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Summary

1. A new synthesis yielding 40–60% of glycocholic acid is reported.

2. The following new compounds are described: triformylcholic acid, triformylcholyl chloride and triformylcholyl amide.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Activity and Activation Energy in Heterogeneous Catalysis of Gas Reactions[1]

BY H. H. STORCH[2]

In a number of heterogeneous catalytic reactions[3,4,5] the use of the rate equation $k = Ae^{-E/RT}$ has led to an apparent relationship of the type $A = C_0e^{cE}$ where C_0 and c are constants, E is the activation energy, and A the activity constant. Unfortunately the energetics of the particular reactions chosen to illustrate this relationship are not simple. Thus, all but a few of the dehydrogenation reactions cited by Balandin[3] are apparently of first order,[6] and the contributions of the heats of adsorption to the E values are not known. Cremer's[4] comparison of the rates of decomposition of ethyl alcohol at atmospheric pressure by aluminum oxide, reduced indium oxide, and scandium oxide is of doubtful value because of the very marked retardation by water vapor and the lack of measurements on the order of the reaction, thus making impossible any precise statement concerning the significance of the E values. The same objections may be made to the use of similar data of Adkins and Perkins[7] on the decomposition of various alcohols by aluminum oxide and of Adkins and Nissen[8] on the decomposition of formic acid by various aluminum oxide catalysts.

The data of Eckell[5] on the oxidation of carbon monoxide by $Al_2O_3 + Fe_2O_3$ catalysts indicate a first order reaction with respect to the partial pressure of carbon monoxide; hence there is some uncertainty concerning the effect of possible variations in the heats of adsorption on the E values for the various catalysts. There is also a definite uncertainty as to the influence of adsorbed water vapor, for the water-gas reaction, $CO + H_2O = CO_2 + H_2$, may well be the rate-controlling step.

The problem of the relationship between activity and activation energy has also been discussed in connection with the activated adsorption of gases, particularly of hydrogen by similar catalysts.[9] In the experiments on activated adsorption the order of the reaction has not in any case been definitely determined, and the temperature coefficients are very variable depending upon the amount of gas adsorbed. The activation energies calculated from such measurements cannot therefore be conclusively designated as an invariant characteristic of a given surface reaction.

For the purpose of this discussion it seemed desirable to use data for zero order decompositions of a single reactant in which there is no retardation by reaction products and for which the rate measurements were made with a known degree of precision. These restrictions limit the discussion to the data of Palmer and Constable[10] on the dehydrogenation of various alcohols by copper catalysts, of Dohse[11] on the dehydration of various alcohols by bauxite, the dehydrogenation of methanol by zinc oxide,[12] and of Schwab and Schultes[13] and of Hüttig *et al.*[14]

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(3) Balandin, *Z. physik. Chem.*, **B19**, 451 (1932).

(4) Cremer, *ibid.*, **A144**, 231 (1929).

(5) Eckell, *Z. Elektrochemie*, **39**, 807, 855 (1933).

(6) That the assumption made by Balandin of zero order for all the reactions is erroneous can readily be seen from an inspection of the data of Zelinsky and Balandin [*Z. physik. Chem.*, **A126**, 267 (1927)].

(7) Adkins and Perkins, THIS JOURNAL, **47**, 1163 (1925).

(8) Adkins and Nissen, *ibid.*, **45**, 809 (1923).

(9) Howard and Taylor, *ibid.*, **56**, 2263 (1934).

(10) Palmer and Constable, *Proc. Roy. Soc.* (London), (a) **A107**, 255 (1925); (b) **A108**, 355 (1925); (c) **A113**, 254 (1927).

(11) (a) Dohse and Kälberer, *Z. physik. Chem.*, **B5**, 131 (1929); (b) Dohse, *ibid.*, **B6**, 343 (1930).

(12) Dohse, *ibid.*, **B8**, 159 (1930).

(13) Schwab and Schultes, *ibid.*, **B9**, 265 (1930).

(14) Hüttig, Schreiber and Kittel, *ibid.*, **A171**, 83 (1934).

on the decomposition of nitrous oxide by various metal oxides.

Constable[10b] was the first experimenter who indicated clearly the experimental relationship between the activity and activation energy in contact catalytic reactions. Table I gives some of his data on the dehydrogenation of ethyl alcohol by copper catalysts formed by reduction of the oxide at various temperatures. There is obviously a linear relationship between $\log_{10} A$ and E. Constable[10b] applied the theory of probability to Taylor's concept of active centers[15] and showed that the distribution of active centers corresponding to a given E value is an exponential function of E, in other words, that the relationship $A = C_0 e^{cE}$ is a reasonable consequence of Taylor's theory.

TABLE I

DEHYDROGENATION OF ETHYL ALCOHOL BY COPPER CATALYSTS

Reduction temp., °C.	E, kcal.	$\log_{10} A$, molecules per sec. per g. of catalyst
225	25.61	28.69
235	25.03	28.51
257	23.89	27.93
266	22.07	27.20
275	21.61	27.15
350	21.59	26.87

In order to penetrate further the origin of such a relationship it must be possible to answer questions concerning the mechanism of energy exchange between the catalyst and the adsorbed reactant. The energy imparted to the latter by gas bombardment is probably of minor importance, as the number of collisions with the surface of gas molecules possessing energy greater than E is enormously larger than the observed reaction rate in all of the experiments discussed in this paper. The frequency of energy transfer between the catalyst centers and the adsorbed reactant for zero order reactions would be expected to be of the order of magnitude of the vibration frequency of these centers, namely, about 10^{13} sec.$^{-1}$. If the number of active centers (S) were directly measurable, the frequency of energy exchange (Z) could be readily calculated, as the product of these two quantities (SZ) must be equal to the activity constant (A) expressed in molecules sec.$^{-1}$. This statement assumes, of course, that S and Z do not vary appreciably with temperature; this is true of S for a zero order reaction and approximately true of Z for relatively short temperature ranges.

Such a calculation is possible for the data of Dohse[11] on the dehydration of various alcohols by bauxite given in Table II. Here the reaction is of zero order in the pressure range 0.1–10 mm. if the water is removed continuously. For the very low initial pressures the water is retained by the catalyst, and there is a sufficiently large difference between the adsorptions of the olefin and the alcohol to make rate measurements possible up to the point of complete covering of the active centers. Beyond this point the half-life period, which had thus far remained constant with varying amounts of alcohol adsorbed, increased very sharply with increased initial alcohol adsorption. This made it possible to calculate the number of active centers directly, and the figure given by Dohse[11b] is 2×10^{19} per g. of bauxite. Beyond the point at which a complete monomolecular layer existed on the catalyst surface, circulation of the gas by a mercury diffusion pump through a tube of barium oxide removed the water with sufficient rapidity to avoid any retardation.

TABLE II

DEHYDRATION OF ALCOHOLS ON BAUXITE

Alcohol	E, kcal.	$\log_{10} A$, molecules per sec. per g. of catalyst
Propyl	28.5	29.2
Butyl	28.0	29.0
s-Butyl	24.0	28.9
i-Propyl	26.8	29.6
t-Butyl	20.0	29.1

In Table II the activity factor A is constant within a factor of about 5, despite the fact that the energies of activation range from 20 to 28.5 kcal. Using $S = 2 \times 10^{19}$, one finds $Z = 0.4 \times 10^{10}$ to 2×10^{10} sec.$^{-1}$ for the frequency of efficient energy exchange between the catalyst and the adsorbed alcohol.

One finds upon examination of the data of Palmer and Constable[10a,c] given in Table III that in the dehydrogenation of various alcohols by copper, the activity factors vary by a factor of as much as 250. Since, as shown in Table I, appreciable variation of A is to be expected due to small differences in conditions used for preparation of the catalyst, it was necessary to measure the E and A values for ethyl alcohol with every new catalyst preparation to have a common basis for comparison of the data for the other alcohols. The ratio A_x/A_e of Table III is the activity factor for any alcohol based on $A = 1$ for ethyl alcohol. This ratio is unity for all the primary alcohols except isoamyl for which it is 2.5, whereas

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[15] Taylor, *J. Phys. Chem.*, **28**, 911 (1924).

for the secondary alcohols the ratio is 250. The latter variation is obviously a peculiarity of the dehydrogenation reaction rather than of the copper catalyst, since both bauxite and copper gave identical values of A for the primary alcohols, and the dehydration on bauxite showed little or no difference between A values for primary, secondary and tertiary alcohols.

TABLE III

DEHYDROGENATION OF ALCOHOLS ON COPPER

E_x, activation energy for various alcohols in kcal. E_e, activation energy for ethyl alcohol in kcal. A_x, activity factor for various alcohols in molecules per second per gram of catalyst. A_e, activity factor for ethyl alcohol in molecules per second per gram of catalyst

Alcohol	E_x	E_e	$\log_{10} A_x/A_e$
Propyl	22.5	22.5	0.0
Butyl	23.0	23.0	.0
i-Butyl	21.2	21.1	.0
i-Amyl	19.7	18.9	.4
i-Propyl	26.7	22.8	2.4
Cyclohexanol	27.3	21.3	2.4
Allyl	18.6	18.6	0.0
Allyl ⟶ propionaldehyde	8.4	18.6	−3.5

Table III also contains data on the dehydrogenation of allyl alcohol by copper. Here there are two concurrent reactions: dehydrogenation to acrolein and rearrangement of hydrogen atoms in the allyl alcohol to yield propionaldehyde. The A_x/A_e value for the dehydrogenation is unity, that is, the dehydrogenation energetics are in complete agreement with that of other primary alcohols; however, the A_x/A_e value for the rearrangement shows that the activity factor for the latter is about 3000 times smaller than that for the dehydrogenation reaction. One is tempted at first to argue that the number of catalyst centers sufficiently active to cause the rearrangement with the relatively low E value of 8.4 kcal. may well be 3000 times scarcer than those which are capable of effecting the dehydrogenation. Constable,[10c] however, has found that sintering the copper catalysts results in a much higher ratio of propionaldehyde to acrylic aldehyde in the products. Hence it appears that the explanation just given is not correct, as one would expect the very active centers to be those most readily destroyed by sintering. It is apparent therefore that there is some factor inherent in the bond energy distribution of the adsorbed reactant that is different for the two types of reaction of allyl alcohol.

A somewhat similar situation is encountered in the dehydrogenation of methyl alcohol by zinc oxide. The data of Dohse[12] show two consecutive dehydrogenation reactions, both of zero order and both free from retardation by the products. The E value for the first reaction $CH_3OH \longrightarrow H_2CO + H_2$ is 22.5 kcal. and $\log_{10} A = 26.4$. The second reaction, $H_2CO \longrightarrow H_2 + CO$, has an E value 35.0 kcal. and $\log_{10} A = 30.6$. The activity factor for the formaldehyde decomposition is about 6000 times larger than that for the dehydrogenation of methanol. While there is no criterion which would enable one to infer that the number of active centers capable of dehydrogenating methanol to yield formaldehyde cannot be 6000 times smaller than those which are capable of effecting the formaldehyde decomposition, the data on allyl alcohol should make one less confident that this is the explanation. The alternative explanation is again some factor which is a function of the bond energy distribution of the adsorbed molecules and does not depend directly on the nature of the catalyst center. To make this statement more specific—if we exclude a variation in the number of active centers there appear to be only two possible explanations of the relationship $A = C_0e^{cE}$ namely: (1) that the frequency of energy transfer by vibrational collisions (Z) on the catalyst surface is a function of the type of adsorption involved. Thus, it is conceivable that if multiple adsorption precedes the $CH_3OH = H_2CO + H_2$ reaction, whereas the H_2CO molecule is only singly adsorbed, the frequency of energy transfer in the former reaction will be reduced greatly by the small changes in amplitude which must occur when two (or more) catalyst centers are bound together by a stretched C–H or O–H bond. (2) That in reactions involving the addition, subtraction, or transfer of hydrogen atoms a considerable fraction of the rate, particularly for reactions where $E <$ about 20 kcal., is to be ascribed to a quantum mechanical leakage through the energy barrier.

The latter explanation may be rather difficult to test experimentally. The only experiments which suggest themselves concern the possibility of finding a contact catalytic reaction involving hydrogen, for which the activation energy increases from almost zero at relatively low temperatures to a constant value at higher temperatures, and the relatively complete absence of any such behavior for reactions which do not involve hydrogen. This would involve rate measurements of a precise nature on rates ranging from very low to very high values.

To test the first explanation and at the same time exclude the second, a search was made of the literature to find a series of measurements of a zero order decomposition, not involving hydrogen, of a single reactant by various similar catalytic surfaces where no retardation by the products existed. A mildly satisfactory case was found in the decomposition of nitrous oxide by various catalyst.[13,14] These data are shown in Table IV. The reaction is close to zero order, for Schwab and Schultes[13] found rate = constant × $\sqrt[3]{N_2O}$. There are no data to indicate whether retardation by the products exists, but neither oxygen nor nitrogen is adsorbed very strongly by these oxide catalysts, and it is not likely that retardation occurs. It will be noted that the activity constants are identical for cupric oxide and magnesium oxide. The $MgO \cdot Fe_2O_3$ prepared at 750° was ferromagnetic, whereas that prepared at 680° was not. Despite a continuous variation in the magnetic susceptibility with temperature of preparation of the catalyst, no change in rate or E occurred until the catalyst was definitely paramagnetic, which point is associated with the formation of a magnesium ferrite and a corresponding change in crystal structure. The activity factor decreased by about 7000 upon formation of the ferromagnetic material, the activation energy decreasing at the same time from 38.0 to 26.1 kcal. Here one is confronted with the fact that increase in temperature of preparation of the catalyst, instead of destroying the active centers associated with low activation energies, appears to create such centers. Hence, it is apparent that some change in the manner of adsorption of the reactant must have occurred due to the transition to the magnesium ferrite lattice.

TABLE IV

DECOMPOSITION OF NITROUS OXIDE

Catalyst	E, kcal.	Log$_{10}$ A, molecules per sec. per g. of catalyst	Distance between metal and oxygen atoms, Å.	
CuO	24.0	26.07	1.87	2.33
MgO	28.1	26.02	..	2.11
$Mg(FeO_2)_2$[a]	26.1	24.8	1.94	2.03
$MgO \cdot Fe_2O_3$[b]	38.0	28.56	?	?
ZnO	44.5	31.07	..	3.25

[a] Prepared by heating at 750° for six to twelve hours.
[b] Prepared by heating at 680° for six to twelve hours.

In view of the apparent identity of the CuO and MgO activity factors and of the fact that the 7000-fold difference between the two $MgO \cdot Fe_2O_3$ catalysts probably is due to a change in frequency of energy transfer caused by a corresponding change in the manner of adsorption of nitrous oxide, it seems plausible to assume that the 10,000-fold difference in activity factor between zinc oxide and cupric oxide (or magnesium oxide) should be explained in the same fashion.

Discussion

Consideration of the data thus far presented leads to the conclusion that changes in the frequency of energy transfer (Z) with the type of adsorption constitute an important factor in determining the relationship $A = C_0e^{cE}$. It is not possible at present to decide whether or not leakage of hydrogen atoms through the energy barrier in reactions involving hydrogen is also a contributing factor. Since, however, all of the data presented are consistent with the assumption of variation of Z with type of adsorption, it does not seem necessary to include the additional hypothesis of H-atom leakage.

It would be desirable to make x-ray measurements to determine the spacings between atoms of a group of similar catalysts which are effective in the zero order decomposition of a single reactant. Such data, combined with a direct determination of the number of active centers by Dohse's[11b] method, should yield quantitative data concerning the variation of Z with distance between catalyst atoms. The atomic distances listed in Table IV indicate that there may be a correlation between them and the activity factors.

Summary

A survey of available data shows that the relationship $A = C_0e^{cE}$ between the activity A and the energy of activation E for contact catalytic reactions cannot be due entirely to a probability distribution of active centers. Two other factors may be important in determining this relationship, namely: (1) that the frequency of energy exchange in the adsorbed phase may be reduced markedly when multiple adsorption occurs and hence be a function of the spacing of the catalyst atoms; (2) that in reactions involving hydrogen and having a relatively low activation energy a considerable fraction of the rate is to be ascribed to a quantum mechanical leakage through the energy barrier.

In the data reviewed there is considerable evidence in favor of the first hypothesis but none either for or against the second. Experiments are suggested which may result in further evidence concerning these two hypotheses.

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