Letters to the Editor

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NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 976.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

Mechanism of Thermal Change in Gaseous Organic Compounds

INVESTIGATIONS in this laboratory have shown that thermal change in gaseous organic compounds commonly leads to the formation of paired products through a single chemical process, so that, although the rate of change in the reactant is determined solely by initial concentration and temperature, the relative rates of formation of the products may be determined by other conditions. In such cases the initial rates of reaction show acceleration, the $x - t$ graphs being linear, or curved towards the x-axis; but after a relatively short period the slopes of the graphs suddenly diminish. Further, the main process seems generally to be associated with a primary or *background process*, represented by,

$$A \rightleftharpoons B \; (+ C),$$

leading to equilibrium in the system A, B, (C).

The main process seems to be initiated by binary collisions AB, collisions AA, and generally also BB, leading only to change in the equilibrium system. The main process may be represented by,

$$\begin{array}{ccccccccc} a & & b & & c & & d & & e \\ A + B & \rightarrow & A'\,B' & \rightarrow & A'\,B' & \rightarrow & A'\,B' & \begin{array}{c}\nearrow \\ \searrow\end{array} & \begin{array}{c}C \\ D\end{array} \\ \text{Molecules} & & \begin{array}{c}\text{activated} \\ \text{state}\end{array} & & \text{complex} & & \begin{array}{c}\text{unstable} \\ \text{intermediate}\end{array} & & \begin{array}{c}\text{paired} \\ \text{products}\end{array} \end{array}$$

The change $c \rightarrow d$ is such that the probability of reversal is very small, and it is the rate of this process which we generally measure. Since the products which are formed simultaneously may be, on one hand, products of condensation, and on the other, products of disruption of the reacting molecules, it is suggested that these survive as entities to the *unstable intermediate* stage, and that free radicals are not accountable for the processes involved.

Re-investigation of the data obtained by Dr. Hockin, Dr. Pearce and myself from the study of the thermal decomposition (550°–630°) of ethane, and of ethane – ethylene – hydrogen equilibrium mixtures, has thrown some light on the whole problem of the thermal changes in simple organic compounds. In both cases methane and condensation products are formed, but in the background of the processes which give rise to these products is the equilibrium reaction represented by,

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2.$$

However, in this case the background reaction can be studied independently, and a great deal is known about it. Also, by working with ethane – ethylene – hydrogen equilibrium mixtures, we can virtually eliminate the disturbing effect introduced by the operation of the background reaction when working with pure ethane. It is possible to make up an unlimited number of mixtures in which the ratio $(C_2H_4)(H_2)/(C_2H_6)$ corresponds to equilibrium conditions at the temperature of the experiment, and using the computative method described in one of our papers[1], I have found that the rate of formation of the products, expressed in terms of the rate of disappearance of 2-carbon hydrocarbon, conforms to the expression,

$$d(CH_4 + R)/dt = K(C_2H_6)(C_2H_4),$$

with reasonable exactitude in the case of about a hundred experiments.

Starting with pure ethane, it is found that the initial rate of reaction is accelerated. This may be accounted for qualitatively by the fact that the ethylene concentration is increasing from the commencement. However, the acceleration is greater than can be accounted for in this way, and the fact that the break does not occur in the $x - t$ graph until some little time after the ethylene concentration has reached a maximum suggests that the acceleration may be partially due to some chain mechanism arising from the background reaction. After the break, the rate of reaction seems to conform to the bimolecular equation. The ratio $(CH_4)/(CH_4 + R)$ seems to vary between limits 0·5 and unity with the hydrogen concentration, but no quantitative relationship has been worked out. The bimolecular reaction involving ethane alone results only in the formation of ethylene and hydrogen, and the bimolecular condensation of ethylene, as studied by Pearce, seems to be a heterogeneous process.

The work carried out by Dr. Seddon and myself on acetaldehyde was that in which it was shown originally that the *paired products* may result from a single chemical process. They are methane and carbon monoxide, which constitute the main product when the reaction is conducted in an empty tube, and propylene, carbon monoxide, and water, which may constitute the main product when the tube is packed. The thermal decomposition process is accelerated initially; and, from analogy with the case just considered, it seems fair to associate this process with the development of a system represented by,

$$CH_3.CHO \rightleftharpoons CH_2{:}CHOH,$$

in the background. The constituents of the system are known, though nothing is known about their equilibrium relations.

The thermal decomposition of methyl nitrite has been studied by Mr. A. G. Carter and myself. Contrary to the conclusion of Steacie and Shaw, we find that the decomposition process shows strong initial acceleration, and that paired products result, the processes being represented by,

$$\begin{aligned} 2\,CH_3NO_2 &= 2\,NO + CH_2O + CH_4O, \text{ or} \\ &\; N_2O + 2\,CH_2O + H_2O. \end{aligned}$$

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There is evidence here that the process must be bimolecular. However, though there is plenty of evidence to show that methyl nitrite does not behave like a normal ester, there is no evidence as to the nature of a background process, should such exist. The thermal decomposition of methylamine has been studied by Messrs. Bosanquet, Carter, Wilshire and myself, in continuation of the work of Emeléus and Jolley. Their work suggested that the two methods of decomposition represented by,

$$CH_3NH_2 = HCN + 2\,H_2, \quad \text{and}$$
$$CH_3NH_2 + H_2 = CH_4 + NH_3,$$

are related. We find further evidence in support of this view, and also that the processes are initially accelerated. The process represented by the first equation is definitely reversible, and it can be supposed that a background reaction operates in this case, though its nature is again unknown.

A similar mechanism must operate in the case of other gaseous reactions to which I have made reference in recent letters to NATURE.

We have also studied the thermal decomposition of certain 3-carbon compounds, but detailed analysis shows that the processes are extremely complex. One can, in such cases, express the rates of decomposition, if measured by observing increase in pressure at constant volume, by means of an equation analogous to that representing unimolecular change. Taking the two sets of results together, however, it seems to me that such procedure is likely to be much more misleading than helpful.

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[1] *J. Soc. Chem. Ind.*, 53, 323 (1934).

Action of Co-zymase as the Specific Co-enzyme of Lactic Dehydrogenase from Heart Muscle

EARLIER work on the mechanism of enzymatic dehydrogenation has shown that, in presence of a thermolabile apo-dehydrogenase of protein character, co-zymase takes up hydrogen from a substrate and is thereby reduced to a dihydro-form[1]; the dehydrogenation of alcohol may be represented by the equation

$$\text{alcohol} + D^A\text{-}Co^I \rightleftarrows \text{aldehyde} + D^A\text{-}Co_I H_2 \qquad (1)$$

where D^A is the specific alcohol apo-dehydrogenase and Co^I co-zymase. The apo-dehydrogenases are specific with respect to substrates and to one or other of the two known co-dehydrogenases, co-zymase (Co^I) or Warburg's co-ferment (Co^{II})[2]. Recently, we showed that lactic apo-dehydrogenase from heart muscle and alcohol apo-dehydrogenase from yeast are not identical, but both form active holo-dehydrogenases only with Co^I and not with Co^{II} [3].

Green and Brosteaux[4] have just confirmed our result that lactic dehydrogenase is not activated by Co^{II}, but have not decided whether the necessary co-dehydrogenase is identical with Co^I. Our earlier proof of the identity of lactic co-dehydrogenase with co-zymase, based on parallelism between fermentative and co-dehydrogenase activity, is confirmed conclusively by the following experiments, which show that alcohol co-dehydrogenase and lactic co-dehydrogenase are completely interchangeable. The identity of the former with co-zymase is quite certain.

(1) 2·0 ml. *M*/2 sodium lactate, 1·4 ml. *M*/2 disodium hydrogen phosphate and 0·1 ml. lactic dehydrogenase (D^L) from heart muscle (clear solution) were mixed in an absorption cell and the extinction (ε) at λ = 334 mμ was measured photo-electrically. After addition of 0·4 mgm. co-zymase, the extinction increased rapidly, corresponding with the formation of reduced co-enzyme (Fig. 1). Equilibrium was reached after 10 minutes. After a further 15 minutes, 0·1 ml. *M*/10 sodium pyruvate was added (*a*) which caused the extinction to fall rapidly to a value representing the absorption of the excess of pyruvic acid. This experiment indicates the reversibility of the process

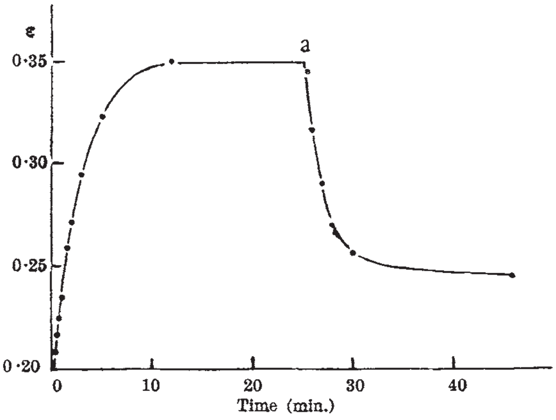

FIG. 1.

$$CH_3.CHOH.COOH + D^L\text{-}Co \rightleftarrows CH_3.CO.COOH + D^L\text{-}CoH_2 \quad . \; . \; . \; . \quad (2)$$

The effect of *p*H and temperature on this equilibrium is being further investigated.

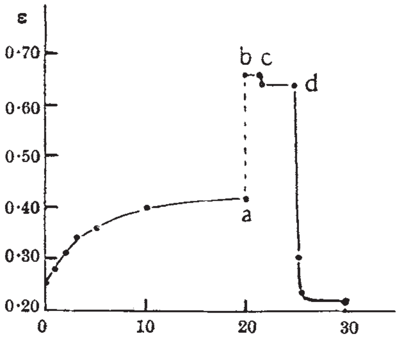

FIG. 2.

(2) In a similar experiment (Fig. 2), after production of the reduced co-enzyme, the mixture was heated (*a*) for 5 minutes at 75°, thus destroying the lactic apo-dehydrogenase. After filtration, the extinction of the clear filtrate was again measured (*b*). The increase is due to a displacement of the equilibrium by rise of temperature in favour of the reduced co-enzyme prior to destruction of the enzyme. No reaction occurred on addition of 0·1 ml. *M*/100 acetaldehyde (*c*), but on subsequent addition of 0·1 ml. alcohol apo-dehydrogenase from yeast (*d*),

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