

USSR/Chemistry - Chain Reactions,  
Atomic Energy

Apr 53

"The Theory of Chain Reactions in the Calculation of the Diffusion of Active Centers," N. S. Akulov

Zhur Fiz Khim, Vol 27, No 4, pp 614-615

In all chain reactions which occur in nature, diffusing active centers interact with the medium, forming active centers of another type. The view of V. V. Vovodskiy and A. S. Kompaneyets (Zhur Eksp i Teor Fiz, Vol 23, p 229, 1952) that there is only one type of active center in the chain fission of U, i.e. the neutron, is erroneous. One must consider

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at least 2 types of centers, i.e. slow and fast neutrons. Although Vovodskiy and Kompaneyets use with small changes equations developed in the author's (Akulov's) book, they claim credit for independent work in arriving at the same result as the author.

270123

VOYEVODSKIY, V. V.

USSR/Chemistry - Combustion Kinetics

Sep 53

"The Problem of the Existence of Three Limits of Spontaneous Ignition of Combustible Mixtures,"

V. V. Voyevodskiy, Inst of Chem Phys, Ac Sci USSR

Zhur Fiz Khim, Vol 27, No 9, pp 1420-1426

The alleged theory of three limits of ignition about which N. S. Akulov talks and for which he claims credit does not exist. Akulov's deductions are not in accordance with exptl facts. His criticism of N. N. Semenov's theory, which does explain exptl results satisfactorily, is not justified and involves

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rejection of everything that has been done by USSR workers in this field during the past 20 yrs. There is no reason for acceptance of Akulov's empirical formulas, because all phenomena can be explained from a unified theoretical point of view.

FBI



VOJEVODSKIN V.V.

The mechanism and kinetics of polymerization of  $\epsilon$ -caprolactam S. M. Skuratov, A. A. Stremelnik, V. V. Ch...

...the results reported by S. et al. (CA 46, 13067) are described in greater detail. When  $\epsilon$ -caprolactam is polymerized in the presence of acids, the max. rate of polymerization occurs at 30% transformation of monomer instead of 42% when pure H<sub>2</sub>O is used. When BuNH<sub>2</sub> is present, the value is 45-6% and with NaOH, 50%. Since both pos. and neg. ions affect the reaction rate, the amino acid formed during the polymerization must act as a dipolar ion. H. M. Leicester

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VOYEVODSKIY, V.V.

The Committee on Stalin Prizes (of the Council of Ministers USSR) in the fields of science and inventions announces that the following scientific works, popular scientific books, and textbooks have been submitted for competition for Stalin Prizes for the years 1952 and 1953. (Sovetskaya Kultura, Moscow, No. 22-40, 20 Feb - 3 Apr 1954)

<u>Name</u>	<u>Title of Work</u>	<u>Nominated by</u>
Malbandyan, A.B. Voyevodskiy, V.V.	"The Mechanism of the Oxidation and Combustion of Hydrogen"	Institute of Chemical Physics, Academy of Sciences USSR

SO: W-30604, 7 July 1954

VOYEVODSKIY, Vladislav Vladislavovich.

A cademic degree of Doctor of Chemical Sciences, based on his defense, 29 December 1954, in the Council of the Inst of Chemical Physics Acad Sci USSR, of his dissertation entitled: "Free Radicals in Chain Gas Reactions".

A cademic degree and/or title: Doctor of Sciences

SO: Decisions of VAK, List no 8, 2 April 55, Byulleten' MVO SSSR, No. 14, July Moscow pp 4-22, Uncl.  
JPRS/NY-429

"APPROVED FOR RELEASE: 08/09/2001

CIA-RDP86-00513R001861110018-4

APPROVED FOR RELEASE: 08/09/2001

CIA-RDP86-00513R001861110018-4"



Voyevodskiy, V.V.

AID P - 1118

Subject : USSR/Chemistry  
Card 1/1 Pub. 119 - 1/5  
Authors : Kursanov, D. N. and Voyevodskiy, V. V. (Moscow)  
Title : Some new data on hydrogen exchange between organic radicals and ions  
Periodical : Usp. khim., 23, no. 6, 641-653, 1954  
Abstract : Hydrogen exchange of free organic radicals and of organic cations is reviewed. Experimental data on the hydrogen exchange of carbonyl compounds with D<sub>2</sub>SO<sub>4</sub> are compiled in a table. One table, 38 references (19 Russian: 1934-54).  
Institution : None  
Submitted : No date

USSR/Chemistry - Analysis methods

Card 1/1 : Pub. 147 - 15/27

Authors : Kardaleyshvili, R. E.; Lavrovskaya, G. K.; and Voyevodskiy, V. V.

Title : Micro-method of analyzing heavy water

Periodical : Zhur. fiz. khim. 28/12, 2195-2198, Dec 1954

Abstract : A new compensation method for measuring vapor pressures was utilized in determining the deuterium content of water. This method permits carrying out heavy water analyses (deuterium content in water) in 0.5 mg of water with an accuracy of up to 1 - 0.05 mol%; regardless of the D<sub>2</sub> content in the water. The installations used in connection with this compensation method are described. Eight references; 5 USSR; 1 USA; 1 English and 1 German (1936-1953). Table; graphs; drawings.

Institution : Academy of Sc. USSR, Institute of Chemical Physics and the V. M. Lomonosov State University, Moscow

Submitted : June 23, 1954

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**CIA-RDP86-00513R001861110018-4"**

VOYEVOVSKIY, V.V.

~~The kinetics and heat effect of the reaction of polymerization of enantholactam. M. Skuratov, V.V. Voevodskiy, A. A. Gerasimov, P. S. Lomozov, K. G. Murav'eva, and N. V. Zolotareva. *Doklady Akad. Nauk SSSR* (Moscow), *Doklady Akad. Nauk SSSR* 95, 591-4 (1954). The H<sub>2</sub>O-catalyzed polymerization of enantholactam (I) was studied calorimetrically in a manner analogous to the method as previously in studying the polymerization of caprolactam (II) (cf. *C.A.* 49, 8206c, 49, 15987c). The polymerization of I is autocatalytic, with an induction period somewhat smaller than that of II. The period required for the attainment of the max. reaction velocity decreases as the amt. of catalytic H<sub>2</sub>O is increased, but the degree of conversion 20-25% of I at the point of max. velocity is independent of the amt. of H<sub>2</sub>O present. The heat of polymerization of I, 5.19 kcal./mole, is about 2 kcal./mole greater than that of II, which indicates that the ring strain in I is 2 kcal./mole greater than in II. An effective activation energy of 23 kcal./mole is required in the polymerization of I. A rate equation, derived from a proposed reaction scheme, on introduction of the activation energy becomes  $W = A_0 \frac{1000}{RT} [H_2O] [B] (B_0 - B)^{3/2}$ , where  $W$  is the rate of change of  $B$ ,  $B$  is the concn. of I, and  $B_0$  is the initial concn. of I. Donald B. Miller~~

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Voyevodskiy, V. V.

AF701597

TREASURE ISLAND BOOK REVIEW

AID 803 - S

VOYEVODSKIY, V. V. (Institute of Chemical Physics, Academy of Sciences, USSR).

DISKUSSIYA (Discussion). In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vol. 8. Izdatel'stvo Akademii Nauk SSSR, 1955. Section I: Effect of illumination on the adsorbability of solids. p. 73-74.

An outline of the photodesorption of CO from a Ni-surface is given. The process consists of the absorption of light, deactivation by means of recombination, surface reaction preceding desorption of CO, and desorption of CO.

1/1



Voyevodskiy, V.V.

AF701597

TREASURE ISLAND BOOK REVIEW

AID 807 - S

VOYEVODSKIY, V. V. (Institute of Chemical Physics, Academy of Sciences, USSR).

O TSEPNYKH MEKHANIZMAKH V GETEROGENNOM KATALIZE (Chain mechanisms in heterogeneous catalysis). In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vol. 8. Izdatel'stvo Akademii Nauk SSSR, 1955. Section II: General problems of the theory of catalysis. p. 97-109.

An explanation of the mechanism of catalytic processes is given, based on the formation of intermediate products with a higher reactivity than the initial substances. Three types of heterogeneous active centers are discussed: 1) free lattice valence (formed by thermal or chemical action); 2) heterogeneous radical, i.e., a particle chemically combined with the surface and 3) homogeneous radical (or atom), whose bond with the surface is intermediate between a strong chemical bond and physical adsorption. The mechanisms of hydrogenation, of catalytic cracking in the presence of carbon and formation of hydrocarbons and alcohols from CO and H<sub>2</sub> are discussed at some length. The processes determining the direction and velocity of heterogeneous chain transformation are governed by the action of the catalyst

1/2

VOYEVODSKIY, V. V., O tsepnykh mekhanizmax v ..... AID 807 - S

on 1) the continuation and 2) initiation (and breaking) of the chains. 22 refs., 14 Russian, (1944-1955).

2/2

Voyevodskiy, V.V.

AID 816 - S

AF701597

TREASURE ISLAND BOOK REVIEW

VOYEVODSKIY, V. V. (Institute of Chemical Physics, Academy of Sciences, USSR)  
DISKUSSIYA (Discussion). In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vol. 8. Izdatel'stvo Akademii Nauk SSSR, 1955. Section II: General problems on the theory of catalysis. p. 154-155.

In reply to his opponents, Voyevodskiy states that his theoretical explanation of catalysis by chain reactions, though in need of experimental or theoretical confirmation introduced clarity into the mechanism of heterogeneous catalysis. The further study of the chain theory of heterogeneous catalysis should be concerned with:

1. the properties and structure of active heterogeneous compounds and
2. the kinetics of catalytic processes.

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VOYEVODSKIY, V. V. and TIKHOMIROVA, N. N.

"Determination of the Velocity Constants of the Reaction of Hydrogen Atoms with Hydrocarbons at Increased Temperatures," pp. 172-186 of the book Chain Reactions of Oxidation of Hydrocarbons in the Gas Phase, AS USSR, Moscow, 1955.

Translation 1071268

VOYEVODSKIY, V.V.

*Chem*

✓ The role of free valencies in heterogeneous catalysis. V. V. Voevodskii, P. F. Vol'kenstein and N. N. Bogdanov. *Voprosy Khim. Khimich. Reaktivnoi Spetsiatsii, Akad. Nauk S.S.S.R.* 1955, 423-40. A preliminary sketch of the principal features of a theory of catalysis. A catalyst crystal can be viewed as a single giant mol. that affects heterogeneous reactions in a way similar to that of free radicals in homogeneous reactions. In both cases, reactions proceed by essentially similar mechanisms. In all catalytic reactions the process is caused and directed by free valencies, and the catalyst plays a role not unlike that of a "radical". The phys. nature of free valencies on the catalyst crystal surface, and the different bond types between the adsorbed atoms and the crystal surface are discussed. The reaction mechanisms are based on the participation in the reactions of free valencies and of the heterogeneous radicals formed during the process on the catalyst surface. The introduction of a chain catalysis mechanism gives a novel explanation of the mechanism of acceleration caused by the catalyst. This acceleration may be a result of formation of free valencies that causes chain generation on the catalyst at much higher velocities than in the gas phase. A 2nd catalyst function may consist in the formation of heterogeneous radicals on the crystal surface, by way of which chain-growth reactions are realized. The chain-growth may frequently be impeded by the high endothermicity of the compds. formed in the elementary stages. When the chain development via the heterogeneous radicals happens to be energetically more probable, catalysts can greatly accelerate the process. A complete absence of information with regard to bond energies of single atoms and of at. groups with the catalyst may be the principal difficulty that at present interferes with the evaluation of velocity relations in elementary heterogeneous radical reactions. A rough evaluation of the heats of reactions at elementary stages makes such stages appear probable, but any concrete schemes must still be considered purely hypothetical.

W. Li. Sternberg

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*PM*

VOYEVOODSKIY, V.V.

USSR.

✓2645

MICRO METHOD OF ANALYSIS FOR HEAVY WATER. B.

E. Mardalishvili, L. S. Litrovskaya and V. V. Voevodskii

(Moscow State Univ. Zhur. Fiz. Khim. 41:154-161, 1965)

Dec. In Russian

A compensation method of measuring vapor tensions for determining the D content of water is described. The D in 0.5 mg of water can be determined with an accuracy of 0.05 to 0.1 mole % (G.Y.)

(2)

*BMZ JSA*



Voyevodskiy V.V.

USSR/Kinetics - Combustion. Explosions. Topochemistry. Catalysis. B-9  
Abs Jour : Referat Zhur - Khimiya, No 6, 1957, 18564

Author : V.I. Tsvetkova, V.V. Voyevodskiy, N.M. Chirkov.  
Inst : Academy of Sciences of USSR. (*Inat. Chern. Physical*)  
Title : Kinetics of Slow Oxidation of Carbon Monoxide.

Orig Pub : Zh. fiz. khimii, 1955, 29, No 2, 380-389; in symposium  
Tsepnyye reaktsii uglevodorodov v gazovoy faze, M., AN  
SSSR, 1955, 161-171.

Abstract : The kinetic curves of CO oxidation at 450 to 630° and a pressure of 150 to 500 mm of mercury column in presence of steam or H<sub>2</sub> have a shape characteristic of non-ramified chain reactions. It is shown that H<sub>2</sub> catalyzes the reaction six times more than steam. The phenomenon of "saturation" of the mixture with steam and H<sub>2</sub> was disclosed; it consisted in that the reaction speed approached a constant magnitude when the contents of these substances in the mixture increased. The activation energy of the

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VOYEVODSKIY, V.V.

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat.Zhurnal Khimiya, No 3, 1958, 7186.

Author : R. Ye. Mardaleysvili, G.B. Pariyskiy, V.A. Poltorak,  
V.V. Voyevodskiy.

Inst : Academy of Sciences of USSR.

Title : Reaction of Deuterium Atoms with Alkenes. Dependence of Methane Deuterization on Concentration of Deuterium Atoms in System.

Orig Pub: Izv. AN SSSR. Otd. khim. n., 1956, No 5, 516-524.

Abstract: The exchange reaction of alkyl radicals with D<sub>2</sub> (RZh-Khim, 1956, 74392) was studied with the application of the mass-spectrometric analysis of D content in the being produced methane. The radicals were formed according to the reaction  $D + M \rightarrow R$ , where M was C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and iso-C<sub>4</sub>H<sub>8</sub>. In the cases of C<sub>2</sub>H<sub>4</sub> and iso-C<sub>4</sub>H<sub>8</sub>, the D content in methane increased,

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VOYEVODSKIY, V.V.

B-9

USSR/Physical Chemistry - Kinetics. Combustion.  
Explosives. Topochemistry. Catalysis

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 3774

Author : Voyevodskiy V.V.  
Title : Interchange of Free Alkyl Radicals with Molecular  
Deuterium

Orig Pub : Ukr. khim. zh., 1956, 22, No 1, 42-44

Abstract : There is proposed a new hypothetical elemental reaction of isomerization of alkyl radicals in beta-position, with formation of a hydrogen bridge, which supplements the author's notions concerning the mechanism of interchange and isomerization of free radicals (RZhKhim, 1956, 74392).

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CHIRKOV, N.M.; VOEVODSKIY, V.V.

Nikolai Nikolaevich Semenov, founder of the theory of chain reactions; on the 60th anniversary of his birth. N.M. Chirkov, V.V. Voevodskii. Zhur.fiz.khim. 30 no.4:722 Apr. '56. (MLRA 9:9)

(Semenov, Nikolai Nikolaevich, 1893-)

V. VOYEVODSKIY, V.V.

B-4

USSR/Physical Chemistry - Molecule. Chemical Bond

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 3462

Author : Vedeneyev V.I., Voyevodskiy V.V.

Title : Cleavage Energy of C - Cl Bonds of Different Chlorides

Orig Pub : Zh. fiz. Khimii, 1956, 30, No 4, 789-793

Abstract : Fulfillment of the correlation  $E_i = \alpha - \beta D_i(1)$ , wherein  $E_i$  -- energy of activation of exothermic reaction,  $D_i$  -- cleavage energy of  $R_1X$  molecule ( $R_1$  -- alkyl radical), and  $\alpha$  and  $\beta$  -- constants, is illustrated by several examples. Equation (1) is used to calculate the cleavage energy of C - Cl bonds on the basis of known values of  $D(C_2H_5-Cl)$  and  $D(CH_3-Cl)$ . Calculated values of cleavage energy are in satisfactory agreement with the available experimental values. The conclusion is drawn that equation (1) can be utilized to evaluate the cleavage energy values of bonds on the basis of known values of energy of activation, and vice versa.

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WZKUCISKY, T. V.



VOYEVODSKIY, V. V.

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.  
Catalysis, B-9.

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 390

Author: Voyevodskiy, V. V., and Kabachnik, M. I.

Institution: ~~None~~

Title: On Completing the Reactions Involving Isomerically Active Particles

Original

Periodical: Zh. fiz. khimii, 1956, Vol 30, No 4, 945-948

Abstract: On the basis of the Polanyi relations for single-type free radical reactions, it is shown that whenever during a chemical reaction the formation of free radicals which are sufficiently rapidly interconvertible is possible, the direction of the reaction will be determined preferentially by the most stable of these radicals. Its reduced chemical activity is compensated by its considerably greater concentration.

Card 1/1

VOYEVODSKIY, V.V.; VEDENEYEV, V.I.

Possible mechanism of degenerated branching in hydrocarbon  
oxidation reactions. Dokl. AN SSSR 106 no.4:679-682 P 156.  
(MLRA 9:6)

1. Institut khimicheskoy fiziki Akademii nauk SSSR Moskovskiy  
gosudarstvennyy universitet imeni M.V. Lomonosova.  
(Hydrocarbons) (Oxidation)

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**VOYEVODSKIY, V. V.**  
USSR/Physical Chemistry - Kinetics, Combustion, Explosions,  
Topochemistry, Catalysis.

B-9

Abs Jour : Referat Zhur - Khimiya, No 1, 1958, 501  
Author : V.V. Voyevodskiy.  
Inst :  
Title : Heterogeneous Catalysis and Chain Processes.  
Orig Pub : Khim. nauka i prom-st', 1957, 2, No 2, 160-166  
Abstract : Review.  
Bibliography with 14 titles.

Card 1/1

~~VOYEVODSKIY, V.V.~~

Mechanism of homogeneous and heterogeneous homolytic deuterium  
exchange. Probl. kin. i kat. 9:33-44 '57. (MIRA 11:3)  
(Deuterium) (Catalysis)

20-114-5-36/54

AUTHORS: Lyadova, Yu. I., Vedeneyev, V. I.,  
Voyevodskiy, V. V.

TITLE: Investigation of the Kinetics and the Mechanism of the  
Thermal Decomposition of Isobutylene (Issledovaniye  
kinetiki i mekhanizma termicheskogo raspada izobutilena).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 114, Nr 6, pp. 1269-1271 (USSR)

ABSTRACT: The third author (references 1,2) suggested a chain-reaction of the thermal decomposition of olefines which is based upon the redistribution of the H-atom between a radical of the allyl-type and the olefine-molecule, where an alkyl radical and a diene develop. He succeeded in determining from this point of view the composition of the products of this composition of olefines of various structure. It was, however, not possible to extend these conceptions to the cracking of such simple olefines as  $C_3H_6$  and  $i-C_4H_8$ , as no H-atoms capable of redistribution reactions exist in the allyl-radicals developing of it. In another paper (reference 2) the third author advocated the opinion that in the case of the two above-mentioned olefines the formation of the reaction products is always preceded by an addition

Card 1/4

Investigation of the Kinetics and the Mechanism of the Thermal  
Decomposition of Isobutylene

20-114-6-36/54

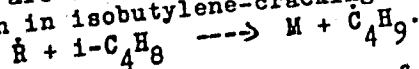
of the allyl-radical to the double bond of the olefine. The authors intended to obtain additional data on the chain character of this decomposition as well as to check the hypothesis concerning the transfer of the H-atom to the olefine double bond. The cracking of isobutylene was studied at between 542 and 620° and at a pressure of 100-500 mm torr. Furthermore experiments with a mixture of  $i\text{-C}_4\text{H}_8$  and  $\text{C}_2\text{H}_4$  were made at 542-600° and 200-600 mm pressure. The thermo-chromatical gas-analysis showed that the main products (gases) of the isobutylene-cracking are  $\text{C}_3\text{H}_6$ ,  $\text{CH}_4$ ,  $i\text{-C}_4\text{H}_{10}$ ,  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  beside small quantities of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ . Figures 1 and 2 show the modification of the composition of these gases with a modification of pressure, as well as the percentage of conversion. The extrapolation of the curves which describe the dependence of the composition of the gas products on the percentage of conversion to the zero-percentage of the conversion makes it possible to determine the primary reaction-products and their relations. From the cracking of  $i\text{-C}_4\text{H}_8$  up to 10% isobutane is obtained

Card 2/4

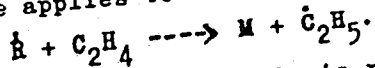
Investigation of the Kinetics and the Mechanism of the Thermal Decomposition of Isobutylene 20-111-536/54

as one of the primary products. This quantity increases with increasing pressure and with decreasing temperature. This shows that the addition reaction of the H-atom to the double bond of isobutylene takes place under the conditions given here. In order to further determine the problem of the transfer of the H-atom to the olefine double bond, the cracking of mixtures of  $i-C_4H_8$  with  $C_2H_4$  was studied. The

results in table 1 permit the following conclusions:  
1) They confirm the conception on the chain mechanism of the reaction. On the other hand the development of ethane in large quantities furnishes another proof that the transfer reaction of the H-atom to the olefine double bond is possible. The authors are of opinion that their tests confirm the assumed reaction in isobutylene-crackings:



The same applies to the mixture of isobutylene-ethylene:



The comparison of the analysis results of the primary gas



20-114-6-36/54

Investigation of the Kinetics and the Thermal  
Decomposition of Isobutylene

products and the composition of the liquids leads to the conclusion that the cracking-scheme suggested by the third author of  $C_3H_6$  and  $i-C_4H_8$  is insufficient. New ways of the transformation of the radical  $i-C_4H_7$  must be introduced to this scheme. The decomposition to  $\dot{C}H_3$  and "allene" may be supposed as such, as well as the transfer reaction of the methyl-radical from  $i-C_4H_7$  to the isobutylene molecule. Allene-formation was observed in the cracking of isobutylene (reference 4). Under the conditions given here it is, however, unstable and completely disappears from the gas phase during the duration of test. There are 2 figures, 1 table, and 5 references, 2 of which are Slavic.

ASSOCIATION: Institute for Chemical Physics AS USSR (Institut khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: January 14, 1957, by N. N. Semenov, Academician

SUBMITTED: January 12, 1957

AT: Library of ...

Card 4/4

VOYEVODSKIY, V. V.

20-1-32/54

AUTHOR

TSETKOV YU. D., VOYEVODSKIY V. V., RAZUVAYEV G. A.,  
SOROKIN Yu. V., DOMRACHEV G. A.

TITLE

Electron Spin Resonance in Some Sandwich Type Chromaromatic Compounds.  
(Elektronnyy paramagnitnyy rezonans v nekotorykh khromaromaticheskikh soyedineniyakh sandvichevogo stroyeniya -Russian)  
Doklady Akad. Nauk SSSR, 1957, Vol 115, Nr 1, pp 118- 121 (U.S.S.R.)

PERIODICAL

ABSTRACT

In recent times increased interest was devoted to the study of the mentioned compounds of the ferrocene type,  $(Fe(C_5H_5)_2)$ , the ferrocene ion and analogous molecules with aromatic addenda. In spite of a great number of papers on this subject, there hitherto exists no general theory which might explain the present data on the "sandwich" structure of these molecules. Their formation and steadiness cannot be fully explained by the generally accepted conception of valence. The data obtained indicate that in the majority of compounds of this type the linkage of addenda with the complex-forming atoms is of a covalent character. This is especially indicated by magnetic measurements. According to the latter these materials are either diamagnetic or they possess a magnetic momentum which corresponds to one, two or at most three non-paired electrons. The ion salts of these metals of such compounds by the method of electronic paramagnetic resonance (called EPR in the following) have hitherto been described in publications. The present paper gives measurements of the EPR spectra of the following compounds:  $Cr(C_6H_6)_2J$  (I),  $Cr(C_6H_5)_2J$  (II) and  $Cr(C_6H_5 - C_6H_5 - C_6H_5)_2OC_6H_5$  (III). The static magnetic susceptibility

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Electron Spin Resonance in Some Sandwich Type Chromo- 207-1-32/54  
matic Compounds.

of these materials corresponds to a single- non-coupled electron. The presence of a hydrogen-overrefined structure of the absorption line in solutions of the materials II and III can be explained in two ways. 1. The non-coupled electron and the positive charge of the complex are located on the chromium atom. The estimation made on the basis of this assumption shows that the density of the non-coupled 3d-electron on the positions of the hydrogen atoms of the aromatic rings is sufficient to effect an "overrefined" cleavage of the EPR spectrum. 2. The non-coupled electron and the positive charge are located on the aromatic addenda of the complex. The overrefined structure is in this case due to the interaction of the non-paired  $\pi$ -electron of the aromatic ring with the hydrogen atoms of this ring. The extent of cleavage, the number of components and the ratio of their intensities are in this case dependent on the distribution of electron density on the addenda molecule. The following facts speak in favor of the first assumption: a) presence of the anisotropy of the g-factor in the materials I and II, b) the value of the g-factor is less than that of a free electron. The true picture of density distribution of the non-coupled electron is probably a superposition of the two extreme cases mentioned above. (2 illustrations, 2 Slavic references.)

Card 2/3

*Inst. Chem. Physics AS USSR; Gor'kiy State Univ.*

VOYEVODSKIY, V. V.

AUTHORS:

Kazanskiy, V. B., Voyevodskiy, V. V.

20-4-29/51

TITLE:

Note on the Rôle of Hydrogen Atoms in the Catalytic  
Oxydation of Hydrogen on Palladium (O roli atomov vodoroda  
v reaktsii kataliticheskogo okisleniya vodoroda na palladii).

PERIODICAL:

Doklady AN SSSR, 1957, Vol. 116, Nr 4, pp. 633-636 (USSR)

ABSTRACT:

Wagner (Vagner) and Hauffe (Khauffe) (reference 2) investigated the mechanism of the catalytic oxydation of hydrogen on metallic palladium by comparing the stationary concentration of hydrogen atoms at the surface of the catalysator with the concentration corresponding to equilibrium. On this occasion the authors established, that a chain-like mechanism of this reaction is possible. The authors of this paper examined the final conclusions by Wagner (Vagner) and Hauffe (Khauffe) by an independent method, using a different experimental procedure. According to modern conceptions a dissociation of the hydrogen molecules at the surface of the metal takes place in the adsorption and dissolution of hydrogen in metallic palladium, resulting in the formation of adsorbed atoms. The solution

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Note on the Role of Hydrogen Atoms in the Catalytic  
Oxydation of Hydrogen on Palladium

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and diffusion of hydrogen within the metal apparently takes place in the form of ions. The authors compared the stationary concentration of the hydrogen atoms on the surface of the palladium with the concentration corresponding to equilibrium with the help of a diffusion process in a vacuum circulation apparatus. A capillary tube consisting of palladium served as a catalysator. The numerical data of the experimental arrangement are given here, and the occurrence of the experiments is explained. The results from some of the experiments of the authors are compiled in a table. According to these data the stationary concentration of the hydrogen atoms in the reaction zone is considerably smaller than the concentration corresponding to equilibrium. For the purpose of a more precise investigation of the mechanism of the reaction, the authors computed the deviation of the stationary concentration of the hydrogen atoms at the surface of the catalysator from the equilibrium concentration with the assumption of a radical mechanism. The data computed in this way were then compared with the experiment. Oxygen does not modify the mechanism of this reaction. The

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Note on the Role of Hydrogen Atoms in the Catalytic  
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good accordance of the experimental data with the computed values speaks in favour of the radical mechanism of the oxydation of hydrogen on metallic palladium. The data obtained here without doubt speak for the fact, that in the case of palladium the reaction takes place with an interaction between the hydrogen atoms adsorbed at the surface of the catalysator and oxygen.

There are 1 figure , 2 tables, and 11 references, 5 of which are Slavic.

ASSOCIATION: Moscow State University imeni M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosov), Institute for Chemical Physics AN USSR (Institut khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: April 12, 1957, by N. N. Semenov, Academician

SUBMITTED: April 5, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/51-5-1-17/19

AUTHORS:

Voyevodskiy, V.V., Molin, Ya.N. and Chibrikov, V.M.

TITLE:

Electron Paramagnetic Resonance Spectra of Cr-Aromatic Compounds with Various Substituents (Spektry elektronnoye paramagnitnoye rezonansa Cr-aromaticheskikh soedineniy s razlichnyimi zamestitelnyami)

PERIODICAL:

Optika i Spektroskopiya, 1958. Vol 5, Nr 1, pp 90-92 (USSR)

ABSTRACT:

The present note reports continuation of the work described in Ref 1-2 on electron paramagnetic resonance spectra of solutions of  $(C_6H_5)_2CrI$ ,  $(C_6H_5 \cdot C_6H_{11})_2CrI$ ,  $(C_6H_5 \cdot C_6H_5)(C_6H_5)CrI$  and  $(C_6H_5 \cdot C_6H_5)_2CrI$ . These compounds are denoted I, II, III and IV respectively in the present note. The purpose of the work was to find the effect of substitution of the distribution of density of unpaired electrons. Isopropyl alcohol, acetone, pyridine and water were used as solvents. All measurements were made at room temperature using a spectrometer working at 9300 Mc/s. The modulation depth of the magnetic field was 2 Oe. The g-factor, the total line-width in Oe, the separation of the hyperfine structure components ( $\Delta H$ ) and the number of resolved hyperfine structure (h.f.s.) components for the compounds I-IV in isopropyl alcohol are given in the table

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Electron Paramagnetic Resonance Spectra of Cr-Aromatic Compounds with Various Substituents

on p 91. The consistency of g and ΔH in the series of compounds I-IV indicates that introduction of a substituent into the benzene ring does not materially change the distribution of density of unpaired electrons between Cr and the benzene rings. Improvement of the resolution of the spectra (see the figure on p 92) on going from the compound I to the compound IV was observed. The authors make the following conclusions. (1) In dilute solutions the h.f.s. component width ceases to depend on concentration below a certain concentration which is different for different solvents. (2) The width of h.f.s. components in dilute solutions depends on the nature of the solvent. (3) On increase of the solution concentration the h.f.s. disappears at different concentrations in different solvents. The main reason for the disappearance of the h.f.s. is the exchange interaction between paramagnetic particles. The authors thank Professor G.A. Razuvaev (Gor'kiy Institute of Organic Chemistry) and Professor F. Hein (Institute of Inorganic Chemistry, Jena, Eastern Germany) for supply of the compounds studied. There are 1 figure, 1 table and 5 references, 3 of which are American and 2 Soviet.

Card 2/2

ASSOCIATION: Institut khimicheskoy fiziki, AN SSSR (Institute of Chemical Physics, Academy of Sciences of the U.S.S.R.) 1. Metalorganic compounds-Spectro-  
SUBMITTED: January 27, 1958 graphic analysis 2. Metalorganic compounds-Magnetic properties 3. Cyclic compounds-Properties 4. Chromium iodine compounds-Properties



VOYEVODSKIY, V.V.

57-1-19/30

AUTHOR: Molin, Yu. N., Voyevodskiy, V. V.

TITLE: Investigation of Action of the Ionizing Radiation on Quartz by the Method of Electron Paramagnetic Resonance (Issledovaniye vozdeystviya ioniziruyushchego izlucheniya na kvarts metodom elektronnoogo paramagnitnogo rezonansa)

PERIODICAL: Zhurnal Tekhnicheskoy Fiziki, 1958, Vol. 28, Nr 1, pp. 143-149 (USSR)

ABSTRACT: The investigation of the paramagnetic resonance absorption was carried out on a spectrometer of the Superheterodyn type with 9.300 mc and of a sensitivity of  $5 \cdot 10^{14}$  of the diphenylpicrylhydrazil - (DFPH) - radical-particle. (ref. 10, 11.) The samples of the crystalline quartz are produced of rock crystal.

The quartz samples were irradiated with  $\gamma$ -rays of  $Co^{60}$ . Irradiation and measuring were carried out at room temperature. On the occasion of the investigation of the temperature influence on the behaviour of the defects the samples were heated in the electric furnace (outside of the resonator). Molten quartz which has been irradiated with  $\gamma$ -rays and crystalline quartz irradiated with  $\gamma$ -rays and neutrons were investigated. The molten quartz which had

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Investigation of Action of the Ionizing Radiation on  
Quartz by the Method of Electron Paramagnetic Resonance

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not been irradiated gave no signals of paramagnetic absorption. On the occasion of irradiation the quartz became violet and showed two absorption lines. These lines are called  $\alpha$  and  $\beta$  signals according to their sequence in the magnetic field. The paramagnetic centres which give the  $\alpha$  and  $\beta$  signals are here called  $\alpha$  and  $\beta$  defects. The  $\alpha$  signal showed no sign of saturation. Saturation of the  $\beta$  signals occurred without change of the signal. Width and shape of the  $\beta$  signal seem to be due to the anisotropy of the  $g$ -factor. The shape of the saturation curve of the  $\beta$ -signal was analysed according to the methods described in Refs 13 and 14 and a value of the order of magnitude of  $10^{-5}$  sek was obtained for the time of the spin-lattice-relaxation  $T_1$ . The investigation of the dependence of the concentration of the  $\alpha$  and  $\beta$ -defects on the irradiation dose showed that in the case of doses of an order of magnitude of  $10^7$  the defect concentration reaches saturation. In the first part of the curve the concentration of the  $\beta$ -defect is proportional to the square root of the irradiation dose. Because of insufficient accuracy of the spectrometer the first section of the curve for the  $\alpha$ -effect

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Investigation of Action of the Ionizing Radiation on  
Quartz by the Method of Electron Paramagnetic Resonance

could not be recorded. In accordance with ref. 7 and 8 it could be observed that on the occasion of the heating of the irradiated molten quartz up to 300 and 400°C it turned from violet into blue. The heating was accompanied by changes in the spectrum of the paramagnetic absorption. It could be observed that when the  $\alpha$ -signal disappears the  $\beta$ -signal increases simultaneously. The initial concentration of the  $\alpha$ -defects is about three times greater than that of the  $\beta$ -defects. The grinding of irradiated quartz into powder does not change the intensity of the  $\alpha$  and  $\beta$ -signals. It influences, however, the behaviour of the  $\beta$ -signal on the occasion of heating. Due to the grinding the temperature at which the  $\beta$ -defect disappears changes by 350°. The following was observed on the occasion of the investigation of crystalline quartz:

- 1) The monocrystal gave no signal of paramagnetic absorption after irradiation with  $\gamma$ -rays ( $10^7$  röntgen), neither at room temperature nor at the temperature of liquid nitrogen.
- 2) At the same irradiation fine polycrystalline powder gave a weak signal which as to its shape and position on

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Investigation of Action of the Ionizing Radiation on  
Quartz by the Method of Electron Paramagnetic Resonance

57-1-19/30

the spectrum was similar to the  $\beta$ -signal in molten quartz. In the case of great amplitudes of the radiation-frequency-field this signal "saturated" like the  $\beta$ -signal. 3) After irradiation by means of a nuclear reactor ( $\gamma$ -rays, neutrons) the monocrystal gave the same signal as in case 2, it was only somewhat more intense. Besides, some weak signals were observed in the range of  $g \approx 2$ . The dependence of the concentration of the  $\beta$ -defects on the irradiation dose observed here, can be explained by considering the finite number of traps and by taking into consideration that simultaneously with the process of capturing of free electrons and holes through the traps also processes of recombination of free electrons with the captured holes and of the free holes with the captured electrons occur. It is presumed that paramagnetic absorption in irradiated quartz is due to the electrons and holes captured by the structural defects. A simple table is given on the basis of which the fundamental qualitative rules of the accumulation-kinetics of paramagnetic defects can be explained. The behaviour of the  $\alpha$  and  $\beta$ -defects on the occasion of heating can equally be explained on the basis

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Investigation of Action of the Ionizing Radiation on  
Quartz by the Method of Electron Paramagnetic Resonance

57-1-19/30

of this model. There are 6 figures, and 14 references,  
1 of which is Slavic.

ASSOCIATION: Institute for Chemical Physics AN USSR Moscow  
(Institut khimicheskoy fiziki AN SSSR Moskva)

SUBMITTED: May 3, 1957

AVAILABLE: Library of Congress

Card 5/5

20-118-6-26/43

**AUTHORS:** Ivanov, O. A., Fok, N. V.,  
Voyevodskiy, V. V.

**TITLE:** Reaction Between Methyl Radicals Obtained According to the  
Method of Polanyi and Deuterium (Reaktsiya metil'nykh  
radikalov, poluchennykh po metodu Polyani, s deyeriyem)

**PERIODICAL:** Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 6,  
pp. 1142-1145 (USSR)

**ABSTRACT:** First previous papers dealing with the same subject are  
shortly referred to. The authors produced the methyl radicals  
according to the method of Polanyi (Polyani) according to the  
reaction  $\text{CH}_3\text{J} + \text{Na} = \text{CH}_3 + \text{NaJ}$ . The reaction passed in presence  
of molecular deuterium which was used as carrier gas for sodium  
vapors. The scheme of the experimental arrangement is  
illustrated in a figure. The reaction container in which the  
jets of  $\text{CH}_3\text{J}$  combine with those of deuterium consisted of a  
quartz cylinder with a nozzle. In one series of experiments  
the inner surface of the reaction container was covered with  
sodium which was applied in form of drops or as reflecting

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20-118-6-26/43

Reaction Between Methyl Radicals Obtained According to the Method  
of Polyani and Deuterium

coating. The deuterium used for the experiments was produced electrolytically from  $D_2O$ . The authors detected the composition of the methanes obtained in a pure quartz container in the temperature interval of from 20-480°C. Under these conditions mainly  $CH_4$  and  $CH_3D$  are obtained. The quantity of the semi-deuterized methanes is small and reaches the value 18-20% only in a small temperature interval near 200°C. The ratio  $CH_3D/CH_4$  increases in the interval of from 20-100°C from 0,6 to 2, and remains constant in the case of further temperature rise. The deuterium content in the investigated methanes is considerably changed in the case of a deposit of metallic sodium on the surface of the container. Here the connection between the portion of the different deuterized methanes and the temperature depends on the kind of applying of sodium to the surface. In covering the container surface with a reflecting sodium the percentage of to a great extent deuterized methanes ( $CD_4$ ,  $CD_3H$

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20-118-6-26/43

Reaction Between Methyl Radicals Obtained According to the Method  
of Polyani and Deuterium

and  $CD_2H_2$ ) is at room temperature by 5 to 8 times greater than in a pure quartz container. In the case of a temperature rise the percentage of the to a great extent deuterized methanes decreases. In the case of sodium drops the surface reaction is insignificant and its portion of the volume of the methane produced amounts to totally only 1/5. Here the methanes obtained from the radicals  $CH_3$  contain much more deuterium than in the case of a reflecting coating sodium. The maximum of the deuterization at 70-80°C is striking. At higher temperatures  $CH_4$  and  $CH_3D$  predominate again. In the case of sodium drops the light methane is not exchanged with  $D_2$  as it is the case in the case of existence of a reflecting coating. This exchange has to take place with participation of the methyl radicals independently of the kind of mechanism of the production of  $CH_2D_2$ ,  $CH_3D$  and  $CD_4$ .

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20-118-6-26/h

Reaction Between Methyl Radicals Obtained According to the Method  
of Polyani and Deuterium

There are 3 figures and 8 references, 3 of which are Soviet.

ASSOCIATION: Kafedra khimicheskoy kinetiki Moskovskogo gosudarstvennogo  
universiteta im. M. V. Lomonosova  
(Chair of Chemical Kinetics, Moscow State University  
imeni M. V. Lomonosov )  
Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute of Chemical Physics, AS USSR)

PRESENTED: July 26, 1957, by N. N. Semenov, Member, Academy of Sciences  
of USSR

SUBMITTED: July 19, 1957

Card 4/4

AUTHORS:

Chernyak, N. Ya., Bubnov, N. N.,  
Voyevodskiy, V. V., Polak, L. S., Tsvetkov, Yu. D.

SOV/20-120-2-34/63

TITLE:

The Formation of Free Radicals and of Atoms in the Radiolysis of Hydrocarbons at a Temperature of 77°K (Ob obrazovanii svobodnykh radikalov i atomov pri radiolize uglevodorodov pri temperature 77°K)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 2, pp. 346 - 348 (USSR)

ABSTRACT:

References are made in publications to free radicals formed during the action of ionizing radiation, as by X-rays,  $\gamma$ -radiation, fast electrons etc. This is caused by a rupture of C - C and of C - H bindings. When fluid hydrocarbons are radiolysed, the life of the free radicals is very short. The main products of radiolysis, apart from liquid products with one or two conjugated double bindings, are  $H_2$  and  $C_{14}H_{30}$ . The latter compound is considered to be a dimer of the heptyl radical. The method of determining the radical is shortly described. The following hydrocarbons were investigated: hexane,

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The Formation of Free Radicals and of Atoms in the  
Radiolysis of Hydrocarbons at a Temperature of 77°K

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heptane, octane, dodecane, cetane, isooctane, cyclohexane, benzene and toluene. In all cases intensive signals of paramagnetic electron resonance with a g-factor of  $\sim 2,0$  are observed. In paraffin-type hydrocarbons and in cyclohexane a hyperfine structure was very clearly observed. According to the attached photographs the hyperfine structure is considerably changed if the structural properties of the initial molecule change. Another peculiarity of the spectra of paramagnetic electron resonance of the hydrocarbons which are irradiated in a frozen state is the existence of considerable concentrations of hydrogen atoms. This is also indicated by two narrow signals which are located symmetrically at a distance of about 250 Oersted (Ersted) from the signals of the alkyl radical. The hydrogen atoms probably do not become stabilized in the volume of the frozen hydrocarbons but on the internal surface of the quartz ampoule. In a table the quantitative measurements performed on the basis of the example of heptane concerning the concentration of the free radicals with a dose of  $\sim 10^7$ r are compared with the data of the chemical analysis of a sample irradiated under absolutely identical conditions. The results

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The Formation of Free Radicals and of Atoms in the  
Radiolysis of Hydrocarbons at a Temperature of 77°K

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obtained by both measurements agree in a satisfactory manner.  
There are 2 figures, 1 table, and 4 references, 2 of which are  
Soviet.

ASSOCIATION: Institut nefti AN SSSR (Petroleum Institute, AS USSR) Institut  
khimicheskoy fiziki, AN SSSR (Institute of Chemical Physics  
AS USSR)

SUBMITTED: January 11, 1958

1. Hydrocarbons--Temperature factors    2. Free radicals  
--Production    3. Atoms--Production    4. Hydrocarbons  
--Test results

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SOV/20-122-2-27/42

5(4)  
AUTHORS:

Tikhomirova, N. N., Lukin, B. V., Razumova, L. L.,  
Voyevodskiy, V. V., Corresponding Member, Academy of Sciences,  
USSR

TITLE:

Using Electron Paramagnetic Resonance and Roentgenography in  
Studying the Structure of the Carbonization Products Obtained  
From Carbon-Containing Substances

(Issledovaniye stroyeniya produktov karbonizatsii  
uglerodsoderzhashchikh veshchestv metodom elektronnoogo para-  
magnitnogo rezonansa i rentgenografiyey)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 2, pp 264-266  
(USSR)

ABSTRACT:

The method of paramagnetic electron resonance permits im-  
mediate detection of free radicals in the investigated system  
and a measurement of their concentration. In order to find  
the possibilities which are given by the investigation of  
the structure of carbonized substances by the  
method of paramagnetic electron resonance (and simultaneous-  
ly by radiography), the authors investigated the structural  
variations caused by the carbonization of polyvinyl chloride

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SOV/20-122-2-27/42

Using Electron Paramagnetic Resonance and Roentgenography in Studying the Structure of the Carbonization Products Obtained From Carbon-Containing Substances

and polyvinylidenechloride. The carbonization was carried out in an inert atmosphere in the temperature interval of 350-700°C. The signal of the electron paramagnetic resonance (which indicates the existence of free radicals) appears in the first stages of the carbonization of polyvinyl chloride and polyvinylidenechloride (beginning with 350°). A diagram shows the variation of the signal width for the 2 investigated substances as a function of the carbonization temperature. A relatively wide line (7 Gauss) in polyvinyl chloride is an argument in favor of an essential influence of the hyperfine splitting up on hydrogen nuclei. Such great widths are characteristic of some natural coals. In the case of polyvinylidenechloride (especially in the initial stages of carbonization) the line of paramagnetic electron resonance is by far narrower than that of the product of the carbonization of polyvinyl chloride. According to radiographic data, an increase of the calcination temperature to 450° only slightly changes the character of the products of the carbonization of polyvinyl chloride. Other results are then discussed.

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Using Electron Paramagnetic Resonance and Roentgenography in Studying the Structure of the Carbonization Products Obtained From Carbon-Containing Substances

According to these results, the appearing of a wide signal is connected with the existence of free valences near the individual carbon nets or blocks in which conduction electrons appear. There are 2 figures.

SUBMITTED: June 28, 1958

Card 3/3

5(4)

SOV/20-122-6-27/49

AUTHORS:

Tsvetkov, Yu. D., Bubnov, N. N., Makul'skiy, H. A.,  
Lazurkin, Yu. S., Voyevodskiy, V. V., Corresponding Member,  
AS USSR

TITLE:

The Investigation of the Spectra of the Electron Paramagnetic  
Resonance of Some Polymers Which Were Irradiated at 77°K  
(Issledovaniye spektrov e.p.r. nekotorykh polimerov, obluchennykh  
pri 77°K)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 6, pp 1053-1056  
(USSR)

ABSTRACT:

The authors carried out the above investigation for the purpose of solving several problems connected with the structure and chemical behavior of organic radicals in the solid phase as well as with the mechanism of chemical transformations in solid organic bodies under the influence of ionizing radiation. Polyethylene, polyvinyl chloride, "Teflon" (polyethylene tetrafluoride), polydimethyl siloxane, polyisobutylene, polymethyl methacrylate and natural rubber were investigated. Carrying out of the experiments is described in short. At 77°K a very intensive signal of paramagnetic electron resonance

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The Investigation of the Spectra of the Electron Paramagnetic Resonance of Some Polymers Which Were Irradiated at 77°K

with a g-factor near 2.0036 was observed in all samples. After "thawing" of the sample down to room temperature the signal was in all cases found to change. In some cases, the signal vanished completely as a result of "thawing" (polyisobutylene, polydimethyl siloxane, natural rubber). In the case of other materials the character of the signal and its fine structure changed considerably. A comparison of all data obtained gave the following result: The character of the spectra obtained by investigating not "thawed" samples can be fully explained by the assumption that the predominant primary chemical act in irradiation is the stripping of one of the C-H bonds in the main chain (or in the absence of a main chain the stripping of a C-H bond in a lateral chain). The spectrum of paramagnetic electron resonance recorded at 77°K consists of 6 components. The even number of the spectrum in this as well as in other cases is connected with the formation of the radical  $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$ . The authors then discuss several details, especially such as concern the investigation of Teflon. By the irradiation of Teflon at low temperatures it is possible

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The Investigation of the Spectra of the Electron Paramagnetic Resonance of  
Some Polymers Which Were Irradiated at 77°K

to obtain materials with fully satisfactory mechanical  
properties. These substances contain a large quantity  
(~0.1 %) of free radicals. There are 2 figures and 7 ref-  
erences, 4 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute for Chemical Physics of the Academy of Sciences,  
USSR)

SUBMITTED: July 24, 1958

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SOV/20-123-2-23/50

5(1.3)  
AUTHORS:

Moiseyev, V. D., Lyadova, Yu. I., Vedeneyev, V. I., Heyman,  
M. B., Voyevodskiy, V. V., Corresponding Member, AS USSR

TITLE:

Ways of the Formation of Propylene and Ethylene in Isobutylene  
Cracking (Puti obrazovaniya propilena i etilena pri krekinge  
izobutilena)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 2, pp 292-294  
(USSR)

ABSTRACT:

As is known, up to 50% of the initial substance in thermal isobutylene decomposition are transformed into liquids (olefins, aromatic compounds). Apparently the polymerization of the initial olefin forms the first stage of the liquid formation, with dimeric and trimeric olefin being formed. The latter themselves are capable of being transformed in various ways with the final result being liquid cracking products. The ratio between carbon and hydrogen in these products is about 1 (Ref 2), whereas it is 2 in isobutylene. From this may be supposed that hydrogen and methane are separated in the formation of the liquids; in principle, also heavier cracking gases with 2 and 3 carbon atoms each in the molecule can be formed. The problem

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## Ways of the Formation of Propylene and Ethylene in Isobutylene Cracking

concerning the type and amount of the gases escaping from the liquids or in their formation is not investigated at all. Propylene is one of the main products of isobutylene cracking. If it were formed from isobutylene only, its formation velocity would decrease with the exhaustion of the isobutylene. If propylene is, however, formed from the liquid or from any other intermediate product of low stability (not from radicals), its formation velocity in the beginning of the reaction must be equal to zero, and then increase according to the law of successive reactions. If both ways of the formation of propylene are correct the two pictures must agree. This was the case in the present experiments. The change of the formation velocity of propylene was investigated by the isotopic kinetic method (Ref 3). Ye. D. Fedorov took part in the synthesis of the marked propylene (with  $C^{14}$  on the hydroxyl group). This propylene (15 torr) was subjected together with isobutylene (285 torr) to a cracking in vacuum at  $542^{\circ}$ . The course of the specific activity  $\alpha$  and of the  $C_3H_6$  concentrations are given in figure 1. Figure 2 gives the formation velocity of propylene  $w_1$ . In the

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## Ways of the Formation of Propylene and Ethylene in Isobutylene Cracking

beginning of the reactions this value  $w_1$  is not equal to zero; it increases during the first 10-12 minutes, i.e. to about 20% isobutylene transformation. This  $w_1$  increase tends to show that a considerable propylene amount in isobutylene cracking is not formed from isobutylene but from any intermediate products of the cracking, obviously from liquids. As may be seen from figure 2, the formation velocity of propylene passes a maximum within the range of 10-14 minutes and then decreases. The authors consider it to be premature to draw any conclusions. The ethylene activity determined in some experiments besides the specific activity of propylene is given in figure 3. As this activity is much lower than that of propylene, this tends to show that only part of the ethylene is formed from propylene. Also ethylene can be formed either from isobutylene directly or from liquids. Based on the experimental results obtained it is not possible to make a decision as to the way of formation prevailing. The fact that propylene is formed from liquids tends to show the possibility of the ethylene formation from the latter. There are 3 figures and 4 references, 2 of which are

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SOV/20-123-2-23/50

Ways of the Formation of Propylene and Ethylene in Isobutylene Cracking

Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of  
Chemical Physics, AS USSR)

SUBMITTED: July 28, 1958

Card 4/4

5(4)  
AUTHORS: Molin, Yu. N., Koritskiy, A. T., Buben, N. Ya.; Voyerodskiy, V.V.,  
Corresponding Member, Academy of Sciences, USSR

TITLE: The Investigation of Free Radicals Formed in Solid Bodies in  
the Process of Irradiation by Fast Electrons (Issledovaniye  
svobodnykh radikalov, obrazuyushchikhsya v tverdykh telakh  
v protsesse oblucheniya bystryimi elektronami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 5, pp 882-883  
(USSR)

ABSTRACT: The authors endeavored to detect radicals of short life-times  
in solid bodies formed by fast electrons. The present paper  
gives data concerning radicals of life-times of some minutes.  
The authors constructed an apparatus for the immediate re-  
cording of the spectrum of the paramagnetic electron resonance  
during the irradiation of the investigated specimen. Prepara-  
tion of the samples is discussed in short. The experiments  
were carried out at room temperature. The authors observed a  
signal of paramagnetic electron resonance during the irradia-  
tion of the specimen and after the interruption of the irradia-  
tion. More than 20 various substances were investigated,  
namely polymers (polyethylene, nylon, caprone, polymethyl

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SOV/20-123-5-31/50

The Investigation of Free Radicals Formed in Solid Bodies in the Process of Irradiation by Fast Electrons

metacrylate, teflon, and various specimens of rubber), solid organic acids and their salts (oxalic acid and their salts, succinic acid and their sodium salt, stearic acid and citric acid), aromatic compounds (naphthalene,  $\alpha$ -naphthol,  $\beta$ -naphthol, benzoyl peroxide, metol). In all the investigated samples, the concentration of the radicals reached saturation at doses of some dozens of megarad. In the case of the majority of the investigated substances, the produced radicals were rather stable, their life-time amounted to some hours (in some cases also to longer periods). Some details are given in short. During the irradiation of polyethylene, the authors could record the radical  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  which is not stable at room temperature. The spectrum of this radical is shown in a figure. According to measurements at temperatures below room temperature, the rate of conversion of the primary radical into the second one decreases with a decrease of temperature. There are 1 figure and 1 Soviet reference.

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The Investigation of Free Radicals Formed in Solid Bodies in the Process  
of Irradiation by Fast Electrons

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR  
(Institute of Chemical Physics o. the Academy of Sciences,  
USSR)

SUBMITTED: August 11, 1958

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VOEVODSKIY V. V.  
VOEVODSKIY, V. V.

"Low-Temperature Radical Reactions in Solid Bodies."

paper to be submitted Fourth Intl. Symposium on Free Radical Stabilization, Washington,  
D. C., 31 Aug - 2 Sep 1959.

Voyevodskiy, V.V.

The Chemical Society of the USSR held its annual meeting 28 Oct.-1 Nov. 1958 in Leipzig. The following papers were presented by the USSR delegation

F. Vilesov and A. Terzina - Physics Inst., Leningrad "Photoelektronische Katalyse der Oberfläche von Halbleiterkatalysatoren".

Ye. Shilov and A. Yarnikov - Inst. Organic Chemistry, AS USSR "Über den Mechanismus der katalytischen Wirkung von Aminosäuren in den Reaktionen der Carbonylverbindungen."

A. Shekhter - Inst. Scientific Information, AS USSR "Zur Elektronenmikroskopie heterogener Katalysatoren."

M. K. Lantsev - Inst. Chemical Physics, AS USSR "Homogene Katalyse auf Chemische Induktion bei Langsamen Oxydations-Kettenreaktionen."

A. Ye. Braunshcheyn - Inst. Biological & Medical Chemistry, AS USSR "Allgemeine Fragen der biologischen Katalyse im Licht der Wirkungsweise der Pyridoxalenzyme."

F. Vol'kenshteyn - Inst. Physical Chemistry, AS USSR "Zur Elektronentheorie der Chemisorption und Katalyse an Halbleitern."

V. Kozlovskiy and V. Voyevodskiy - Inst. Chemical Physics, AS USSR "Über den Mechanismus einiger katalytischer Reaktionen an Palladiummetall unter Beteiligung von Wasserstoff "orientiert"."

G. K. Borovkov - Serepov Physical-Chemical Inst., Moscow "Wechselwirkung zwischen Katalysator und Reaktionsystem."

A. A. Selandin - AS USSR "Zum Aufbau der Katalyse."

20: Известия Академии Наук СССР, Серия Химическая, 1959, № 1, 1-10.

KORITSKIY, A.T.; MOLIN, Yu.N.; SHAMSHEV, V.N.; BUBEN, N.Ya.;  
VOYEVODSKIY, V.V.

Study of radicals by means of electronic paramagnetic resonance during the irradiation of polyethylene by fast electrons. Vysokom.soed. 1 no.8:1182-1193 Ag '59.  
(MIRA 13:2)

1. Institut khimicheskoy fiziki AN SSSR.  
(Polyethylene) (Radicals(Chemistry))

TSVETKOV, Yu.D.; LEBNEDEV, Ya.S.; VOYEVODSKIY, V.V.

Free radical reactions in irradiated polytetrafluoroethylene.  
Part 1: Use of electron resonance (ER) in studying radical conversions and in the determination of the coefficient of diffusion of oxygen in polytetrafluoroethylene. Vysokom. soed. 1 no.10:1519-1525 0 '59. (MIRA 13:3)

1. Institut khimicheskoy fiziki AN SSSR.  
(Radicals(chemistry)) (Ethylene) (Oxygen)

TSVETIKOV, Yu.D.; LEBEDEV, Ya.S.; VOYEVODSKIY, V.V.

Reactions of free radicals in irradiated polytetrafluoroethylene.  
Part 2: Determination of the rate constants for the reactions  
 $RO_2 \rightarrow R + O_2$  and  $R + O_2 \rightarrow RO_2$ . Vysokom.soed. 1 no.11:1634-1642  
N '59. (MIRA 13:5)

1. Institut khimicheskoy fiziki AN SSSR.  
(Radicals (Chemistry) (Ethylene) (Oxygen)

TSVETKOV, Yu.D.; MOLIN, Yu.N.; VOYKOVODSKIY, V.V.

Electron resonance spectra of some irradiated polymers.  
Vysokom.soed. 1 no.12:1805-1811 D '59. (MIRA 13:5)

1. Institut khimicheskoy kinetiki i goreniya AN SSSR  
(Sibirskoye otdeleniye).  
(Polymers--Spectra)

SOV/51-6-4-26/29

24(7), 5(3)

AUTHORS:

Chernyak, N. Ya., Butnov, N.N., Polyak, L.S., Tsvetkov, Yu. D. and  
Voyevodskiy, V.V.

TITLE:

On Certain Regularities in the Electron Paramagnetic Resonance Spectra  
of Alkyl Radicals (O nekotorykh zakonomernostyakh v spektrakh  
elektronnogo paramagnitnogo rezonansa alkil'nykh radikalov)

PERIODICAL: Optika i Spektroskopiya, 1959, Vol 6, Nr 4, pp 564-565 (USSR)

ABSTRACT:

In the study of the electron paramagnetic resonance (e.p.r.) spectra of radicals formed on  $\gamma$ -irradiation of frozen hydrocarbons (at 77°K), it was found that the hyperfine structure (h.f.s.) varies with the position of the hydrocarbon in its homologous series. Fig 1 shows the spectra of radicals of normal paraffin hydrocarbons from  $C_{11}H_{23}$  to  $C_{16}H_{33}$  obtained under conditions described earlier (Ref 1). The samples were of 97-98% purity. Fig 1 shows that h.f.s. of the even ( $C_{12}H_{25}$ ,  $C_{14}H_{29}$ ,  $C_{16}H_{33}$ ) and odd ( $C_{11}H_{23}$ ,  $C_{13}H_{27}$ ,  $C_{15}H_{31}$ ) hydrocarbons differ considerably. In odd hydrocarbons the h.f.s. is well resolved and the intensities of the central components differ only slightly from one another. In even hydrocarbons the resolution is much poorer and the intensity distribution is close to binomial. In paraffin hydrocarbons from n-C<sub>5</sub> to n-C<sub>10</sub> the spectra are more complex and more similar to

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## On Certain Regularities in the Electron Paramagnetic Resonance Spectra of Alkyl Radicals

one another. Two of them are shown in Fig 2, where curves 1 and 2 represent the e.p.r. spectra of  $C_6H_{13}$  and  $C_7H_{15}$  respectively. The spectra of radicals of cyclic hydrocarbons (with five or six C atoms, shown in Fig 3) are in many respects similar to the corresponding spectra of the odd and even terms of the series  $C_{11}-C_{16}$ . The simplest spectrum is that of cyclo- $C_6$ . The hyperfine splitting and component intensities may be explained by assuming that the spectrum is a triplet (with 37 oversted splitting and 1:2:1 ratio of intensities of the components) and each components of the triplet is split into two lines (20 oversted separation). Such a spectrum occurs in the radical cyclo- $C_6H_{11}$ . Following Ingram (Ref 3) it is assumed here that of four hydrogen atoms in the  $\beta$ -position, the free valence, only two take part in the hyperfine splitting. This produces a triplet. Interaction with a hydrogen atom in the  $\alpha$ -position produces the doublet splitting of each triplet component. In the case of cyclo- $C_5H_{10}$  the molecule is almost planar and both hydrogen atoms of the  $\beta$ -groups  $CH_2$  in the radical should be equivalent with respect to free valence and the number of h.f.s. components should increase. The spectra shown in Fig 3 confirm these deductions. The authors conclude by pointing out that the e.p.r. spectra

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On Certain Regularities in the Electron Paramagnetic Resonance Spectra of Alkyl Radicals

can be used in molecular structure studies and in chemical analysis. There are 3 figures and 3 references, 2 of which are Soviet and 1 English.

SUBMITTED: August 28, 1958

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SOV/51-6-4-27/29

24(7), 21(1)

AUTHORS:

Bubnov, N.N., Voyevodskiy, V.V., Polyak, L.S. and Tsvetkov, Yu. D.

TITLE:

Electron Paramagnetic Resonance Spectrum of Hydrogen Atoms Stabilized on Solid Surfaces (O spektrakh elektronnoy paramagnitnoy rezonansy atomov vodoroda, stabilizirovannykh na tverdykh poverkhnostyakh)

PERIODICAL:

Optika i Spektroskopiya, 1959, Vol 6, Nr 4, pp 565-566 (USSR)

ABSTRACT:

It was reported (Refs. 1, 2) that H atoms, formed on  $\gamma$ -irradiation of frozen hydrocarbons and other compounds, can be stabilized on various surfaces. The present paper reports studies of the effect of the nature of the stabilizing surface on the magnitude of h.f.s. splitting of the electron paramagnetic resonance (e.p.r.) spectra of H atoms and the width of the e.p.r. absorption lines. The H atoms were stabilized on quartz, silica gel and molybdenum glass. They were formed by irradiation of these three substances with  $\gamma$ -rays at 77°K. It may be assumed that formation of H atoms is due to rupture of bonds in H<sub>2</sub>O molecules adsorbed on these surfaces or rupture of bonds in SiOH groups (Ref 3). The magnitude of h.f.s. splitting in all the three cases was found to be close to 500 oersted which does not differ greatly from splitting in a free H atom (Ref 4). Width of the components of the hydrogen doublet depends strongly on the nature of the surface: on

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Electron Paramagnetic Resonance Spectra of Hydrogen Atoms Stabilized on Solid Surfaces

quartz it is close to 0.8 oersted (curve 1 in a figure on p 566), on silica gel it is near 2.4 oersted (curve 2) and on molybdenum glass it is 4.5 oersted (curve 3). Since the hyperfine splitting in the e.p.r. spectra of H atoms stabilized on various surfaces is close to the hyperfine splitting of free atoms, the binding of H atoms to these surfaces does not alter greatly the spin density of the unpaired electron in hydrogen. On the other hand, dependence of the width of the hydrogen doublet components on the nature of the stabilizing surface indicates that there is a definite interaction between the unpaired electron and the surface. In view of this the authors suggest further studies of the nature of binding of H atoms to solid surfaces. This is an abridged translation. There is 1 figure and 4 references, 2 of which are Soviet and 2 English.

SUBMITTED: August 29, 1958

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SOV/51-6-6-18/34

24(7), 5(3)  
AUTHORS:

Buben, N.Ya., Vovodskiy, V.V., Koritskiy, A.T., Molin, Yu.N.,  
Chkheidze, I.I. and Shamshev, V.E.

TITLE:

Electron Paramagnetic Resonance Studies of Free Radicals Formed by  
Irradiation with Fast Electrons (Issledovaniye metodom elektronnoy  
paramagnitnoy rezonansy svobodnykh radikalov, obrazuyushchikhsya v  
protsesse oblucheniya bystryimi elektronami)

PERIODICAL: Optika i spektroskopiya, 1959, Vol 6, Nr 6, pp 806-807 (USSR)

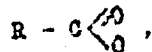
ABSTRACT: An electron paramagnetic resonance (e.p.r.) spectrometer with high-  
frequency modulation of magnetic field working at 9400 Mc/s was used  
to measure the effects of fast-electron irradiation in situ. The  
samples irradiated were kept at temperatures from -180 to +150°C and  
the radiation dose reached  $10^6$  -  $10^7$  rad/sec. At room temperature  
radicals produced in various polymers, solid organic acids and their  
salts and in some aromatic compounds were found to be stable (their  
lifetime was of the order of several hours and sometimes longer). At  
low temperatures e.p.r. resonance showed the presence of atomic hydrogen  
in irradiated aqueous solutions of sulphuric acids and some of its salts.  
Irradiation at low temperatures and subsequent warming up produced changes  
in the e.p.r. spectra which could be either reversible (caprone) or

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**Electron Paramagnetic Resonance Studies of Free Radicals Formed by Irradiation with Fast Electrons**

irreversible (dicarboxylic acids, polyformaldehyde). Such studies were made on radicals produced by electron irradiation in oxalic acid, polyethylene and paraffin. In oxalic acid the e.p.r. signal is a single line whose width is due to interaction between an unpaired electron and magnetic moments of protons. The observed e.p.r. spectrum of oxalic acid is not related to the presence of water of crystallization but it is due to radicals of the type



formed by removal of the hydrogen atom from the carboxyl group. E.p.r. studies showed that radicals formed by electron irradiation of oxalic acid had disappeared at the rate given by  $dn/dt = -Kn^2$  (at 25°C  $K = 10^{-21} \text{ cm}^3/\text{sec}$ ). The presence of water of crystallization affects strongly the rate of disappearance of these radicals: the value of  $K$  in anhydrous acid is higher than in the hydrated compound. Irradiation of polyethylene at room temperature produces  $\text{CH}_2\text{--}\dot{\text{C}}\text{H--}\text{CH}_2$  radicals which are stable at low temperatures. Changes in the e.p.r. spectrum of

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Electron Paramagnetic Resonance Studies of Free Radicals Formed by Irradiation with Fast Electrons

irradiated polyethylene show that the initially produced radical transforms into a secondary radical which is more stable; the rate of this conversion decreases with decrease of temperature. The e.p.r. spectrum of paraffin showed that the original radical is the same as that in polyethylene, i.e. it is due to removal of the hydrogen atom from one of the methylene groups, but the lifetimes of the original radicals in polyethylene and in paraffin are different. There are 3 Soviet references.

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TIMOMIROV., N.N.; VOITOVSKIY, V.V.

Method for the analysis of the form of electron paramagnetic  
resonance lines. Opt. i spektr. 7 no. 6:829-832 D 15.  
(M.I. 14:4)

(Paramagnetic resonance and relaxation)



5 (4), 5 (3)  
AUTHORS:

Poroykova, A. I., Voyevodskiy, V. V.,  
Nalbandyan, A. B.

SOV/76-33-6-26/44

TITLE:

Photoinitiation of Propane Oxidation in the Presence of  
Ammonia and Hydrogen Sulphide (Fotoinitsirovaniya oksileniya  
propana v prisutstvi ammiaka i serovedoxda)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6,  
pp 1336-1344 (USSR)

ABSTRACT:

The thermal oxidation of low, gaseous paraffin hydrocarbons proceeds only at high temperatures at a noticeable rate; the high temperature leads to a decay of the intermediate products so that these products as well as the reaction kinetics cannot be investigated under these conditions. A photochemical reaction initiation (RI) is, besides the catalysis, an important method of (RI). The photochemical oxidation of low gaseous hydrocarbons was first investigated by A. B. Nalbandyan et al (Refs 1-3), and among other things, a reaction mechanism of the propane oxidation at low temperature was suggested (1) - (8). The photolyses (P) of the ammonia (I) and hydrogen sulphide (II) have been insufficiently examined up to now; on the other hand, it

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Photoinitiation of Propane Oxidation in the Presence of Ammonia and Hydrogen Sulphide SOV/76-33-6-26/44

must be assumed that at a (P) of (I) or (II) in the presence of a mixture of propane (III) and oxygen (IV), the resulting inorganic radicals will form propyl radicals with the molecules of (III), thus initiating the (III)-oxidation. The latter has already been observed (Refs 16, 17), the mode of origin of the formed acetone could not be clarified. The present experiments were carried out in a vacuum device (Fig 1), which was equipped with 2 quartz lamps PRK-2. The reaction products were frozen out by liquid nitrogen. The experiments led to the following statements: Isopropylhydroperoxide (V), acetaldehyde and formaldehyde form at 200-220°C as main products of the photochemical propane oxidation. The (RI) with (I) gives at 220°C a yield of reaction products of  $\gamma \geq 5$  per decomposed (I)-molecule, which is considered as a confirmation of the chain mechanism in the process. The present results as well as those obtained by A. B. Nalbandyan et al permit the assumption that the propane oxidation, photoinitiated with mercury (Refs 1-3), ammonia or hydrogen sulphide, proceeds according to the same chain mechanism, independent of the type of initiator. The acetone which - as

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Photoinitiation of Propane Oxidation in the Presence of Ammonia and Hydrogen Sulphide SOV/76-33-6-26/44

mentioned above - is observed in static experiments, is produced by the decay of (V). There are 5 figures, 1 table, and 23 references, 7 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki Moskva (Academy of Sciences of the USSR, Institute of Chemical Physics Moscow)

SUBMITTED: November 27, 1957

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5 (4)  
AUTHORS:

Poltorak, V. A., Leytis, L. Ya.,  
Voyevodskiy, V. V.

05826  
SOV/76-33-10-24/45

TITLE:

On the Part Played by the Surface in Thermal Propane Decomposition

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 10, pp 2259 - 2263  
(USSR)

ABSTRACT:

The fact that thermal decomposition is never completely inhibited by various inhibitors is ascribed by Hinshelwood (Ref 1) to the two parallel mechanisms of decomposition, namely, the chain mechanism (inhibited by the inhibitor) and the molecular mechanism (which is not inhibited at all). This assumption is, however, irreconcilable with experimental results obtained from the cracking of hydrocarbons in the presence of deuterium-bearing molecules. Hinshelwood et al. (Ref 9) found that the rate of thermal decomposition of 2-methyl pentane was independent of a variation in the ratio S:V (S = surface of the reaction vessel, V = its volume). Rice and Herzfeld (Ref 10) have, however, shown that the absence of any dependence of the reaction rate on the ratio S:V is not indicative of the homogeneity of a chain formation or destruction. Since the hypothesis of a homogeneous

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On the Part Played by the Surface in Thermal Propane SOV/76-33-10-24/45  
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mechanism of chain formation or destruction could not explain experimental observations, V. V. Vovodskiy and V. A. Poltorak (Ref 11) assumed that the formation and destruction of the chains be heterogeneous processes and the observations are to be attributed to variations in the surface of the reaction vessel. Consequently, they suggested a definite course of this process. In order to check this hypothesis, the authors investigated systematically the influence exerted by the ratio S:V on the kinetics of propane cracking. Further, they examined the possibility of intoxicating or activating the vessel surface. The reaction rate was determined from the pressure rise (measured by means of a diaphragm gauge) at a propane pressure of 25 torr and a temperature of 610 C. For this purpose, they used a quartz tube with and without content (twelve-fold variation of the S:V value). When the S:V value was increased by twelve times, the reaction rate dropped to one-fourth. Experimental pretreatment of the vessel surface with various salt solutions indicated that an  $Mg(ClO_4)_2$  solution increases the reaction rate (Fig 4). Intoxication of the reaction vessel by pretreatment with a mixture

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On the Part Played by the Surface in Thermal Propane Decomposition SOV/76-33-10-24/45

of  $\text{NO} + \text{H}_2\text{S}$  indicates that at the beginning the reaction proceeds like an inhibited reaction, is then accelerated and finally passes through a maximum (Fig 3). In order to explain the problem as to whether the afore-mentioned hypothesis is correct, or whether the influence exerted by the surface of the reaction vessel upon the thermal decomposition should be explained in another way, further investigations are needed. There are 4 figures and 12 references, 4 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova  
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: March 25, 1958

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24(7)

AUTHORS:

Blyumenfel'd, L. A., Voyevodskiy, V. V. SOV/53-68-1-4/17

TITLE:

Radiospectroscopy and the Problems of Modern  
Theoretical Chemistry (Radiospektroskopiya i  
problemy sovremennoy teoreticheskoy khimii)

PERIODICAL:

Uspekhi fizicheskikh nauk, 1959, Vol 68, Nr 1,  
pp 31-49 (USSR)

ABSTRACT:

This article is an elaborated reproduction of a lecture held by the authors at the 12th All-Union Conference on Spectroscopy (November 1958, Moscow). It gives a survey of the investigations carried out in the USSR in the field of radiospectroscopy as well as of the most important pertinent methods and results of investigations. Radiospectroscopic investigation may be applied to the following problems: investigation of the mechanism of chemical radical- and chain reactions, polymerization, rapid reactions proceeding in liquids within less than millionths of seconds (ion interaction, charge exchange between ions, isotope exchange); processes taking place in living tissue, particularly fermentative catalysis; investigation of the structure of various materials and polymers under the action of temperature, ionizing

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Radio spectroscopy and the Problems of Modern  
Theoretical Chemistry

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radiation, and mechanical destruction of the chemical structure as well as the investigation of the effect exercised by ionizing radiation on biological matter. In addition, there are problems of remote action in chemical reactions, in heterogeneous catalysis and biochemical processes, explanation of the mechanism of a number of important processes, for instance, photosynthesis of organic matter from carbonic acid and water, muscular contraction, reflexibility of the nerves, further, problems of low-temperature chemistry in connection with the possibility of producing and using especially active particles which are able to carry out chemical reactions at very low temperatures. The most important and most carefully developed method of investigation is that of paramagnetic electron resonance (this phenomenon was discovered by Ye. K. Zavoyskiy in 1944; the first theory was established by Ya. A. Frenkel' (Refs 1, 2) ). The methods of investigation based on the phenomenon as well as the phenomenon itself, and numerous investigations and results are mentioned and discussed. The major part of the data referred to was published in Western

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articles. The authors then discuss the method of nuclear magnetic resonance which in principle does not differ from the former. A more detailed description is given of line widths of solid compounds and some liquids as well as their variation during phase transitions, further, investigations of the line spectrum of magnetic resonance. Another method is that of nuclear quadrupole resonance, which is only touched. Finally, reference is made to microwave spectroscopy in gases which is applied to investigations of chemical reactions in the gas phase, especially of reactions of negligible quantities of active free radicals. Some possibilities are discussed in short. There are 5 figures and 48 references, 20 of which are Soviet.

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5(4)

AUTHORS:

Molin, Yu. N., Koritskiy, A. T.,  
Buben, N. Ya., Voyevodskiy, V. V., Corresponding Member, AS USSR

SOV/20-124-1-35/69

TITLE:

Investigation by the Method of Paramagnetic Electron Resonance of Free Radicals Formed During Irradiation of Oxalic Acid (Issledovaniye metodom elektronogo paramagnitnogo rezonansa svobodnykh radikalov, obrazuyushchikhsya pri obluchenii shchhavelevoy kisloty)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 127-128 (USSR)

ABSTRACT:

The procedure developed by the authors for the purpose of observing free radicals by the method of paramagnetic electron resonance in connection with the action of fast electrons on matter also permits the investigation of the creation and annihilation of radicals in solids. The present paper contains preliminary data concerning the properties of radicals formed by the irradiation of oxalic acid with 1.6 Mev electrons. The signal of paramagnetic absorption in oxalic acid consists of a single line having a width of about 4.5 Oe. The corresponding g-factor is similar to that of diphenyl-picryl hydrazyl (2.0036).

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After irradiation has been discontinued, signal intensity decreases at a rate that depends on temperature. A diagram shows one of the curves for the variation of radical concentration, which was plotted at room temperature. In the temperature interval of  $+10^{\circ}$  to  $+40^{\circ}$  the recombination of radicals is described by the equation  $dn/dt = -kn^2$ , where  $n$  denotes the concentration of the radical and  $k$  a temperature-dependent constant. At  $+25^{\circ}$  the value  $k \approx 9 \cdot 10^{-22} \text{ cm}^3/\text{sec}$  was found by employing the usual methods. According to the quadratic law of recombination it would be expected that, at constant temperature, the steady concentration of radicals after saturation is proportional to the square root of the efficiency per dose of irradiation. A table contains data on the dependence of the steady concentration of the radical on the density of the electron flux. Accumulation of radicals is, however, not described by a simple kinetic equation  $dn/dt = w_0 - kn^2$ , but it is of complicated character. For the purpose of determining the nature of the radical in oxalic

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acid, the authors compared the spectra of the paramagnetic resonance of irradiated oxalic acid, succinic acid, and stearic acid as well as of some of their salts. The following was found: also in the rather complicated spectra of succinic acid and stearic acid signals of paramagnetic resonance occur which are analogous to the signal in oxalic acid. In the spectra of the salts, such signals are either of only weak intensity or they lack entirely. The experimentally determined law of quadratic recombination is indicative of the fact that the radicals are destroyed by the interaction of two radicals. Either the diffusion of a radical in matter by the transition of a hydrogen atom from the neighboring molecule to the radical, or dislocation of a free electron according to the system of conjugate hydrogen bonds may be considered as possible mechanisms. Further investigations are necessary for the purpose of determining the true mechanism. There are 2 figures, 1 table, and 2 Soviet references.

ASSOCIATION:  
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Institut khimicheskoy fiziki Akademii nauk SSSR (Institute for Chemical Physics of the Academy of Sciences, USSR)