

The Spectra of the Negative Ions of Naphthacene and 5,12-Dihydronaphthacene in 1,2-Dimethoxyethane

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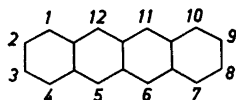
The spectra of the ions produced by the action of potassium metal on naphthacene and 5,12-dihydronaphthacene in dimethoxyethane in a high vacuum have been recorded. The mononegative ion of naphthacene took up a proton and formed a compound with a spectrum that was almost identical with that of the ion produced from dihydronaphthacene. When the sealed ampoules containing the samples were opened, naphthacene, dihydronaphthacene, and traces of a stable reduction product were found to be present in both solutions.

The spectra of the negative ions of phenanthrene and 9,10-dihydrophenanthrene in dioxan greatly resemble each other. When the ampoule containing the solution of phenanthrene is opened, the phenanthrene is found to have been converted into a number of reduction products, mainly, however, into dihydrophenanthrene.¹⁻³

When the ampoules containing similarly treated solutions of phenanthrene and 9,10-dihydrophenanthrene in dimethoxyethane are opened, both compounds are found to be present in their original concentrations.¹

The spectra of the mono- and dinegative ions of naphthacene in tetrahydrofuran have been recorded previously⁴ and are used for comparison in this study. It has been reported that a trinegative ion has also been produced from naphthacene.⁵

The aim of the present study was to determine whether the negative ions of naphthacene have a tendency to change into dihydronaphthacene and whether the spectrum of the mononegative ion of 5,12-dihydronaphthacene resembles that of any ion of naphthacene.



EXPERIMENTAL

1,2-Dimethoxyethane, a product of Fluka AG, was boiled over sodium wire for 24 h and then distilled. The middle fraction boiling at 85°C was treated as described previously.

5,12-Dihydronaphthacene was a product of Fluka AG reported to be 96 % pure. It was purified further by recrystallization from xylene containing maleic anhydride as proposed by Clar.⁵ The spectrum of the compound was in agreement with previously reported data for the compound.⁶

Naphthacene was a product of K & K laboratories, Inc., that gave a spectrum in good agreement with previously reported spectral data.^{7,8} It was used as received.

The cuvettes employed were 1-cm quartz and glass cuvettes.

Ions of naphthacene. Spectrum 0 in Fig. 1 was recorded before the reaction with

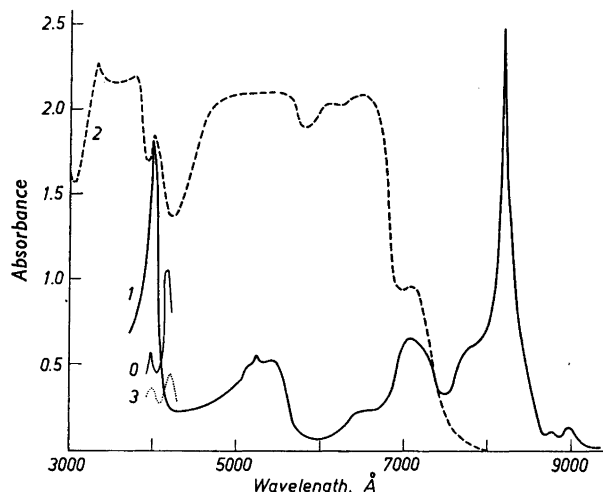


Fig. 1. Spectra recorded before and after naphthacene in dimethoxyethane had reacted with potassium in a high vacuum at room temperature.

potassium and reveals that the initial concentration c_0 of naphthacene calculated from the absorbance at 4160 Å was 3.8×10^{-4} M. Spectrum 1 in the same figure that was recorded after the solution had been in contact with potassium for one hour shows that the reaction had begun. The solution was initially green and became carmine red while spectrum 1 was being recorded. Spectrum 2 was recorded when the solution had been in contact with potassium for 72 h and was violet in colour. Spectrum 3, which was recorded after the ampoule had been opened, revealed that the naphthacene concentration had decreased to 1.6×10^{-4} M. The concentration was deduced from the absorbance at 4160 Å where 5,12-dihydronaphthacene does not absorb. When the absorbances of naphthacene at 2710 Å and 2800 Å calculated from this final concentration are compared with the absorbances at these wavelengths in spectrum 3, it is found that also other reduction products than 5,12-dihydronaphthacene must have been formed.

Ions of 5,12-dihydronaphthacene. The initial concentration of 5,12-dihydronaphthacene, computed from the absorbance of the solution at 2700 Å, was 1.4×10^{-4} M. A reaction had taken place after the solution had been in contact with potassium for 20 h (spectrum 1 in Fig. 2); the solution was carmine red except in the vicinity of the metal surface where it was green. Spectra 2, 3, and 4 were recorded after the solution had been in contact with potassium for 1, 1 and 3 days after the preceding spectrum was recorded. Spectrum 5 was recorded after the solution had been out of contact with potassium for

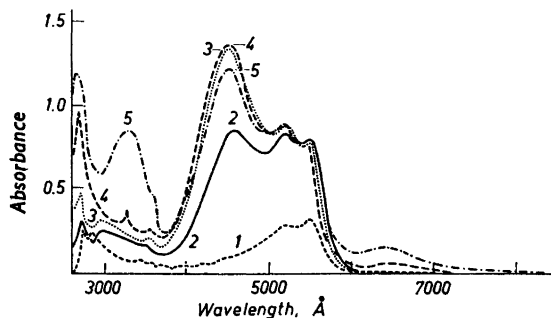


Fig. 2. Spectra recorded before and after 5,12-dihydronaphthacene in dimethoxyethane had reacted with potassium in a high vacuum at room temperature. Initial 5,12-dihydronaphthacene concentration 1.4×10^{-4} M.

2 days after spectrum 4 was recorded. When the ampoule was opened, only about 10 % of the 5,12-dihydronaphthacene had changed into naphthacene as deduced from the absorbance at 4160 Å.

The same experiment was carried out on a solution in which the initial concentration of 5,12-dihydronaphthacene was 4.4×10^{-4} M. Spectrum 1 in Fig. 3 shows that the reaction had begun when the solution had been in contact with potassium for 5 min. Spectrum 2 was recorded when the time of contact had been 10 h and spectra 3 and 4 when 1 and 1 days had elapsed from the recording of spectrum 2. Spectrum 5 was taken when the solution had been out of contact with the metal for 2 days after the recording of spectrum 4. Spectrum 6, recorded after the ampoule had been opened, shows that naphthacene had been formed in the solution. The concentration of naphthacene as deduced from the absorbance at 4720 Å was 1.4×10^{-4} M, which is 32 % of the initial 5,12-dihydronaphthacene concentration. Also in this case the final products included other compounds than naphthacene and 5,12-dihydronaphthacene.

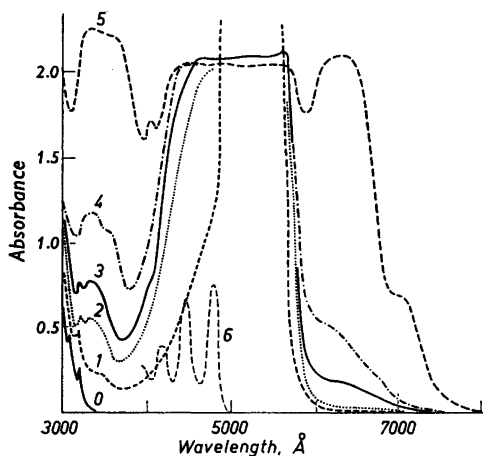
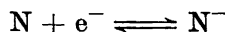


Fig. 3. Spectra recorded before and after 5,12-dihydronaphthacene in dimethoxyethane had reacted with potassium in a high vacuum at room temperature. Initial 5,12-dihydronaphthacene concentration 4.4×10^{-4} M.

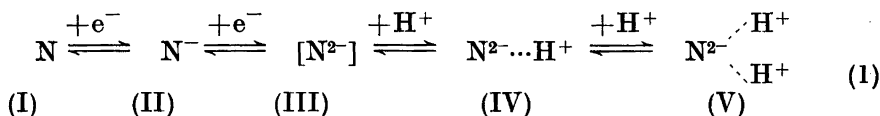
RESULTS AND DISCUSSION

Naphthacene. The spectrum (1 in Fig. 1) of the mononegative ion of naphthacene⁴ exhibits sharp peaks at 4020 Å and 8240 Å, a broad band at 7100 Å, and small peaks at 8800 Å and 9000 Å.

The reaction (N = naphthacene)



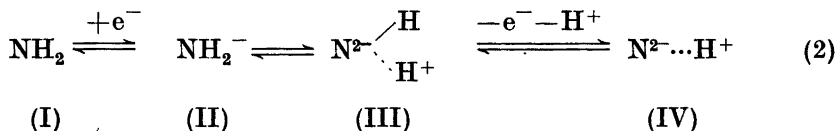
had evidently taken place. The broad band in the 5200–5500 Å region is not due to the mononegative ion or to the dinegative ion, bands of which were not clearly observed in any of the recorded spectra. Spectrum 2 in Fig. 1 shows weak bands at 6100 and 3350 Å which may be due to traces of the dinegative ion. At the same time as the broad band at 5200–5500 Å, the bands in the 6400–6550 Å and 3300–3750 Å regions increase in size. The following reactions may be assumed to have taken place:



The mononegative ion is first reduced to a dinegative ion which immediately takes up one loosely bound proton and then another. The different species are in equilibrium because when the solution was not in contact with the potassium surface for 1 day at 45°C, the absorption peaks of the mononegative ion reappeared in the spectrum. When the solution is in contact with potassium, the equilibrium between the species IV and V dominates.

5,12-Dihydronaphthacene. The bands at 5200 Å and 5500 Å in spectrum 1 (Fig. 2) reveal that the reaction had begun. There is also a peak at 4540 Å that increased in height in later spectra. Bands at 6400 Å and 3300 Å simultaneously appeared in spectrum 4.

The spectra in Fig. 3 relate to a dihydronaphthacene in which initial hydrocarbon concentration was three times as great as in the preceding solution. Spectrum 1 refers to the initial stage of the reaction and contains a strong broad band in the 4900–5600 Å region which spreads out and decreases in height as the reaction proceeds. Bands at 3300 Å and 6400 Å appear in the later spectra. The reaction sequence may be written:



A mononegative ion is first formed from dihydronaphthacene: its absorption bands are seen in spectrum 1 in Fig. 2 and in spectrum 1 in Fig. 3. Bands are seen in the spectrum for the dilute solution at 5200 Å and 5500 Å, but the absorbances of the more concentrated solution (Fig. 3) are so large that the locations of the maxima cannot be determined. An absorption band has appeared at 4540 Å in Fig. 2 which is due to the species III in eqn. (2). This

absorption band refers to a species different from species II, as revealed by the differences in the absorbances in spectra 2 and 1. The band is broader in Fig. 3. The species evidently is not the dinegative ion of dihydronaphthacene, for its spectrum resembles that of an ion produced from naphthacene (spectrum 3 in Fig. 1). For the same reason it cannot be the mononegative ion of dihydronaphthacene to which a proton is loosely attached. The great changes that have occurred since the recording of spectrum 1 suggest a considerable change in the electronic structure. The simultaneous variation of the bands at 3300 Å and 6400 Å shows that these bands belong to the same species IV in eqn. (2). The absorbance at 6400 Å increased when the solution was not in contact with potassium for three days. Species IV is then more readily formed because reduction is at a minimum in the solution. The species III and IV are in equilibrium. The ionic species III predominates and changes into dihydronaphthacene when the ampoule is opened, whereas species IV changes into naphthacene. A high initial dihydronaphthacene concentration seems to favour the species IV, and hence the formation of naphthacene (spectrum 6 in Fig. 3). In a naphthacene solution in which only traces of the dinegative ion are present, species IV reverts to naphthacene, whereas species V, which resembles the dihydronaphthacene derivative III, is reduced to dihydronaphthacene when the ampoule is opened. Other reduction products had evidently been produced in small amounts in all the sample solutions. For example, the species II formed in the dihydronaphthacene solution may add a proton and change into stable reduction products. A marked difference in the behaviour of phenanthrene and 9,10-dihydrophenanthrene is the ease with which a part of the dihydronaphthacene is oxidised to naphthacene and a part of the naphthacene changes into dihydronaphthacene. Attempts were made to estimate rate constants from the variation of the absorbance bands, but the bands overlapped to such an extent that no satisfactory values were obtained. The values obtained were, however, in qualitative agreement with the observations described above.

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