

THE MAGNETIC STUDY OF QUINHYDRONE

THE structure of quinhydrone has been the subject of extensive investigations. Majority of the experimental evidence is against the view advocated by Willstätter and Piccard that the hydroxyl groups of the benzenoid component of quinhydrone is linked co-ordinately to the carbonyl oxygen of the quinonoid component. Pfeiffer² regards quinhydrone as an additive compound with its components held together by residual valencies of the nuclei. Another view of more recent origin is that in the compound the two components are held together due to the interaction between the strongly polar quinonoid groups and the anisotropic, polarisable quinol nucleus. This view is supported by X-Ray analysis of crystals of quinhydrone in which discrete existence of quinonoid and quinoloid units has been shown.³ A mechanism of how the union is affected is obvious on the above view. The polar quinonoid groups induce corresponding moments in the quinol nucleus and the union is thus affected by the electrostatic interaction between the permanent and induced moments. A similar view has been put forward in case of molecular compounds of sym. Trinitrobenzene.⁴ The 'London' Forces thus involved are intermediate between van der Waals's forces and true covalencies. Such weak electrostatic interactions between the two components as in the case of quinhydrone should not effect the magnetic susceptibilities of the two components largely and it should be expected that the molecular magnetic susceptibility of quinhydrone should not differ very much from the sum of the molecular magnetic susceptibilities of quinone and quinol. This should particularly be true in case of quinhydrone since both the components are symmetrical with respect to the substituent groups.

The magnetic susceptibilities of quinone, quinol and quinhydrone were determined by Palacios and Froz,⁵ and their results showed that molecular magnetic susceptibility (χ_m) of quinhydrone differs considerably from the sum of the molecular susceptibilities of quinone and quinol. We have, therefore, undertaken the determinations of carefully purified samples and the results are tabulated in Table I. The determinations were made on a modified

form of Guoy's Balance. The working of the apparatus was checked by determining χ (mass susceptibility) of a number of substances whose values are known very accurately, e.g., potassium chloride, sodium chloride, benzene, alcohol, etc. Water was taken as reference substance with $\chi = -0.720 \times 10^{-6}$. The results were correct within 0.7 per cent. of the accepted values.

The sum of the molecular susceptibilities of quinone and quinol is thus -102.07×10^{-6} which is nearly equal to χ_m for quinhydrone ($= -102.05 \times 10^{-6}$).

The results support the view about the structure of quinhydrone that the two components are held together in the compound by weak electrostatic forces.

However, it should be clear that this agreement between the sum of χ_m of components and χ_m of the molecular compound may be true in this case only, while, in other similar cases, where the resultant compound may be more or less symmetrical, the diamagnetic susceptibility of the compound may be greater or lesser than the sum of the components.

The results on other similar molecular compounds of *p*-quinone and symmetrical Trinitrobenzene will be published shortly.

Department of Chemistry,
Government College,
Lahore,
November 4, 1944.

SUNDER LAL.
NOOR-UL-HAQ KHAN.

1. Willstätter and Piccard, *Ber.*, 1908, **41**, 1458; *A.*, 1908, **i**, 475. 2. Pfeiffer, P., and collaborators, *Annalen*, 1924, **444**, 241-64, 1914, **404**, 1-23. 3. Stuart Anderson, *Nature* 1940 **140**, 533-84. 4. Fevre, R. W. L., *Trans. Faraday Soc.*, 1937, **33**, 210. 5. Palacios, J., and Froz, O. R., *Anal. Fis. Quim.*, 1935, **33**, 627-42.

A NOTE ON *HELIOTHIS ARMIGERA* HUBN., AS A PEST OF PEA (*Pisum sativum*)

Heliothis armigera Hubn. (*Chloridea obsoleta* F.) is well known as a pest of various crops. It occurs in America as a cotton boll-worm. Fletcher (1914) describes it as a pest of red-gram, Bengal-gram, groundnut, maize (cob), tobacco (seed capsules), ganga (leaves and capsules), safflower (capsules), etc. The writer finds it in Calcutta as a borer of pea-pods, destroying the cotyledons. The only other record of its infestation of pea-pods was from Lyallpur. So far, however, its life-history in pea has not been reported.

This pest was collected from pea-pods obtained from local markets and was reared in the laboratory. The larvæ collected from pea-pods were kept separately in separate glass-vials plugged with cotton, so as to note their individual growth and period of pupation. They were fed with pea-pods. The larvæ were voracious eaters and occurred in great abundance during the months of January and February 1944. Their number decreased from March onwards. The maximum length of a full-fed larva reared in the laboratory was 3.6 cm. They were bright-green in colour,

TABLE I

Substance	M. P.	Molecular weight	$\chi \times 10^6$ Mean of 3 concordant readings	$\chi_m \times 10^6$	$\chi_m \times 10^6$ Reported by Froz and Palacios
1. <i>p</i> -Benzoquinone	117°	108	0.333	35.96	33.3
2. Hydroquinone (Quinol)	171°	110	0.601	66.11	64.58
3. Quinhydrone	171°	218	0.468	102.05	84.2

which showed considerable variation. The larvæ pupated within the vials during the months of February and March. No cocoon was formed, but the pupæ were found to be held by some fine thread-like structures, probably formed by the secretions of the silk-gland. The pupæ were dark-brown in colour and their lengths varied from 1.6 to 1.9 cm. The duration of pupal period varied from 8 to 12 days.

In course of rearing this pest the writer also came across the following species as infecting pods:—(1) *Polyommatus boeticus* L., during the months of December, January and February and (2) *Etiella zinckenella* Tr., during the months of February and March. The last mentioned species is regarded as a minor pest of pulses by Fletcher (1914), but since it occurred in sufficient number, it may be regarded as a major pest like *Heliothis armigera* H., the incidence of the two pests taking place in different periods of the pea-season.

Department of Zoology,
University College of Science,
35, Ballygunge Circular Road,
Calcutta, PRABHAS KUMAR MITRA.
November 4, 1944.

1. Ayyar, R., *A Handbook of Economic Entomology*, 1940.
2. Fletcher, T., *Some South Indian Insects*, 1914.
3. Hampson, G., *Fauna of British India*, 1894, Moths 2.
4. *Rept. Proc. 3rd. Ent. Meeting, Pusa*, 1919, 1, 60.

THE THERMAL DECOMPOSITION OF MERCURIC FULMINATE

HORTSEMA¹ obtained a yellowish product on heating mercuric fulminate to 132° C. which could be heated to higher temperatures without explosive decomposition. He believed that this residue was mercuric oxide and, strangely enough, he found in the gaseous products of decomposition no cyanogen, no carbon dioxide and no carbon monoxide but only oxygen in an almost pure state. Hess and Dietl² found that when 0.5 gm. of fulminate was heated in a test tube at 90-95° C. for 75½ to 97 hours it was transformed into a brownish yellow, non-explosive, difficultly combustible isomerisation or polymerisation product with no change in crystal structure. Langhans,³ working with 15 gm. of fulminate heated in a cylindrical Passburg vacuum drier maintained at 90° C. for 100 hours, obtained the brownish yellow transformation product with similar characteristics, made an exhaustive qualitative study of its chemical properties and named it "Pyrofulmin". Although he never got consistent results on analysing the solid residues obtained from several runs, he concluded from his analytical figures that carbon and oxygen alone disappeared partly and, from his highest values, he worked out the empirical formula of the compound as $Hg_1N_7C_5O_5$. If this formula were correct it is evident that there would have to be some nitrogen in the evolved gases.

Farmer⁴ was the first to study quantitatively the velocity of decomposition of mercuric fulminate *in vacuo* at temperatures between 60°

and 90° C. using 1 to 2 gm. of the substance. He found that the velocity curves are of an abnormal type with an initial quiescent period, decomposition setting in somewhat abruptly, proceeding at first with a nearly constant velocity, which increases slightly until the decomposition ultimately ceases almost abruptly. The main relevant conclusions from his experiments are:—

- (i) The temperature coefficient within the temperature interval is 1.12 per degree centigrade or 1.75 per 5° C., a fact of fundamental importance in the drying and storage of this explosive and its mixtures.
- (ii) The total quantity of evolved gas at 80° C. per gram varies from 44.3 to 48.5 c.c. which corresponds in the mean with 0.58 mol. per mol. of fulminate.
- (iii) The evolution of gas is proportional to the quantity of fulminate.
- (iv) The gas evolved is nearly pure carbon dioxide although on prolonged heating gases unabsorbed by soda lime were given off.
- (v) The residue from the decomposition believed to be a solid autocatalyst is a brown, insoluble material, particles of which retained their original shape.

Garner and Hailes⁵ using a more elaborate and refined technique and working with single crystals, 1 to 5 mgms. in weight, followed the decomposition and detonation *in vacuo* in the temperature range 100° to 120° C. They found that *in vacuo* the thermal decomposition passes into detonation at 105° to 115° C. and that below the ignition temperature the decomposition occurs in three stages:—

- (i) A quiescent period;
 - (ii) a period of acceleration of rate of reaction for which the logarithmic relationship, $\log (dp/dt - dp_0/dt) = kt + \text{constant}$ holds; and
 - (iii) a region where the first order equation applies.
- Stages (ii) and (iii) occur in crushed and ground fulminate also. The critical increment of the thermal reaction is approximately 30 kg. cal. and the volume of the total gas evolved in c.c./gm. lies between 52 and 55 c.c.

The writer has studied the decomposition of several batches of mercuric fulminate of purity 99.3 ± 0.2 per cent. at 100° and 120° C. using 0.1 gm. of the material in the apparatus developed and standardised by Farmer (*loc. cit.*) for the examination of the vacuum stability of certain types of high explosives. A preliminary critical examination with four stability tubes at 100° C. with 0.1 gm. of the explosive in each from a small portion of the same batch has revealed that:—

- (i) apart from small variations in the individual rates, especially in the early stages, owing probably to differences in total effective surface, the general course of the decomposition is substantially the same in all;
- (ii) the decomposition is nearly complete in about 32 hours but, thereafter a slow but continuous evolution of small quantities of gas takes place for a