

PHOTOPOLYMERISATION OF ANTHRACENE IN BENZENE SOLUTION FROM THE MAGNETIC STANDPOINT

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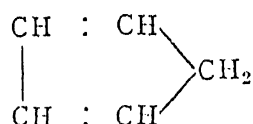
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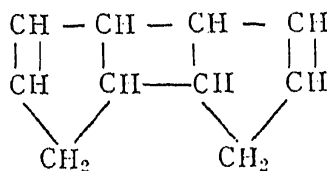
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FARQUHARSON¹ while investigating the magnetic behaviour of cyclopentadiene



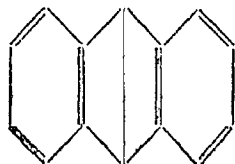
on polymerisation to dicyclo-pentadiene



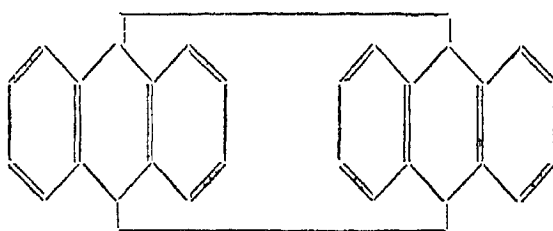
observed that as the polymerisation proceeded, the susceptibility value of the product decreased. Bhatnagar, Kapur and Hashmi² in their studies of the magnetic behaviour of photo-tropic substances observed that the susceptibility value of cinnamylidene-malonic acid on polymerisation to its dimer showed a decrease. A similar behaviour was observed in the case of thiophosgene on its polymerisation to its photodimer. In all these cases, the polymerised product is formed as a result of the disappearance of two double bonds, one from each of the parent molecules, and the formation of a bridged four-membered ring. As the polymerisation in such cases involves the change of $-\text{C}=\text{C}-$ double bonds to single bonds, therefore, according to Pascal's views there ought to be a rise in the diamagnetic susceptibility value of the polymerised product by 5.5×10^{-6} units. Bhatnagar, Kapur and Hashmi (*loc. cit*) suggested that the decrease rather than the increase of the susceptibility value of the polymerised products is probably due to the formation of a bridged ring. The exact value for λ the constitution correction factor for such a ring formation, cannot be deduced from the data already available, because in the case of cyclopentadiene the value of the dimer is not known and in the case of cinnamylidene malonic acid it is

difficult to get the pure polymerised product because of its tendency to oxidise easily.

It is well known that photopolymerisation of anthracene



to dianthracene



in solid state or in benzene solution leads to the disappearance of two double bonds, one from each of the molecules, and the formation of a bridged four-membered ring.³ The present investigation was, therefore, undertaken in order to determine the value of λ , the constitution correction factor for the bridged four-membered ring, by a magnetic study of the products of this photo-polymerisation.

Experimental

Pure anthracene available in the stores was repeatedly crystallised from benzene till pure crystals with m.p. 213° C. were obtained. Particular care was taken to eliminate anthraquinone which, if present in small traces, has been observed to catalyse photochemical oxidation processes.⁴ This was done by heating the hydrocarbon with zinc dust (Sudborough). Anthraquinone is, however, developed in the course of the reaction as has been shown in the sequel. The pure white crystals thus obtained were dissolved in pure thiophene-free benzene which had been kept over sodium wire for a fortnight and had been redistilled before use. The solution was exposed to sunlight in pyrex glass conical flasks and the magnetic susceptibility values of the product separating out from day to day were determined on a modified form of Gouy's magnetic balance.

It was observed that the anthracene solution remained colourless for the first two days and became pale yellow on the third day. It went on deepening in colour on further exposure till after a month it developed a deep orange red colour.

The susceptibility and the melting points of the solids which separated out at different intervals were determined and are tabulated below:—

Time of exposure days	Colour of insoluble product	M.p. of solid separating	$\chi \times 10^6$ of solid separating	Colour of the solution
0	(Pure anthracene)	.. 213	- 0.728	..
1	Colourless 243-44	- 0.635	Colourless
2	Slightly coloured 241-42	- 0.593	Do.
3	Coloured 239-41	- 0.549	Pale yellow
4	Do.	236-39	- 0.546	Yellow
7	Light brown 232-55	- 0.532	Orange
30	Brown 180-85	- 0.286	Red

From the results given above, it is clear that the melting point and the susceptibility of the solid which separates out from day to day go on decreasing, indicating thereby that some other compounds besides dianthracene possessing a rather low magnetic susceptibility are also being formed.

Although the solid that separates out of the irradiated solution of anthracene in benzene after a week is brown, the compound that is crystallised out from this deep orange red solution is orange in colour and when further crystallised from pure acetone comes out as a needle-shaped buff coloured substance, having a susceptibility of -0.573×10^{-6} and a m.p. of 280-82° C.

The analysis of the brown and the buff coloured compounds gave

	C	H	O
	%	%	%
Brown compound ..	81.40	4.85	13.75
Buff needle-shaped ..	80.80	4.00	15.20

(other elements such as nitrogen and sulphur were found to be absent).

It, therefore, appears that the change in colour of the solution is due to the formation of photo-oxidation products of anthracene. Chemical analysis and the physical constants of the buff coloured solid identify it as anthraquinone. (Anthraquinone gives C = 80.77, H = 3.85 and O = 15.38%.)

That the photo-oxidation products are responsible for the colour changes of the irradiated solution were further supported by the fact that when the

photopolymerisation of anthracene in a benzene solution was carried out in vacuum for a month, no such colour developed.

It was observed that dianthracene that separated out from solution of anthracene on exposure to light in vacuum was perfectly white with m.p. 244°C . and susceptibility -0.668×10^{-6} . For comparison the m.p. and the amounts of solid which separated out in vacuum and in contact with air are given below :—

Time days	M.p. of dianthracene		% of dianthracene formed	
	Vacuum	Air	Vacuum	Air
	$^{\circ}\text{C}$.	$^{\circ}\text{C}$.		
1	244	243-44	81.08	72.21
2	244	241-42	88.45	74.13
3	244	239-41	88.90	75.96
4	244	236-39
7	244	232-35	91.54	85.19

From the results it is clear that pure dianthracene is formed only in vacuum, whereas a mixture of compounds separates out in contact with air, and the amount of dianthracene formed in vacuum is more than that formed in air. The energy absorbed in both cases is the same, but whereas in vacuum the whole of this energy is used up in the formation of dianthracene in air it is partly utilized for the photo-oxidation of the hydrocarbon. Therefore, the amount of dianthracene formed in presence of air is less than that formed in vacuum.

If the fluorescent solution, after the removal of dianthracene formed when the exposure of anthracene solution in benzene was carried out in vacuum, is exposed to light in the presence of air, the solution becomes light red. The colour goes on deepening and a brown solid separates out.

This brown compound melts with decomposition at 180°C . and its composition is C, 69.00; H, 4.36; O, 26.64%. Its susceptibility was found to be -0.212×10^{-6} . This analysis corresponds to $\text{C}_{14}\text{H}_{10}\text{O}_4$ (C, 69.42; H, 4.13; O, 26.45%).

The melting point and magnetic susceptibility of the brown compound separating out of the irradiated benzene solution from which dianthracene

has been removed in vacuum is different from that which is obtained from the irradiated benzene solution in air. In order to identify the latter compound and to see whether it was a pure or a mixed specimen, the brown material was shaken with acetone distilled over KMnO_4 . It was noticed that a white insoluble compound (m.p. 243°) approximately 17.09% separated out and a brown soluble compound remained in solution (m.p. 180°). The brown compound had a susceptibility value -0.212×10^{-6} which is the same as that of the brown compound, $\text{C}_{14}\text{H}_{10}\text{O}_4$, mentioned above. The melting point of the white compound corresponds to dianthracene. Moreover, if the susceptibility value of the original compound is calculated according to the mixture law, assuming it to be a mixture of dianthracene and the pure brown compound, it comes to be -0.290×10^{-6} , which is in very good agreement with its experimental susceptibility value of -0.286×10^{-6} .

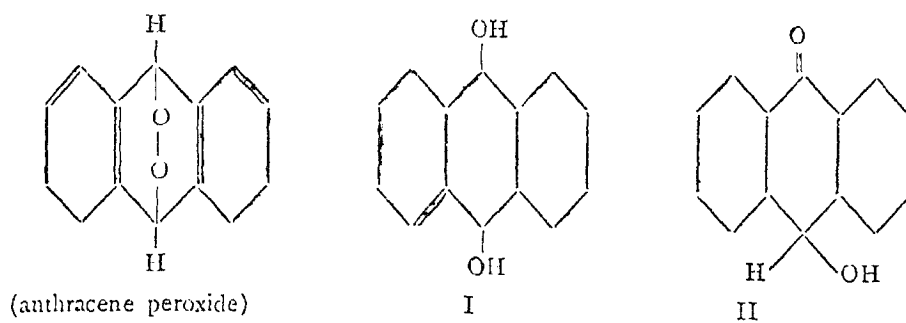
It was also observed that if pure dianthracene (m.p. 244° and $\chi = -0.668 \times 10^{-6}$) separating out from anthracene solution irradiated in vacuum, is kept in benzene and exposed to light in the presence of air, the solution goes on changing its colour from day to day till it develops an orange red colour. The colour of dianthracene also goes on changing and becomes light brown after a fortnight. Its magnetic susceptibility was found to be -0.579×10^{-6} which is much less than the value for pure dianthracene, -0.668×10^{-6} . This is clearly indicative of the formation of photo-oxidation products.

Discussion of Results

The photochemical change of anthracene to dianthracene has been investigated by numerous workers, and it has been regarded that anthracene is one of those substances which is most resistant to self-oxidation. Charles Dufraisse and Marcel Gerard⁵ have, however, found that when a benzene solution of anthracene is irradiated in air, anthracene peroxide ($\text{C}_{14}\text{H}_{10}\text{O}_2$) is formed. The red benzene solution obtained by us after irradiation in air liberates iodine from KI in the presence of acetic acid. 0.0712 gm. of the solid in the deep orange red solution liberates iodine equivalent to 8.30 c.c. N/250 $\text{Na}_2\text{S}_2\text{O}_3$.

If the liberation of iodine from KI is due to anthracene peroxide only, then the amount of anthracene peroxide present in 0.0712 gm. of the solid in solution is only 4.897%.

Anthracene peroxide is isomeric with anthrahydroquinone (I) and oxanthrone (II)⁶



Anthrahydroquinone is brown coloured and melts at about 180°C ., whereas oxanthrone is colourless and melts at 167°C . The brown compound that separates out of the irradiated solution melts with decomposition at 180°C . and has a composition corresponding to $\text{C}_{14}\text{H}_{10}\text{O}_4$, which has two oxygen atoms more than anthrahydroquinone. The mechanism of the formation of this compound can be pictured as follows: In the irradiated solution anthracene peroxide is formed first as suggested by Dufraisse and Gerard, which subsequently undergoes an isomeric change to anthrahydroquinone and ultimately an oxygenated derivative approximating to $\text{C}_{14}\text{H}_{10}\text{O}_4$ is formed although a part of the peroxide equivalent to 4.987% remains dissolved as such in the benzene solution. The oxygenated derivative is apparently anthrahydroquinone containing loosely bound oxygen.

Similar considerations apply to the development of the brown compound when a solution of dianthracene in benzene is irradiated in air. An equilibrium anthracene \rightleftharpoons dianthracene is first established and this is followed by a slow photochemical oxidation of anthracene to its oxygenated derivatives.

The origin of anthraquinone in the solution phase is to be sought in the photochemical oxidation of anthrahydroquinone. The work of Gardner and Goldstein⁷ on the photolysis of chloro-derivative of anthrahydroquinone in which they were able to show that anthrahydroquinone undergoes oxidation to anthraquinone in the presence of air, affords a fair confirmation of this view.

Determination of the value for λ .—It has been shown that when photopolymerisation of anthracene is carried out in air, besides dianthracene, other compounds with low susceptibility values are also formed, but if anthracene solution is exposed to light in vacuum, pure dianthracene alone is formed. Therefore, in order to determine the value for λ , the constitutive factor for a bridged four-membered ring formed as a result of the disappearance of double bonds during the course of polymerisation, the susceptibility value of pure dianthracene formed as a result of the exposure to sunlight of pure anthracene solution in evacuated flasks was determined on a Geuy's balance. Its susceptibility value was found to be -0.668×10^{-6} .

According to Pascal's well-known principle of the additivity of the diamagnetic properties of non-polar compounds the molecular susceptibility χ_M of a molecule can be closely represented as $\chi_M = \Sigma\chi_A + \lambda$, where $\Sigma\chi_A$ represents the sum of the atomic susceptibilities of all the atoms in the molecule and λ is the constitutive factor depending on the nature of linkages between the atoms.

When polymerisation takes place between two molecules of anthracene to form dianthracene the magnetic susceptibility of dianthracene will be given by an expression similar to that given by Pascal for the formation of molecules from atoms, *i.e.*,

$$\chi_M = 2\chi_A + \lambda,$$

where χ_M is the molecular susceptibility of dianthracene, χ_A susceptibility of anthracene, and λ the constitution factor arising from the new ring formed. The experimental molecular magnetic susceptibility value for dianthracene is equal to -237.80×10^{-6} and that for anthracene is equal to -129.7×10^{-6} (-0.7288×178)

$$\begin{aligned}\lambda &= \chi_M - 2\chi_A \\ &= -237.8 + 2 \times 129.7 \\ &= +21.6.\end{aligned}$$

Farquharson and Sastri⁸ determined the values of constitutive correction factor for polymethylene rings and obtained a value of $+3.05 \times 10^{-6}$ for a four-membered ring. Our constitutive factor value for a four-membered ring formed as a result of the disappearance of two double bonds during the course of polymerisation is 21.6×10^{-6} which value is much higher than the one obtained by Farquharson and Sastri. They obtained the constitutive factor value for various polymethylene rings simply by comparing corresponding open-chain and cyclic compounds.

When the polymerisation of compounds such as that of anthracene to dianthracene takes place the following structural changes accompany it:

- (1) The loss of two double bonds, one from each of the molecules.
- (2) The formation of a four-membered ring.
- (3) Change in the effective radius of the polymerised product.
- (4) Influence of various groups on the valency angles of the ring formed.

From the magnetic standpoint the effect of change (1) would be to increase the diamagnetism of the polymerised product formed and the magnetic value for this change can be assessed because λ for $-\text{C}=\text{C}-$ is

known to be 5.5×10^{-6} . If the value 3.05×10^{-6} for a four-membered ring obtained by Farquharson and Sastri (*loc. cit.*) be taken to account for the change, (2) and the effect due to the magnetic changes accompanying processes (3), and (4) be regarded negligible, the effect of polymerisation would be to increase the diamagnetism of the polymerised product. This is contrary to observations.

It is clear, therefore, that the influence of changes (3) and (4) on the magnetic property of the polymerised product cannot be ignored. It is very difficult to obtain an exact magnetic value for the changes (3) and (4).

The large fall in diamagnetism observed on polymerisation can be explained, however, by assuming that the polymerisation of two molecules of anthracene to one molecule of dianthracene is accompanied by a decrease in the radius of the polymerised molecule formed, and the influence of the benzene rings on the valency angles seems to lead to a concentration of the electronic charge in the rings leading to a smaller effective radius and both these factors would contribute to a large fall in diamagnetism.

From these considerations it is obvious that the value of λ , 21.6×10^{-6} will not be the same for all such cases of polymerisation but would be mainly influenced by the magnetic changes accompanying processes (3) and (4). Thus the value of λ when thiophosgene polymerises to its photodimer is $+11.5 \times 10^{-6}$ (Bhatnagar, Kapur and Hashmi, *loc. cit.*).

As polymerisation of anthracene in benzene solution in vacuum proceeds, dianthracene is formed, part of it remains in solution in equilibrium with anthracene. The mass susceptibility χ of the complex in solution at any stage, according to Farquharson (*loc. cit.*) would be

$$\chi = \frac{n\chi_A + (n - 1)\lambda}{n M_A},$$

where n = number of molecules of anthracene which polymerise

λ = polymerisation constitution constant

χ_A = molecular susceptibility of anthracene

M_A = molecular weight of anthracene.

In this expression λ , χ_A and M_A are constants and the curve for the change in the mass susceptibility with the number of simple molecules in the complex will be a hyperbola. Thus at any stage the mass susceptibility can be employed to calculate the composition of the mixture of the polymerised and unpolymerised molecules.

Time in hrs.	$\chi \times 10^{-6}$ of the mixture	% of anthracene in the mixture	
		Calculated from magnetic data	Determined by sublimation
1	0.7278	98.3	98.4
2	0.7273	97.0	97.2
3	0.7264	95.0	95.1
4	0.7254	93.4	93.2

In the second column of the table is given the mass susceptibility value of the solid obtained from time to time by evaporating benzene in vacuum from an anthracene solution exposed to light in vacuum. The third and the fourth columns give the percentage composition of the mixture as calculated from the magnetic data and as determined by subliming off anthracene from the known weight of the mixture, respectively.

It is clear from the table that the percentage composition of the mixture as determined by magnetic data agrees well with those obtained by the sublimation method.

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