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Remarks on the Electronic Spectrum of Nickelocene

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In their discussion on the nickelocene electronic spectrum, Scott and Becker reported three intense bands in the ultraviolet spectral region in addition to other weaker bands at longer wavelengths.[1] The nickelocene spectrum in cyclohexane, as recorded by Scott and Becker at 24 °C, is shown in Figure 1.

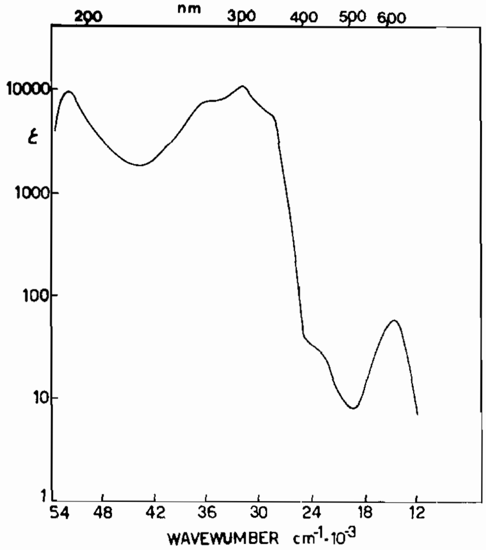

Fig. 1. Absorption spectrum of nickelocene in cyclohexane at 24 °C.

On the basis that the energy levels in the nickelocene complex are not altered in respect to that of ferrocene by the addition of two more unpaired electrons, the mentioned authors proposed the following interpretation: i) the band at 192 nm is an allowed transition one, which is designated as a N–V transition corresponding to the 202.5 nm N–V transition in ferrocene. The shoulder at 270 nm is denoted as a N–V or N–Q transition similar to the 230 and 260 nm shoulders in ferrocene; ii) the relatively intense band at 307 nm is assigned as an intramolecular charge transfer band which fortuitously occurs at approximately the same wavelength as the intermolecular charge transfer band of ferrocene in halocarbon solvents reported in the literature.[2,3]

Moreover, according to these authors the absorption spectrum of nickelocene in CCl_4 shows no new bands other than those found in cyclohexane or ethanol.

While studying the photochemistry of some metal sandwich compounds, we examined the nickelocene photochemical behaviour in cyclohexane, ethanol and halocarbon solutions*. The spectral changes during irradiation suggested that the band at 307 nm was concerned with the nickelocene cation. In fact, it can easily be shown that the band at 307 nm corresponds to the $Ni(C_5H_5)_2^+$ absorption band (Fig. 2, curve A). As a matter of fact, the nickelocene spectrum does not exhibit such a band (Fig. 2, curve B). On the other hand, $Ni(C_5H_5)_2$ oxidation with oxygen causes the formation of a new band with maximum at 307 nm. The spectrum reported in Fig. 2 must be considered as the real nickelocene spectrum in cyclohexane or ethanol solutions.

In order to verify the assignment of the 307 nm band to the nickelocene cation, we have also compared the nickelocene spectra in ethanol with that observed in various halocarbon solvents (Fig. 3). The nickelocene spectrum in halogen containing solvents had an additional intense band at 310 nm, which can be considered the result of nickelocene-to-solvent charge transfer transitions. The general appearance of this absorption is quite typical of a charge transfer to solvent absorption[4] and its wavelength position (shifted by 10 nm towards a longer wavelength in respect to the ferrocene case) reflects the noted easy nickelocene oxidation. Moreover, the increase in the charge transfer to solvent absorption is roughly parallel to the avidity with which the halocarbon solvent acceptor receives electrons.[2] We also have observed that in these solvents ultraviolet

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*Nickelocene from two different sources (Roc/Ric and K & K) was used after purification. No spectral difference was noted between the purified materials. Purification was carried out by rapid recrystallization from light petroleum with use of a solid carbon dioxide–acetone cooling bath, followed by repeated sublimation in vacuo. Bis-cyclopentadienylnickel(II) is thus obtained as dark green needles, m.p. 172 °C (reported 171 - 173 °C).

Solvents were reagent grade and were deoxygenated by bubbling prepurified nitrogen through them for at least 1 hr. All operations were conducted in a vacuum–inert atmosphere box under nitrogen.

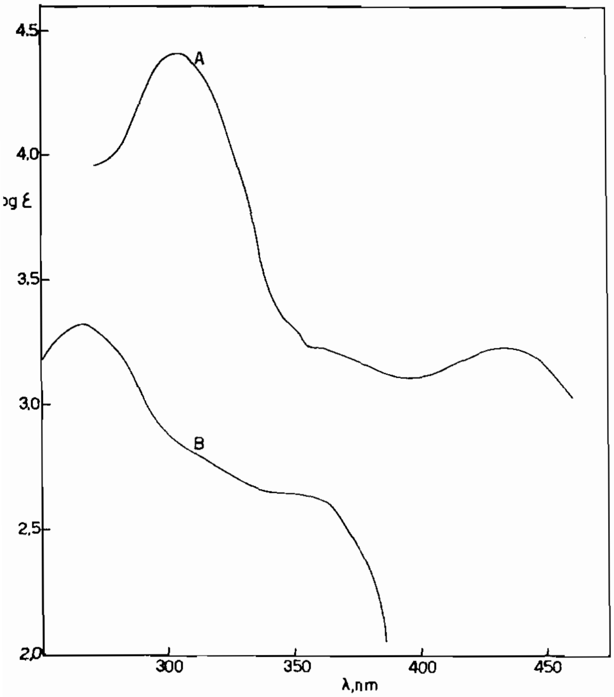

Fig. 2. Curve A: spectrum of nickelocenium tetraphenylborate in ethanol solutions containing 1*M* $HClO_4$.
Curve B: absorption spectrum of nickelocene in cyclohexane or in ethanol at 20 °C.

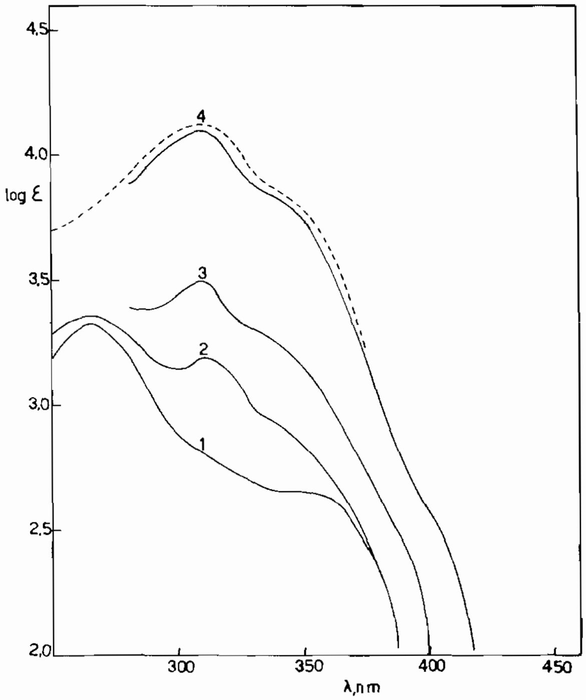

Fig. 3. Spectrum of nickelocene in ethanol and in acceptor solvents. Curve 1, absolute ethanol; 2, dichloromethane; 3, chloroform; 4 (– – –), carbon tetrachloride; 4 (---), 1,2-dichloroethane.

irradiation caused the nickelocene decomposition via a primary photooxidation process. Moreover, we have found, with appropriate Baush and Lomb narrow band pass filters, that the region of absorption required for the $Ni(C_5H_5)_2^+$ cation photoproduction agrees with the charge transfer absorption maxima of 310 nm. This behaviour appears reasonable since the chief characteristic of charge transfer light absorption is that it causes an electron largely localized on the donor to be transferred to the acceptor.[3,5]

It must be noted that the intriguing nickelocene absorption at 307 nm originally reported[1] is now believed to have originated from a spurious source which probably was $Ni(C_5H_5)_2^+$. The nickelocene easy oxidation to the bis-cyclopentadienylnickel(III) ion may confirm this hypothesis.

References

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