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25 July 1980

USSR Report

CHEMISTRY

(FOUO 2/80)

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USSR REPORT

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FUELS

POLYMERS AND POLYMERIZATION

FUELS

UDC 66.092+662.765

GASIFICATION OF LOW OCTANE LIQUID FUELS AND PRODUCTS OF HYDROGENATION INTO A HIGH OCTANE GASEOUS FUEL FOR INTERNAL COMBUSTION ENGINES

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 79 pp 47-52 manuscript received 2 Dec 78

[Article by Ye.G. Gorlov, V.M. Antonova and Ya.M. Paushkin, Institute of Fossil Fuels]

[Text] A study is made of the influence of temperature, the coefficient of discharge of air and the nature of the column packing on the material balance and composition of a gas produced in the gasification of low hydrocarbons, a petroleum fraction and a hydrogenate of coal.

The substitution of liquid high octane fuel with less expensive fuel (not inferior to it in octane number) and the problem of protecting the environment from toxic automobile exhausts can be solved by replacing this fuel with gaseous fuel. At the present time the Siemens and Nissar Motor Co. firms abroad and the Ukrainian SSR Academy of Sciences Institute of Gas in the USSR are developing a process for producing gaseous fuel for internal combustion engines, chiefly by means of the conversion of gasoline with water vapor in a catalyzer, employing the heat of exhaust gases [1-3].

However, the employment of water vapor complicates running these engines: large tanks for storing water, problems relating to its freezing in winter and to cleaning salts from the water, etc.

The purpose of this paper is to study the chemism of the process of the gasification of low hydrocarbons of gasoline fractions and to determine the optimal operating conditions of a gas generator which can be used together with an internal combustion engine.

Subjected to gasification were paraffins, naphthenes and aromatic hydrocarbons, as well as a petroleum fraction (70 to 220°) with the following composition (in percentage by weight): unsaturated hydrocarbons four percent and aromatic 11; density of ρ_{20}^{4}, 0.790; as well as a liquid fraction produced in the hydrogenation of coal (condensation point 300°) with the following composition (in percentage by weight): unsaturated hydrocarbons seven percent, aromatic 36, phenols 10 and sulfur 0.60; density ρ^{4}_{20} , 0.860.

Gasification was carried out in a quartz reactor with a diameter of 20 mm in the temperature range of 700 to 800° and with volumetric rates of 3 to $6\ h^{-1}$. The reactor was heated by means of an electric furnace, which was controlled automatically. The raw material was fed into the reactor by a dispensing injector, and the air by a compressor. The gas produced and the condensate were cooled and analyzed chromatographically. The coke content was determined by weighing. The amount of gas was registered by a gas meter. The gasification process was studied both in a hollow reactor and by employing different column packings.

With incomplete combustion, part of the energy obtained from the raw material is converted into heat, whereby the total caloricity of the gas produced is lower than the caloricity of the original liquid fuel. With a coefficient of discharge of air of $\alpha > 0.4$, losses of heat make up a considerable part, since there is an increase in the role of endothermic cleavage reactions, which consume part of the heat produced in the dissociation of products of high caloricity. On this basis, α should be as low as possible.

With $\alpha = 0.1$, losses of heat are insignificant. A further drop in α results in intensified formation of soot. For example, when α is lowered to 0.05, the amount of soot in a hollow reactor increases almost twofold as compared with $\alpha = 0.1$, and with $\alpha = 0.005$ the reactor is clogged with soot already after 30 min of operation (table 1).

At 800° is reached almost total conversion in a hollow reactor of the hydrocarbons studied, except the aromatic. The results have demonstrated that an increase in the process's temperature promotes gas formation for any hydrocarbon. The reduction in coke formation with a rise in temperature is apparently explained by the increase in the rate of reduction of carbon dioxide with the formation of carbon monoxide.

Coke formation depends on the degree of saturation of hydrocarbons, i.e., on the ratio C:H. Maximum coke formation is observed in aromatic hydrocarbons.

With a rise in temperature the composition of the gas also changes: There is an increase in the content of hydrogen, methane and ethylene.

However, the depth of conversion of hydrocarbons reached is insufficient for stable operation of an engine. With a high yield of condensate having a high octane number (the condensate can contain more than 70 percent aromatic and unsaturated hydrocarbons), will be observed considerable soot formation in the engine.

Table 1. Material Balance of the Process of the Gasification of Hydrocarbons in a Hollow Reactor and Composition of the Gas

1) Параметры	2) Углеводороды													
	3) гептан						4) декап			5) циклогексан			6) толуол	
	7) температура, °C													
	700	750	800	700	750	800	700	750	800	700	750	800	750	800
8) Коэффициент расхода воздуха	0,05			0,1			0,1			0,1			0,1	
9) Материальный баланс, мас.%:														
10) газ	94,4	95,2	95,7	82,6	89,5	92,3	80,4	84,9	89,4	80,7	83,4	88,2	39,1	47,7
11) конденсат	5,2	4,5	4,1	17,2	10,4	7,6	19,3	15,0	10,5	18,8	16,3	11,6	60,5	52,0
12) кокс	0,4	0,3	0,2	0,2	0,1	0,1	0,3	0,1	0,1	0,5	0,3	0,2	0,4	0,3
13) Состав газа, об.%:														
14) H_2	5,4	6,8	7,4	6,1	8,4	9,4	6,8	7,5	9,7	5,9	6,3	6,8	10,8	14,2
CH_4	28,9	32,5	34,1	13,8	17,2	20,4	11,8	13,0	17,6	10,8	11,4	14,9	14,3	15,1
$C_2H_4+C_2H_2$	22,8	24,2	23,5	13,4	15,7	15,7	12,1	13,8	15.7	17,6	18,7	19,6	0,3	0,6
C_2H_6	5,5	1,9	1,1	2,1	1,9	1,5	1,3	1,1	1,0	2,9	2,5	1,7	0,1	-
ΣC_3	2,6	0,2	–	3,7	1,6	1,3	3,1	2,9	2,5	1,7	1,5	1,3	–	-
ΣC_4	–	–	–	1,3	0,9	0,5	0,7	0,6	0,4	1,7	1,5	1,3	–	–
CO	5,0	6,8	6,8	8,4	8,9	9,4	8,4	8,6	8,8	8,1	8,4	8,9	11,2	11,1
CO_2	–	–	–	–	–	–	1,9	1,8	0,5	–	–	–	–	–
N_2	29,4	27,4	27,0	48,4	43,2	40,8	51,3	47,6	44,5	49,4	48,1	45,0	59,6	56,7
O_2	0,4	0,1	0,1	1,8	1,7	0,9	2,2	2,1	1,0	1,9	1,5	0,7	3,8	2,3

[Key on following page]

Key:

1. Parameters
2. Hydrocarbons
3. Heptane
4. Decane
5. Cyclohexane
6. Toluene
7. Temperature, °C
8. Coefficient of discharge of air
9. Material balance, percentage by weight
10. Gas
11. Condensate
12. Coke
13. Composition of gas, percentage by volume
14. H_2, CH_4, $C_2H_4+C_2H_2$, C_2H_6, ΣC_3, ΣC_4, CO, CO_2, N_2, O_2

Note: Parameter of process--volumetric rate, 3 h^{-1}; duration of experiment, 3 h.

For the purpose of increasing the yield of gas the process must be carried out by using column packings, both inert and having a catalytic effect. For this purpose were studied various types of packings: quartz, fireclay, aluminum oxide, silica gel, and commercial aluminosilicate (Al_2O_3, 11 to 13, and SiO_2, 88 to 86 percent by weight).

From fig 1 it is obvious that with an increase in the time the packing functions the depth of conversion of the raw material and the yield of gas and coke are reduced. The greatest reduction is observed at the beginning of the process (in the first 30 min of operation). This is explained by the fact that in the initial period the process of the gasification of hydrocarbons takes place on the entire active surface of the packing. As a result of this, the depth of conversion of hydrocarbons is increased. However, with time the coke formed in the process accumulates and partly deactivates the surface of the packing. As a result there is a reduction in the depth of cracking and accordingly in gas and coke formation. All this is reflected also in the composition of the gas (cf. fig 1).

The reactions of isomerization, dehydrogenation and redistribution of hydrogen take place preferredly on clean surfaces of the catalyzer. In proportion to lengthening of the time the packing is used, the percentage of these reactions is reduced and accordingly there is a reduction in the yield of propane-propylene and butane-butylene fractions, and an increase in the content of hydrogen, methane and ethylene.

Since the normal operation of an engine depends not on the yield of any single gas component, but on the stability of the gas's composition, then all investigations of gasification were made after the instant the gas reached a steady composition, which equaled not less than 30 min of the packing's functioning.

The results presented in tables 2 and 3 demonstrate that the employment of packings increases the depth of conversion of hydrocarbons. This is evidenced especially considerably for aromatic hydrocarbons. The nature of the packing exerts a great influence on the process.

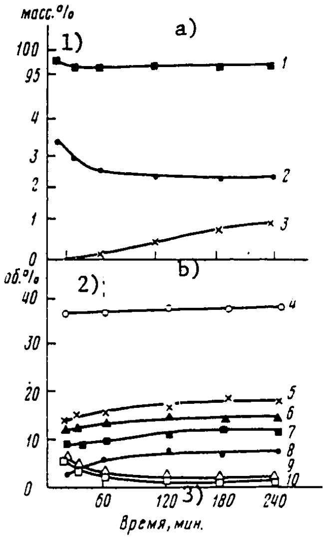

Figure 1. Influence of Duration of Functioning of the Column Packing on the Process of Gasification of Heptane; a--material balance; b--composition of gas: 1--gas, 2--coke, 3--condensate, 4--nitrogen, 5--methane, 6--ethylene, 7--hydrogen, 8--carbon monoxide, 9--propylene, 10--ethane. Parameters of process: packing Al_2O_3; temperature 800°C; $\alpha = 0.1$; volumetric rate 3 h^{-1}.

Key:

1. Percentage by weight
2. Percentage by volume
3. Time, min

Inert column packings such as quartz glass and fireclay influence the conversion of hydrocarbons insignificantly. Packings having a catalytic effect increase the yield of gas on account of a considerable reduction in the percentage of condensate.

At a process temperature of 700 to 800°, when a high depth of conversion of hydrocarbons is reached, from the mechanism of both thermal and catalytic cracking it is difficult to distinguish considerable differences in the nature of the effect of catalytic packings. But it is possible to note that the best catalytic effect on the gasification of hydrocarbons is exerted by aluminum oxide, which possesses aprotonic properties [4]. Furthermore the composition of the gas is changed in the direction of an increase in the content of hydrogen and ethylene.

Table 2. Material Balance and Composition of Gas in the Gasification of Heptane in Employing Different Column Packings

1) Параметры	2) Насадка				
	3) кварцевое стекло	4) шамот	5) силикагель	6) окись алюминия	7) алюмосиликат
8) Материальный баланс, мас.%:					
9) газ	93.5	90,6	94,4	97,1	95,7
10) конденсат	4,8	4,2	2,1	0,7	2,3
11) кокс	1,7	5,2	3,5	2,2	2,0
12) Состав газа, об.%					
H_2	8,50	6,20	7,42	12,25	8,70
CH_4	25,40	19,24	24,53	19,10	22,60
$C_2H_4+C_2H_2$ *	13,37	18,60	13,90	16,64	17,16
C_2H_6	0,80	0,80	1,60	0,89	0,80
ΣC_3	1,10	1,04	0,50	1,43	0,50
ΣC_4	—	—	—	—	0,04
CO	8,78	8,84	8,40	9,20	9,20
O_2	1,25	0,80	0,82	0,74	0,60
13) Теплота сгорания газа, *ккал/нм³*	4910	4940	4880	5080	5000

Key:

1. Parameters	8. Material balance, percentage by weight
2. Packing	9. Gas
3. Quartz glass	10. Condensate
4. Fireclay	11. Coke
5. Silica gel	12. Composition of gas, percentage by volume
6. Aluminum oxide	13. Heat of combustion of gas, kcal//nm^3
7. Aluminosilicate	

Note: Parameters of process--temperature 800°C; $\alpha = 0.1$; time 3 h; volumetric flowrate 3 h^{-1}.

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*C_2H_2 content less than one percent.

Table 3. Material Balance of the Process of Gasification of Hydrocarbons with an Al_2O_3 Column Packing, and Composition of Gas

1) Параметры	2) Углеводороды											8) Нефтяная фракция		9) Гидрогенизат	
	3) гептан			4) декан			5) циклогексан			6) толуол					
	7) Температура, °														
	700	750	800	700	750	800	700	750	800	750	800	750	800	750	800
10) Материальный баланс, мас.%:															
11) газ	87,3	91,6	97,1	81,4	86,5	90,1	81,1	85,9	88,7	50,0	76,9	79,7	89,8	76,2	86,9
12) конденсат	1,2	0,9	0,7	5,1	3,3	3,0	5,2	4,5	4,2	39,4	14,9	10,4	4,8	13,5	6,1
13) кокс	11,5	7,5	2,2	13,5	10,2	6,9	13,7	9,6	7,1	10,6	8,2	9,9	6,4	10,3	7,0
14) Состав газа, об.%:															
15) H_2	10,6	11,3	12,3	6.9	8,1	9,6	6,7	7,0	7,4	16,3	18,2	6,2	7,8	5,8	6,2
CH_4	14,4	17,8	19,1	14,8	16,7	18,3	12,4	13,6	14,0	14,6	16,7	18,8	23,7	14,2	16,7
$C_2H_4+C_2H_2$	16,8	17,3	16,6	14,7	15,6	16,4	16,6	19,0	23,3	0,5	0,3	12,2	13,0	13,7	16,1
C_2H_6	2,3	1,7	0,9	1,1	1,0	0,8	1,4	0,8	0,5	0,6	0,5	1,3	0,5	0,9	0,6
ΣC_3	2,6	1,4	1,4	2,0	2,0	1,9	2,6	1,3	0,6	—	—	1,5	0,6	1,6	0,6
ΣC_4	—	—	—	0,5	0,5	0,3	2,1	1,5	0,8	0,7	0,5	0,5	0,2	0,6	0,4
$CO+CO_2$	8,1	8,9	9,2	10,7	11,1	9,4	8,1	8,5	9,1	9,0	9,6	8,6	10,2	9,7	10,3
N_2	43,6	40,7	39,2	48,6	44,2	43,9	49,0	47,2	43,7	56,3	52,7	50,0	43,6	52,5	44,5
O_2	1,6	1,0	0,7	1,1	0,7	0,5	1,1	1,1	0,7	2,0	1,5	0,8	0,4	1,0	0,6
16) Теплота сгорания газа; *ккал/нм³*	5000	5100	5100	4100	4200	4900	5000	5200	5400	3000	3700	4500	4700	4500	4500
17) КПД газификации	82	86	89	73	80	85	72	79	83	36	38	57	75	50	59

[Key on following page]

Key:

1. Parameters
2. Hydrocarbons
3. Heptane
4. Decane
5. Cyclohexane
6. Toluene
7. Temperature, °C
8. Petroleum fraction
9. Hydrogenate
10. Material balance, percentage by weight
11. Gas
12. Condensate
13. Coke
14. Composition of gas, percentage by volume
15. H_2, CH_4, $C_2H_4+C_2H_2$, C_2H_6, ΣC_3, ΣC_4, $CO+CO_2$, N_2, O_2
16. Heat of combustion of gas, kcal/ /nm^3
17. Efficiency of gasification

Note: Parameters of process--volumetric rate 3 h^{-1}; $\alpha = 0.1$; time 3 h. 1) The efficiency of gasification is given without taking the condensate into account. 2) Content of C_2H_2 less than one percent by volume.

Table 4. Material Balance of Gasification of Heptane, Benzine and Hydrogenate

1) Параметры	2) Углеводороды				
	3) гептан			4) нефтяная фракция	5) гидрогенизат
6) Температура, °C	700	750	800	800	800
7) Материальный баланс, мас.%:					
газ 8)	88,6	92,8	95,7	88,8	75,1
конденсат 9)	9,2	5,3	3.3	9,3	22,9
кокс 10)	2,2	1,9	1,0	1,9	2,0
11) Состав газа, об.%:					
H_2	5,3	7,1	9,7	6,2	7,5
CH_4	13,1	16,1	18,3	18,0	11,0
$C_2H_4+C_2H_2$	12,0	14,1	15,4	11,7	12,1
C_2H_6	3,3	3,1	2,7	2,1	5,0
ΣC_3	5,5	4,1	3,6	5,2	2,3
ΣC_4	1,7	1,3	1,1	0,9	1,4
CO	7,8	8,0	8,2	8,3	7,3
CO_2	1,1	0,3	–	–	1,4
N_2	49,5	45,0	40.3	47,2	51,3
O_2	0,7	0,6	0.6	0,4	0,7
12) Теплота сгорания газа, *ккал/нм*^{3}	5280	5610	5680	5470	4660
13) КПД *	80,5	83,2	87,0	72,0	53,0

[Key on following page]

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*Efficiency of gasification given without taking condensate into account.

Key:

1. Parameters
2. Hydrocarbons
3. Heptane
4. Petroleum fraction
5. Hydrogenate
6. Temperature, °C
7. Material balance, percentage by weight
8. Gas
9. Condensate
10. Coke
11. Composition of gas, percentage by weight
12. Heat of combustion of gas, kcal//nm^3
13. Efficiency

Note: Parameters of process--packing Al_2O_3; volumetric rate 6 h^{-1}; time 3 h; $\alpha = 0.1$.

Simultaneously was discovered an influence of the volumetric rate on the coke formation process. A twofold increase in the volumetric rate drastically reduces the yield of coke (tables 3 and 4).

Conclusions

1. In the incomplete oxidation of n-heptane, n-decane and cyclohexane chiefly gaseous hydrocarbons are produced; the composition of the gas depends little on the nature of the raw material.

2. Under the conditions studied the best catalytic column packing is aluminum oxide.

3. The gas generator reaches the stable mode after 30 min of operation.

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GRAPHITE COMPLEXES WITH TRANSITION METALS - A NEW CLASS OF ORGANOMETALLIC COMPOUNDS

Moscow VESTNIK AKADEMII NAUK in Russian No 3, 1980 pp 21-27

[Article by M. Ye. Vol'pin, Corresponding Member of the USSR Academy of Sciences]

[Text] Not so long ago it seemed that the foundation of chemistry had been built and all that remained to be done was to construct new stories upon it. All kinds of chemical bonds and their nature, all possible types of compounds and basic classes of reactions were considered already known.

In recent decades a radical change of many ideas has occurred in chemistry. One field which proceeded especially intensively was the chemistry of organic compounds of transition metals, i.e. metals with unfilled inner d-shells of the atoms, such as iron, cobalt, nickel, platinum, etc. It turned out that these metals can yield compounds of an entirely new type, not predictable or explainable on the basis of classical ideas, and not even representable by means of the familiar bond dashes.

The study of such compounds forced us, on the one hand, to revise our views on the nature of the chemical bond, and on the other hand it revealed a whole class of new and amazing reactions of metal-complex catalysis passing through the intermediate formation of compounds of this type. Some amazing reactions proved to be possible such as, for example, the stereoregular polymerization of olefins, various reactions of cyclization of olefins and acetylenes, the disproportionation ("metathesis") of olefins, and also the chemical fixation of molecular nitrogen. In this way a vast field of new, nonclassical ideas developed in chemistry.

Below we list some applications of these ideas in the investigation of graphite, the form of free carbon most abundant on earth, a substance which is well studied and widely used in technology.

Graphite represents an aggregate of flat polymeric molecules in which carbon atoms form reticular structures of hexagonal cells of benzene-ring type. In such a system each carbon atom has a free pi-electron in a p-orbit perpendicular to the plane of the molecule. The pi-electrons interact and form a single coupling chain which is responsible for the electric conductivity as well as many other properties of graphite. The parallel lattices of carbon atoms are interconnected not by chemical bonds but by weak Van der Waals forces. Therefore it is possible to introduce various connectors into the space between the networks, such as alkali metals, strong acids, halogenides of transition metals. In this process the networks are as if pulled apart and so-called layered compounds of graphite are formed in which there are no firm covalent bonds in the perpendicular direction, i.e., between the inserted substance and the carbon atoms.

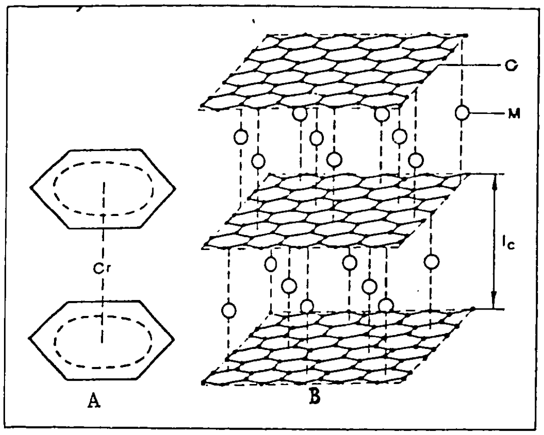


Figure 1. Structure of metal-complex compounds.
A - complex of benzene with chromium (dibenzene chromium),
B - complex of graphite with a transition metal;
C - network of carbon atoms,
M - metal atoms,
I_c - distance between the planes

Within the framework of the neoclassical ideas of modern chemistry of transition metals, entirely new types of compounds are possible. By analogy with the nonclassical monomolecular compounds ("sandwiches") of the dibenzene chromium type $(C_6H_6)_2Cr$, where chromium is linked with two benzene rings, one may try to obtain a whole "flaky pie" where atoms of a transition metal, filling strata between the graphite lattices, would form pi-bonds with the carbon atoms in the perpendicular direction (Figure 1). Such a task was undertaken by the author and Yu. N. Novikov at the Institute of Organoelemental Compounds of the USSR Academy of

Sciences about ten years ago and they struggled with the solution for a long time. As a result they succeeded in developing various methods of synthesis of new type substances by reduction of stratified graphite compounds with metal chlorides using various reducers: alkali metals, aromatic anion radicals, complex hydrides, etc. Recently such compounds were also obtained by a direct method - introducing metal atoms between the graphite layers. In this way, complexes of graphite with chromium, tungsten, manganese, iron, cobalt, nickel, palladium, copper and other metals were obtained.

A difficult task was the investigation of the structure of the new compounds that are solid insoluble powders. The physico-chemical methods usually employed in organic chemistry, such as nuclear magnetic resonance, optical spectroscopy and mass spectroscopy, were not applicable here. Investigation of the structure of these substances turned out to be possible only by such methods as radiography, gamma resonance spectroscopy, X-ray spectroscopy and magnetic methods. We will give only a few examples of determining the structure of metal complexes of graphite.

The transition from a compound of graphite with a metal chloride to a compound with a zero-valent metal is accompanied by a substantial decrease (2-2.5 times) of the thickness I_c of a filled layer in the graphite (Table). Thus, in the initial stratified compination of graphite with molybdenum chloride $MoCl_5$, where there is no chemical bond between the salt and the graphite, the distance I_{c1} between the graphite lattices is equal to the sum of the Van der Waals radii (9.5 Å). In the reduction of this compound and formation of chemical bonds of molybdenum with carbon the distance decreases to I_{c2} = 3.5-3.7 Å, which is very close to the inter plane distance in the analogous monomolecular "sandwich", molybdenum dibenzene (3.5 Å). Magnetic data and the study of X-ray spectra also indicate formation of a pi-complex of graphite with molybdenum. In contrast to the paramagnetic combination with $MoCl_5$, the complex of graphite with molybdenum is dianagnetic similarly as is dibenzene molybdenum.

For the compound of graphite with palladium, investigations of the same kind indicate formation of a pi-complex of graphite with monovalent palladium. The inter-plane distance in such a compound (4.3 Å) is very close to the analogous parameter of the corresponding monomolecular "sandwich" (4.4 Å). In the investigation of the combination of graphite with iron, Mössbauer and X-ray spectroscopy turned out to be very useful, since they directly prove the presence of the chemical bond metal-carbon. In this case both these bonds and the iron-iron bonds were detected, that is, the iron atoms are arranged in the "pie" in a double layer.

Without dwelling on the demonstration of the structure of other complexes with metals, although each of them has its specificity, we turn to their properties.

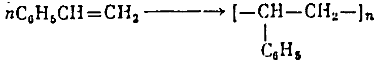
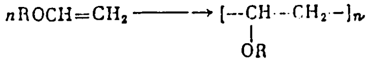
Thickness of the filled layers of stratified compounds of graphite with chlorides of transition metals and with metals

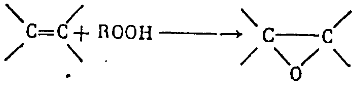
Chlorides of transition metals	Thickness of the filled layer I_{c1} in A	Transition metals	Thickness of the filled layer I_{c2} in A	Thickness difference $I_c = I_{c1} - I_{c2}$
$MoCl_5$	9.3	Mo	3.7	5.6
$MnCl_2$	9.5	Mn	5.8	3.7
$FeCl_3$	9.4	Fe	5.9	3.5
$CoCl_2$	9.4	Co	5.9	3.5
$NiCl_2$	9.3	Ni	5.9	3.5
$PdCl_2$	9.9	Pd	4.3	5.6
$CuCl_2$	9.4	Cu	5.9	3.5

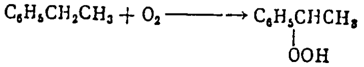
At present the catalytic properties of the graphite complexes have been studied first. Indeed, looking at the layered structure of these compounds, it could have been surmised beforehand that the location of the metal atoms between the conducting carbon lattices would facilitate the reactions of electron transfer from the metal (catalyst) to reacting substances. The fixed distances I_c between the lattices (from 3.5 Å for molybdenum to 6 Å for iron and some other metals) allowed to consider the possibility of selective reactions where some molecules penetrate into the mid-layer space easily and others with difficulty.

It developed that not only complexes of graphite with transition metals, but also layered combination of graphite with salts of metals have a number of interesting catalytic properties.

Combinations of graphite with halogenides of transition metals are very soft catalysts of various cationic processes, for example, alkylation and polymerization of unsaturated compounds. They are much more convenient than the aluminum chloride and ferric chloride used in industry, as they are more stable and difficult to hydrolyze, are less corroded and, most important, they control the polymerization of highly reactive monomers and catalyze selectively the alkylation and acylation of aromatic hydrocarbons.

Alkylation of benzene	$C_6H_6 + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2CH_3$
Polymerization of isobutylene	$nCH_2{=}C(CH_3)_2 \longrightarrow [-CH_2-C(CH_3)_2-]_n$
Polymerization of styrene	 $nC_6H_5CH{=}CH_2 \longrightarrow [-\underset{\substack{\vert\\ C_6H_5}}{CH}-CH_2-]_n$
Polymerization of vinyl ethers	 $nROCH{=}CH_2 \longrightarrow [-\underset{\substack{\vert\\ OR}}{CH}-CH_2-]_n$
Amination of nitrochlorbenzenes	$ClC_6H_4NO_2 + NH_3 \longrightarrow NH_2C_6H_4NO_2$

Epoxidation of olefins 

Oxidation of hydrocarbons 
$C_6H_5CH_2CH_3 + O_2 \longrightarrow C_6H_5\underset{\substack{|\\OOH}}{C}HCH_3$

Electrochemical reduction of nitrogen $N_2 \xrightarrow{\bar{e},\,H^+} NH_2NH_2$

Hydrochlorination of olefins $CH_2{=}CH_2 + HCl \longrightarrow CH_3CH_2Cl$

The compounds of graphite with transition metals can actively catalyze various oxidation-reduction reactions. Thus, of great interest are the properties of these compounds as electrodes, since they act simultaneously as catalysts of electrochemical oxidation reactions of hydrogen in an acidic medium, and reduction of oxygen in an alkaline medium. The activity of an oxygen electrode based on a graphite-cobalt compound in an alkaline medium reaches or even exceeds the activity of silver electrodes. We wish to point out here that a layered compound of graphite with molybdenum pentachloride, introduced into an electrode, catalyzes the electrochemical reduction of molecular nitrogen to ammonia and hydrazine.

Compounds of graphite with cobalt, nickel and other metals, and also with their oxides, catalyze actively and very selectively the dehydrogenation of alcohols to aldehydes and ketones; dehydrogenation only takes place, not accompanied by dehydration.

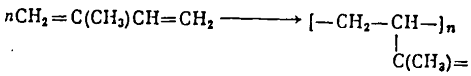
Hydrogenation of olefins $RCH{=}CHR + H_2 \longrightarrow RCH_2{-}CH_2R$
Hydrogenation of carbon monoxide $CO + H_2 \longrightarrow CH_4 + C_2H_6 + \ldots$
Dehydrogenation of alcohols $RCH_2OH \longrightarrow RCHO + H_2$

Electrochemical reduction of oxygen $O_2 \xrightarrow{\bar{e},\,H_2O} OH^-$
Oxidation of hydrogen $2H_2 + O_2 \longrightarrow 2H_2O$

If together with the transition metal an alkali metal, for instance potassium, is introduced into the space between the layers, so that the charge on the transition metal is changed, we obtain catalysts with negatively charged iron, cobalt, nickel or other transition metals, which are very active in the synthesis of ammonia from nitrogen and hydrogen. They permit lowering considerably the process temperature as compared to some industrial catalysts; which gives promise of obtaining low-temperature catalysts for ammonia synthesis. Additionally, compounds of graphite with transition metals and potassium are active catalysts for the hydrogenation of carbon monoxide into hydrocarbons.

Synthesis of ammonia $N_2 + 3H_2 \rightleftharpoons 2NH_3$
Hydrogenation of carbon monoxide $CO + H_2 \longrightarrow CH_4 + C_2H_6 + \ldots$
Hydrogenation of acetylenes $HC{\equiv}CH + H_2 \longrightarrow CH_2{=}CH_2$

Polymerization of isoprene

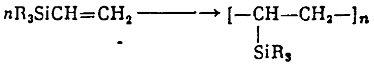


$$nCH_2{=}C(CH_3)CH{=}CH_2 \longrightarrow [-CH_2-\underset{C(CH_3){=}CH_2}{\underset{|}{CH}}-]_n$$

Finally, complexes of graphite with alkali metals, are very promising as catalysts for polymerization reactions. Thus, in the polymerization of organocyclosiloxanes, unlike other catalysts, these result in polymers without terminal groups (possibly of cyclical structure) which are, even without additional treatment, thermally more stable than the polysiloxanes obtained with the usual catalysts.

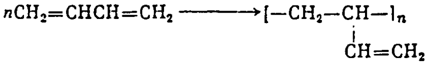
Polymerization of cyclosiloxanes $n(R_2SiO)_4 \longrightarrow [-R_2SiO-]_{4n}$

Polymerization of vinyl silanes



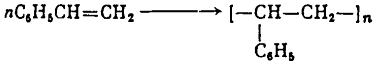
$$nR_3SiCH{=}CH_2 \longrightarrow [-\underset{SiR_3}{\underset{|}{CH}}-CH_2-]_n$$

Polymerization of butadiene



$$nCH_2{=}CHCH{=}CH_2 \longrightarrow [-CH_2-\underset{CH=CH_2}{\underset{|}{CH}}-]_n$$

Polymerization of styrene



$$nC_6H_5CH{=}CH_2 \longrightarrow [-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-]_n$$

One unusual reaction catalyzed by compounds of graphite with transition metals ought to be especially mentioned - the conversion of graphite into diamond. As is known, this conversion is thermodynamically impossible under ordinary conditions and takes place only under pressures greater than 50 kbar and at temperatures of 1500° C and above. This conversion actually consists in cross-linking of graphite layers and formation of chemical bonds between them (Figure 2). For this, however, such an enormous activation energy must be overcome that without a catalyst these reactions do not take place even under the indicated conditions of high pressures and temperature. In the industry, metals are usually employed as catalysts; they are introduced in powder form or as small bits in quantities up to 50% of the charge weight. It is thought that under these conditions the metal fuses and graphite is dissolved in it and later crystallizes in the form of diamond.

Together with Ya. A. Kalashnikov (MGU [Moscow State University]) the question was raised: Could cross-linking of graphite layers be effected by atoms of a metal included in the complex, thus avoiding any dissolution of graphite in the metal? It turned out that complexes of graphite with quite ordinary metals, e.g. iron, actually catalyze the conversion of graphite into diamond at pressures of 60-80 kbar and temperatures of 1200-1600° C. The quantity of the metal in the catalyst is only a few per cent and the reaction proceeds much faster than in the usual diamond synthesis. It is interesting that transparent, well-facetted monocrystallines are obtained in this way, of sizes up to 30 microns, characterized by high purity.

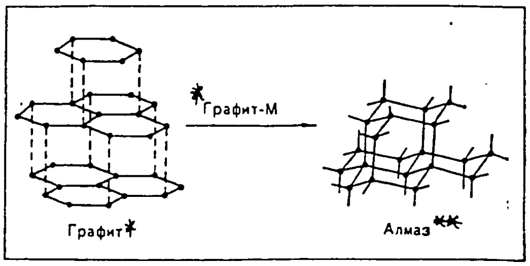


Figure 2. Scheme for the conversion of graphite into diamond (dotted lines indicate the cross-linking of graphite layers)
* graphite ** diamond

Thus, on the one hand, a basically new method of diamond formation was found and on the other hand, diamonds were obtained which differ from the usual synthetic ones and in many respects are close to natural diamonds.

As under the action of complexes of transition metals graphite can be converted into diamond, that is, its very structure can change under the influence of such compounds, it is interesting to consider one more reaction requiring destruction of graphite-like structures. We are referring to the methods of converting coal into hydrocarbon fuel.

Due to depletion of crude oil sources we have an acute problem of coal burning and its conversion into hydrocarbons; and processes which previously were considered economically unprofitable are not developed further and anew, taking into account the fact that the coal reserves on the earth considerably exceed the oil reserves.

Two basic methods of conversion of coal into liquid fuel are known at present. One of them consists of direct hydrogenation of coal under rather struct conditions - at a temperature of about 500° C under hydrogen pressure (method of Bergius). Hydrogen is obtained by conversion of coal with water yielding CO and H_2; thereafter CO, reacting with water, is converted into CO_2 and H_2. In short a three-stage synthesis must be carried out for the hydrogenation of coal.

The other method, the Fischer-Tropsch reaction

$$nCO + (2n +1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O,$$

is thermodynamically possible at not very high temperatures, but it also requires a separate production of hydrogen. By now the interest in this reaction has increased again, although the hydrocarbons thus obtained are so far more costly than petroleum hydrocarbons.

But could not these multiphase processes be replaced by a reaction of carbon with water, without participation of hydrogen, to obtain hydrocarbons and CO_2 directly: $2C + 2H_2O \rightarrow CH_4 + CO_2$? Thermodynamic calculations have shown that even for graphite at temperatures 400-500° C the reaction is sufficiently shifted to have in equilibrium 25% methane, 25% CO_2 and 50% water. If the calculation is done for amorphous carbon, which is less stable than graphite and closer to mineral oil, this reaction turns out to be possible even at 400-500° C. The thermodynamic feasibility of such a reaction may be qualitatively explained by noting that we convert carbon into very low-energy carbon dioxide and very high-energy methane which carries the main part of the whole calorific power of coal.

The thermodynamics of this reaction varies little with temperature. But other reactions, accessory in this case (formation of CO and H_2), shift with temperature very abruptly. Consequently, for the reaction to proceed selectively, it has to be carried out at comparatively low temperatures, up to 400-500° C at most. However, complete destruction of the graphite fragments in coal can hardly be expected at such temperatures. Thus the problem of catalytic decomposition of the carbon lattice of graphite arises again, and here an important part may be played by compounds of transition metals, among them complexes of graphite with transition metals.

The work reported here was initiated at the Institute of Organoelemental Compounds and at present many organizations and institutions participate in it. Synthesis of new compounds and investigation of their catalytic properties is conducted at the Institute of Organoelemental Compounds by the group of Yu. N. Novikov. At the Institute of Physical Chemistry of the USSR Academy of Sciences investigations of graphite complexes are conducted by magnetic and Mossbauer methods. At the Institute of Organic Chemistry imeni N. D. Zelinskiy and at the Institute of Petrochemical Synthesis imeni A. V. Topchiyev of the USSR Academy of Sciences some interesting reactions of these complexes have been studied. Investigations of X-ray spectra are conducted at the University of Rostov and work on diamond synthesis under pressure at the University of Moscow. Also industrial institutes participate in the study of catalytic properties.

* * *

The communication of M. Ye. Vol'pin was received with great interest.

Academician G. A. Razuvayev stressed in his statement that the theoretical significance of the work communicated by the speaker is not inferior to its obvious practical importance. In particular, one may expect the discovery of many interesting directed reactions in the "corridors" between the carbon layers where atoms of one or several metals penetrate.

Academician N. M. Emanuel' pointed out that M. Ye. Vol'pin, after brilliant work on chemical fixation of nitrogen, displayed a whole spectrum of new amazing possibilities of the metal complexes of graphite synthesized by himself. Special attention should be paid to catalytic properties of the new compounds which may allow, in particular, to carry out an extremely important process - the direct oxidation of propylene. N. M. Emanuel' offered the use of installations of the Institute of Physical Chemistry for the study of such possibilities. He also expressed the wish to enlist the cooperation of other institutions with the work already being conducted in order to elucidate more quickly the practical prospects of utilization of the metal complexes of graphite.

The president of the USSR Academy of Sciences, academician A. P. Aleksandrov, assessed the work on the synthesis and study of the new compounds as very important and promising. This is true above all for such applied trends as fixation of nitrogen, obtaining artificial diamonds, and new ways of coal processing: they must be expanded, advocated and supported by all means. A. P. Aleksandrov offered help from the Institute of Atomic Energy in arranging large-scale experiments and in investigations by the method of Mossbauer spectroscopy: he also asked the lecturer to formulate suggestions about other meauures which could be helpful in the conduct of further experiments.

The president backed up the opinion of N. M. Emanuel' on the necessity to accelerate this extremely promising work and the need of participation of a greater number of institutes of various fields.

In conclusion A. P. Aleksandrov congratulated M. Ye. Vol'pin on his great scientific achievements.

[152-12157]

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POLYMERS AND POLYMERIZATION

UDC 541.64

ON THE MECHANISM OF LOW TEMPERATURE SOLID PHASE POLYMERIZATION

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 244, No 6, 1979 pp 1379-1383

[Article by G. N. Gerasimov, M. V. Bazilivskiy, V. A. Tikhomirov, and A. D. Abkin, Scientific Research Physical Chemical Institute imeni L. Ya. Karpova, Moscow]

[Text] Solid phase polymerization reactions initiated by ultra-violet or ionizing radiation are currently attracting great attmetion. The effect of temperature on the rate of such reactions is often not described by the simple Arrhenius equation. Over a certain interval of temperatures this effect markedly diminishes, and with further cooling of the solid monomer, the rate approaches a final limit, so that formation of polymer chains is observed even at 4.2 K. Various hypotheses on the mechanism of low temperature solid phase polymerization have been proposed which are not dependent on thermal activation. According to one of these hypotheses this athermal reaction depends on quantum-mechanical tunneling of the reacting molecules through a potential barrier of the reaction (1). However, the probability of such a process for heavy monomer molecules is very low. It was also proposed that the reaction is controlled by diffusion and that low temperature growth of the chain takes place as a result of diffusion of the monomer caused by irradiation (2, 3). However, athermal polymerization of the solid monomer at low temperature also takes place in the case where the initiating irradiation is not absorbed by the monomer, and acts only on a certain sensibilizing reaction to form active sites (4). For low temperature reactions such sites are either ions or excited molecules (5, 6). Here we will examine a new mechanism describing the most diverse process of this type: ionic polymerization of monomers with Pi-electron bonds.

The attachment of an isolated monomer molecule to a growing ion in a gas most probably takes place without a barrier (7). The barrier in solid phase addition is conditioned by the interaction of reacting particles with the lattice and therefore depends strongly on the position of the particles in the lattice. The polymer chain in a solid monomer forms from the ordered monomeric precursors (5, 8) after irradiation created a primary monomeric ion. Part of the energy expended on ionization of the system is converted into local energy of vibration of the precursor molecules in the vicinity of the excited ion. The barrier of the initial reaction of the monomer ion with the molecule may be overcome as a result of these vibrations, in which case the rate of transition through this barrier does not depend on temperature. The mechanism of the initiating reaction leading to the appearance of precursors of the polymer chain is considered in works (5, 6). In this article is described a model of the development of such a precursor. It is essential that the precursor of a growing chain arises in a metastable position in respect to its surrounding part of the crystal lattice, the status of which ceases to be in equilibrium owing to the nearness of a growing defect. The basis of the proposed scheme rests on two assumptions: first, in a metastable position of the growing chain, the barrier to the chain growth disappears entirely, and second, in the corresponding ordered monomeric system this position of the chain is preserved during the process of its growth, since the reaction develops faster than the diffusion process of relaxation, thereby "confusing" the polymer chain and the solid body lattice to each other. The latter is confirmed by experimental data according to which the structure and conformation of molecules growing in a solid monomeric matrix, as well as the sub-molecular structure of the formed polymer phase are not in equilibrium (5). If our assumptions are correct, during athermal generation of chains under the action of irradiation the overall rate of polymerization will not depend on temperature, and the polymerization may take place even in the vicinity of absolute zero.

The cationic polymerization of ethylene was selected as a model. This is a hypothetical reaction, since crystalline ethylene hardly polymerizes at all, most probably due to the unfavorable positioning of the molecules (9). The lattice being examined here differs from a real crystal of ethylene and contains the molecule precursors needed for reaction (Figure 1), analogous to typical monomeric precursers in polymerizing molecular crystals (5, 10). The lattice is constructed according to general principles determining the structure of crystals: the molecules in the lattice are densely packed and the distance between adjacent atoms of neighboring molecules is approximately equal to the sum of the van der Waals radius of these atoms.

For the sake of definition the act of the formation of a cationic site is considered to be the addition of a proton: a molecule of ethylene I (Figure 1) is converted to an ethyl cation $C_2H_5^+$. The initial reaction of this cation with a molecule of II leads to the formation of a dimer precursor of the growing chain of the butyl cation $C_4H_5^+$. (This reaction, as stated above, takes place probably as a result of the energy which is released locally during the formation of the ethyl cation). We are interested in the next act of chain growth - the interaction of cation $C_4H_9^+$ with Molecule III of the monomer precursor (Figure 2).

Let us select a subsystem of reactants in the crystal. At a given stage it will be entered by a $C_4H_9^+$ Cation and an ethylene molecule III. The other molecules in the system we consider as an immobile crystal background. In this case, the energy of the reactants U consists of the energy of reaction among themselves - chemical energy U_{chem} and the energy or reaction between them and the background - crystalline energy U_{cryst}:

$$U = U_{chem} + U_{cryst}$$

In a gaseous reaction chemical energy is the only component. The specifics of the solid phase reaction is determined by the addition of an additional member U_{cryst}. Optimization of U_{cryst} in a harmonic approximation leads to an important conclusion: a minimum of energy corresponds to the position of a precursor mid-way between the molecule layers of the crystal (Figure 2). This conculsion is also justified in the case of anharmonism if the width of the crystalline potential holes is sufficiently large in comparison with the distance between the layers: the crystalline potentials for molecules I and II, forming the dimer precursor, must effectively cover each other.

The initial stage of addition of III to the dimer precursor is shown in Figure 2. The slight shift of the monomer molecule - the horizontal shift of 0.7 A and the rotation of 20° - leads to configuration 2b, for which it is a simple matter to evaluate the chemical potential energy. Calculating U_{cryst} by an atom-atom scheme with parameters foom work (11) and by utilizing quantum-chemical calculations of U_{chem} for a gas phase reaction (7), it is possible to show that the reaction in configuration 2b takes place without a barrier: the corresponding route of addition although different from the optimal route of a gas phase reaction (7), never-the-less facilitates a sufficiently rapid decrease in U_{chem}. To evaluate the change in U_{chem} in the transition from 2a to 2b, the work method used in (7) is unsuitable. Such an evaluation requires additional research. Preliminary calculations by ppdp and mChpdp methods showed the U_{chem} at this stage of the reaction changes insignificantly; lattice resistance is also low; U_{cryst} increases only by 1-2 kcal/mole. As a whole, hypothesis (1) appears justified.

To check proposition (2) we computed U_{cryst} on the atom-atom scheme for various fragments of the polymer chain C_nH_{2n+1}. The structure of the precursor is such that the growing chain takes on the cis-configuration, in which the carbon atoms are located in a single plane and is unstable in the gaseous phase, but in the lattice corresponds to the metastable state of the chain. During the process of growth, the chain holds its position in the center between the layers of the crystal. According to our estimates, inside the hollow of the crystal arising during polymerization, the polymer fragment may freely transfer to the horizontal direction, if the lattice surrounding the hollow is ordered: in a lattice which is incoherent to the chain, stresses arise which at a definite length of the polymer fragment overcome the barrier for such a displacement. Therefore, hypothesis (2) is also justified. In general, non-barrier growth of a chain may be viewed as movement of the chain into the metastable state between the layers of the lattice, in connection with subsequent "stringing-on" of new monomer molecules to the chain.

Termination of the reaction depends on relaxation processes related to disruption of order in those parts of the crystal associated with the growing chain. Thus, confrontation of a growing chain with a defect causes its deactivation. For example, on collision with a vacancy it is possible for the chain links to transfer from the flat cis- to the non-flat hom-conformation, so that the chain becomes entrapped in the lattice and thereby loses the mobility necessary for reaction. If such a transfer takes place in a terminal link containing a cationic site, then this site breaks off from the monomer precursor and becomes unreactive. However, at higher temperatures conformational changes halting chain growth, may take place in the absence of defects, so that the probability of chain rupture at conformational entrapments increases. On the other hand, chain generation processes related to thermal activation begin to play a role, as well as thermal reactivation from conformational traps. In this case one may expect transition to conventional Arrhenius kinetics, as indeed observed experimentally.

The main conclusion coming from the present work is that in order to understand the mechanism of solid phase reactions, it is absolutely necessary to have the effects of the crystal field clearly in view. The proposed concrete mechanism rests on a number of model assumptions. We submit that in general outline it correctly describes the character of the actual polymerization process, although many details undoubtedly require clarification.

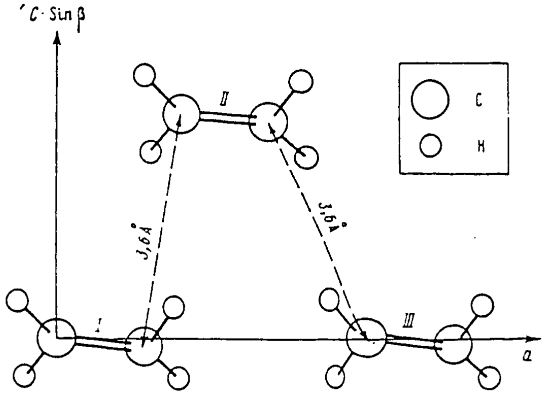

Figure 1. Scheme of monomer precursor in a model ethylene crystal. The crystal is of triclinic modification with the parameters: a=5.0 Å; b=4.36 Å; c=4.07 Å; alpha=54°; beta=56°; gamma=73°. Plane of projection ac.

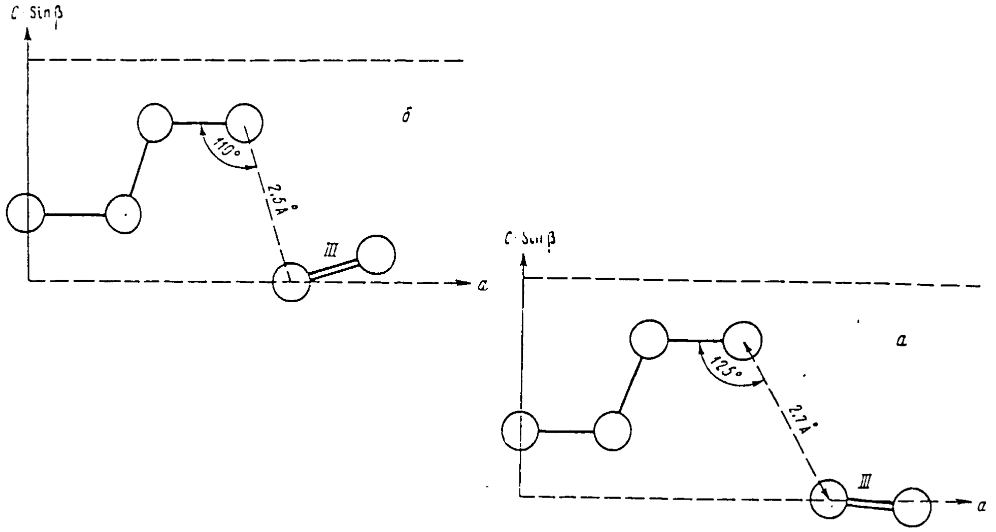

Figure 2. Reaction scheme of a dimeric precursor of a growing chain in model crystal of ethylene; a - initial configuration; b - intermediate configuration. Only the carbon atoms are shown. Crystal layers are designated by dashed lines.

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[8144/1304-P]

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UDC 541(64+14)

SOLID PHASE PHOTOSENSITIZED POLYMERIZATION OF ACRYLONITRILE AT CRYOGENIC TEMPERATURES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 250, No 2, 1980
pp 384-387

[Article by S. M. Dolotov, G. N. Gerasimov, and A. D. Abkin, Scientific-Research Physical-Chemical Institute im. L. Ya. Karpov, Moscow]

[Text] During solid phase polymerization, initiated by irradiation, the influence of temperature on the reaction rate (W) is in many cases not described by the simple Arrhenius equation. At a certain temperature interval this influence markedly diminishes and with further cooling of the monomer W approaches a limit, so that polymerization is observed even in the vicinity of 4.2^{o} K (1-4). Various possible explanations of athermal polymerization at extremely low temperatures have been proposed (5, 6). However, to establish a true mechanism for this unusual reaction, experimental data are lacking. The processes of cryogenic chain polymerization known so far have very low yields (less than 15), which present great difficulties in the theoretical analysis of the results. Furthermore, these processes were initiated with high energy ionizing radiation which is absorbed by the monomer lattice and creates perturbations which are difficult to predict.

In the present article we describe a new effective process of photosensitized chain polymerization of a solid monomer at cryogenic temperatures. This process takes place without the direct action of irradiation on the monomer: light is absorbed only by the sensitizer which leads to the formation of active sites which initiate polymerization of the solid monomer. The process described is unique in having a high velocity and a high conversion of monomer to polymer.

Acrylonitrile (AN) and N, N'-tetramethyl-p-phenylene diamine (TMPhD) were chosen as monomer and sensitizer, respectively. After careful purification, the AN and the TMPhD were condensed under vacuum onto a cooled substrate of CaF_2 which was fixed in a cryostat holder for spectroscopic investigation. The samples were irradiated with light from a high pressure mercury vapor lamp DRSh-500 through a UFS-2 filter, separating out the 260-400 nm region. Conversion of the monomer and a accumulation of the polymer were determined by infra-red spectroscopy at the irradiation temperature. The IR spectra were measured on a "Perkin Elmer-580" instrument. Ultra-violet spectra of the irradiated samples were recorded on a "Beckman Acta II" spectrophotometer.

Condensation of AN vapors at 80° K leads to the formation of a glassy monomer (according to calorimetric data, the glassification temperature (T_{gl}) of AN is 115 K (7); on deposition of AN on a substrate, cooled to 140 K, crystals of the metastable modification AN-AN I are formed (7). The various phase states of solid AN are readily distinguished by the position and width of the bands of valence vibrations of C≡N and C-N in the IR spectra of AN. Condensation, both at 80 and at 140 K yields a glassy TMPhD which is stable at up to 150 K and crystallizes at 150-160 K. Experiments were conducted at 20-150 K in binary systems; TMPhD (glass) - AN (glass) and TMPhD (glass) - AN (crystals of AN I).

The photosensitized reaction in the system AN-TMPhD is conditioned by the electron donor properties of TMPhD and is the result of the photo transfer of an electron from the TMPhD to AN. It is characteristic that in the presence of electron acceptor benzophenone, photosensitizing the formation of excited AN molecules, no low temperature changes in AN were observed. Phototransfer of an electron initiates the anionic polymerization of AN at cryogenic temperatures. The formation of ionic sites is manifested by the appearance in the ultraviolet spectra of the irradiated systems of absorption bands characteristic of the TMPhD cation-radical at 590 and 620 nm. The number of cation-radicals is equal to the number of electrons "captured" in the AN, since, as the experiments showed, the charged are not stabilized in the TMPhD.

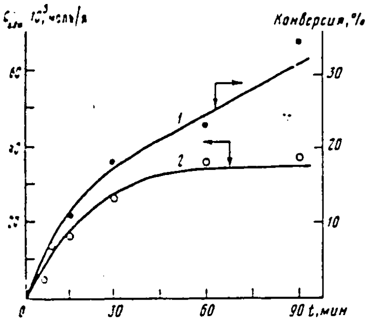
Figure 1 shows a kinetic curve for the polymerization and a curve for the accumulation of ions for glassy AN at 20 K. The reaction takes place without an induction period, although the number of ions in the initial stage gradually increases reaching a constant number after about 30 min. Apparently, the time required for the development of the chain is significantly less than the life-time of the ions in the system. The ratio of the overall polymerization rate (W_{pol}) to the rate of ion formation (W_{ion}) - specific rate (W_{sp}) of polymerization as computed for 1 ion - is equal to the product $\overline{\nu}f$, where $\overline{\nu}$ is the average chain length, and f is the probability of conversion of the primary ionic site to a growing carbion (chain generation). Judging by the data obtained, W_{sp} comprised about 100 at 20 K. This quantity is the lower limit of $\overline{\nu}$ under the given conditions. Therefore, the active site formed in solid AN, causes the conversion of a large number of molecules at cryogenic temperatures.

Cooling of glassy AN results in a step-like drop in W_{pol} at 50 K, conditioned by a corresponding drop in W_{ion} (Figure 2). After heating, W_{ion} increases anew to its previous value. The observed changes in W_{ion} are probably related to the change in interaction between the glassy particles of AN and TMPhD. It may be proposed that elastic deformations, conditioned by cooling of the system, leads to a marked increase in the barrier, thereby inhibiting electron transfer from donor to acceptor. Elastic deformations are reversible, and after reheating of the system, the barrier again decreases. It should be noted that under the action of gamma-radiation on single-component homogeneous glasses, the probability of formation of stabilized charges is the same both at 4.2 and at 77 K (9, 10). The initial value of W_{sp} - $(W_{sp})_0$ remains constant in the interval 20-50 K. In the interval 50-70 K $(W_{sp})_0$ increases by 1.5-2 times, and with further heating of the system to 110 K there is practically no change (Figure 3).

Crystalline AN at cryogenic temperatures polymerizes only to a slight degree (about 10%), after which the reaction terminates (Figure 4). For crystalline AN the rate of formation and the stationary concentration of stabilized ions are lower than in the glassy state. Furthermere, in systems containing crystalline AN no step-like changes in W_{ion} are observed at low temperatures: throughout the entire interval of temperatures under study W_{ion} was practically independent of temperature. The value of $(W_{sp})_0$ of crystalline AN remains practically constant on heating the crystals from 20 to 80 K (Figure 3): the reaction takes place athermally. At about 85 K this value increases by about 2 times. At the same time the character of the kinetic curves changes: polymerization at temperatures above 85 K proceeds to extensive conversions of the monomer. In the interval 90-110 K $(W_{sp})_0$ increases insignificantly: the effective activation energy of the process (E_{eff}) comprises approximately 0.3 kcal/mole. With further heating E_{ff} increases to 2 kcal/mole (Figure 3).

Solid phase polymerization is conditioned by an ordered structure in the lattice of the solid monomer: the reacting molecules form "precursors" of future polymer chains (11, 12). Such aggregates exist not only in crystals, but also in glasses consisting of asymmetric molecules bound strongly together; such an association is characteristic particularly for nitriles (13). The primary site in our case is apparently the anion-radical $(AN)^{\overline{\cdot}}$. Conversion of $(AN)^{\overline{\cdot}}$ to a growing carbion - chain generation - takes place apparently as a result of the addition of $(AN)^{\overline{\cdot}}$ to the monomer (14). It may be supposed that this addition takes place at cryogenic temperatures as the result of local lattice vibrations arising at the moment of formation of $(AN)^{\overline{\cdot}}$ (4); the energy of such vibrations consists partly of the irradiation energy expended on rupture of an electron from the sensitizer. A probable scheme for the further growth of an ionic chain precursor is considered in work (15): the position of the formed precursor in the lattice is metastable, and deformations arise around it which overcome the barrier to ionic growth of the chain. In an ordered configuration of molecules, the activated metastable state of the growing chain is maintained regardless of its length; in this way, athermal cryogenic polymerization becomes possible. Chains are torn off during collision with defects, and for further growth of these chains thermal activation is required, which takes place, apparently, at higher temperatures (Figure 3); the reactivation energy depends on the depth of the traps into which the chains fall.

Chain development is facilitated wherever the monomeric "precursors" are weakly bound to the surrounding lattice. Glassy AN, apparently, consists of just such labile precursors. It may be assumed that in AN crystals at cryogenic temperatures, only those precursors near certain extended defects are labile, while extension of the reaction throughout the entire bulk of the crystal during heating takes place in connection with thermal disintegration of the lattice of crystalline AN. Supplementary kinetic investigations now under way will more definitely characterize the reaction.



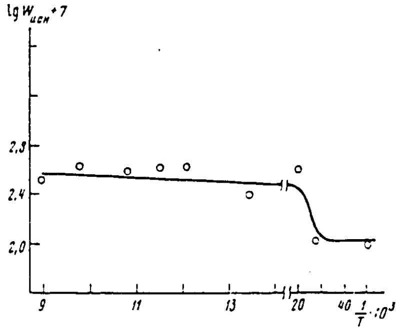
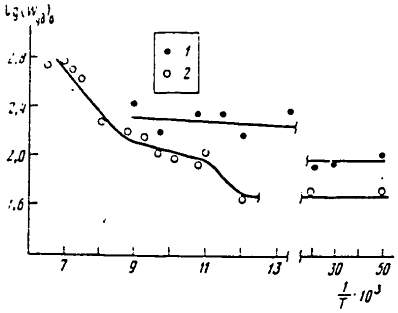


Figure 1. Relationship of monomer conversion (1) and ion yield (2) on irradiation time during polymerization of glassy AN; at 20 K.

Figure 2. Relationship of rate of formation of ion to temperature for glassy AN; rate expressed in mole/l.s



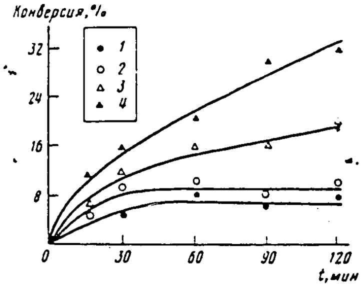


Figure 3. Relationship of initial specific rate of polymerization of glassy (1) and crystalline (2) AN to temperature.

Figure 4. Kinetic curves for polymerization of crystalline AN at 20 (1), 82 (2), 90 (3) and 103 K (4).

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