Photochemistry and Absorption Spectrum of Acetone

IT has been generally assumed that the explanation of the diffuse absorption spectra of aldehydes and ketones in the ultra-violet is the occurrence of a process of predissociation involving the splitting of a C – H or C – C link[1]. Against this observation are the following observations :

(1) The vapours of aldehydes and ketones exhibit fluorescence.

(2) The unimolecular decomposition is always accompanied by bimolecular polymerisation.

(3) The quantum efficiency of decomposition is diminished on passing from C – H to C – C compounds.

(4) Complex ketones decompose in quite a different way from acetone, giving very little carbon monoxide.

(5) The photodecomposition is not a chain reaction.

The photo-reactions of acetone illustrate (1) and (2). In the gaseous state it decomposes with a quantum efficiency of about 0·2 only[2], and we have found that in the liquid state it polymerises (without decomposition) with about the same quantum efficiency. As it is difficult to assume a back reaction to explain the low efficiency[3], it seems more probable that no splitting of a link occurs in the excited molecule. Instead, two processes may occur : (i) bimolecular interaction to give polymerisation, (ii) unimolecular decomposition through the similar interaction of two parts of the molecule, for example,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO \longrightarrow \begin{matrix}CH_3\\|\\CH_3\end{matrix} + CO.$$

In the case of the ketone $\begin{matrix}CH_3CH_2CH_2CH_2\\CH_3\end{matrix}\!>\!CO$ the products are not unexpectedly $\begin{matrix}CH_3-CH\\\|\\CH_2\end{matrix}$ and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO$.[4]

Unless the above unimolecular dissociation takes place within a rotational period it becomes necessary to find another explanation of the diffuseness of the absorption spectrum of some of these substances. We have recently examined the absorption spectrum of acetone, using pressures 0·5–200 mm. in absorbing columns up to one metre. With pressures higher than a few mm. a region of continuous absorption extends from *c.* 3200 A. to 2400 A., with a maximum at about 2800 A. This is the region characteristic of compounds containing the > C = O group. At lower pressures in longer columns and under higher dispersion (Hilger E_1 spectrograph) this continuum splits up into about four groups each containing about 25 diffuse bands. The centres of the respective groups lie at *c.* 3150, 2900, 2710 and 2570 A. The corresponding intervals are 2740, 2420 and 2010 cm.$^{-1}$. (A strong Raman frequency of acetone is 2900 cm.$^{-1}$.) The width of the bands is of the order 2·5 A. (*c.* 30 cm.$^{-1}$) and their separation uniformly about 4 A. With increasing pressure the bands widen and the groups extend so as to produce an effectively continuous absorption.

This type of equally spaced diffuse narrow diffuse bands is similar to that found in other *Y*-shaped molecules[5]. Assuming that the CH_3 groups of acetone behave as single masses of 15, and using probable interatomic distances, the moments of inertia of the *Y*-shaped molecule are such that the rotation lines in the bands should be separated by only *c.* 0·4 cm.$^{-1}$. There will, moreover, be a double series of *P* and *R* branches. It seems therefore inherently impossible to detect the fine structure in this spectrum, and the diffuseness of the bands can be attributed to an unresolved close packing of the rotation lines without calling upon the additional hypothesis of predissociation.

In the case of formaldehyde, where the moments of inertia are much smaller, it is not surprising that a region of fine structure is observed followed by diffuse bands, indicating unimolecular rearrangements within periods greater or less than those of rotation.

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Activated Adsorption and Para-Ortho Hydrogen Conversion on Charcoal

THE para-ortho hydrogen conversion was used by us among other reactions, at the suggestion of Prof. A. Frumkin, in order to investigate the chemical properties of hydrogen adsorbed on charcoal at high temperatures.

It has been shown in a qualitative way by Harkness and Emmett[1] and by Rummel[2] that adsorption of hydrogen on the surface of catalysts diminishes their activity in the ortho-para hydrogen conversion at 90° K.

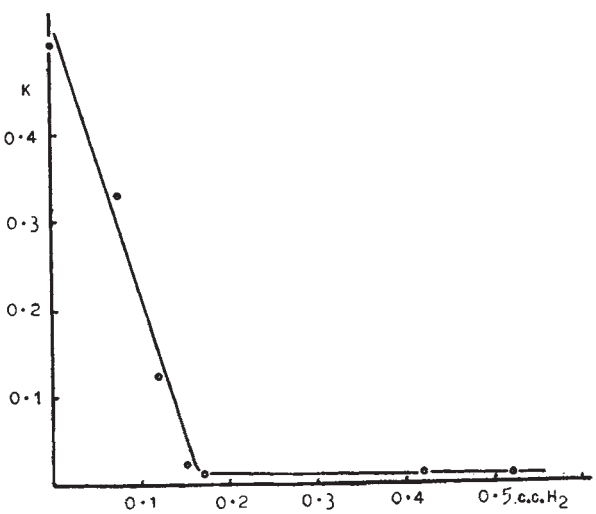

FIG. 1. Adsorption of hydrogen on charcoal at 500° C.

We have investigated the relation between the velocity of the para-ortho conversion at 20° C. and the quantity of gas adsorbed in the activated form. The charcoal was outgassed at 950°, then allowed to cool to the temperature of hydrogen adsorption, and after a definite amount of gas was adsorbed, further cooled to room temperature. The velocity of the

para-ortho conversion was measured at 20° C. using the dynamic method. These experiments (Fig. 1) have shown that the half period of the reaction τ falls in an almost linear way when the quantity of hydrogen adsorbed at 500° increases. The adsorption of 0·17 c.c. hydrogen on 1 gm. of charcoal brings down the velocity to almost zero; this quantity of hydrogen covers less than one thousandth part of the surface. Further increase of the quantity of adsorbed hydrogen has practically no influence on the velocity of the reaction. The poisoning action of hydrogen adsorbed at high temperatures is also observed when the para-ortho conversion was carried out at 300°, but the measurements in this case are inaccurate because hydrogen is already adsorbed with a measurable velocity in the activated form at 300° and the catalyst is therefore gradually poisoned during the reaction.

The change in catalytic activity caused by the activated adsorption cannot be explained merely by a diminution of the van der Waals' adsorption[3], as experiments which we have carried out have shown that the latter is practically uninfluenced by a previous activated adsorption of 0·17 c.c. of hydrogen.

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A Reducing Substance in Brain Tissue

EXPERIMENTS in this laboratory on the chemical basis of some histological staining reactions of brain tissue have shown that all the brain tissues examined (mouse, rat, guinea pig, ox) contain a substance which has the peculiar property of reducing silver nitrate in neutral or acetic acid solution at room temperature, although ammoniacal silver nitrate is not readily reduced in the cold. Extracts of brain tissue containing this substance reduce phenol 2 : 6 dichloroindophenol under the conditions described by Harris and Ray[1] and Birch, Harris and Ray[2] for the estimation of ascorbic acid in tissues, and aqueous alcoholic extracts of ox brain tissue contain the reducing equivalent of 12–15 mgm. of ascorbic acid per equivalent of 100 gm. of tissue, as determined by this method. But the general properties of this substance (or substances) clearly differentiate it from ascorbic acid, as shown in the following table:

Brain reducing substance	Ascorbic acid
Readily reduces acid ammonium molybdate at room temperature.	Does not readily reduce acid ammonium molybdate at room temperature.
Does not reduce ammoniacal silver nitrate at room temperature.	Instantaneously reduces ammoniacal silver nitrate at room temperature.
Insoluble in absolute acetone.	Soluble in acetone.
Precipitated by mercuric acetate.	Not precipitated by mercuric acetate.
No anti-scorbutic activity.	Anti-scorbutic activity.

Daily doses of ox brain extract containing the reducing equivalent of 6 mgm. of ascorbic acid failed to prevent the appearance of the symptoms of scurvy in guinea pigs fed on a scorbutic diet, and it is clear that estimations of ascorbic acid in brain tissue by the indophenol titration method yield fallacious results.

The activity of solutions of this reducing substance is easily destroyed in both acid and alkaline solutions, which renders concentration difficult, but experiments are proceeding with the view of its isolation; solutions are somewhat stabilised by the addition of cyanide, which suggests the possibility that sulphur is concerned in the activity of this substance. A crystalline semicarbazone, m.p. 251°–252° C. (uncorrected), has been isolated from active extracts, but it is not yet possible to determine whether or not this is a derivative of the active substance.

The possibility of identity of the reducing substance from brain tissue, and that obtained from tumour tissue by Boyland[3] and Harris[4] is under consideration, but it is not proposed to name the substance from brain tissue yet.

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Serum Phosphatase in the Domestic Fowl

IT has been suggested that skeletal reserves of calcium may be available for eggshell formation in the domestic fowl[1]. If this suggestion is correct, alterations in the metabolic activity of the bony tissues might be expected in association with the laying period in the hen. Moreover, plasma phosphatase has been used to study alterations in calcium and phosphorus metabolism in sheep[2], and the association of increased serum phosphatase with clinical disorders of bone is now fairly well established. As opportunity has arisen, therefore, serum phosphatase estimations have been made on birds at different stages of the reproductive cycle, using Bodansky's technique[3] and his definition of the unit of phosphatase. Some of the results secured so far are given:

Birds used.	Units of Serum Phosphatase.
3 Cockerels	4·1; 4·0; 3·0.
15 Laying Pullets.	9·2; 7·5; 27·1; 10·2; 28·3; 8·3; 8·3; 16·4; 13·0; 9·2; 15·4; 6·9; 27·7; 16·7; 22·6.
2 Pullets in moult after laying.	24·0; 13·9.
9 Pullets, sexually immature.	4·4; 3·2; 2·0; 4·3; 1·7; 3·8; 3·6; 5·3; 2·8.
1 Pullet nearing laying (weight of largest ovum in ovary = 4·4 gm.)	12·1.

The values for cockerels and sexually immature pullets are comparable, those for laying and moulting birds are higher. There may well be a physiological increase of serum phosphatase in the laying hen, although it is realised that the increase may be related to functions other than bone metabolism and shell formation.

The values obtained from laying birds are very variable, and it will be desirable to study these variations in relation to egg production.

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