RADIOISOTOPES IN SCIENTIFIC RESEARCH

VOL II

RADIOISOTOPES IN SCIENTIFIC RESEARCH

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Investigations on the Mechanism of Catalysis Based on Isotopic Data

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Abstract

Radioisotopes have been extensively used in work on the mechanism of catalysis carried out in our Institute.

A study was made, in collaboration with M.M. Sakharov et al., of the distribution of radiocarbon in the hydrocarbons obtained by hydrogenation of carbon monoxide on cobalt-thoria catalysts, various labelled compounds being added to the primary gas mixture. It was thus possible to show that the reaction proceeds along two-dimensional growth-chains. Two dimensional relay chains were detected during hydro-polymerisation of a mixture of ethylene and carbon monoxide. The carbide and the dehydration-condensation theories of alkane synthesis have thus been proved to be in error. A radical-ionic mechanism of chain growth seems more probable.

Further studies made in collaboration with L.I. Margolis et al. of the distribution of radiocarbon from different labelled molecules in the products of oxidation of olefines and paraffins on certain oxides and metallic silver have demonstrated the occurrence of independent and simultaneous formation of a number of products of partial and complete oxidation. The results point to the existence of a destructive chain mechanisms in hydrocarbon oxidation.

A study of homomolecular exchange of oxygen on catalysts showed the significance of the ion-radical O_2^- as a primary active form accounting for the formation of labile intermediate forms (ion-radicals of the peroxide type).

Radiochromatographic methods for analysis of catalysts have been devised in collaboration with M.I. Janovski et al. in order to study the occurrence of successive stages in catalytic reactions.

The kinetics of catalysis and chemisorption are characterized by a strong influence of the composition of the absorption layer and its degree of covering on the velocity constants, the thermal coefficient and the activation energy for surface processes. Methods worked out in collaboration with N.P. Keier have been used to establish the relative importance of 'biographical' non-uniformity and interactions within the layer. In this way we set up the distribution functions and interaction rules. Measurement of energetic values characterizing some metallic and semi-conducting catalysts have shown that no appreciable effect is produced by interaction. In the case of catalytic decomposition of alcohol and certain reactions of acetylene, the occurrence of particular reactions on well-defined groups of active sites was demonstrated unambiguously. The activity of these sites is primarily related to valency defects of the crystal lattice, mainly micro-impurities of electron acceptors and donors dissolved or adsorbed in the lattice. The capture of impurities during the formation of catalysts has been traced radiochemically. This work was done in collaboration with G.M. Zabrova et al.

The theory of catalysis is on the verge of establishing scientific principles of selecting new catalysts including synthetic organic catalysts, artificial analogues of enzymes. Even a

partial solution of these problems would signify an enormous success on the way to a complete control over chemical transformations. This, however, requires a profound knowledge of the mechanism of catalytic processes and of the relationship between the catalytic properties of substances and their chemical composition and structure. It is not surprising that of late the most refined modern methods of research have been used to study the mechanism of catalysis and the nature of catalytic activity, and that the interest in employing isotopes for this purpose has greatly increased.*

Our laboratory started work on the application of artificial radioactive isotopes for the study of catalysts and catalytic processes as far back as in the 1930's (1). This paper will present the latest results revealing new peculiarities of the catalysis mechanism.

1. CHAINS IN CATALYSIS

For a long time the problem of chains in heterogeneous catalysis was identified with the problem of continuation, in the gas or liquid phase, of reactions initiated on the surface of a solid catalyst. Such a course of catalytic reactions has been reliably proved in several cases, yet it plays a subsidiary role in heterogenous catalysis. Ordinarily, at temperatures which are not too high, the entire catalytic process is fully localized on the surface of a solid, and in order that the chains in the catalysis could acquire a general significance, they should develop on the surface without escaping from the volume of the gas. This conclusion is not categorical for liquids.

The question of the probability of the existence of such chains has been raised many times by N.N. Semenov and in recent years was discussed in several theoretical papers (2), reviving the old idea of F. London concerning the accelerating action of the free valencies of the catalyst's surface. The arguments presented in these papers favouring the reality of a "flat" chain mechanism cannot be regarded as decisive, owing to factors limiting the possibility of such a course of catalytic processes. It appeared probable that the employment of labelled molecules would serve to clarify this problem.

It has been proved that in homogeneous kinetics there exist two basic types of chain processes which should be more correctly termed as *relay* and *polymerization* chains. The polymerization chains observed in cases of repeated mutual approach of product molecules, for instance during the formation of polymers $(C_2H_4)_n$ from C_2H_4, are characterized by the linking of the molecules of the monomer to the initial centre, link after link. This is the simplest variant of growth chains, where the added links are not in general identical with the molecules of the primary substance, but represent the product of their more or less complex chemical transformation (Diagram 1a).

This is the way in which big molecules are formed in certain processes for producing plastic materials by condensation. According to the principle of microscopic reversibility, the existence of growth chains leads inevitably to the existence of destruction chains where bigger molecules diminish in size due to repeated, successive removal of their separate parts (Diag. 1b). Depolymerization chains are an example of this. Relay or intermolecular chains are characterized by the transfer of the reaction from one molecule to another (Diagram 1d).

(a) *Search for Relay Chains*

Flat relay chains have been postulated by some investigators for individual reactions on the basis of kinetic data. These indirect data are most convincing for ethylene hydrogenation (3), and for the isotopic exchange of molecular hydrogen (4). However, attempts to prove this mechanism unambiguously have failed thus far. In particular, when studying surface oxidation of hydrogen diffusing through a membrane of a palladium capillary and identified as atomic hydrogen, V.V. Voyevodsky, V.B. Kazansky (5), and others did not find any chains. Working with T.I. Adriyanova, we tried to discover flat chains in catalytic cracking of normal octane with alumina-silica catalysts, by introducing C^{14}-labelled additions (6). In this way we succeeded in showing that when the cracking process is accelerated by ethylene, this carbon enters into many reaction products. However, these data may be interpreted with equal success as the initiation of flat chains and as the activation of the catalyst surface by the olefin.

To establish the role of flat relay chains in catalysis, more precise and regular

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* An indication of this is the USSR Scientific Conference on Application of Isotopes in Catalysis held in Moscow in March–April, 1956.
see "Probl. of Kinet and Catal", Vol. IX, Moscow, 1957.

experiments with labelled molecules are necessary. By analogy with homogeneous processes such a mechanism is possible for the transfer of reactions from molecules of hydrocarbon to each other during deuteron exchange.

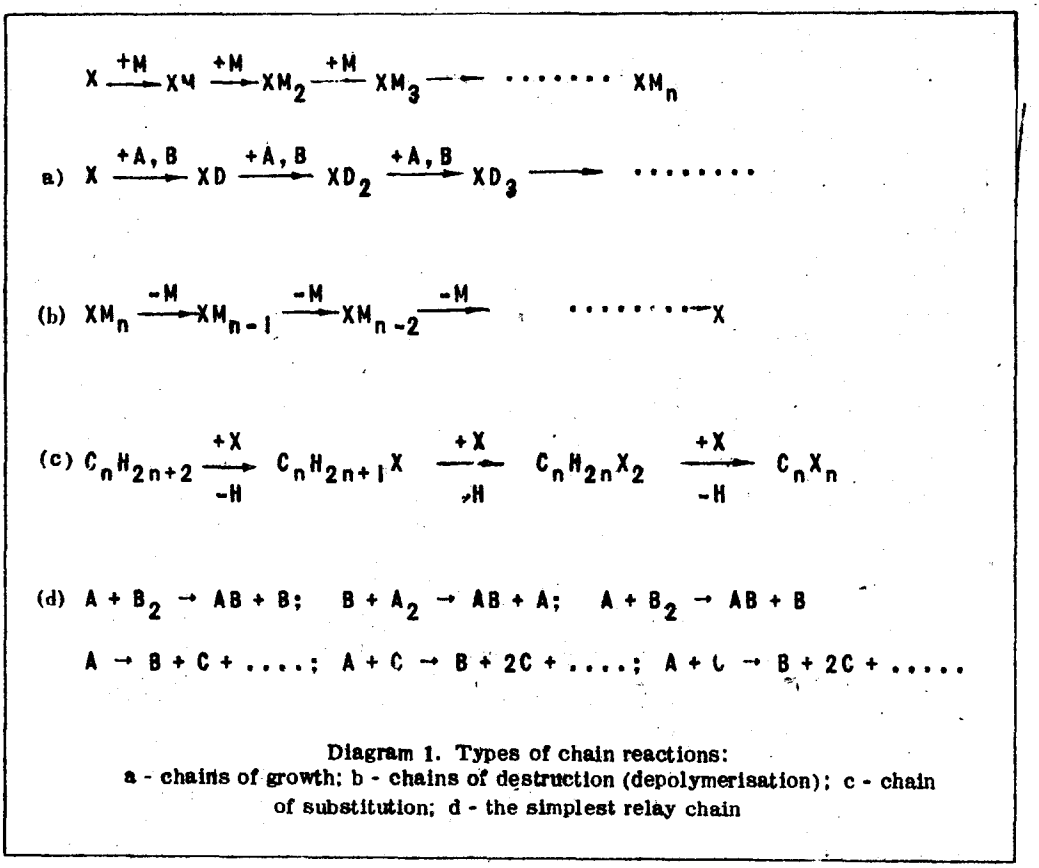

Diagram 1. Types of chain reactions:
a - chains of growth; b - chains of destruction (depolymerisation); c - chain of substitution; d - the simplest relay chain

(b) *Growth Chains in the Synthesis Process as Determined on the Basis of Radiocarbon Distribution*

More clear-cut results in favour of the existence of growth chains were obtained for reactions of hydrogen with carbon monoxide and with its ethylene mixtures. The first direct indication of the participation of flat chains in such processes was obtained by Emmett, Kummer and others (7) in attempts to use C^{14}-labelled alcohols for proving the dehydration-condensation mechanism of alkane formation from carbon monoxide and hydrogen. Using ammonia synthesis type iron catalysts these investigators observed a sharp drop in specific radioactivity of the products with the growth of the number of C atoms in a molecule. Molar radioactivity proved to be constant for all the members of the homologous series of alkanes except for the initial ones ($C_1 - C_3$ in experiments with C_2H_5OH). Regarding these data, in the first place, as a confirmation of the Storch-Anderson mechanism of hydrocarbon chain formation, the authors interpret the results of radiometrical study of the products and the increased content of oxgen compounds as a proof of initiation by alcohols of a condensation process attended by an elongation of the carbon skeleton.

The catalysts used yield many olefins in the by-products owing to which the data obtained with these catalysts are not typical of the synthesis of alkanes with normal structure. Therefore we conducted a similar study with classical Fischer-Tropsch cobalt-thoria catalysts. At the same time we increased the range of labelled substances introduced into the system. In the various experiments these were: C^{14}-labelled ethanol, ethylene, acetaldehyde, methyl formate, carbon monoxide and dioxide.

Fig. 1, III shows that the peculiar C^{14} distribution described by Emmett and Kummer may also be observed in synthesis with a Co/ThO_2 catalyst when introducing labelled ethanol into the initial gas mixture (8). The molar radioactivity of the products is practically constant for hydrocarbons from C_6 to C_{20} and is somewhat reduced for hydrocarbons C_2–C_4. In keeping with this, radioactivity related to one C atom changes but slightly for the first members of the series and drops parabolically beginning with C_6 (Fig. 1, IV). A similar picture is observed with labelled acetaldehyde. This fact is probably associated with its reduction to alcohol proceeding intensely under synthesis conditions. In experiments with labelled ethylene a similar C^{14} distribution in the products may be easily obtained just as in experiments tests with labelled ethanol and acetaldehyde (see Fig. 1,II) (9). This by no means proves the dehydration-condensation scheme of the growth of the carbon chain in the form of an alcohol radical. We shall note further that the observed distribution may be obtained not only in the case of chain initiation by a substance containing labelled molecules, but also when it breaks the chain.

The significance of the observed C^{14} distribution for the determination of the character of the participation of substances in the process is shown by the experimental tests with labelled CO, which participates both in the generation and in the growth of chains, since all the carbon which participates in the process is labelled. In this case specific radioactivity is constant. An essential factor characterizing the participation of the molecules of the labelled addition in the chain process is the ratio of specific activities of the products and the addition. When the molar concentrations in the mixture are close, these values for C_7 are equal to 0·017 with an ethanol addition and 0·07 with an ethylene addition. Taking into consideration the contribution of the radioactive addition it may be supposed that the alcohols participate in the process not directly but through the olefins which are formed during their dehydration. Therefore, in the further study of the chain process ethylene was used. At the C_2H_4 concentration above 4·8 volume per cent, the molar radioactivity of the products begins to increase with an increase in the number of carbon atoms in the alkane (see Fig. 1,I) (9).

This fact as well as some others make it possible to discard the explanation of the distribution observed by the break of the chains by ethanol and to go somewhat further in characterizing the chain process. The olefins at small concentrations play the role of the initiators of the process by forming initial centres of the polymerization chain. When the concentration increases, they begin to participate in the growth of the chain. Due to this there takes place a smooth transition to hydrocondensation where, according to Eidus, Zelinsky and Yershov (10), the bulk material for the chain polymerization is provided by olefin while carbon monoxide plays the principal part in the initiation. This picture seems to be not corroborated by the data of A.W. Fletcher and E.Y. Gibson(11)on hydropolymerization of ethylene in the presence of labelled carbon monoxide. The fact that chains similar in nature are initiated by ethylene at a high CO content and by carbon monoxide at a low content of CO requires explanation. It is possible that the picture is complicated by the contamination of the surface; in particular, the initiation of hydrocondensation by carbon monoxide may be true, and may reflect the inhibition of olefin hydrogenation enabling the ethylene to go through a series of initial stages of polythene type catalytical polymerization without being transformed into ethane. At high carbon monoxide concentrations there is a possibility of self-contamination of the initial stage relieved by ethylene. In this connection it would be interesting to determine the C^{14} distribution in the polymerization products during "initiation" by labelled CO. An essential contribution to the understanding of the mechanism of this process is made by the experiments with labelled cobalt carbide where the C^{14} distribution in the alkanes is the same as in synthesis from CO. This points to the inability of carbide to initiate a chain type synthesis of alkanes and speaks against the carbide stage in the Fischer-Tropsch mechanism.

The use of the C^{14} molar distribution to detect chains is limited by processes which by means of a uniform mechanism yield a mixture of products with a wide range of molecular weights. Perhaps this method could be used for the study of the formation of higher olefins, higher alcohols and other oxygen compounds from CO and also for the study of certain enzymatic processes in biological synthesis and in the synthesis of polymers.

(c). *Destructive Chains in Organic Compound Oxidation*

Catalytical oxidation by molecular oxygen is the most direct and, from the point of view of raw materials, the most profitable way of obtaining organic oxygen compounds. Owing to the difficulty of choosing selective catalysts and controlling them, this method is as yet most insufficiently developed. A distinction is made between deep-oxidation

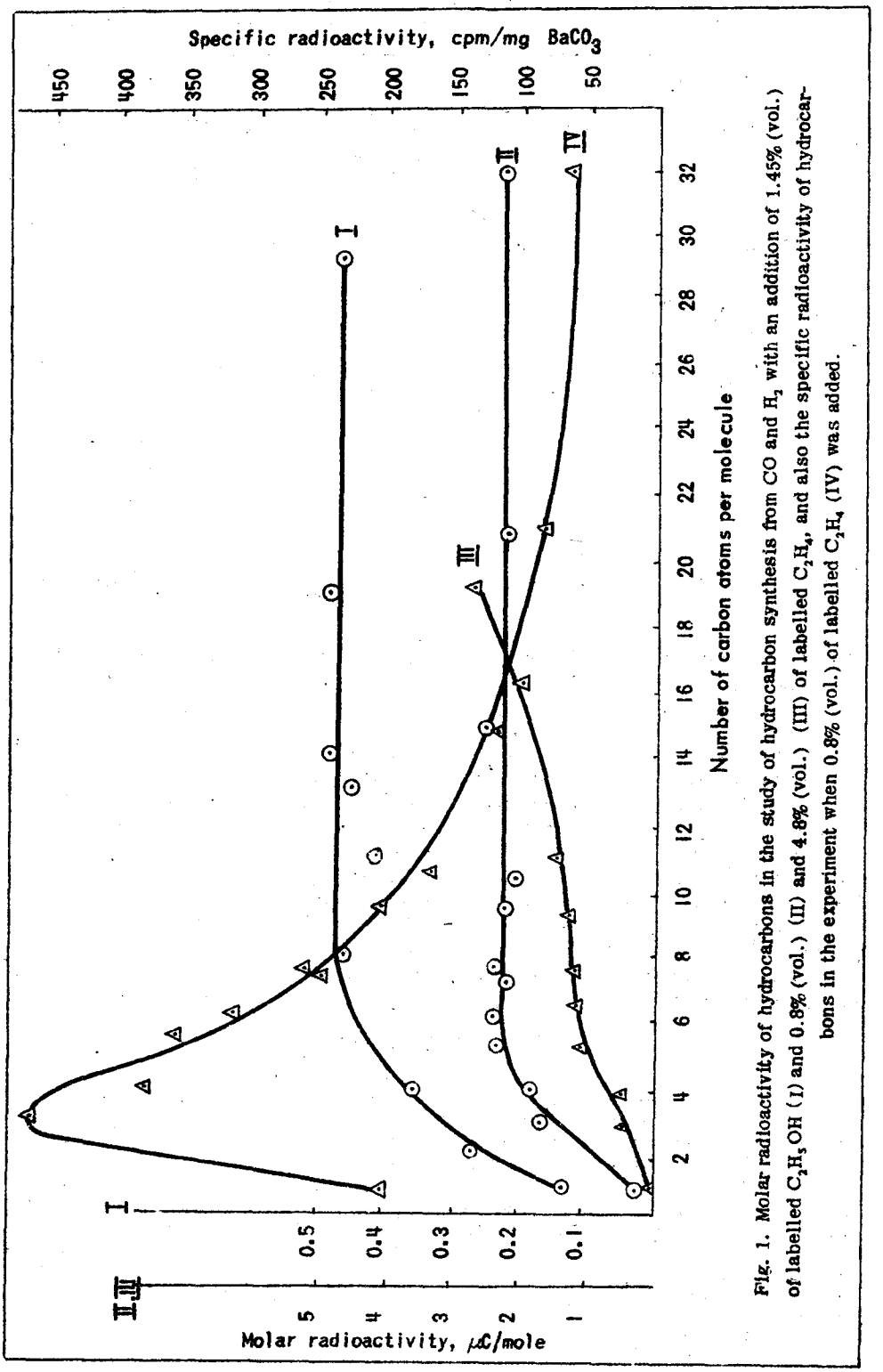

Fig. 1. Molar radioactivity of hydrocarbons in the study of hydrocarbon synthesis from CO and H_2 with an addition of 1.45% (vol.) of labelled C_2H_5OH (I) and 0.8% (vol.) (II) and 4.8% (vol.) (III) of labelled C_2H_4, and also the specific radioactivity of hydrocarbons in the experiment when 0.8% (vol.) of labelled C_2H_4 (IV) was added.

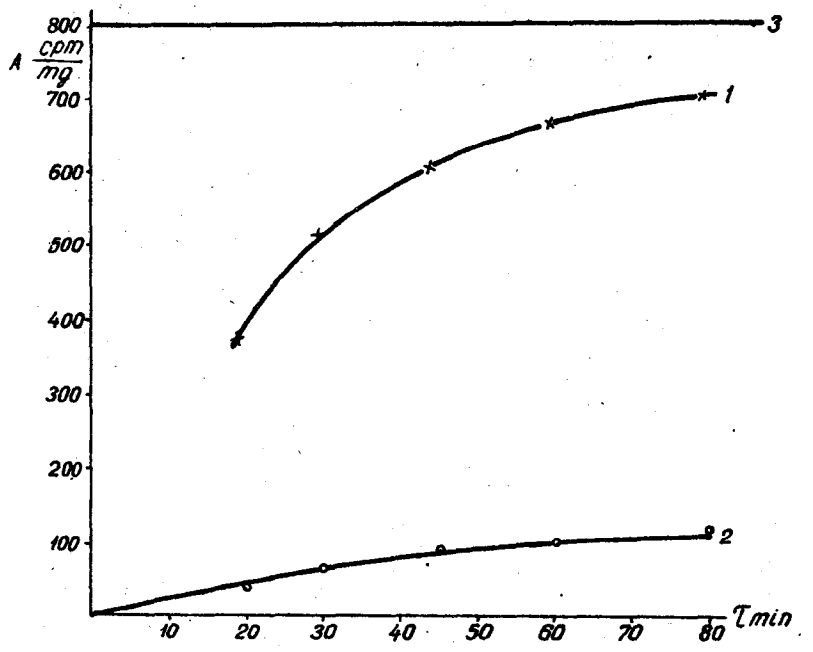

Fig. 2. The dependence of C^{14} content in CO_2 and C_2H_4O in the oxidation of labelled ethylene mixtures (1), ethylene oxide (2) and CO_2 (3) upon the contact time.

catalysts which accomplish the process almost completely to carbon dioxide and water, and moderate-oxidation catalysts with which, along with CO_2 and H_2O a more or less complex mixture of organic oxidation products is formed (12). Unlike homogeneous oxidation for which chain mechanisms with the participation of free hydrocarbon and peroxide radicals have been generally accepted for a comparatively long time, until recently stage schemes which lead the process from hydrocarbon to carbon dioxide through a number of stable forms of intermediate oxidation have been predominating almost entirely in the theory of contact oxidation. This interpretation of the mechanism implies that the various products of the reaction are obtained from one another, and the predominance of one of them signifies only a more or less successful termination of a uniform process at a definite stage. In particular, the well-known Bone sequence may be assumed for methane:

$$CH_4 \rightarrow CH_3OH \rightarrow CH_2O \rightarrow HCOOH \rightarrow \begin{matrix} CO_2 \\ \searrow\ \nearrow \\ CO \end{matrix}$$

with various by-processes yielding methyl formate and other products with two and more atoms of carbon. The same scheme, but beginning with another link, is also used for the oxidation of organic oxygen compounds. For more complex molecules, for instance, for propylene or naphthalene, the number of such stable steps on the "chemical product ladder" may be very great. Certain facts disagree with this concept. In particular, it cannot explain, without making additional hypotheses, the very weak dependence of the chemical composition of the products upon the integral transformation degree, for instance, complete oxidation to CO_2 and H_2O on the contacts of deep oxidation when only a negligible part of hydrocarbon is expended, the bulk of the oxygen remaining unused. This encouraged us to study the actual genetic relations of the various products of oxidation reactions by means of C^{14}-labelled molecules beginning with the oxidation of ethylene with selective silver catalysts employed to obtain ethylene oxide (13). To illustrate this, we present diagrams of radioactivity change

with time for C_2H_4, CO_2 and C_2H_4O during the oxidation of mixtures of labelled ethylene with unlabelled ethylene oxide (Fig. 2). These tests are a convincing proof of the fact that the bulk of carbon dioxide is obtained from initial ethylene, by-passing ethylene oxide, while the

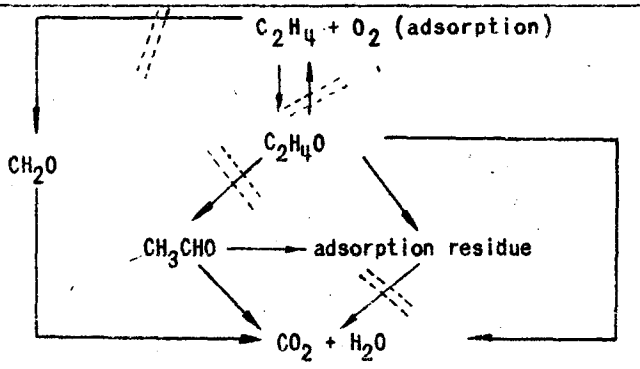

Diagram 2. Twigg's pattern of ethylene oxidation on silver.

formation of CO_2 and C_2H_4O at temperatures up to 250° represents two independent parallel processes (14)

$$C_2H_4 \rightarrow C_2H_4O \ldots\ldots \rightarrow CO_2$$

The distribution of C^{14} in the products during the oxidation of ethylene mixtures with CH_2O, CH_3CHO, CO, etc., was studied for the same reaction. It must be noted that according to the generally adopted scheme of Twigg (15), CO_2 is formed from olefin through CH_2O, ethylene oxide isomerizes into CH_3CHO, which further on oxidizes to CO_2 (Diagram 2).

All this seems to be wrong. The distribution of C^{14} did not confirm the reversibility of formation of C_2H_4O. The rejected stages of Twigg's scheme are crossed on diagram 2. Similar results were obtained by the study of the oxidation of ethylene, propylene and propane upon a series of oxide catalysts (Cu_2O, V_2O_5, etc), and also for the oxidation of a number of aliphatic oxygen compounds. Recently published data speak in favour of a similar course of moderate oxidation of aromatic hydrocarbons (16). In this way we succeeded in excluding for ethylene every possible variant of oxidation with an intermediate formation of stable substances. When heavier molecules are oxidized, the number of variants increases greatly, however, and it seems that in these cases, too, each of the stable oxidation products is formed along its own independent line without an intermediate formation of other stable substances. The same is true of the oxidation of any of the products of incomplete oxidation, as can be seen from Diagram 3. To explain this, we have to assume

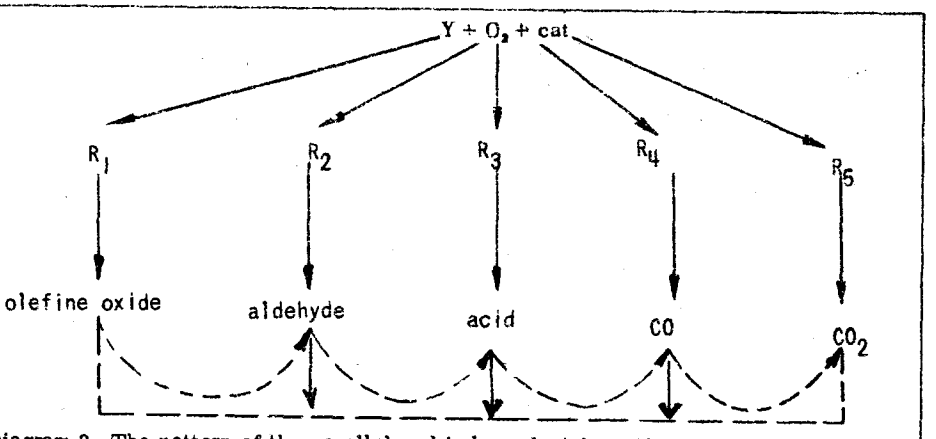

Diagram 3. The pattern of the parallel and independent formation of various products during the catalytic oxidation of hydrocarbons.

that in a catalytic oxidation, every molecule, once it begins to react, undergoes without interruption a whole series of successive rapid processes resulting in the formation of only labile products, and drops out of the game as soon as any separable stable product of oxidation is formed. With deep-oxidation catalysts this will be carbon dioxide for molecules of any complexity, and therefore the molecule either does not react at all, or is oxidized completely, entailing the destruction of the entire carbon skeleton. With moderate-oxidation catalysts there is a possibility of the termination of the process with the products of incomplete oxidizing destruction, and even with one of the products retaining an intact carbon skeleton. In other words, each of the initial reacting molecules participates but once in a single chain process.

The simultaneous and independent formation of many oxidation products may be attributed to differences in the catalytic properties of various parts of the surface, or to the possibility of several directions of chain oxidation upon the same area. Using our terminology, all these are destructive chains.

(d) *Substitution chains in isotopic exchange*

We can find in isotopic exchange all the mechanisms that are known for ordinary chemical reactions (17); in particular, the existence has been proved of relay atomic chains during the homogeneous thermal exchange of D_2 with H_2 and during the photochemical and radiation-chemical exchange of N_2^{14} with N_2^{15}, and O_2^{16} with O_2^{18}.

A mass-spectrometric study of the products of isotopic exchange of various donors of deuterium (D_2SO_4, D_2, etc.) with hydrocarbons has shown that during the exchange in homogeneous solutions and on solid catalysts, a distribution of the products with a different degree of deuterium substitution, incompatible with the scheme of independent successive exchange, is often obtained. Thus, when the transformation fraction during the exchange of *iso*pentane is negligible, C_5D_{12} or $C_5D_{11}H$ molecules may predominate in the products, molecules of C_5DH_{11} and $C_5D_2H_{12}$ appearing towards the very end of the exchange. A detailed analysis has shown that in order to obtain such a distribution only active molecules should participate in the exchange* which while in the active state manage to exchange several times one of the H atoms for a D atom without returning to their initial inactive state (17). Fig. 3 shows the time change of the composition of molecules of various substitutions in the case of the usual stage mechanism of substitution and of the chain mechanism of substitution. This type of chain process which is similar in its nature to growth and destruction chains, is known thus far only in isotopic exchange. (Diag. 1c). Since, as regards the deep mechanism this exchange does not differ in principle from some reactions of hydrogen substitution, one may expect similar mechanisms in the catalysis of such reactions, *e.g.* during the formation of di- and poly-substituted products in halogenation. There is also a possibility of a chain mechanism of multiple joining of atoms or groups to molecules. The possibility of a chain interpretation of some regularities of catalytic hydrogenation is worthy of attention, in particular with regard to the formation of cyclanes without traces of cyclic olefins and di-olefins from benzene and its homologues. If this interpretation is correct then the reverse reactions of aromatization of six-member cyclanes should also proceed chainwise. The common feature for the processes studied is the successive chain repetition of a number of unitype chemical reactions (joining, splitting off, substitution) with one and the same molecule. All these are fixed intramolecular restricted chain reactions without a relay transfer of the reaction from molecule to molecule.

(e) *Active forms of catalysis and the origin of fixed chains*

Interesting indications as to the nature of the active forms that participate in heterogeneous chain catalysis are offered by the study of the isotopic exchange of diatomic gases. Ever since the early works of Polanyi, it has been usual to associate the activation of molecules with their dissociation during adsorption. Direct tests with active gases adsorbed on metals and the study of chemisorption on thoroughly degassed surfaces show that free atoms when adsorbed on the surface may lose a substantial part of their chemical mobility (18). This is confirmed by new data on emission microscopy and electronography of adsorbed gases.

Recently, on the basis of kinetic and electfochemical data non-dissociated molecules

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* With a completed exchange the distribution of D among all the forms corresponds exactly to their statistical probability in equilibrium.

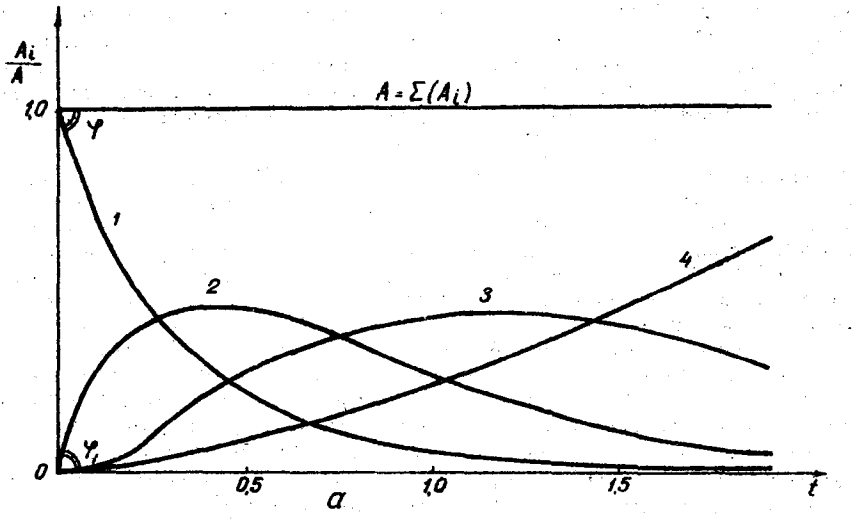

Fig. 3. (a) The change of A_0, A_1, A_2, A_3 with time during non-chain successive substitution of X for AX_3. The value of K_1 is taken as 1. The non-dimensional value of the fraction of molecules with a given atom content X from O (A_0) to 3 is graded along the axis of the abscissa;

1 $\frac{A_0}{A}$; 2 $\frac{A_1}{A}$; 3 $\frac{A_2}{A}$; 4 $\frac{A_3}{A}$.

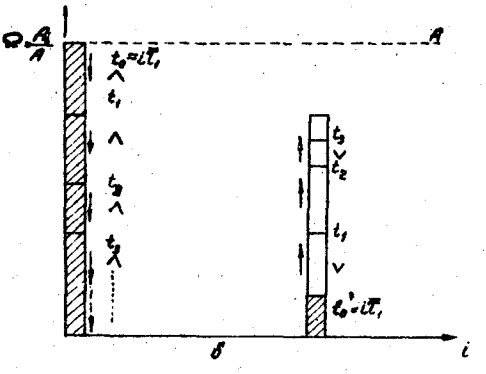

Fig. 3. (b) The ideal case of the change with time of the content of molecules of different substitution with regard to D in chain isotopic exchange C_nH_{2n+2} with D_2; i is number of D atoms in a molecule.

have been more and more used in the reaction schemes in radical and ion-radical forms. Re-adsorption with dissociation in mixtures of molecules of different isotopic compositions. should invariably bring about homomolecular exchange. The absence of exchange under well chosen conditions, on the contrary, excludes adsorption with dissociation.

L.Y. Margolis applied this criterium in her effort to find out the state of oxygen on the surface of metal (Ag; Pt) and oxide ($MgCr_2O_4$; Cu_2O and V_2O_5) catalysts. In all cases by lowering the temperature we can completely stop the homomolecular exchange of

$$O_2^{16} + O_2^{18} \leftrightarrows 2O^{16}O^{18}$$

preserving the catalytic oxidation of ethylene and hydrogen. This is a serious argument against the dissociation of O_2 into atoms during adsorption, resulting in catalysis. Similar results were obtained jointly with A.V. Krylova for nitrogen in the synthesis of ammonia. The published data concerning this point are contradictory. We have studied the exchange of $N_2^{15} + N_2^{14} \leftrightarrows 2N^{14}N^{15}$ within the range of 400 to 650°C upon iron catalysts with and without additions accepted in the nitrogen industry. Up to 520° the homomolecular exchange proved to be negligible. The decomposition of ammonia and its synthesis upon the same contacts proceed well already at 300—400°. Beginning with 550° the exchange becomes noticeable, but there is no conformity between the specific activity of the contacts in the synthesis and the exchange. This speaks against adsorption with dissociation as the primary act of the catalysis of reactions with O_2 and N_2. Apparently the primary act is accompanied by a decrease of the number of electrons binding the O (or, accordingly the N) atoms in a molecule with the formation of new bonds with the solid and the recovery of one electron from the lattice, according to the following scheme:

$$\text{Cat} + N \equiv N \rightarrow \overset{+}{\text{Cat}} - \overset{-}{(N = N)} \xrightarrow{H_2(2H)} \overset{+}{\text{Cat}} - \overset{+}{(HN - NH)} \rightarrow \ldots \rightarrow 2NH_3$$

$$\text{Cat} + O = O \rightarrow \overset{+}{\text{Cat}} - \overset{-}{(O - O)} \xrightarrow{C_2H_4} \text{Cat} - (O_2C_2H_4) \rightarrow C_2H_4O \rightarrow 2\,CO_2 + 2\,H_2O$$

Similar mechanisms of activating adsorption are probable for the reaction of unsaturated binary compounds (CO, C_2H_2 and others). Conversely, the participation of non-dissociated molecules of H_2 in the catalysis is doubtful.

The results obtain with N_2 and O_2 show that homomolecular isotopic exchange can by no means always be used as a model reaction for finding out the regularities of catalysts selection for conventional chemical processes. This is equally true of the isotopic exchange of initial molecules with catalysts. In particular, for oxide catalysts isotopic O_2 exchange with the lattice begins as a rule at higher temperatures than the oxidation catalysis, and in this case the catalytic series do not coincide with the activity series in respect to isotopic exchange. An important fact is the absence of isotopic exchange of oxide contacts with O_2 during the oxidation of CO and hydrocarbons in the case of a rapid removal of CO_2 and H_2O, precluding the transfer of O with their participation. It shows the possibility of catalysis without the catalysts oxygen entering the products of the reaction, *i.e.* without the transfer of oxygen. The redistribution of the electrons of the catalyst, not the break off the bond and the redistribution of its atoms, forms the basis of primary activation in oxidation catalysis. A certain idea of the nature of further intermediate forms of catalysis is offered by the above-mentioned data about the early appearance of products of high deuterium substitution during exchange. The comparative study of the exchange of saturated molecules and radicals; the influence of the skeleton structure upon the isotopic exchange and of other regularities of hydrogen exchange brings us to a conclusion that this behaviour during exchange is inherent to free radicals and ions, *i.e.* radicals of the carbonium-ion type (17). Since this exchange occurs with a number of metals and with oxide catalysts of acid type, it is natural to suppose that on the typical contacts of the two principal classes of catalysts* the reacting organic molecules represent ion-radicals as was indicated on the grounds of other consideration by us (19) and by M.I. Temkin (20).

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* Oxidation-reduction and acid-base, see (17).

$$C_nH_{2n+2} + Cat \rightarrow C_n^+H_{2n+1}(adc) + H^-(adc) \rightarrow C_n^+H_{2n+1}(adc) \xrightarrow{D_2} C_n^+H_{2n}D(adc) \xrightarrow{D_2}$$
$$\rightarrow C_n^+H_{2n-1}D_2 \xrightarrow{D_2} \cdots\cdots \rightarrow C_n^+D_{2n+1} \rightarrow C_nD_{n+1}H$$

According to Campbell's data (17) on initial exchange of half of the hydrogen atoms in cyclanes for deuterium, these molecules are comparatively strongly fixed and oriented. The isotopic data bring us to the following picture of the chain process. During chemisorption with the transfer of electrons or protons, or as a result of an auxiliary chemical reaction, surface ion-radicals are formed. Owing to the considerable heat of adsorption, the average lifetime of these active forms on the surface greatly exceeds the average time necessary for a unit reaction of the addition of a new link, destruction or isotopic exchange. The molecular ion-radical retains its active state changing the size and the isotopic composition until, owing to a subsidiary reaction, it is transformed into a stable molecule which breaks away from the surface (chain rupture). Also possible though less probable is an escape into the volume of a free neutral radical which is capable of causing a volume chain reaction under favourable conditions. Initial adsorption in the form of atoms or saturated ions often results in a very stable adsorption without the ability of chain development.

The above picture requires a fundamental revision of the complete stage schemes of many individual catalytic reactions. The solution of this problem is greatly hampered by the low concentrations of the greater portion of the intermediate active substances formed during chain reactions of the above type, and by the impossibility of their separation in a stable form. Since we do not have an opportunity of analysing here the solutions contemplated for separate processes, we should note that even in those cases where experimental data do not point to chain mechanisms, experiments with labelled molecules and isotopic exchange, as a rule, introduce substantial corrections into stage schemes.

Of a number of stage schemes that we have checked only two did not require a radical revision, *i.e.* the Gorin-Kagan scheme of butadiene synthesis and the scheme of CO oxidation upon active oxides. However, those are the very schemes for which earlier, too, non-stable intermediate forms, *i.e.* crotyl alcohol and croton aldehyde, in the first case, and CO in a labile "presorption state", in the second case, were postulated by the kinetic data. However, in these cases, too, the isotopic methods have revealed substantial new aspects of the processes. For the second reaction this is the absence of initial O_2 dissociation and of a direct participation of the oxide lattice oxygen in the CO oxidation by the transfer mechanism and for the first it is an intensive redistribution of hydrogen between ethyl alcohol and acetaldehyde (21), the inadequacy of the deoxygenation scheme of Kwatlabaum, the elucidation of further transformations of the independently formed diethyl ether and ethylene (21) and the establishment of the nature of the subsidiary transformations of the butadiene (22) formed.

2. THE NATURE OF THE ACTIVE SURFACE OF CATALYSTS

The most characteristic catalytic phenomena are associated with specific active structures of the solid and its surface. The study of the catalysis mechanism cannot be isolated from the study of their nature. One of the key problems is the cause of the sharp dependence of the energetic characteristics of chemisorption and catalysis upon the coverage and upon the qualitative composition of the adsorption layer. The dependence of E and Q on θ which determines the basic regularities of catalysis kinetics may be a sequence of the "biographical" heterogeneity of the surface and of the interaction of the adsorbed molecules, and in this respect the manifestations of heterogeneity and interaction are very much alike. Due to the development of electronic concepts in catalysis, many authors are now inclined to attribute the principal role in this case, to the interaction by means of the electron-hole gas of the lattice. In recent years several isotopic methods have been developed enabling the effects caused by heterogeneity and by interaction to be distinguished (23). Thus, by covering the surface of a catalyst by an absorbent in portions of different isotopic compositions and by studying the distribution of isotopes during desorption, catalytic reaction and isotopic exchange, the biographical heterogeneity can be easily detected. This differential isotopic method helped to show unambiguously the progress of various catalytic reactions of acetylene upon the various parts of the surface and to obtain similar results for the decomposition of ethanol on zinc oxide. Heterogeneity with regard to chemisorption is