

POLYMERS OBTAINED BY CATALYTIC DECOMPOSITION OF DIAZOALKANES IN HETEROGENEOUS SYSTEMS

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Since polymethylene was first prepared by Bamberger and Tschirner¹ in 1900, the reactions of diazoalkanes which result in the formation of polymers have presented several points of special interest, in addition to the fact that diazomethane gives a practically unbranched hydrocarbon polymer.

The polymerization of the residues derived from diazoalkanes by elimination of elementary nitrogen may well be interpreted in terms of carbene intermediates, especially when the reaction is subjected to heterogeneous catalysis.

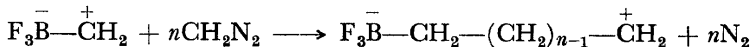
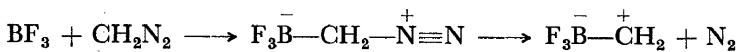
Methylene radicals were first demonstrated by Staudinger and Kupfer², in 1912, in the decomposition of diazomethane. They are involved in many known reactions, and may be called radicals, or di-radicals according to Semenov³, or active divalent carbon molecules. The $:\text{CH}_2$ residue has been called carbene: this term can be extended to include the alkylidenes which have two free electrons attached to one carbon atom.

In recent years, there has been a marked increase in reaction mechanisms involving carbene intermediates, and, consequently, an understandable interest in the chemistry of divalent carbon⁴.

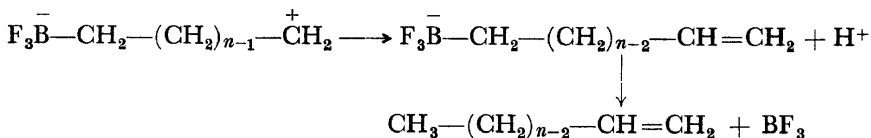
The purpose of this lecture is to describe the experimental work which has been carried out on this subject in the Chemistry Department of the University of Torino, and to discuss, where possible, energy and geometric factors of the surfaces involved. The work is far from complete and quite a lot of experiments have still to be performed, but we hope that the results so far obtained will be of interest.

Meerwein and Burneleit⁵ observed that polymethylene is produced from diazomethane in the presence of aluminium alcoholates or boric esters. Metallic copper and copper salts as well as some boron compounds, such as boron trifluoride and boron alkyls, are suitable catalysts for the preparation of high molecular weight compounds from the decomposition of diazomethane and higher diazoalkanes. Feltzin, Restaino and Mesrobian⁶ undertook a kinetic study of the polymerization of six different diazoalkanes in ethereal solution, using either boron trifluoride or copper stearate as catalysts. They observed that the reactivity of the straight-chain diazoalkanes decreases as the number of carbon atoms in the chain increases. The mechanisms probably differ with each of these catalysts. In the case of boron trifluoride the polymerization can indeed be attributed to an alkylation catalyzed by Lewis acids, as suggested by Kantor and Osthoff⁷,

and the first step would be the formation of a diazonium-like addition product which subsequently gives rise to a carbonium ion. The latter can then act as a Lewis acid and attack a second molecule of diazoalkane, thus initiating the chain growth:

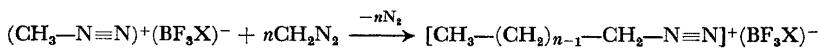
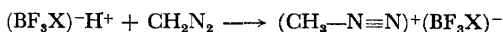


Kantor and Osthoff proposed disproportionation as a way of chain termination:

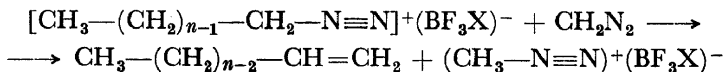


A similar mechanism has been proposed by Bawn and Rhodes⁸.

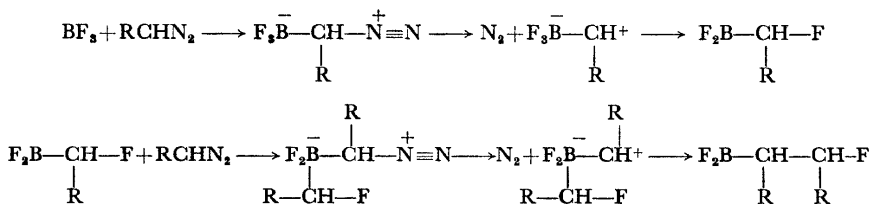
Feltzin and co-workers⁶, as well as Plesch⁹, suppose that polymerization is initiated not by boron trifluoride itself, but by a complex acid of the type $\text{H}^+(\text{BF}_3\text{X})^-$, where $\text{X} = -\text{OH}, \text{RO}-, \text{etc.}$, which would be very easily formed in the presence of traces of water or alcohols. The polymerization would then proceed in the same way as a cationic polymerization:



Termination would occur by transfer of a proton to the monomer:



These mechanisms have been criticized by Bawn and Ledwith¹⁰ who, on the basis of the results of their experiments, suggest that the initiation step would be the co-ordination of boron trifluoride to a diazoalkane molecule, followed by spontaneous nitrogen evolution and consequent intramolecular rearrangement:



and so on. This process can continue either until all the diazoalkane has been consumed or until chain termination occurs by transfer of an hydride ion.

Our work started some years ago because we were interested in the effect of short branching on hydrocarbon polymers, and so we prepared a number

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of polymers by diazoalkane decomposition. Since boron compounds, which are quite efficient catalysts in the polymerization of diazomethane and give polymethylene in quantitative yields, do not display such a high efficiency towards higher diazoalkanes⁶, and copper and copper salts catalyze polymer formation with high yields from higher diazoalkanes^{6, 8}, but are not so active in polymerizing diazomethane¹¹, we tried to find some more efficient catalysts: auric chloride, a Lewis acid derived from gold which belongs to the same subgroup of the periodic table as copper, was then examined.

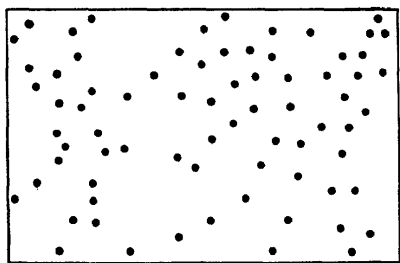


Figure 1. Schematic representation of a gold colloid, as seen under an electron microscope

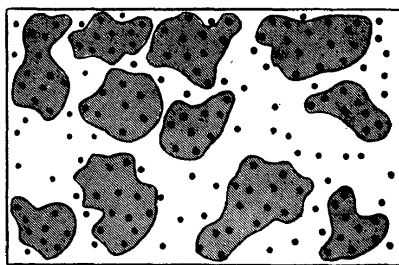


Figure 2. Schematic representation of a gold colloid after reaction with diazomethane, as seen under an electron microscope

From the initial experiments¹² it appeared that gold chloride in ethereal solution was reduced at once to a red/gold colloid, and that the yield of polymethylene was nearly quantitative. Similar results have been obtained with diazoethane, diazopropane and diazobutane, although the reduction of the gold salt is not as fast and the yields of the polymer are lower than with diazomethane.

One interesting result of these experiments was that diazoethane gave low yields of crystalline polyethylidene, insoluble in cold solvents¹³, in addition to the amorphous polymer which is soluble in cold ethyl ether. It was also observed¹² that even when practically all the gold chloride had been reduced to gold, the diazomethane decomposition continued. It was thus reasonable to assume that metallic gold was the active catalytic surface. This hypothesis has been confirmed by a detailed study of the catalytic action of gold surfaces¹⁴, and by a more general investigation of metallic surfaces active in promoting polymer formation from the decomposition products of diazoalkanes¹⁵.

DIAZOMETHANE

Let us first consider the preparation of polymethylene from diazomethane. On the addition of an ethereal solution of diazomethane to one of gold chloride, the gold salt is reduced at once to a red/gold colloid. The polymer, insoluble in the reaction medium, surrounds the colloidal gold particles; there is reason to believe that the polymer may act as a protecting agent as the reaction product, when dissolved in hot xylene, retains its red colour even after several hours¹².

The results of examination with an electron microscope¹⁴ are schematically represented in *Figures 1 and 2*. The particles of colloidal gold formed

under our experimental conditions, have a diameter of about 200 Å and the field looks like that shown in *Figure 1*. After the reaction with diazomethane for one minute, the field observed looks like that shown in *Figure 2*; the gold particles are surrounded by the polymer, as represented by the shaded areas. A few minutes later, practically all the gold particles are embedded in the polymer.

The polymer aggregates containing colloidal gold are active catalysts for diazomethane decomposition leading to further polymer formation: it is very probable that the gold particles embedded in the polymethylene are prevented from coalescing, and nitrogen, which is emitted during the polymer formation makes the lumps porous.

The fact that a gold film, obtained by evaporating the metal under high vacuum, decomposes diazomethane to give almost quantitative yields of polymethylene, confirms that the effective agent acting on the ethereal solution of diazomethane is the gold metal.

An investigation on the course of the decomposition of diazomethane, using gold chloride as catalyst, showed that the reaction is approximately first-order with respect to the diazomethane concentration, and that the rate is proportional to the gold chloride concentration. This suggests that, the gold particles being practically monodispersed, the rate of diazomethane decomposition is proportional to the total surface area of the colloid. The apparent activation energy of the reaction is about 10 kcal/mole¹². The diffusion of the reagent through the polymer layer in which the gold particles are embedded is not the rate determining process.

The *molecular weight* of the polymethylene is in the range 10^4 to 5×10^4 ; it decreases with increasing gold chloride concentration and reaction temperature. When polymethylene, which occludes colloidal gold is used as a catalyst for decomposing an ethereal solution of diazomethane, further polymer is formed, as has already been mentioned, but the average molecular weight of this new polymer does not differ appreciably from that of the gold-containing polymer used as a catalyst¹². This means that the polymer chains already formed do not grow further, but that new chains are produced. Only polymethylene containing colloidal gold displays such an activity towards diazomethane; polymethylene alone is not effective.

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When the action of metallic gold in the decomposition of diazomethane had been verified, the research was extended to the action of gold on diazoethane, and to a study of the activity of other metals towards the formation of polymers from the decomposition products of diazoalkanes. The most remarkable points which arose from the investigations on diazoethane were:

- (i) the formation of a highly crystalline polyethylidene on the decomposition of diazoethane in ethereal solution using gold as catalyst¹³;
- (ii) the dependence of the yield of polymer formed from the decomposition products of diazoethane on the metal used as a catalyst¹⁵;
- (iii) the fact that the chromatographic analysis of the gases, evolved in addition to nitrogen during the reaction, gave some indication of the

relationship between the ability of different metal surfaces to isomerize or to dimerize the $:\text{CH}-\text{CH}_3$ fragment released from the decomposition of diazoethane, and the ability of the metal to give polymer¹⁶.

The reduction of gold chloride to colloidal gold at 0° by diazoethane is not as fast as that by diazomethane: initially there is only a slight change in the colour of the liquid but, after some time, the liquid becomes darker and ultimately blue flakes separate. When all the diazoethane has been decomposed, the liquid is colourless.

The blue flakes suspended in the liquid are efficient agents for decomposing a fresh solution of diazoethane (their behaviour is similar to that of polymethylene containing colloidal gold). By repeating this operation several times, the flakes become larger.

By extracting these flakes first with hot chloroform, then with xylene at 100° and, finally, with α -chloronaphthalene at 150° , and by dropping the filtrates into an excess of cold methanol, a series of polymer fractions can be obtained. These fractions are insoluble in cold solvents, and their crystallinity increases in ascending order from the fraction soluble in hot chloroform to that soluble in α -chloronaphthalene. The over-all yield of crystalline polyethylidene is about 5 per cent. The infra-red spectra of these crystalline polymers (*Figure 8*) are very similar to that of amorphous polyethylidene which can be obtained by dropping the liquid, from which the blue flakes of insoluble polyethylidene have been separated, into an excess of methanol.

The crystallinity in polyethylidene arises, of course, from a sterically ordered arrangement of the methyl-side groups connected to the tertiary carbon atoms constituting the main chain. As far as we know, our crystalline polyethylidene is the first synthetic crystalline polymer, whose main chain is formed by a sequence of tertiary carbon atoms which have a methyl side-group. From the work still in progress on the crystalline structure of polyethylidene, it seems that the probable configuration of the chain in the crystalline state is that of a di-syndiotactic polymer with the chain fully extended in the plane¹⁷.

There is no doubt that the catalyst displays, at least partly, a stereoregulating activity, and that this is peculiar, up till now, to metallic gold. As already mentioned, the flakes of polyethylidene containing gold catalyze the decomposition of diazoethane with formation of both crystalline and amorphous polyethylidene^{12, 13}. Furthermore, gold films, obtained by evaporating gold metal under high vacuum, decompose diazoethane and give, together with the amorphous polymer, small amounts of crystalline polyethylidene^{14, 15}.

Metal surfaces were prepared by evaporation of metals under high vacuum¹⁴. The high vacuum apparatus is shown in *Figure 3*. The reaction vessel *A* was sealed to the vacuum line, carefully evacuated and outgassed, until the pressure in the system was about 10^{-5} mm Hg. The metal to be investigated (1–2 mg), supported on a tungsten filament or on a graphite rod, was then slowly heated and outgassed. When an increase in pressure in the system was no longer noticeable on further heating, the temperature of the supporting filament was increased until the films appeared on the walls of the flask, whose temperature was kept rigorously at 25° .

A solution of about 2g of diazoethane (prepared by the method of Arndt¹⁸ from *N*-nitrosoethylurea) in 100 ml of ethyl ether, carefully dried on potassium hydroxide pellets, was distilled from the storage vessel *B*, which had been previously evacuated, into the reaction flask *A* by surrounding this latter with a liquid nitrogen bath. The action vessel was sealed off and transferred to a thermostated bath.

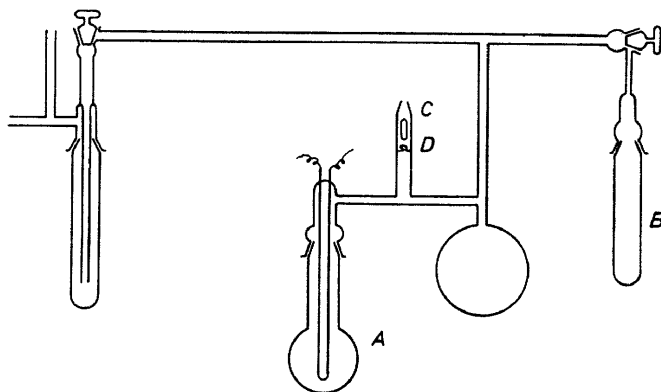


Figure 3. High vacuum apparatus for the preparation of the metal films used for the decomposition of diazoethane solutions

When all the diazoethane had been completely decomposed (this usually took a few days), the reaction vessel was connected to the sampling line of a gas fractometer by means of the ground joint *C*. The break seal *D* was then broken, and the chromatographic analysis of the gases, which were evolved in addition to nitrogen during the reaction, was made according to methods which have already been described¹⁶.

So far twenty-one metals have been studied. They are grouped according to the periodic table in *Figure 7*. The figures represent the relative over-all yields of polymer. In *Figure 4*, some of the metals are subdivided into two groups, according to whether or not they give a polymeric product from the decomposition of diazoethane. In *Figure 4* the percentage of the main light hydrocarbons which are formed in side reactions are also reported, for the two groups of metals. It can be seen that, besides nitrogen, ethylene, *trans*-but-2-ene and *cis*-but-2-ene are the most important gaseous products arising from the metal catalyzed decomposition of diazoethane in ethereal solution.

The following conclusions can be drawn from the results shown in *Figure 4*:

(i) the light hydrocarbons evolved when polymer-forming metals, such as copper and gold, are used to decompose diazoethane are essentially a mixture of *trans*-but-2-ene and *cis*-but-2-ene (apparently dimers of the :CHCH₃ carbene), together with small amounts of ethylene;

(ii) when metals, such as silver and palladium, which do not promote polymer formation, are used as catalysts for decomposing diazoethane in ethereal solution, ethylene represents the main fraction of the light hydro-

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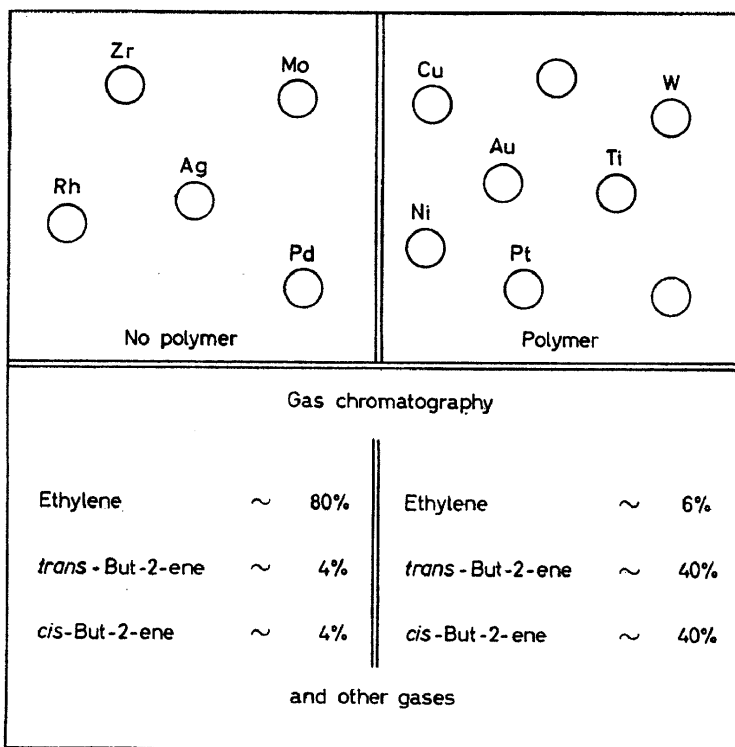


Figure 4. Main results of the chromatographic analyses of the gases evolved, besides nitrogen, in the metal-catalysed decomposition of diazoethane

carbons evolved, as the result of isomerization of the carbene residue which is apparently released from diazoethane;

The chromatographic analyses referring to above experiments were undertaken when diazoethane had been completely decomposed. In other experiments, using slightly different experimental techniques, it was possible to follow the course of the hydrocarbon evolution as a function of time.

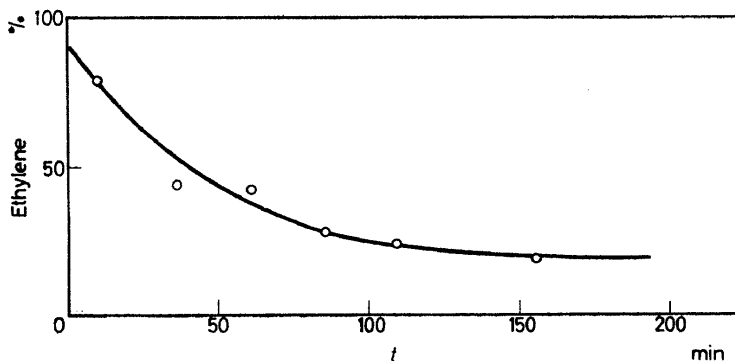


Figure 5. Plot of the variation of ethylene percentage with time, in the gold chloride-catalysed decomposition of diazoethane in ethereal solution

Using an ethereal solution of gold chloride as a catalyst, we were able to observe that, at the beginning of the reaction, the composition of the mixture of the light hydrocarbons formed differs appreciably from that at the end of the reaction: ethylene predominates over the butenes, and the amount of *trans*-but-2-ene is greater than that of *cis*-but-2-ene. This can be seen from the data plotted in *Figure 5*, which represents the variation of the amount of ethylene with time, and in *Figure 6* where the ratio *trans*-but-2-ene/*cis*-but-2-ene is plotted against time for a typical run.

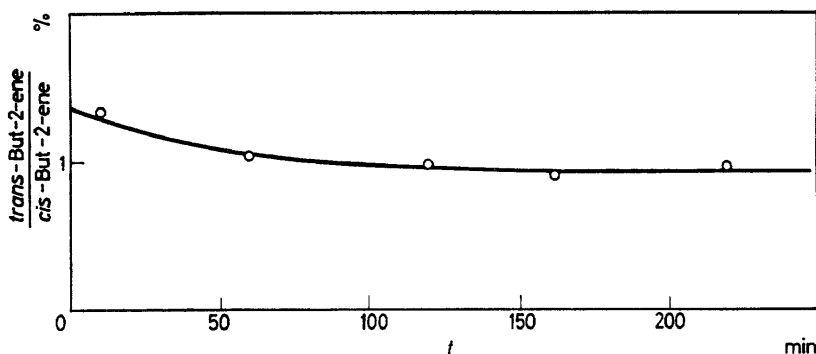


Figure 6. Plot of the variation of the ratio *trans*-but-2-ene/*cis*-but-2-ene with time, in the gold chloride-catalysed decomposition of an ethereal solution of diazoethane

From these results we might infer a change of the conditions prevailing at the surface of the metal, as shown by the initial isomerization of the ethylidene fragment to ethylene, and then by the dimerization of the $:\text{CHCH}_3$ carbene to the two isomeric forms of but-2-ene. The isomerization of the $:\text{CHCH}_3$ fragment could also be explained without the necessity of postulating a surface, since the surface might effectively decompose diazoethane but not adsorb the fragment released from the decomposition. In this case, the energy let free in the decomposition of diazoethane could be sufficient for the isomerization of the ethylidene fragment. This argument, of course, would not be valid when dimerization and polymerization of the fragments occur.

HIGHER DIAZOALKANES

The higher diazoalkanes studied were diazopropane, and diazobutane, in ethereal solution. They were decomposed by gold chloride and polyalkylidenes were formed. The reactions were much slower than those of the two diazoalkanes previously described, and the yields of polymer were lower, namely about 10 per cent.

The behaviour of diazopropane and diazobutane when gold was used as a catalyst, was similar to that of diazoethane and some crystalline fractions of polypropylidene and polybutylidene were obtained. The analysis, by gas chromatography, of the low molecular weight products formed, together with the polymer, is still in progress, but, so far, propylene and but-1-ene have been detected besides nitrogen.

DISCUSSION

Inspection of the elements we have studied so far, which are arranged according to the periodic classification in *Figure 7*, shows immediately that, apart from magnesium and aluminium, which play an important role as catalysts in polymer chemistry, the transition elements of the first long and of the first very long period favour polymer formation from the decomposition of diazoethane. The transition elements of the second long period which have been studied, namely zirconium, molybdenum, rhodium and palladium gave practically no polymer.

Mg 57												Al 7
Ca --	Sc --	Ti 67	V 31	Cr 13	Mn 30	Fe 64	Co 26	Ni 38	Cu 90	Zn 25	Ga --	
Sr --	Y --	Zr 0	Nb --	Mo 3	Tc --	Ru --	Rh 0	Pd 0	Ag 0	Cd 22	In --	
Ba --	La --	Hf --	Ta 30	W 45	Re --	Os --	Ir --	Pt 27	Au 14	Hg --	Tl --	

Figure 7. Metals tried for the decomposition of diazoethane in ethereal solution, arranged as in the periodic classification of the elements; the figures represent the over-all yield of polymer

The elements of sub-group IB follow the behaviour of their predecessors in the period: copper gives a large yield of polymer, gold gives a lower but very controlled yield, and silver, like palladium, gives no polymer at all. When we pass to the elements of sub-group IIB, in addition to zinc we see that cadmium, in contrast to its predecessor in the period, silver promotes polymer formation: passing from the electronic structure $4d^{10}5s^1$ of silver to the $4d^{10}5s^2$ of cadmium is very beneficial, and then the completion of the s electron shell is, of course, very important.

In going from copper to zinc and from silver to cadmium the metal lattice changes from face-centered cubic to hexagonal compact: this means that the structural co-ordination forces change in a logical manner.

The yields of polymer cited do not, of course, give a proper measure of the reactivity of a given metal towards polymer formation from the decomposition products of diazoethane, but they clearly show whether or not polymer is formed.

We have tried to establish many relationships between different properties of the elements investigated and their polymer-forming activity. In some cases they are partially satisfactory, but are never generally valid. The same thing happens, as is well known, with attempts to establish similar relationships with other catalytic phenomena. We have attempted to find separately a correlation between polymer forming ability of the metals investigated and their d -character, lattice constants, ionization potentials, work functions, heats of atomization and other properties, but always with only partial success.

There are many factors to be considered, and it is difficult to define accurately the state of a surface and how it might change during a reaction

on it. We can only cite some experimental facts which are similar to ours.

If we compare the bond energies for surface hydrides, which can be calculated with the aid of the electronegativity values of the elements (in some cases in good agreement with the experimental values), we find a partially satisfactory correlation between the activities of those hydride-forming metals¹⁹ with their activity in the hydrogenation of acetylene to ethylene and ethane. However, the order of the metal activity is practically reversed when we turn to the formation of low polymers from acetylene. Copper which was nearly at the end of the list of active metals for hydrogenation, has now jumped to the first place. In the case of nickel, which is active for both hydrogenation and polymerization, Sheridan¹⁹ suggested that the (110) face of the nickel crystal is suitable for the growth of a polymer from acetylene held on the 3.5 Å spacing, whilst the 2.47 Å spacing of the (110) face of the nickel crystals would favour, following Twigg and Rideal²⁰, the hydrogenation of the olefinic bond. In this case the different action of a metal surface can be explained by invoking a *geometric factor*.

We can also recall the fact, noted by several authors²¹, that a high catalytic activity towards hydrogenation reactions is peculiar to those metals which show a high paramagnetic susceptibility, *viz.* nickel, palladium and platinum. Copper and gold, on the contrary, which show low paramagnetic susceptibility, are much less active, although they follow nickel and palladium in their respective periods. Thus, it seems that polymer formation in the hydrogenation of acetylene is catalyzed by metals which have low paramagnetic susceptibility; the same can be said for our polymer formation. We might then infer that an *electronic factor* could also explain the behaviour of the metals in which we are interested.

In our series of experiments on diazoethane we have shown by chromatographic analysis¹⁶, that, in addition to the formation of polyhydrocarbons with tertiary carbon atoms, the products arising from side reactions are predominantly olefins. Although we do not want to state categorically that olefinic complexes with metals might be an explanation of the experimental facts, it is logical to infer that some similarity might exist with the possible formation of olefinic complexes on the metal surface.

It is well known that the metals of the transition series can form complexes with olefins, and Chatt²¹ says: “. . . Only those metals with filled *d*-orbitals at an energy level close to that of the valency electrons, and not buried by *s*- or *p*-electron shells, form olefinic complexes; those are the metals at the end of the transition series. The great importance of the donation of the electron pairs from *d*-orbitals in metals is demonstrated by the greater (qualitatively observed) stability of platinous complexes relative to palladous and the very high stability of the cuprous relative to argenteous olefin complexes . . .”. These observations correspond to ours for the same pairs of metals.

Another argument which might explain the activity of copper and gold and the inactivity of silver towards polymer formation in the decomposition of diazoalkanes, is that although the first two metals have completed *d*-bands, the energy for the transition from the *d*-level to the following *s*-level is about the same; namely 3.25 eV for copper²² and 3.0 eV for gold²³, whilst for silver it is higher, 4.0 eV²⁴. This might be the reason why silver does

not chemisorb ethylene or acetylene, since chemisorption of these gases would be endothermic, and thus precluded on thermodynamic grounds.

An interesting experimental fact in our researches is given by the *action of the solvent* in the two cases studied, namely copper and gold surfaces. If we change the solvent from ethyl ether to a saturated aliphatic hydrocarbon, such as pentane, the reaction of diazoethane upon copper does not give rise to polymer formation; the change of solvent does not produce noticeable differences in the yield of polymer in the case of gold. In the case of copper the fact that ethyl ether is a complex-forming solvent which can contribute to the formation of co-ordinate links and to solvation, may be relevant. It is also to be pointed out that any carbene intermediate, owing to its electronic structure, might behave as a Lewis acid and react with an eventual electron-donating reagent^{25,26}. It is well known from the literature²⁶ that the carbenes released from the photolytical decomposition of diazomethane, in ethyl ether, react with it and, as a consequence, a $-\text{CH}_2-$ group is added to one of the two hydrocarbon radicals of ethyl ether. A specific action of the solvent cannot then be disregarded in our case, at least as a reaction occurring near the metal surface where carbenes are supposed to be liberated. These explanations, of course, do not hold for metallic gold.

With reference to the gases formed in the decomposition of diazoethane catalyzed by metals, we would like to point out that the decrease in the ratio *trans*-but-2-ene/*cis*-but-2-ene with time opposes the thermodynamic equilibrium, since *cis*-but-2-ene has a larger free energy of formation (16.046 cal/mole) than *trans*-but-2-ene (15.315 cal/mole). However, although the bond strength in the olefin metal complexes, is not accurately known, olefinic hydrocarbons which have a *cis* configuration co-ordinate more strongly than those with a *trans* configuration²⁷. There may be some correlation with our results here.

The *influence of hydrogen* upon the activity of metal surfaces is also noteworthy. Using gold films, for instance, we observed that the over-all yield of polymer increases noticeably from 14 per cent, in the absence of this gas, to 50 per cent when the decomposition of diazoethane is carried out in the presence of hydrogen at a pressure of 300 mm Hg. The increase in the yield of polymer is roughly proportional to the pressure of hydrogen in the system. With a silver surface in the presence of hydrogen, the over-all amount of but-2-enes raises from 9.6 per cent to 66 per cent, although no polymer is formed. Thus hydrogen seems to have quite a remarkable effect on the behaviour of some metal surfaces in such experiments as ours.

Among the metals we have studied, gold is unique in its ability to give rise to small amounts of highly crystalline polymers from the decomposition of aliphatic diazo compounds. It shows a stereoregulating action here. A geometric factor, connected with this metal, can then be taken into account. Geometric factors, as previously mentioned, might be important in heterogeneous catalysis. For instance, the extent of the geometrical fit might be all important. This is shown by Rideal²⁰ and Beeck²⁸, in the case of ethylene on nickel, where a distance of about 2.5 Å between nickel atoms on the surface is considered to be the most convenient for the production of a $\text{Ni}-\text{CH}_2-\text{CH}_2-\text{Ni}$ complex, with a minimum of valency strain at the

two tetrahedral carbon atoms. This is confirmed by the fact that the (110) plane of nickel, which presents distances of 2.48 and 3.51 Å, hydrogenates ethylene five times faster than a nickel powder consisting of a random mixture of (100), (110) and (111) planes.

The fact that the polymer-forming ability of gold and its stereoregulating action are practically unaffected by the solvent might imply a reaction mechanism in which a geometric factor of the surface is important.

It is very often difficult, and somewhat uncertain, to define the state of a surface on which adsorption of the reactants and subsequent reaction occur. We may assume that the forces which cause adsorption depend upon the real distance between an adsorbed molecule, or atom, and the adsorbing surface. The equilibrium distance between adsorbed molecules and the surface is determined by the equilibrium of all the attraction and repulsion forces acting on the surface. Furthermore, the metals might be considered as adsorption agents with an ideal polarizability, and, consequently, we do not know whether the metallic properties leading to this ideal polarization should be assumed to start at the outer peripheries of the surface atoms of the metals, or whether we must assume that these properties are found in a plane through the centres of the surface atoms.

It has also to be borne in mind that, in many cases of chemisorption, normal covalent bonds are formed by sharing of the electrons of the adsorbed molecule, either with the atoms of the metals on which they are adsorbed, or with the metal as a whole. Dipoles on the surface of the metals might then be formed, and the direction of these dipoles might be of great importance for chemisorption and catalysis. In many cases the dipoles point their negative end away from the metal, as observed in the adsorption of hydrogen on nickel²⁹, but in other cases, such as in the adsorption of ethylene and of acetylene³⁰, the adsorbed molecules form dipoles pointing their positive poles away from the metal surface. So we do not propose to sketch a particular mechanism for the gold surface in our experiments, but merely to point out that some geometric factors ought to be important.

The main experimental findings which have been reported previously in describing our work, chiefly on diazoethane, are:

- (i) but-2-enes are the main by-products when the metal surface catalyzes polymer formation in high yields;
- (ii) ethylene is the main product when the metal surface does not give rise to polymer;
- (iii) gold alone, among the metals investigated, shows a stereoregulating activity;
- (iv) the polyalkylidene molecules contain vinyl groups, as shown by the infra-red spectra (*Figures 8, 9, 10*).

The infra-red spectra of the three crystalline polyalkylidenes which have been obtained, are very similar to those of the corresponding atactic polymers. In all spectra, there is evidence of unsaturation of the vinyl type, especially in the polyethylidene molecule. The infra-red spectra of amorphous polypropylidene and polyethylidene are practically identical with those described by Buckley, Cross and Ray³¹. The infra-red spectrum of polybutylidene was first reported by us³². From the infra-red spectrum

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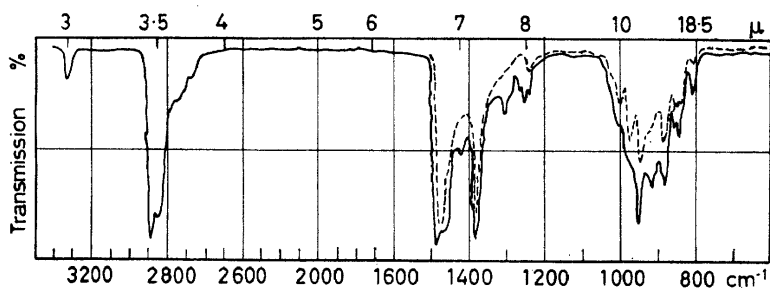


Figure 8. Infra-red spectra of amorphous and crystalline polyethyldiene

of amorphous polyethyldiene the presence of unsaturation of the type $R_1R_2C=CHR_3$ can also be envisaged.

From the above four points and the discussion, we can draw some working

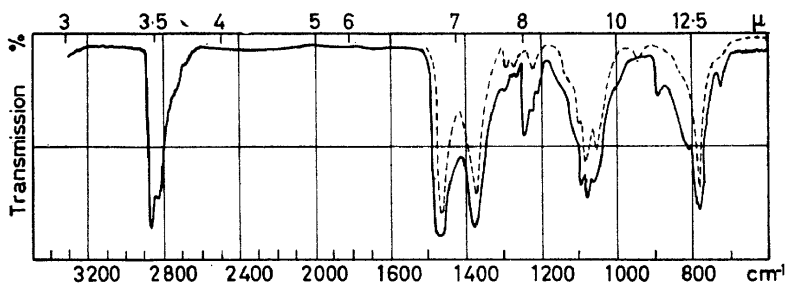


Figure 9. Infra-red spectra of amorphous and crystalline polypropyldiene

hypotheses for the mechanism of the reaction, chiefly for diazoethane. Although we do not want to emphasize the present point of view, our mechanism is described *via* carbene residues, and thus possesses the advantage of a simple model for describing the reaction.

It is reasonable to assume that, when diazoethane molecules reach the active sites of the metal surface, they are decomposed with evolution of

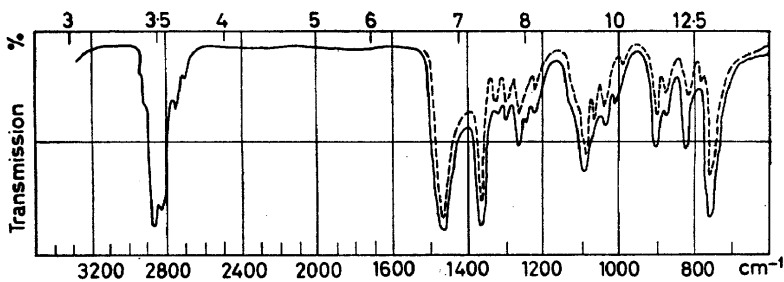
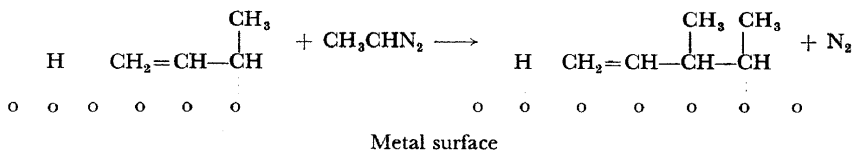
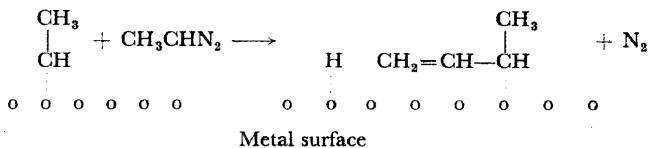


Figure 10. Infra-red spectra of amorphous and crystalline polybutyldiene

nitrogen, and that the residue so released is held on the metal surface. The carbenes can then undergo three different types of reactions, namely isomerization to ethylene, dimerization to but-2-enes, and polymerization. We previously pointed out that for isomerization there is no need for a metal surface, and it would now be appropriate to note that but-2-ene formation can occur either by reaction of two ethylidene fragments adsorbed on neighbouring sites of the metal, or by reaction of an adsorbed ethylidene fragment with a molecule of diazoethane coming from the solution.

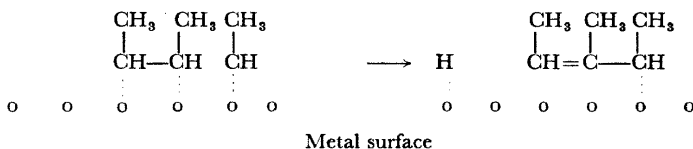
In view of the presence of vinyl-type unsaturation in polyethylidene and the higher polyalkylidenes which we prepared, the initiation step of a polyethylidene chain could be the addition of a diazoethane molecule to the carbene held on the metal surface:



The process might continue until termination occurs by addition of the hydrogen atom released in the initiation step, and so polyethylidene molecules having one double bond of the vinyl type per molecule should be formed.

Chain termination processes, including chain transfer with diazoethane or with solvent, especially when ether is the medium in which the reaction occurs, cannot be disregarded.

A second process which could also give rise to polyethylidene formation would be one initiated by the addition of an ethylidene fragment, adsorbed on a neighbouring site, to a but-2-ene molecule, adsorbed on the metal in a very active form:



The chain would grow in a similar way through addition of active ethylidene fragments adsorbed on the metal surface, to the carbon-metal bond of the growing chain. A mechanism of this type, which can involve a two sites attachment in the formation of the transition complex, could probably explain the formation of a stereoregular polymer, using as catalyst a metal having the proper geometric and electronic factors. The limits would be

very critical indeed, but might be met, in the case of gold, by some faces of the lattice, or by some of the surface atoms.

The experiments which form the basis of these working hypotheses are still largely qualitative. Much work is in progress in the Chemistry Department of the University of Turin with a view to obtaining further results which will help to throw light on what we believe to be an interesting subject.

Summary

The authors make a survey upon the state of the researches made on the reaction of polyalkylidene formation by catalytic decomposition of diazoalkanes upon metallic surfaces. From the experiments it is concluded that the metal surfaces tried up till now, twenty one in number, can be divided into those metals which enhance polymer formation and metals which are almost inactive in this respect, although active in decomposing diazoalkanes.

Metallic gold has been confirmed to be, up to the present time, the only metal endowed with stereospecific regulating properties, giving small amounts of highly crystalline polyalkylidenes: particularly studied is the polymer from diazoethane, namely polyethylidene. The interest of such a tactic-model chain lies in the fact that it has the backbone composed only of tertiary carbon atoms.

The authors have drawn, from the large series of experimental facts and from the tentative explanation of these, some hypotheses about a supposed mechanism of the reaction of polyalkylidene formation from the decomposition products of diazoalkanes, utilizing the conception that the active molecular fragments are the carbenes released from the diazoalkanes in the act of liberating nitrogen. Some tentative explanations are also given for the different mechanism involving a stereospecific action of a clean metal surface.

In the discussion, many points have been taken into consideration concerning the state of the metal surface catalytically active: experimentally, the influence of absorbed gases and of the solvent has been observed, and considerations have been made upon some factors, such as geometric and electronic parameters of the metals, and the formation of surface complexes.

The mechanism of the reaction leading to polymer formation from the decomposition products of diazoalkanes discussed here involves, essentially, three different stages: isomerization, dimerization and polymerization of the active carbene released from diazoalkanes.

References

- ¹ E. Bamberger and F. Tschirner. *Ber.*, **33**, 955 (1900)
- ² H. Staudinger and O. Kupfer. *Ber.*, **45**, 501 (1912)
- ³ N. N. Semenov. *Some Problems of Chemical Kinetics and Reactivity*, Vol. I, p. 135, Pergamon Press, London (1958)
- ⁴ See e.g., H. Zollinger. *Azo and Diazo Chemistry*, p. 110, Interscience Publishers, Inc., New York (1961)
- ⁵ H. Meerwein and W. Burneleit. *Ber.*, **61**, 1840 (1928)
- ⁶ J. Feltzin, A. J. Restaino and R. B. Mesrobian. *J. Am. Chem. Soc.*, **77**, 206 (1955)
- ⁷ S. W. Kantor and R. C. Osthoff. *J. Am. Chem. Soc.*, **75**, 931 (1953)
- ⁸ C. E. H. Bawn and T. B. Rhodes. *Trans. Faraday Soc.*, **50**, 934 (1954)
- ⁹ P. H. Plesch. International Symposium on Macromolecular Chemistry, Milan-Turin, 1954, *Suppl. to Ricerca sci.*, **25**, 140 (1955)
- ¹⁰ C. E. H. Bawn, A. Ledwith and P. Matthies. *J. Polymer Sci.*, **34**, 93 (1959)
- ¹¹ C. E. H. Bawn, A. Ledwith and J. Wittleston. I.U.P.A.C. Symposium on Macromolecular Chemistry, Wiesbaden, 1959, *Short communications, Paper III/A/15*
- ¹² G. Saini, E. Campi and S. Parodi. *Gazz. chim. ital.*, **87**, 342 (1957)
- ¹³ G. Saini and A. G. Nasini. *Atti accad. sci. Torino*, **90**, 586 (1955-56)
- ¹⁴ G. Saini, G. Ostacoli and S. Parodi. *Chim. e ind. (Milan)*, **40**, 467 (1958)
- ¹⁵ L. Trossarelli, E. Campi and A. G. Nasini. I.U.P.A.C. Symposium on Macromolecular Chemistry, Wiesbaden, 1959, *Short communications, paper III/A/16*

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- ¹⁶ A. G. Nasini, G. Saini, L. Trossarelli and E. Campi. *J. Polymer Sci.*, **48**, 435 (1960)
¹⁷ A. G. Nasini, L. Trossarelli and G. Saini. *Makromol. chem.*, **44-46**, 550 (1961)
¹⁸ F. Arndt. *Organic Syntheses*, Coll. Vol. II, p. 165, John Wiley, New York (1943)
¹⁹ J. Sheridan. *J. Chem. Soc.*, **1945**, 133
²⁰ G. H. Twigg and E. K. Rideal. *Trans. Faraday Soc.*, **36**, 533 (1940)
²¹ J. Chatt, in P. H. Plesch. *Cationic Polymerization*, p. 44, W. Heffer & Sons Ltd., Cambridge (1953)
²² A. M. Krutter. *Phys. Rev.*, **48**, 664 (1935)
²³ F. Goos. *Z. Physik*, **100**, 95 (1936)
²⁴ W. Meier. *Ann. Physik*, **31**, 1017 (1910)
²⁵ H. Staudinger, E. Anthes and F. Pfenninger. *Ber.*, **49**, 1928 (1916)
H. Staudinger and T. H. Reber. *Helv. Chim. Acta*, **4**, 1 (1921)
²⁶ H. Meerwein, H. Rathjen and H. Werner. *Ber.*, **75**, 1610 (1942);
V. Franzen and L. Fikentscher. *Ann.*, **617**, 1 (1958)
²⁷ H. J. Lucas, R. S. Moore and D. Pressman. *J. Am. Chem. Soc.*, **65**, 227 (1943)
²⁸ O. Beeck. *Discussions Faraday Soc.*, **8**, 118 (1950)
²⁹ See J. H. De Boer. *Advances in Catalysis*, p. 43, Vol. VIII, Academic Press Inc., Publishers, New York (1956)
³⁰ J. C. P. Mignolet. *Discussions Faraday Soc.*, **8**, 105 (1950)