Schwartz and Rasp, estimating the diastatic value by the production of achroodextrin from starch, reported that rabbit saliva (quantity unstated) would hydrolyse 2 c.c. of a 1 per cent starch solution in times varying from 50 to 81 minutes with an average of 68 minutes. I have been able to obtain complete hydrolyses of the same volume of starch solution in times varying from 30 seconds to 7 minutes. This marked difference in results seems to arise from the method by which the saliva is obtained from the animal. Schwartz and Rasp procured the secretion by placing in the rabbit's mouth a small wad of cotton wool which absorbed any free saliva in the mouth cavity. This was then placed in the given quantity of starch solution. I have been able to obtain the saliva by a suction method directly from the mouth, the fluid being collected in a small glass vessel. In this way, up to 0·3 c.c. can be procured in 3–5 minutes. I have also demonstrated that by placing a shred of cotton wool in the saliva so obtained, its activity is very considerably impaired. The low diastatic activity observed by Schwartz and Rasp, then, seems to lie in the fact that the enzyme is readily adsorbed by the cotton wool and so removed from the sphere of activity.

Work is at present in progress to try to account for the marked fluctuations in reaction time observed with saliva obtained by the suction method.

Rabbit saliva, like human saliva, has no effect whatsoever on uncooked or unbroken starch grains, owing to the resistant sheath of amylopectin in which the individual grains are enclosed. Work done by Pozerski[3] (1927) suggests that only a very small percentage of the grains are broken in the process of mastication. This brings to light the rather interesting problem of the possible utility of the enzyme in rabbit's saliva.

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Photodecomposition of Aldehydes and Ketones

WE have recently extended our study of primary photochemical change by an investigation of the photodecomposition of the homologues of acetone in cyclohexane solution. It has been shown that in the gas phase there are two main types of decomposition. Type I occurs in short-chain aldehydes and ketones, and consists of an elimination of carbon monoxide, and the formation of an approximately equivalent amount of saturated hydrocarbon, resulting from the primary rupture of one of the carbonyl bonds; for example, in the case of acetone at 60° C. we have[1,2,3,4]:
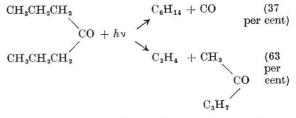
$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$$
$$CH_3CO \rightarrow CH_3 + CO$$
$$2CH_3 \rightarrow C_2H_6.$$

Type II, on the other hand, may be described as a species of cracking of the hydrocarbon chain in the $\alpha \rightarrow \beta$ position to the carbonyl group, with the production of an olefine, and occurs increasingly with the higher homologues[2,5].

Thus with methyl-n-butyl ketone we have:

$$CH_3CH_2CH_2CH_2 \qquad CH_3CH:CH_2 + CH_3$$
$$CO + h\nu \rightarrow$$
$$CH_3 \qquad\qquad CO.$$
$$\qquad\qquad\qquad CH_3$$

It has been shown that some carbonyl compounds in the gas phase decompose simultaneously in the two ways. This is the case with di-n-propyl ketone, in which both types have approximately equal probabilities of occurrence:

$$CH_3CH_2CH_2 \qquad\qquad C_6H_{14} + CO \quad (37 \text{ per cent})$$
$$CO + h\nu$$
$$CH_3CH_2CH_2 \qquad\qquad C_2H_4 + CH_3 \quad (63 \text{ per cent})$$
$$CO$$
$$C_3H_7$$

In solution and in the liquid state these results are considerably modified. Liquid acetone and acetone dissolved in benzene show no reaction whatever. In cyclohexane solution, however, as has been shown by Bowen[6], some reaction occurs with the solvent. Thus Type I decomposition is completely suppressed, and the excited molecules first formed must persist long enough to be deactivated by collision, or for reaction with the solvent.

With 10 per cent solutions of methyl-n-butyl ketone and di-n-propyl ketone in cyclohexane, however, at 20° C. we find a steady evolution of gas—practically pure propylene in the first case, and 98 per cent ethylene in the second, while in the irradiated solution of methyl-n-butyl ketone we have detected the presence of free acetone. It is therefore clear that while photodecomposition of Type I is almost completely suppressed, decomposition of Type II continues apparently unabated in solution. This is particularly apparent in the case of di-n-propyl ketone, in which both types occurred nearly equally in the gas phase.

At temperatures of c. 100° C., on the other hand, we have found that decomposition of Type I can also readily occur. For example, while pure liquid di-n-propyl ketone at 20° C. gives 98 per cent ethylene, at 90°–95° C. it gives a mixture consisting of c. 61 per cent ethylene, 30 per cent carbon monoxide and 9 per cent of ethane. At the same time the absolute amount of reaction according to Type II appears to be approximately independent of temperature.

It may be concluded from these results that:

(a) The mechanism of Type II decomposition is entirely separate from that of Type I.

(b) Molecules of the carbonyl substance can be activated in two alternate ways. In the first case (Type I), the excited molecule has a comparatively long life and is subject to strong deactivation by collision with the solvent, but the probability of reaction increases with temperature. In the second case (Type II), the time between excitation and reaction is so short as to be comparatively uninfluenced by the solvent molecules.

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