STUDIES IN CATALYSIS

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Frequently the term catalysis is associated with important processes such as the fixation of atmospheric nitrogen, hydrogenation or "hardening" of vegetable oils, vulcanization of rubber, manufacture of Bakelite, and many other operations of a similar nature. Usually the function of a catalytic agent is to initiate reactions or to accelerate those which without this aid would proceed too slowly to be of value.

At present considerable attention is being given to another sort of catalysis. It has been known for sometime that the rate of decomposition of unstable materials like smokeless powder and hydrogen peroxide can be greatly decreased by the addition of a small amount of compounds known as stabilizers or negative catalysts. The writer has recently studied problems of this general type in detail with the hope of establishing the mechanism of negative catalysis and of ascertaining principles which might be of general use in choosing inhibitors or stabilizers.

When chloroform is exposed to light, even in stoppered bottles of ordinary glass, it gradually develops an acid reaction and acquires some properties of an oxidizing agent. Compounds found in chloroform which has undergone decomposition are phosgene, hydrogen chloride and chlorine. Probably the reactions involved are as follows: $HCCl_3 + O_2(air) = HCl + Cl_2 = C\begin{cases} O \\ | \\ O \end{cases}$;

$2\,Cl_2 = C\begin{cases} O \\ | \\ O \end{cases} = 2\,Cl_2\,CO + O_2$. Obviously these substances render chloroform unfit for use as an anaesthetic. It is customary to add a small amount of ethyl alcohol to chloroform to minimize the changes which have been mentioned. The decomposition of chloroform has received attention from many investigators. Results obtained have been explained by saying that stabilizers reacted with the products of decomposition. On this basis one would expect that only materials easily oxidized or chlorinated would be effective as inhibitors. There are several serious objections to this point of view, including the fact that very small amounts of preservatives are sufficient for large quantities of chloroform.

A short time ago a theory was put forward by Taylor in which it was stated that, in certain cases at least, the so-called inhibitors function by formation of molecular compounds with the active molecules of the substance being preserved. On this basis inhibitors are true negative catalysts

and not reagents. *This idea has been the guiding principle in our work.* In the case of chloroform one would say that the chloroform molecules have a greater affinity for the stabilizer than for the oxygen of the air. Since molecular compounds are very loose combinations which are formed and decomposed extremely rapidly, a comparatively small quantity of stabilizer is able to care for large quantities of chloroform.

We have repeated some early and recent experimental work and have investigated many stabilizers not previously studied. There seems to be a remarkable parallel between molecular compound formation and negative catalysis. Substances such as ethyl ether, phenol, resorcinol and benzene are stabilizers for chloroform. Evidence of molecular compound formation is available for each of these compounds. It seems unlikely that benzene would be oxidized by decomposed chloroform. Also we have been unable to find any conclusive evidence of chlorination of these four preservatives. On the other hand, carbon tetrachloride is not useful as a negative catalyst. One would not expect this material to form a molecular compound with chloroform. Of course the evidence regarding some of the substances investigated cannot be so readily interpreted as the facts we have just mentioned. In the limited time available it is not possible to give many details, but the writer is prepared to say that in dealing with more than twenty-five compounds, including amylene, benzene, *m*-xylene, toluene, naphthalene, liquid petrolatum, nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene, methyl alcohol, ethyl alcohol, phenol, resorcinol, α-naphthol β-naphthol, pyrogallol, ethyl ether, diamyl ether, phenetole, carbon tetrachloride, acetic acid, cinnamic acid, benzidine and dianisidine, no really serious contradiction of his thesis has been found.

In the prevention of the fading of dyes we have another field in which inhibitors can be employed. Apparently in certain cases loss of color on exposure to light is due to oxidation. One might expect that some of the compounds which retard the decomposition of chloroform would also increase the fastness of certain coloring matters to light. Skeins of cotton and wool were dyed with representative colors of the azo, basic and acid types. In every case investigated it has been found that the fugitive dyes could be more or less protected against the action of light by treatment of the dyed wool or cotton with a dilute solution of phenol or of resorcinol. A piece of yarn colored with malachite green faded a great deal after one week of exposure to light; no color change was apparent in one month, after treatment with resorcinol solution. Among the thirty colors investigated were also shades of blue, yellow, orange, brown and black. It seems advisable to attempt utilizing the information obtained, by synthesizing dyes of molecular structure such that there would be present groups similar to those found in stabilizers. By a rather indirect use of this idea we have succeeded in obtaining from primuline, which usually is described as yield-

ing somewhat fugitive developed colors, a series of brilliant azo dyes very fast to light.

Although the work mentioned in this paper deals with only a small part of the subject the evidence which has been secured indicates that the idea of molecular compound formation should be thoroughly tested. Since the organic chemist specializes in problems connected with molecular structure and the residual affinity of atoms or groups he may find this theory useful in the choice of negative catalysts for many purposes.

ON THE MEASUREMENT OF CRITICAL THERMAL INCREMENT FOR BIOLOGICAL PROCESSES

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The attempt to classify biological activities upon the basis of their velocities as affected by temperature[1] involves for a number of cases the adjustment of curves to data inevitably subject to several sources of variation. One of these arises from the fact that the measurements may be secured with different individuals at each of several temperatures. The latitude of variation in series of data obtained in this way may be large, and unless great numbers of observations are available interpretation may be difficult.[2] Indication already obtained as to the theoretical significance of the exact quantitative relationship between velocity of a vital process and temperature make it desirable to demonstrate the limits of variation in material which is as nearly as possible biologically homogeneous.

An illustration is provided by the frequency of the heart-beat in the silkworm. Larvae were bred from eggs given by Dr. R. W. Glaser. The caterpillars used came from eggs laid by one female; this fact, coupled with the highly inbred character of these animals, insures exceptional genetic uniformity. The heart-beat was counted for each of a number of individuals of the same age, reared throughout under identical conditions.[3] The details of these experiments well be described in another place. It is sufficient here to state that a larva when under observation was motionless and quietly feeding on a mulberry leaf, in a closed glass chamber immersed in water. The temperature was obtained with a thermometer reading to 0.01°C. We shall deal merely with the temperature affect above 15°C. Below this temperature, complications ensue and there occur changesw hich are only slowly reversible. It is significant that 15° is in this instance as