The Spectrum of the Negative Ion of 1,2,3,4,9,10-Hexahydrophenanthrene in 1,2-Dimethoxyethane

JORMA ELORANTA and MIKKO VUOLLE

Department of Chemistry, University of Helsinki, Helsinki, Finland

The negative ion of 1,2,3,4,9,10-hexahydrophenanthrene has been prepared by allowing potassium metal to react with the hydrocarbon in 1,2-dimethoxyethane in a high vacuum. The ion gives rise to a peak at 4060 Å in the visible range, but this peak slowly shifts to longer wavelengths, up to 4250 Å. This shift results from the addition of a proton to the ion. The spectrum of the ion clearly differs in details from the spectra of the ions of phenanthrene and its other hydrogenated derivatives. The electron spin resonance spectrum of the hexahydrophenanthrene ion shows that the ion is an anionic free radical (AFR).

This study belongs to a series [1-3] in which the spectra of negative ions of phenanthrene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, and 1,2,3,4,5,6,7,8-octahydrophenanthrene have been discussed.

The isolation of 1,2,3,4,9,10-hexahydrophenanthrene in a form sufficiently pure for the study proved difficult. The order of hydrogenation of phenanthrene as well as the possibility of discontinuing the hydrogenation at a certain stage were studied.

It was expected that the spectrum of the 1,2,3,4,9,10-hexahydrophenanthrene ion would resemble the spectra of the ions of phenanthrene and its other hydrogenated derivatives, although there might be differences in details. The spectra of the ions of the compounds formed on successively adding hydrogen to the phenanthrene nucleus, would be expected to differ more and more from the spectrum of the phenanthrene ion as a consequence of the changes in the π-electron distribution. If the spectra of the ions of phenanthrene and its various hydrogenated derivatives differ clearly from one another it may be concluded from what hydrocarbon an ion has been formed. It is, however, possible that the hydrocarbon is first partly reduced and an ion is then formed from the reduced form. The sample may even contain ions produced from several hydrogenated forms.

EXPERIMENTAL

The 9, 10-dihydrophenanthrene was a product of pure grade from Koch-Light Laboratories. 1,2-Dimethoxyethane, a product from Fluka AG, was purified and treated as described previously. [1,2] 1,2,3,4,9,10-Hexahydrophenanthrene was prepared by the high-pressure hydrogenation of 9,10-dihydrophenanthrene in cyclohexane. The initial hydrogen pressure was 125 atm. and the temperature 104°C. The hydrogenation was discontinued when the amount of hydrogen consumed was the theoretical amount required for the preparation of hexahydrophenanthrene. The residue remaining after the solvent had been evaporated was distilled *in vacuo* and three main fractions were collected. The fraction boiling at the highest temperature, which had a refractive index that was closest to the value reported by Belleau for hexahydrophenanthrene,[4] was fractionally distilled in a Widmer column. The main fraction, which boiled at 153−155°C/5 mm Hg and had a refractive index (n_D^{22}) of 1.588, was used in the experiments.

Spectra in the ultraviolet, visible, and near infrared regions were recorded with a Becman DK-2A or DU spectrophotometer. The cuvettes were 0.1, 0.5 and 1.0 cm quartz cuvettes.

The infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer employing cells fitted with sodium chloride windows. As hexahydrophenanthrene is a liquid at room temperature, no solvent was employed.

The gas chromatograph was an Wilkens Aerograph autoprep 705. As the hydrogenated derivatives of phenanthrene have relatively high boiling points, temperatures between 250 and 280°C had to be employed when recording the chromatograms. No decomposition of hexahydrophenanthrene was noted at these temperatures.

The electron spin resonance spectra were recorded with a spectrometer AL 340 SY. As the concentration of the compound under study has to be much higher when recording ESR spectra than when recording ultraviolet spectra, separate samples were prepared.

When the reactions were followed by recording ultraviolet, visible, and near-infrared spectra, the samples were prepared as described previously.[1,2] The sample turned green in the vicinity of the metal surface immediately when it was brought into contact with the latter. After the solution had been in contact with the metal several days, it turned yellow but reverted to green within a few hours when it was no longer in contact with the metal. An equilibrium prevailed between the yellow and green forms because the reaction progressed in either of the two directions depending on whether the solution was or was not in contact with the metal mirror. The solution became colourless immediately after the sample was exposed to air, but began to turn yellow a few minutes later. This reaction, caused by moisture and oxygen of the air, interfered with the accurate determination of the final concentration of the compound. The yellow species that was formed gave an absorption peak at 3580 Å; this was evidently formed by polymerisation of the solvent since hexahydrophenanthrene and traces of octahydrophenanthrene were found to be present in the sample.

RESULTS AND DISCUSSION

Mejer[5] prepared 1,2,3,4,5,8-hexahydrophenanthrene by reducing tetrahydrophenanthrene in liquid ammonia and reported the ultraviolet and infrared spectra of the compound dissolved in methanol. Bands occurred at 2690 Å (log ε = 2.5) and 2380 Å (log ε = 3.1). Belleau[4] synthesized 1,2,3,4,9,10-hexahydrophenanthrene which had a refractive index (n_D^{23}) of 1.592 and gave in methanol absorption bands at 2680 Å (log ε = 3.86), but he did not publish the whole ultraviolet spectrum.

In this study 1,2,3,4,9,10-hexahydrophenanthrene dissolved in dimethoxyethane was found to give absorption bands at 2660 Å (log ε = 3.82) and 2100 Å (log ε = 4.48) (Fig. 1). The location of the band in the ultraviolet, the molar absorptivity (ε) and the refractive index (n_D^{22} = 1.588) are in agreement with Belleau's values but deviate from Mejer's values. Despite the fact that the
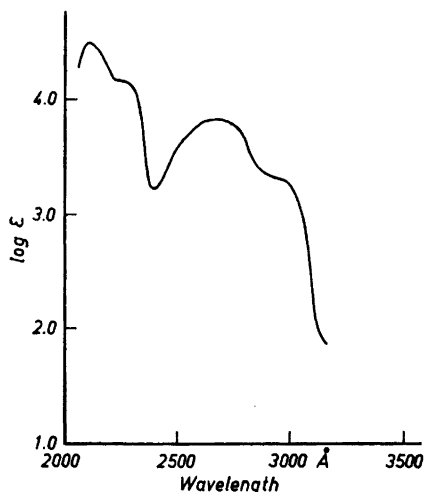
Fig. 1. The ultraviolet spectrum of 1,2,3,4, 9,10-hexahydrophenanthrene in 1,2-dimethoxyethane.

theoretical weight of hydrogen was consumed, it is possible that octahydro-phenanthrene may have been formed and a part of the dihydrophenanthrene may have remained unchanged. In dimethoxyethane 1,2,3,4,5,6,7,8-octa-hydrophenanthrene gives an absorption band at 2700 Å (log ε = 2.60) [3,6,7] and 9,10-dihydrophenanthrene a band at 2620 Å (log ε = 4.60).[2] The absorption bands and molar absorptivities of the last two compounds deviate so much from each other that the synthesized product whose spectrum is given in Fig. 1 could not have been a mixture of octa- and dihydrophenanthrenes.

The infrared spectrum of the studied product has absorption bands at 720, 740, 768, and 790 cm^{-1}. These same bands occur in the infrared spectrum of a mixture of octa- and dihydrophenanthrene, and hence the product may have been a mixture.

The gas chromatogram, however, showed that the product is a homogeneous substance that contains at most 0.1 % of an impurity.

Because low yields of 1,2,3,4-tetrahydrophenanthrene were obtained when dihydrophenanthrene was hydrogenated in ethanol under high pressure in the presence of Raney nickel according to Durland and Adkins,[8] an attempt was made to discontinue the hydrogenation of dihydrophenanthrene in cyclohexane when tetrahydrophenanthrene had formed. The resulting product contained, however, approximately equal proportions of hexahydrophenanthrene and unchanged dihydrophenanthrene according to the ultraviolet and infrared spectra.
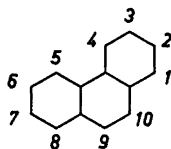
Various hydrogenated derivatives of phenanthrene are formed when the latter is hydrogenated under different conditions. 9,10-Dihydrophenanthrene seems to be the product first formed in all cases. The method employed in this study apparently does not yield any 1,2,3,4-tetrahydrophenanthrene, for 1,2,3,4,9,10-hexahydrophenanthrene is the product formed from 9,10-dihydrophenanthrene. When the hydrogenation is continued further the product is evidently 1,2,3,4,5,6,7,8-octahydrophenanthrene; this reaction presupposes intramolecular rearrangement.[5] Amos [9] has calculated the spin density net charge for the different carbon atoms in the positive phenanthrene ion and found the charge to decrease in the order 9,10,1,3,4,2. If the negative ion is an intermediate in the reduction of phenanthrene [10] and the negative charge is preserved during continued hydrogenation, the mentioned order would seem natural. However, intramolecular rearrangement in some solvents may lead to deviations from the above order because the π-electron density changes as the hydrogenation progresses. If the molecular rearrangement is not prevented by the solvent, the product seems to be one in which as many of the benzene rings as possible remain intact.

Spectrum 1 in Fig. 3 is the spectrum of the sample before the reduction with potassium began. The initial concentration, c, of the hexahydrophenanthrene was then 3.3×10^{-3} M (as determined from the absorption at 2660 Å). Both hexahydrophenanthrene and its ion are evidently present in the early stages of the reaction, but the former does not absorb in the visible range and the latter does not absorb strongly at 2660 Å. The decrease in the concentration of hexahydrophenanthrene was determined by measuring the change in absorption at 2660 Å. The molar absorptivities for the ion at 4060 Å and 3300 Å were found to be 2000 and 1300, respectively. Fig. 3 shows that there were low maxima at 3220 Å and 3160 Å in the spectra recorded in the early stages of the reduction. Curve 5 in Fig. 3 refers to another sample (5 mm cell) than the other curves. In curve 5 the absorbance at 3220 Å is even greater than the absorbance at 3300 Å. The peaks at 3160 Å and 3220 Å disappear rapidly, but the peak at 3300 Å disappears slowly as the reduction proceeds. The peaks at 3160 Å and, at least partly, the peak at 3300 Å relate to a very unstable intermediate in the formation of the negative hexahydrophenanthrene ion.
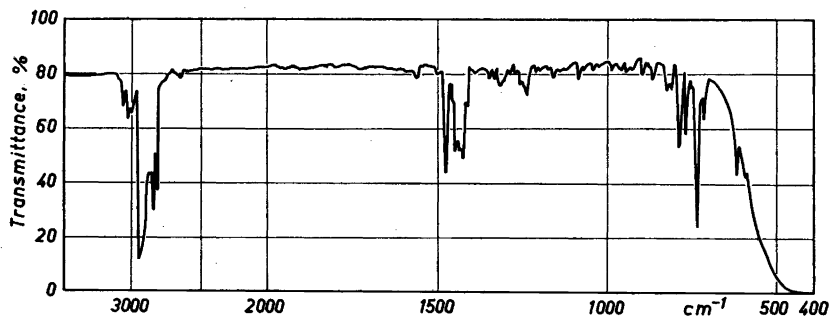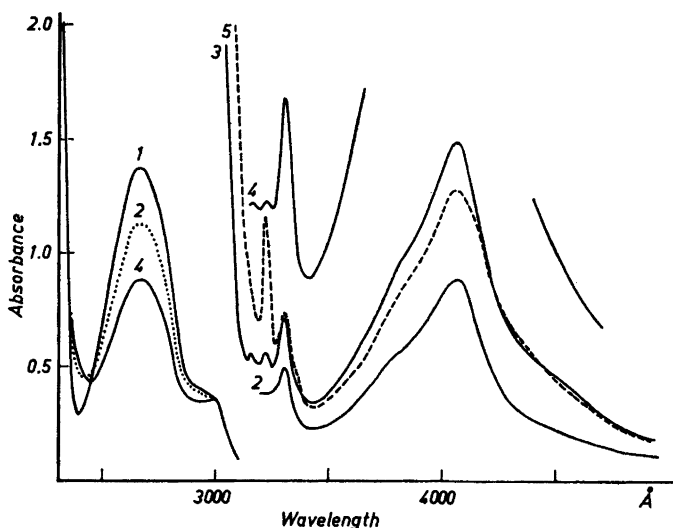

Fig. 2. The infrared spectrum of 1,2,3,4,9,10-hexahydrophenanthrene.

Fig. 3. Spectra recorded in the early stages of the reaction of 1,2,3,4,9,10-hexahydro-
phenanthrene with potassium metal in 1,2-dimethoxyethane. A 1 mm quartz cell was
used when the wavelength was less than 3000 Å and a 1 cm quartz cell when the wave-
length was greater than 3000 Å. Spectrum 5 refers to another sample in a 5 mm
quartz cell.

The absorbance at 3300 Å is observed also in the early stages of the reduc-
tion of 1,2,3,4-tetrahydro- and 1,2,3,4,5,6,7,8-octahydrophenanthrenes, and is
very strong with the latter compound but weak and appears later with the
former compound. Absorption bands were not observed at 3160 and 3220 Å
in the spectra of the ions of phenanthrene or its other hydrogenated deriva-
tives.[2,3]

Several absorption bands are found in the 3000 — 4000 Å range in the
spectrum of phenanthrene, which are not present in the spectrum of 9,10-
dihydrophenanthrene. These bands have been ascribed to the reactivity of
the bond between carbon atoms 9 and 10, even to the dissociation of the
hydrogen atoms at these positions.[6] If 1,2,3,4,5,6,7,8-octahydrophenanthrene
is formed by way of the 1,2,3,4,9,10-hexahydrophenanthrene ion in the reduc-
tion, the hydrogen atoms at positions 9 and 10 must shift. The peaks that
first appear and later disappear in the 3000 — 3300 Å region in the spectra of
the hexahydrophenanthrene ion may be due to the loosening of the bonds
holding the hydrogen atoms at positions 9 and 10 when the ion is being formed.

Fig. 4 shows that the band at 4060 Å shifts to longer wavelengths as the
reaction proceeds (solution in contact with potassium mirror). The longest
wavelength where this band was observed was 4250 Å. Because only one band
was observed and this moved back and forth between 4060 and 4250 Å, an
equilibrium between the hexahydrophenanthrene ion and a complex formed
by this ion and a proton is involved.[13] The shift to longer wavelengths may
be caused by the formation of a weak band with a solvent molecule or an ion
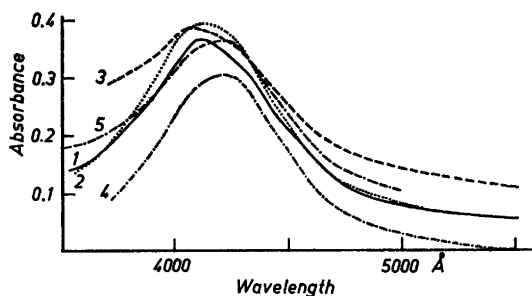
Fig. 4. Spectra recorded in the later stages of the reaction of 1,2,3,4,9,10-hexahydro-phenanthrene with potassium metal in 1,2-dimethoxyethane. 1 mm quartz cell.

pair. In the case of phenanthrene in dioxan a shift to shorter wavelengths was observed, but two bands were observed during the whole reaction when phenanthrene was dissolved in dimethoxyethane. The ESR spectrum showed clearly that the hexahydrophenanthrene ion is an anionic free radical; the spectrum had a clear maximum. According to the ESR spectra, the concentration of the ion gradually decreases and the species formed is diamagnetic. When the shift of the band in the visible region seen in Fig. 4 is compared with the shifts of the bands of the ions of other hydrogenated phenanthrene derivatives, it is seen that the bands in the spectra of hexa-, tetra-, and dihydrophenanthrene ions in dimethoxyethane are located at 4060, 4060, and 4040 Å, respectively. In the case of the dihydrophenanthrene ion, the absorption band widens over the range 4000 — 4400 Å with its maximum at 4200 — 4300 Å. Two bands at 4060 Å and 4480 Å are found initially in the spectra of the tetrahydrophenanthrene ion and finally there is only one band at 4240 Å. With hexahydrophenanthrene ion the band is located between 4060 and
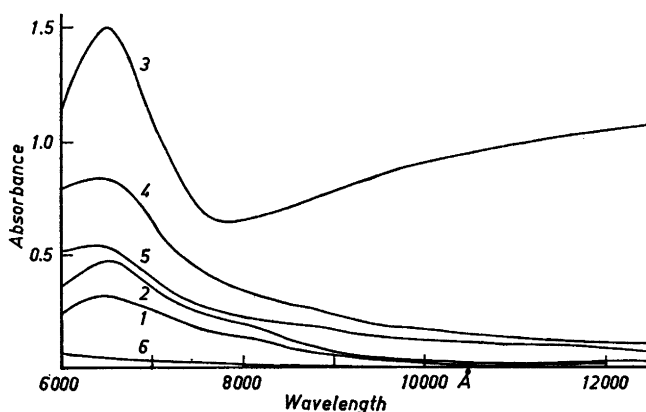

Fig. 5. Near infrared spectra recorded when 1,2,3,4,9,10-hexahydrophenanthrene in dimethoxyethane reacted with potassium metal. 1 cm quartz cell.

4250 Å. These three ions behave similarly. In the case of the hexa- and di-hydrophenanthrene ions the peak is not double and the proton becomes attached directly to the mononegative ion. There is no sharp peak at 4060 Å in the spectrum of the octahydrophenanthrene ion, but a broad band at 4240 — 4300 Å. The addition of the proton is evidently rapid in this case and bands due to the free ion are not seen. A double peak was observed in the spectrum of the phenanthrene ion, similarly as in the spectrum of the tetrahydro-phenanthrene ion. A sharp peak was found at 6500 Å in the near infrared when the hexahydrophenanthrene ion (Fig. 5) was present (green solution). Curves 1, 2, and 3 in Fig. 5 were recorded in the early stages of the reduction; there is a broad low band at 13 000 Å only in spectrum 3. Because this band occurs, like the bands in the 3000 — 3300 Å region, only in the early stages of the reduction it may be due to an unstable intermediate or to solvated electrons.[11,12] When a proton adds to the hexahydrophenanthrene ion (yellow solution) the band at 6500 Å disappears, but this band reappears when the solution is allowed to stand a couple of hours at room temperature without being in contact with the metal. A band is seen near 6500 Å also in the spectra of the ions of phenanthrene,[2] 9,10-dihydrophenanthrene,[2] 1,2,3,4-tetrahydro-phenanthrene,[3] and 1,2,3,4,5,6,7,8-octahydrophenanthrene,[3] but the band location varies between 7200 and 6200 Å. The band is located at a much longer wavelength in the spectrum of the octahydrophenanthrene ion than in the spectra of the other ions. A further band is found at 13 000 Å in the spectrum of the hexahydrophenanthrene ion when this ion is being formed and one at 10 000 — 12 000 Å in the spectrum of the phenanthrene ion over a longer period. This also indicates a loosening of the bands holding the hydrogen ions at positions 9 and 10 when the hexahydrophenanthrene ion is formed. When a proton has become attached to the ion, the spectra, and hence the degrees of solvation and the π-electron structures, of the ions of hydrogenated phenan-threne derivatives are closely similar, but in the early stages of the reduction the ions can readily be identified from their spectra.

REFERENCES

1. Eloranta, J. *Acta Chem. Scand.* **18** (1964) 2259.
2. Eloranta, J. and Vuolle, M. *Suomen Kemistilehti* **B 38** (1965) 151.
3. Eloranta, J. *Suomen Kemistilehti* **B 39** (1966) 143.
4. Belleau, B. *J. Am. Chem. Soc.* **75** (1953) 1159.
5. Mejer, S. *Bull. Acad. Polon Sci. Ser. Chim.* **10** (1962) 463.
6. Askev, F. A. *J. Chem. Soc.* **1935** 514.
7. Nes, W. N. and Mosetting, E. *J. Am. Chem. Soc.* **76** (1954) 3183.
8. Durland, J. R. and Adkins, H. *J. Am. Chem. Soc.* **59** (1937) 135.
9. Amos, T. *Mol. Phys.* **5** (1962) 91.
10. Lipkin, D., Calliano, F. R. and Jordan, R. W. *Chem. Ind.* **41** (1963) 1657.
11. Linschitz, H., Berry, M. and Scweitzer, D. *J. Am. Chem. Soc.* **76** (1954) 5833.
12. Eloranta, J. and Linschitz, H. *J. Chem. Phys.* **38** (1963) 2214.
13. Buschow, K. and Velthorst, N. *Z. physik. Chem. (Frankfurt)* **41** (1964) 45.