium is readily oxidised to $AAB^{\dot{-}}$ and AAB.

With the aid of the absorption data of the neutral as well as radical anion species of the several reduction products of nitrobenzene, we are able to explain all the bands in the time-dependent spectrum of $N^{\dot{-}}$ and also the bands reported by Nagakura and coworkers.[2] It is now apparent that only the band at 440 mμ is characteristic of $N^{\dot{-}}$. We have also examined the esr spectrum of $N^{\dot{-}}$ as a function of time. A freshly prepared brown solution of $N^{\dot{-}}$ exhibited a 54-line spectrum[7]; the line shapes changed with time, eventually leading to a completely different spectrum.

The 440 mμ band of $N^{\dot{-}}$ showed the expected solvent dependence, the bands being sharper in 1,2-dimethoxyethane. The spectra showed distinct bands due to intimate and solver separated ion pairs in equilibrium. It appears that the two bands reported by Kemula and

Sioda[1] are due to these two species caused by the presence of the supporting electrolyte. The λ_{max} of N- increased with the radius of the cation (Li^+, 440; Na^+, 444 and K^+, 470 mμ in THF solution); the ratio of the intimate and solvent separated species also varies with the solvent and the cation. The 444 mμ band of N- also showed substituent effects. Electron-donating substituents like p-OCH_3 and p-$N(CH_3)_2$ do not shift the bands appreciably, whereas electron-withdrawing groups like p-NO_2 and p-CN produce large bathochromic shifts. These substituent effects appear to be in the right direction since electron-withdrawing groups can interact with electron rich π-system by resonance interaction while the donating groups cannot.[8]

The results indicate the difficulties that one might encounter in interpreting the esr and optical spectra of radical anion species produced by alkali metal reduction. Further work on the spectroscopy and chemistry of N- and other radical ions is currently in progress.

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