Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
43. J.Kay, R.Malsan, and F.Rowland, J.Amer.Chem.Soc., 81, 5050 (1959).
44. J.Lee, B.Musgrave, and F.Rowland, J.Amer.Chem.Soc., 82, 3545 (1960).
45. E.Rack and A.Gordus, J.Chem.Phys., 34, 1855 (1961).
46. E.Rack and A.Gordus, J.Phys.Chem., 65, 944 (1961).
47. E.Rack and A.Gordus, J.Chem.Phys., 36, 287 (1962).
48. R.Wolfgang, J.Chem.Phys., 39, 2983 (1963).
49. D.Urch and M.Welch, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
50. H.Moser and R.Shores, J.Phys.Chem., 66, 2272 (1962).
51. W.Breckenridge, W.Root, and F.Rowland, J.Chem.Phys., 39, 2374 (1963).
52. E.S.Filatov, An.N.Nesmeyanov, and Yu.B.Chepyzhev, Vestnik Moskov.Gos.Univ., No.6, 46 (1963).
53. J.Lee, B.Musgrave, and F.Rowland, J.Phys.Chem., 64, 1950 (1960).
54. J.Lee, B.Musgrave, and F.Rowland, J.Chem.Phys., 32, 1260 (1960).
55. J.Root and F.Rowland, J.Amer.Chem.Soc., 85, 1021 (1963).
56. E.Lee, J.Root, and F.Rowland, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
57. J.Root and F.Rowland, J.Chem.Phys., 38, 2030 (1963).
58. E.Lee and F.Rowland, J.Amer.Chem.Soc., 85, 2907 (1963).
59. F.S.Yakushin, Uspekhi Khim., 31, 241 (1962) [Russ.Chem.Rev., 123 (1962)].
60. J.Thompson and W.Miller, J.Chem.Phys., 38, 2477 (1963).
61. L.Groshev, Dokl.Akad.Nauk SSSR, 100, 651 (1955).
62. S.Wexler and T.Davies, J.Chem.Phys., 20, 1688 (1952).
63. S.Wexler, Phys.Rev., 87, 543 (1952).
64. H.Suess, Z.phys.Chem., B45, 312 (1940).
65. W.F.Libby, J.Amer.Chem.Soc., 69, 2523 (1947).
66. C.Hsiung and A.Gordus, J.Chem.Phys., 36, 947 (1962).
67. A.Gordus and C.Hsiung, J.Chem.Phys., 36, 954 (1962).
68. H.Suess, Z.phys.Chem., B45, 297 (1940).
69. R.Williams and W.Hamill, J.Chem.Phys., 18, 783 (1950).
70. W.Hamill and J.Young, J.Chem.Phys., 20, 888 (1952).
71. E.P.Cooper, Phys.Rev., 61, 1 (1942).
72. J.Magee and E.Gurnee, J.Chem.Phys., 20, 894 (1952).
73. R.Hahne and J.Willard, J.Phys.Chem., 68, 2582 (1964).
74. M.Milman, Radiochim.Acta, 1, 15 (1962).
75. M.Milman, Radiochim.Acta, 2, 181 (1964).
76. G.Walton, Radiochim.Acta, 2, 108 (1964).
77. J.Willard, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
78. P.Shaw, Radiochim.Acta, 1, 177 (1963).
79. L.Spicer and A.Gordus, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
80. E.S.Filatov, Uspekhi Khim., 31, 752 (1962) [Russ.Chem.Rev., 383 (1962)].
81. A.Halpern and A.Sokolovska, J.Inorg.Nuclear Chem., in the press (1965).
82. T.Carlson and R.White, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
83. B.Knight, G.Miller, and P.Shaw, J.Inorg.Nuclear Chem., 23, 15 (1961).
84. N.Colebourne, J.Todd, and J.Wolfgang, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
85. J.Willard, Ann.Rev.Nuclear Sci., 3, 193 (1953).
86. J.Willard, Ann.Rev.Phys.Chem., 6, 141 (1955).
87. J.C.Lorquet, S.G.ElKomoss, and J.L.Magee, J.Chem.Phys., 37, 1991 (1962).
88. P.Bridgman, Proc.Amer.Acad.Arts Sci., 49, 1 (1913).
89. M.Milman, J.Amer.Chem.Soc., 86, 3567 (1964).
90. R.Woodworth and P.Skell, J.Amer.Chem.Soc., 81, 3383 (1959).
91. K.Kopesky, G.Hammond, and P.Leermakers, J.Amer.Chem.Soc., 84, 1015 (1962).
92. W.Doering, R.Buttery, R.Laughlin, and N.Chaidhuri, J.Amer.Chem.Soc., 78, 3224 (1956).
93. E.Muller, "Neuere Auschauungen der organischen Chemie" (Translated into Russian), Inostr.Lit., 1960, p.217.
94. C.MacKay and R.Wolfgang, J.Amer.Chem.Soc., 83, 2399 (1961).
95. C.MacKay, P.Polak, H.E.Rosenberg, and R.Wolfgang, J.Amer.Chem.Soc., 84, 308 (1962).
96. C.MacKay and R.Wolfgang, Radiochim.Acta, 1, 42 (1962).
97. E.N.Avdonina, Radiokhimiya, 5, 633 (1963).
98. B.G.Dzantiev and A.P.Shvedchikov, Radiokhimiya, 6, 373 (1964).
99. V.V.Pozdeev, B.G.Dzantiev, and An.N.Nesmeyanov, Radiokhimiya, 3, 613 (1962).
100. E.N.Avdonina, Radiokhimiya, 4, 617 (1962).
101. A.Sokolovska, L.Haskin, and F.Rowland, J.Amer.Chem.Soc., 84, 2469 (1962).
102. An.N.Nesmeyanov and E.S.Filatov, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
103. A.Sokolovska, Paper Presented at the Symposium on the Chemical Effects of Nuclear Transformations, Vienna, 1964.
104. J.Garland and F.S.Rowland, Radiochim.Acta, 4, H2, 115 (1965).
105. F.Rowland and P.Coulter, Radiochim.Acta, 2, 163 (1964).
106. R.Odum and R.Wolfgang, J.Amer.Chem.Soc., 85, 1050 (1963).
107. F.Rowland, Paper Presented at the American Chemical Society Meeting, April, 1963.
108. N.V.Vol'kenshtein, "Stroenie i Fizicheskie Svoistva Molekul" (The Structure and Physical Properties of Molecules), Izd.Akad.Nauk SSSR, 1955, p.128.
109. A.M.Brodskii and A.Ya.Temkin, Dokl.Akad.Nauk SSSR, 152, 127 (1963).

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THE USE OF ELECTRON PARAMAGNETIC RESONANCE FOR THE STUDY OF CATALYSTS

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I. INTRODUCTION

The essential features of the EPR method (electron paramagnetic resonance) have been described in detail in many monographs and reviews[1-6].

The efficiency of this method in the study of catalysts is because in most cases the catalysts are paramagnetic. The nature of the paramagnetic centres may be different but they are all, in the final analysis, produced by unpaired electrons, which give EPR signals. The intensity and shape of the lines in the EPR spectrum can give information on the concentration and state of the paramagnetic centres, with which the catalytic activity of the contacts is usually associated (at any rate in reactions taking place by a radical mechanism). Here it must be borne in mind that both the bulk properties and the surface properties are reflected in the EPR. It is known that the paramagnetism of catalysts, which are most frequently studied in the isolated state at room temperature, does not reflect completely the paramagnetic state of the contacts during catalysis. Moreover, new paramagnetic centres may be produced during catalysis, so that in the comparison of the dynamic paramagnetism of the contacts with their catalytic activity, allowance must be made for the fact that the correlations will be justifiable only if the above features are taken into account.

In a number of studies it has been shown that the irradiation of catalysts by γ-rays, a neutron beam, etc., alters their catalytic activity[7]. Other work, often carried out with the same materials, has established that this irradiation generally leads to the production, in the catalyst, of defects which can be detected using the EPR method. It is convenient to compare the data obtained by different authors on the change in catalytic activity after irradiation on the one hand with the parameters of the EPR signals of the same catalyst on the other. This is particularly necessary since a simultaneous comparison of these two parameters has been made in very few studies.

In the discussion of the factual material, we have used the classification of catalytic reactions proposed by Polyakin[8], who divides all catalytic reactions into three main types: reactions involving the pairing and unpairing of electrons; reactions taking place with electron transfer (oxidation); and reactions involving the donation and withdrawal of an electron pair (acid–base reactions).

II. REACTIONS INVOLVING THE PAIRING AND UNPAIRING OF ELECTRONS

Reactions of this type which have been studied by the EPR method include deuterium exchange in molecular hydrogen, hydrogenation, dehydrogenation, and radical polymerisation†. For these reactions to take place, it is usually necessary that the catalyst surface have paramagnetic centres ("free valencies"[12]) or, at least, that such centres be readily produced under the catalysis conditions by the influence of heat and the reaction mixture. The interaction between the surface paramagnetic centres in this case is not significant. Since the completion of the catalytic act in this type of process does not require the transfer of electrons, dielectric substances (for example, SiO_2 or Al_2O_3) with paramagnetic centres on their surface may also act as catalysts here. If the catalytic act takes place on those paramagnetic centres which are detected by the EPR method, we should expect that the intensity of these signals and the catalytic activity should change in the same sense.

1. Deuterium Exchange in Molecular Hydrogen

The reaction $H_2 + D_2 \rightleftharpoons 2HD$ takes place at a satisfactory rate on a number of catalysts. In recent years it has been studied on silica gel and on alumina as a model reaction for determining the influence of the irradiation of these oxides on their catalytic activity.

It has been established[13] that thoroughly dehydrated and ignited (8 h at 200–300°C in a vacuum) silica gel containing less than 0.1% Fe and Al, after irradiation at room temperature by γ-rays from ^{60}Co (5–10 Mrad), gives a relatively weak EPR signal [a quintet with g-factor equal to the g-factor of diphenylpicrylhydrazyl (DPPH) and splitting 22 G]. It is suggested that the observed paramagnetic centre is formed by the removal of a hydrogen atom from a surface hydroxyl group and that the hyperfine structure (HFS) is due to the interaction of the unpaired electron with the protons of neighbouring OH-groups or adsorbed water molecules. It is considered that the increased catalytic activity of irradiated silica gel in the isotopic exchange $H_2 + D_2 \rightleftharpoons 2HD$ may be associated with these paramagnetic centres. It is also suggested that the EPR spectrum after irradiation does not reveal all the paramagnetic centres produced by irradiation.

Silica gel which has been degassed at 500°C and then irradiated at room temperature with the same dose gives a narrow singlet (g-factor = 2.0004). In Molin and Voevodskii's opinion[14], shared by Kazanskii, this signal is due to electrons trapped in oxygen vacancies of the lattice. Kohn[15] also studied the paramagnetic resonance absorption of silica gel which had been degassed at ~500°C and then irradiated at 50°C by γ-radiation from ^{60}Co (dose 10^{19} eV × × g^{-1}) or by X-rays with an energy of 50 keV. The work was carried out with silica gel in which the concentration of impurities (Fe, Al, Mg) did not exceed 0.1–0.01%. Kohn, like Kazanskii, detected an EPR signal (singlet) stable at room temperature (in a vacuum). Kohn also attributed the signal to the trapping of electrons in the oxygen vacancies of the lattice, but whereas Kazanskii and coworkers identified the paramagnetic centres observed in the EPR spectrum with the colour centres of the silica gel (the so-called F-centres), Kohn showed that the F-centres, which are also produced after irradiation, are not associated with the paramagnetic centres. Similarly the F-centres are not associated with the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$. In actual fact, as noted by

† The o-$H_2 \rightleftharpoons p$-H_2 process is not considered, since it takes place on all paramagnetic substances[9-11].

Taylor and Kohn[16-18], the main bulk of the hydrogen is chemisorbed on the *F*-centres so strongly that these centres cannot react further with hydrogen. Only ~ 5% of the sorbed hydrogen is capable of undergoing exchange with gaseous H_2 or of removal by evacuation at room temperature. Calculations show that this quantity of mobile hydrogen would be sufficient to ensure the increased catalytic activity of the irradiated silica gel. According to Taylor and Kohn's data[17], however, the rate of the exchange of this mobile fraction of the sorbed hydrogen is not sufficiently high for the exchange to be a stage in the catalytic process $H_2 + D_2 \rightleftharpoons 2HD$.

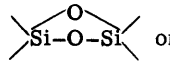
In Kazanskii's experiments, the EPR line did not become broader when oxygen was admitted, and from this it was concluded that the signal is due to bulk defects. Kohn, however, found that this signal disappears when oxygen is added ("the oxygen effect"). The accumulated data suggest that some of the paramagnetic centres are also present on the surface of the contact.

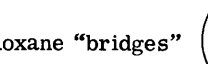
Kohn and Taylor[19] studied the change in the catalytic activity of silica gel which had been degassed at 450–600°C and subjected to γ-irradiation with a dose of approximately 10^{19} eV g^{-1} (concentration of Fe, Al, and Mg impurities less than 0.1–0.01%) with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ at room temperature (static method), and established that after irradiation the silica gel is 100–2000 times more active than before irradiation. At the same time, the activation energy is reduced from 9 kcal × × $mole^{-1}$ to 2 kcal $mole^{-1}$. From this it might be concluded that the increase in the catalytic activity of the silica gel after irradiation is associated with the generation of the defects responsible for the appearance of the narrow EPR signal. In a recent paper, however, Taylor[18], referring to Kohn's results[20], points out that when the silica gel is heated at a temperature close to its melting point, its catalytic activity approaches that of the irradiated contact. The heating was carried out[20] for 16 h at 920°C. After this treatment, the rate constant for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on commercial silica gel, even at -78°C, was equal to 5×10^{-7} min^{-1} m^{-2} — for comparison it should be noted that the rate constant for the reaction $H_2 + D_2 \rightleftharpoons$ $\rightleftharpoons 2HD$ at room temperature on an analogous silica gel specimen after irradiation with γ-rays from ^{60}Co (activity 600 c for 1 min at 35°C) is equal to 5.5×10^{-5} min^{-1} m^{-2}. Unfortunately, Kohn does not give the value of the rate constant at room temperature for silica gel which had been heated at 920°C, and this makes comparison difficult. On other modifications of SiO_2, this thermal treatment gives an even greater effect: the rate constant is equal to 10^{-3} min^{-1} m^{-2} on quartz, and 10^{-4} min^{-1} m^{-2} on quartz glass and cristobalite (these substances have a surface area of approximately 6–8 m^2 g^{-1}).

Kohn[20] also showed that the catalytic activity of silica gels is directly proportional to the concentration of aluminium present. After degassing at high temperature followed by irradiation (35°C, 600 c, ^{60}Co γ-radiation, 1 min), the rate constant at 25° on silica gel shown by spectroscopic analysis to contain no aluminium, was equal to 3.7×10^{-6} min^{-1} m^{-2}, whereas for silica gel specimens containing 0.01% Al^{3+}, 0.1% Al^{3+}, and 0.5% Al^{3+}, the values (min^{-1} m^{-2}) were 3.5×10^{-5}, 5.5×10^{-5}, and 1.6×10^{-4} respectively. An analogous direct relationship between the activity and the aluminium content is observed for silica gel specimens degassed at 500° and 625°C, but in this case the absolute values of the rate constants are smaller by 1–2 orders of magnitude. (An increase in the catalytic activity of silica gel after the introduction of additional quantities of Al was established by Kohn and Taylor[17]). It may also be noted that silica gel with maximum purity, even after extensive irradiation (6×10^{20} eV g^{-1}), adsorbs very little hydrogen, the quantity adsorbed being smaller by a factor of ~ 100 than the quantity adsorbed by irradiated commercial silica gel[16,17].

On the basis of these facts, Kohn[20] suggests that the increased catalytic activity of irradiated silica gel is due to a complex consisting of adsorbed hydrogen and a positive hole, trapped on an aluminium atom. Kohn himself, however, considers that this suggestion is only a rough approximation, since it does not explain a number of facts: the increase in activity after irradiation by ultraviolet light[16,17] or by γ-rays followed by ultraviolet light[16,17], or the poisoning of the catalyst by dry oxygen[21].

The facts indicate that the catalytically active centre in silica gel contains aluminium. In Kohn and Taylor's opinion[17], it cannot be assumed that the aluminium impurity in the silica gel forms a γ-Al_2O_3 phase and that it is the presence of this phase which determines the catalytic activity of the silica gel. This cannot be assumed chiefly because pure γ-Al_2O_3, ignited at 520°C, shows almost no change in activity after irradiation, whereas the catalytic activity of silica gel containing aluminium impurity and heated at the same temperature, increases after irradiation by a factor of 100–2000, as already noted. Kohn and Taylor[17] conclude that the aluminium must be introduced into the silica gel structure. At the same time it is undoubtedly true that heating (degassing) the silica gel increases its activity, the values of the catalytic activity after high-temperature treatment and irradiation being of the same order of magnitude. On this basis, Taylor[18] suggested that the observed changes in catalytic activity are more probably associated with the sorbed molecules (that is, with the removal of water or with the interaction of radiation with the complex catalyst — "poison"), than with the actual solid.

It is generally assumed[22] that the thermal dehydration of silica gel leads to the formation of so-called "siloxane bridges"  on its surface.

It may be suggested that the catalytically active centres of silica gel with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ are alumosiloxane "bridges" , formed during the thermal or radiation dehydration of the contact. Hydrogen is probably activated on these strained energy-rich structures.

The ability of these "bridges" to activate hydrogen should naturally decrease with decrease in the temperature of catalysis. At the temperature of liquid nitrogen, these "bridges" are apparently almost inert with respect to this reaction. At the same time, the γ-irradiation of previously calcined silica gel at the temperature of liquid nitrogen will probably activate these "bridges", making them able to activate hydrogen even at -196°C. At low catalysis temperatures therefore, we should expect that previously calcined silica gel specimens will have a much lower catalytic activity than contacts which have been calcined and then irradiated. The difference in the catalytic activity of silica gel after thermal treatment, and also after thermal treatment followed by irradiation (at the

temperature of liquid nitrogen) should increase with decrease in the temperature of catalysis. This is probably the reason for the observed marked difference in the catalytic activity of silica gel at -196°C after thermal treatment on the one hand and after irradiation at the temperature of liquid nitrogen on the other hand. In fact, for example, the rate constant for deuterium exchange on silica gel containing 0.01% aluminium, after irradiation for 16 h at -196°C, is greater than 3×10^{-4} min^{-1} m^{-2} (at -196°C), whereas the rate constant for the same silica gel specimen after heating at 900°C amounts to less than 3×10^{-7} min^{-1} m^{-2}.

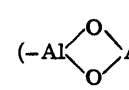
The suggestion regarding the possible part played by alumosiloxane "bridges" as active centres for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on the surface of a silica gel catalyst cannot be taken as proved. It is definitely established, however, that the higher the calcining temperature, that is, the more complete the dehydration of the silica gel, the higher the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$. After thermal treatment the silica gel does not show EPR signals, so that the catalysis here is not associated with paramagnetic centres.

Analogous relationships are observed for the catalysis of the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on alumina. Here also it has been established that the higher the temperature of preliminary heating (activation) of the catalyst in a vacuum, the less marked the effect of subsequent irradiation[18,23-25] (the irradiation was carried out in a vacuum for 3 min at -78°C from a ^{60}Co source at a rate equal to 2×10^{17} eV × × g^{-1} min^{-1}; the catalytic activity was also measured at -78°C). For a catalyst previously heated at 650°C, however, the activity decreased by almost one-half after irradiation. The lower the temperature of preliminary heating of the catalyst, the more rapid the decrease in the catalytic activity induced by the irradiation: the time taken amounted to 2-4 d (at room temperature) for a catalyst heated at 400°C, and to several hours, even at -78°C[23] ("annealing") for a catalyst heated at 200°. At the same time, alumina gives an intense EPR signal after irradiation (both after irradiation at the temperature of liquid nitrogen in a vacuum[26] and after irradiation by ^{60}Co γ-rays with an energy of 1.25 MeV at room temperature[25]).

Kazanskii[26] observed a correlation between the decrease in the intensity of one of the components of the complex EPR signal observed at -196°C and the decrease after annealing in the induced catalytic activity of catalysts previously heated at 200-500°C. On this basis it was suggested that "the additional activity of the irradiated alumina gel and the labile EPR signal are produced by the same centre".[1] It is quite probable that the irradiation of γ-Al_2O_3 previously heated at 650°C also leads to the appearance of EPR signals. At the same time, the catalytic activity of γ-Al_2O_3 decreases after this thermal treatment, as already noted. There are thus grounds for assuming that the above suggestion is erroneous.

Taylor[18] considers that the increase in catalytic activity after irradiation is associated with the removal of sorbed molecules of "poisons" (for example, water) from the surface, not only for silica gel but also for all non-metallic catalysts. This applies particularly to γ-Al_2O_3. Kolbanovskii and coworkers[25] also point out that the activation of γ-Al_2O_3 is most probably due to the removal of sufficient quantities of water from the catalyst.

It may be assumed that dehydration of the alumina gel surface leads to the formation of aloxane "bridges"



(-Al<O>Al-), which can probably act as active centres for the reaction $H_2 + D_2 \rightleftharpoons 2HD$. This assumption makes it possible to explain the regularities observed. In fact, if the preliminary heating of γ-Al_2O_3 is carried out at an insufficiently high temperature, this leads to the formation, on the surface of the catalyst, of a certain quantity of aloxane "bridges" and thus to the production of a definite stable catalytic activity. If this catalyst is then irradiated at low temperature (-78° or -196°C), new aloxane "bridges" are formed, accompanied by the liberation of water. In the process, the catalytic activity evidently increases. It must be assumed, however, that under these conditions the water remains in the catalyst. The aloxane "bridges" are probably less stable than alumosiloxane bridges. (For an approximate estimate of the bond strength, we may note that the energy of rupture of the Al-O- bond at 298°C is 116 kcal $mole^{-1}$, whereas that of the Si-O- bond is 193 kcal $mole^{-1}$;[27] the rate of rehydration of calcined alumina gel is greater than that of calcined alumina-silica and, more particularly, silica gel[28]). It may therefore be assumed that the aloxane "bridges" will react more readily than alumosiloxane bridges with the water remaining in the catalyst, particularly with increase in temperature (the so-called "low-temperature annealing"). If, however, the heating is continued until the water is almost completely removed and formation of the aloxane "bridges" on the surface takes place to the maximum extent, subsequent irradiation can only break down these bridges and thus decrease the catalytic activity. This interpretation explains why the effect of irradiation is greater, the lower the temperature of preliminary heating of the catalyst. On the other hand, it also explains why the irradiation of alumina gel specimens heated at 650°C leads to a decrease in catalytic activity. The phenomenon of the "annealing" of the induced catalytic activity is also explained.

It follows that the increase sometimes observed in the catalytic activity with respect to deuterium exchange in molecular hydrogen on silica gel and alumina gel after irradiation is not due to defects giving an EPR signal. The fact, observed in a number of instances, that the intensity of the signal and the catalytic activity change in the same sense, does not reflect their correlation as cause and effect but merely indicates that both these parameters are determined by the same factor (in this case radiation dehydration). It is not excluded, however, that some paramagnetic centres produced during irradiation may catalyse the isotopic exchange.

A parallelism between the intensity of the signal and the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ is not observed on sugar carbons[29]. The maximal activity is shown by carbon heated at 905°C, for which the intensity of the EPR signal is a minimum. The maximal intensity (and minimal width) is shown by the EPR signal for carbon heated at 607°C. In Turkevich and Laroche's opinion, the high activity of carbon heated above 607°C is because treatment of the carbon in this way produces antiferromagnetic regions on which hydrogen is readily chemisorbed. Activation of hydrogen in the catalysis of the reaction $H_2 + D_2 \rightleftharpoons 2HD$ also apparently takes place on these regions.

The intensity of the EPR signal induced by irradiation is found to change in the same sense as the activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ for two catalysts: ZnO and TiO_2 (anatase). Thus Kohn and Taylor[30] showed that after irradiation with ^{60}Co γ-rays (10^{18}-10^{29} eV g^{-1},

at -78°C) the activity of pure zinc oxide for this reaction increases by a factor of 3–10, the time required for the induced activity to decrease by half being greater than one month. Terenin and coworkers[31] detected the gradual appearance of two EPR signals after the irradiation of zinc oxide with ultraviolet light (and even with visible light) at 77°K, in air: one signal had g-factor 1.964 and line width ΔH = 4.5 G, and the second had g-factor 2.018 and ΔH = = 3.0 G. Analogous signals gradually appeared after irradiation in a vacuum at the same temperature.

Schneider[32] also detected an EPR signal with a g-factor 1.657 and ΔH = 4.6 G after the irradiation of zinc oxide with ultraviolet light in a vacuum at room temperature.

Terenin[31] suggests that the singlet with g-factor 1.914 is produced by centres freed from oxygen during photodesorption — unpaired electrons in donor levels — and that the singlet with g-factor 2.018 is due to chemisorbed oxygen atoms. The intensity of these signals decreases rapidly when irradiation is stopped.

It can be seen that soft irradiation which does not lead to the displacement of atoms in the lattice, on the one hand increases the catalytic activity of ZnO in the reaction $H_2 + D_2 \rightleftharpoons 2HD$, and on the other induces EPR signals in the catalyst.

Mishchenko and coworkers[33] established that changes in the same sense are shown by the intensity of the EPR signal induced in titanium dioxide (anatase) by γ-irradiation with ^{60}Co (at -196°C in a vacuum, integral dose 1.7×10^7 r) and its catalytic activity in deuterium exchange in molecular hydrogen at -196°C. An interesting feature is that Kohn and Taylor[30] detected an increase in the catalytic activity of TiO_2 (rutile) with respect to this reaction, only after treatment by irradiation in a reactor. Here, however, the catalysis was carried out at -78°C, that is, a significantly higher temperature.

The above examination suggests that in pure ZnO and TiO_2 (anatase) the centres responsible for the EPR signals are simultaneously the centres for the activation of hydrogen in the reaction $H_2 + D_2 \rightleftharpoons 2HD$.

2. Hydrogenation–Dehydrogenation Reactions

A number of recent papers have compared the paramagnetic properties, influence of irradiation, and catalytic activity for platinum and palladium catalysts deposited on various carriers, and also for other catalysts, with respect to hydrogenation–dehydrogenation reactions.

(a) Hydrogenation reactions. Nicolau and coworkers[34] studied the hydrogenation of p-nitroanisole and crotonic acid on a catalyst consisting of 5% Pt on diamagnetic carbon, and showed that this catalyst gives a narrow EPR signal (singlet with ΔH = 2–5.4 G). Nicolau and coworkers[35] had previously established that this signal is due to the introduction of the electrons of the platinum into a so-called "pseudo-sandwich" complex with carbon. It was shown that not all of the electrons of the platinum enter complexes of this type, since the observed intensity of the signal is smaller than the calculated value by approximately four orders of magnitude.

Specimens of the catalyst were heated in air in the range 50–500°C. It was found that the higher the temperature of preliminary annealing, the lower the intensity of the EPR signal and the catalytic activity. After heating at 500°C, both quantities decrease to zero. Distinct changes in the same sense are thus shown by the catalytic activity with respect to the hydrogenation of these compounds and the concentration of unpaired electrons bound in the "pseudo-sandwich" complexes. In the hydrogenation of nitrobenzene and p-nitrotoluene on catalysts consisting of Ni on zeolite, 1% Pt on active carbon, and 5% Pd on carbon black, Graham[36] observed an increase in the activity of the catalysts after irradiation by X-rays, β-rays, deuterons, or neutrons. He found that the lower the melting point of the metal catalyst, the more ready its activation during irradiation and the more rapid the decrease in this induced catalytic activity. In Graham's opinion, the generation of active centres involves the creation of defects on the surface, and the decrease in catalytic activity is due to their elimination by surface diffusion and annealing. It is quite probable that under appropriate conditions these defects may be revealed in the EPR spectrum, although Graham unfortunately did not carry out these measurements.

At the same time, Minachev[37] did not observe an increase in the catalytic activity of a catalyst consisting of 0.5% Pt on alumina–silica with respect to the hydrogenation of cyclohexane, after irradiation of the contact with ^{60}Co γ-rays (energy of γ-quanta 0.6 MeV).

A parallelism between the appearance of a narrow EPR signal and catalytic activity with respect to hydrogenation is also observed for titanium dioxide.

According to the data of Gray and coworkers[38], TiO_2 with maximum purity does not catalyse the hydrogenation of benzene, and Chester[39] reports that thoroughly oxidised titanium dioxide does not give an EPR signal. TiO_2 which has been partly reduced by hydrogen is a satisfactory catalyst for the Fischer–Tropsch synthesis[38]. At 4.2–2.16°K, this catalyst gives an EPR spectrum consisting of 2–4 lines (ΔH = 18–30 G).[39] With increase in temperature the signal is converted into an asymmetric singlet. (It should be noted that Nicolau also detected a narrow singlet in TiO_2 at room temperature[40].) The nature of this signal is not clear. In Chester's opinion[39] the signal may be due to Ti^{3+} ions in the interstices or at lattice sites in the Ti lattice, perturbed by adjacent oxygen vacancies. It may also be due to electrons (trapped spontaneously) in the interstices. It is not excluded that the signal is given by certain unidentified centres produced as a result of the introduction of hydrogen (but not H and OH). In any case, the signal from a catalyst with oxygen content reduced as a result of heating in a vacuum is quite different.

It was pointed out above that the catalytic activity of pure zinc oxide with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ increases after irradiation. At the same time, previously irradiated zinc oxide (^{60}Co source, $6–10 \times 10^3$ r min^{-1} in a vacuum at 15° ± 5°) shows a lower catalytic activity in the hydrogenation of ethylene at 0° than a non-irradiated specimen[41]. The probable reason for this is that the activation of the ethylene necessary for its hydrogenation does not take place on the hydrogen-activation centres induced by irradiation and revealed in the EPR spectrum.

The irradiation of zinc oxide during catalysis (^{60}Co source, 2.5×10^{19} eV g^{-1} h^{-1}) increases its catalytic activity with respect to the synthesis of methanol from hydrogen and carbon monoxide[42]: the effect was maximal at the lowest catalysis temperature (201°C) — catalytic activity increased by a factor of 4–5.

Kohn and Taylor[17] tried to hydrogenate ethylene on irradiated industrial silica gel. Moderate activity was

detected. For example, after irradiation (1 g silica gel, dose rate 2×10^{17} eV g^{-1} min^{-1}) all the ethylene was hydrogenated in 4 d at room temperature (the catalytic activity was measured by a static method in a system with a volume of 30 cm^3, and the molar ratio of hydrogen and ethylene in the mixture was 2 : 1). There is no sense in relating this induced catalytic activity to the EPR signal induced by irradiation and observed at room temperature. It is known[43] that ethyl radicals adsorbed on the surface of irradiated silica gel are destroyed even at -70°C.

The intensity of the narrow EPR signal and the catalytic activity do not always change in the same sense. An important part is played by the chemical character of the paramagnetic centre. The intensity of the EPR signals and the catalytic activity will change in the same sense only when the paramagnetic centres are chemically capable of catalysing the hydrogenation (or dehydrogenation) of a given substance. In addition to the examples examined above where a change in the same sense does not take place, no parallelism is observed between the intensity of the narrow and broad signals for alumina–chromium oxide catalysts and their activity with respect to the hydrogenation of ethylene. The maximal activity with respect to this reaction was shown by chromium oxide which had been heated to 700°C and exhibited antiferromagnetic properties[44]. The intensity of the EPR signals of this catalyst was low, however, and its width was approximately 500 G.

(b) Dehydrogenation reactions. In the dehydrogenation of cyclohexane on silica gel, alumina, alumina–silica catalyst, ZrO_2, MgO, ZnO, or NiO irradiated with electrons (energy 0.8 MeV) or with ^{60}Co γ-radiation (dose rate 400 r s^{-1}), a correlation was observed between the appearance of the EPR signal and the induced catalytic activity[45]. The irradiation was carried out in ampoules containing the catalyst and cyclohexane (the ampoules were first evacuated and heated at 400°C). After this treatment, a signal due to the $C_6H_7^{\cdot}$ radical was detected in SiO_2, Al_2O_3, and Al_2O_3–SiO_2, unidentified weak signals were detected in ZrO_2 and MgO, and no EPR signal was detected in ZnO or NiO. From this it was concluded that SiO_2, Al_2O_3, and Al_2O_3–SiO_2 exhibit maximal catalytic activity and ZrO_2 lower catalytic activity, and that in ZnO and NiO there is almost no induced catalytic activity. At the same time, as the authors of the paper point out, NiO and ZnO have a high "thermal" catalytic activity (at 300°C) with respect to the dehydrogenation of cyclohexane, whereas the other oxides examined above do not catalyse this reaction at all at the same temperature.

Nicolau[46] showed that platinum, deposited on a carrier containing diamagnetic carbon (the carrier was first immersed in sugar solution and then heated for 1 h at 800°C), brings about intensive catalysis of the dehydrocyclisation of 1,1,3-trimethylcyclopentane, whereas the catalytic activity of Pt/Al_2O_3 and Pt/SiO_2 is smaller by a factor of 3.5–9. The catalytic activity of the $Pt/C + Al_2O_3$ catalyst is higher than that of $Pt/C + SiO_2$. It is significant that only catalysts containing carbon give EPR signals (concentration of paramagnetic centres 9×10^{16} spin g^{-1}, ΔH = 10 G and 2.3×10^{16} spin g^{-1}, ΔH = 12 G respectively). It can be seen that here also the intensity of the narrow EPR signal and the catalytic activity with respect to the dehydrogenation change in the same sense.

Summarising the results for hydrogenation–dehydrogenation reactions, it may be noted that in most cases a parallelism is observed between the intensity of the narrow EPR signals and the catalytic activity. We would emphasise again, however, that a significant part is played by the chemical character of the centre responsible for the appearance of the signal. Thus the centres responsible for the catalysis of the dehydrogenation of cyclohexane on SiO_2, Al_2O_3, and Al_2O_3–SiO_2 are evidently not identical to the centres which are responsible for the catalysis of $H_2 + D_2 \rightleftharpoons 2HD$. In actual fact, it was shown that the reaction $H_2 + D_2 \rightleftharpoons 2HD$ takes place on previously calcined silica gel and alumina gel which give no EPR signal, whereas the dehydrogenation of cyclohexane does not take place on these catalysts even at high temperature. Hydrogen and cyclohexane are apparently activated on different centres in these catalysts.

As already noted, irradiated zinc oxide is inactive with respect to the dehydrogenation of cyclohexane but effectively catalyses deuterium-exchange in molecular hydrogen (see above). In this case also the hydrogen-activation centres produced during irradiation are probably not capable of activating cyclohexane (the statement that here there is a rapid decrease in the intensity of the EPR signals of zinc oxide[45] is apparently without foundation, since the entire catalyst–hydrocarbon system is subjected to irradiation).

3. The Radical Polymerisation of Ethylene

The polymerisation of ethylene is catalysed by a number of catalysts containing transition metal ions[47]. Some of these catalysts have recently been studied by the EPR method. Chromium oxide catalysts have been studied in most detail in this connection. These catalysts are usually prepared by impregnating carriers (alumina or alumina–silica) with chromic acid solution with subsequent activation.

Sometimes the catalyst was activated by heating for 4 h at 350°C, followed by reduction with hydrogen at the same temperature[48,49]; sometimes the catalyst was activated by heating in air at 500°C for 4 h [50] or at 350°C [51], or in a vacuum at 350°C for 4 h [51], or at 400°C for 3 h [52]; sometimes the catalyst was treated with organic solvents[53,54]. O'Reilly and MacIver[55] prepared an alumina–chromium oxide catalyst by impregnating γ-Al_2O_3 with chromium nitrate, followed by roasting and reduction at 500°C. Some reduced specimens were activated by heating at 500°C. An analogous catalyst can also be obtained by coprecipitating chromium and aluminium nitrates, followed by roasting at 500–1400°C. In this work[56] some specimens were reduced by hydrogen at 500°C.

The concentration of chromium in the catalysts was varied from 0.5 wt.% to ~67 wt.%, calculated as Cr_2O_3. Usually, however, the total chromium concentration amounted to 2.5–3 wt.%, and then, after activation by heating in air or in a vacuum, the catalysts prepared by the impregnation method gave an EPR spectrum at room temperature containing signals of two types: a broad line (ΔH = 500–1300 G, g-factor 1.97–1.98) and a narrow line (ΔH = 16.7–50 G, g-factor 1.97–1.99)[2,48,49,51–53,55]. In a reduced alumina–chromium oxide catalyst prepared by the impregnation method (in this case the chromium concentration calculated as Cr_2O_3 was varied from 0.078 wt.% to 10.1 wt.%), O'Reilly and MacIver[55] detected an additional asymmetric signal, whose parameters were not given (it is merely stated that at a frequency of 9.5 Gc s^{-1} this signal has a maximum close to 1500 G). The intensity of

this signal is a maximum at low chromium concentrations and changes little on oxidation. Moreover, the quantity of chromium responsible for this signal is independent of temperature in the range from -195° to +162°C.

The EPR spectrum of a coprecipitated alumina–chromium oxide catalyst[56] at Cr_2O_3 concentrations of 8.05–66.4 wt.%, in addition to a broad absorption line, shows another signal with parameters: ΔH = 200–750 G, g-factor 1.975 ± 0.01. After heating at 500–900°C, specimens with a low Cr_2O_3 concentration (8.05 wt.%) show only the broadest line, whereas specimens with a high Cr_2O_3 concentration (66.4 wt.%) show only the narrower absorption line (ΔH = 200–750 G). After roasting at 1400°C, however, at all Cr_2O_3 concentrations, only this last signal is observed.

Let us now consider how different authors explain the origin of the observed EPR signals. It is suggested[1,48,49,51,53] that the broad signal of the impregnated contacts is due to Cr_2O_3 microcrystallites. O'Reilly and MacIver[55] consider that the state of α-Cr_2O_3 responsible for the broad signal corresponds more closely to Cr_2O_3 gel, which is paramagnetic at room temperature (α-Cr_2O_3 is antiferromagnetic and has a Curie point of +30°C.[57]) In the coprecipitated catalyst, the broad signal is again, in the opinion of MacIver and coworkers[56], due to Cr_2O_3 microcrystallites, amorphous towards X-rays. The narrower signal (ΔH = = 200–750 G), observed only for the coprecipitated contact, is given by a solid solution of Cr_2O_3 in Al_2O_3.[56]

Finally, in the opinion of MacIver and coworkers[55,56], the asymmetric signal on both types of catalyst is due to Cr^{3+} ions which are interacting weakly with one another and are situated in the lattice sites of the carrier, both on the Al_2O_3 surface and close to the surface.

As will be shown later, however, the narrow EPR signal is of the greatest interest from the viewpoint of the catalytic properties of deposited chromium oxide contacts, so that we shall examine its nature in more detail.

The narrow line is symmetrical on alumina gel and asymmetrical on Al_2O_3–SiO_2.[51] O'Reilly[2], and also Kossee and van Reijen[53], consider that the narrow line is due to Cr^{5+} ions. O'Reilly considers that this line cannot be due to diluted Cr^{3+} or Cr^{4+} ions, since then the spectra should have shown a fine structure, but this was not observed. Kossee and van Reijen[53], who observed only a narrow signal with careful reduction (by boiling in organic solvents) of CrO_3 deposited on alumina, established that these specimens have a magnetic moment which is very close to the value corresponding to the spin of one unpaired electron. These authors therefore conclude that the narrow signal is due to quinquevalent chromium ions. Kazanskii and coworkers[51], in their latest work, also concluded that this signal is due to Cr^{5+} ions. They consider, with some justification, that O'Reilly's proof is inadequate, and give additional data in support of this conclusion. A constant value for the g-factor at different frequencies (3.2 cm and 21.8 cm) can be observed only if the narrow signal is due to Cr^{5+} ions. If the signal were due to Cr^{4+} or Cr^{3+} ions, the value of the g-factor should have increased on going from high to low magnetic fields. The detection of HFS [hyperfine structure (Ed. of Translation)] for the narrow signal on an alumina–silica catalyst[58] is also a weighty argument in support of the suggestion that the narrow line is due to Cr^{5+} ions. In actual fact, the HFS indicates the absence of strong exchange interaction, so that the fine structure, if it had been observed (in this case, if the signal had been due to Cr^{3+} or Cr^{4+} ions), should have been clearly defined.

Further support for this conclusion regarding the origin of the narrow line in the EPR spectrum of the chromium oxide catalyst for the polymerisation of ethylene is provided by the fact, established by a number of authors, that the narrow signal is not shown by the catalysts after intensive reduction by hydrogen[50,51,55] and that this signal appears after contacts which have been previously completely reduced are oxidised[51,55]. Moreover, the narrow signal is never observed from activated CrO_3 in the absence of carrier, so that stabilisation of the Cr^{5+} ions takes place on the surface of the carrier[51,52].

Evidence that the Cr^{5+} ions are situated on the surface of the carrier is provided by the oxygen effect (for the narrow EPR signal) detected by Kazanskii and coworkers[51]. Moreover, Nicolau and Thom[59] established that at constant surface area of the carrier (γ-Al_2O_3) the intensity of the narrow signal remains constant with change in the chromium concentration from 1 wt.% to 20 wt.%. In their opinion, this indicates that the paramagnetic centres responsible for the signal are situated chiefly on the surface of the catalyst. There is no agreement regarding the state in which the Cr^{5+} ions are present on the surface of the chromium oxide catalyst. O'Reilly[60], on the basis of the fact that the width of the narrow line remains constant with change in the concentration of chromium in the alumina–chromium oxide catalyst, suggests that the Cr^{5+} ions form a phase. Kazanskii and coworkers[51] agree with this conclusion and support it with the fact that the value of the Weiss constant which they calculated for the alumina–chromium oxide catalyst is +25, that is, it is greater than zero. This means that exchange interaction takes place between the Cr^{5+} ions, which therefore form a phase[51].

MacIver[55] states that Cr^{5+} ions are Cr^{6+} ions on which an electron is "trapped". For coprecipitated alumina–chromium oxide catalysts[56] he gives some evidence that the Cr^{6+} ions are present in small Cr_2O_3 crystals on the surface of the carrier. The maximum intensity of the narrow signal is observed at a chromium concentration of 4.55 wt.%, which corresponds to the maximal Cr_2O_3 surface area. The intensity of the signal decreases at a chromium concentration greater than 7.6 wt.% Cr_2O_3, that is, in the range where an appreciable increase in the dimensions of the Cr_2O_3 granules takes place. MacIver and coworkers also established that the asymmetric signal attributed to isolated Cr^{3+} ions remains unchanged under conditions in which reduction of Cr^{5+} ions takes place. In their opinion, both facts indicate that the Cr^{5+} ions are situated on the catalyst surface not in isolation but in small Cr_2O_3 crystallites. We have already noted, however, that the narrow signal has never been observed from activated CrO_3 in the absence of a carrier. In our opinion, this fact can be reconciled with MacIver's suggestion that the Cr^{5+} ions are situated on the Cr_2O_3 surface only if it is assumed that the Cr^{5+} ions are distributed on the interface between the Cr_2O_3 microcrystallites and the carrier.

Comparison of the results of statistical calculations with experimental data, in particular with data on the EPR of alumina–chromium oxide catalysts, established[56] good agreement between experiment and calculation for a model with random distribution of isolated Cr^{5+} ions on the surface.

Thus MacIver's results, contrary to O'Reilly and Kazanskii's suggestion, indicate that Cr^{5+} ions do not form a phase on the surface of the alumina.

As already noted[58], Cr^{5+} ions on the surface of an alumina–silica carrier do not give an HFS and thus do not form a phase; the signal is anisotropic. To explain these facts it was postulated[58] that Cr^{5+} ions are introduced into the alumina–silica support, in other words, that replacement of some of the Si^{4+} ions by Cr^{5+} ions takes place in the tetrahedra of the surface layer of the alumina–silica. The quinquevalent chromium ions form a surface compound with the alumina–silica support[54]. The quantity of Cr^{5+} ions formed in an alumina–silica catalyst after its activation is small[52] and amounts to 3–4%; 85–88% of the chromium remains in the form of Cr^{6+} ions.

It can thus be seen that on an alumina–silica carrier the quinquevalent chromium ions are present in the form of a dilute solid solution on the surface, whereas on alumina, in the opinion of some authors, they form a phase, while in the opinion of others a phase is not formed. The evidence in support of the suggestion that a Cr^{5+} phase is not formed on the surface of an alumina–chromium oxide catalyst is more convincing.

The Cr^{5+} ions may, in fact, be distributed on the surface sufficiently closely for the observed exchange interaction to take place between them[51] but at the same time at such a distance from one another that no formation of a phase takes place at this stage. The Cr^{5+} ions may, for example, form a sufficiently "concentrated" two-dimensional surface solution. It is evident, moreover, that even if the appearance of HFS indicates unambigously that the Cr^{5+} ions are present in the form of a dilute solid solution, the absence of HFS cannot be taken as proof that these ions form a phase.

Let us examine the relationship between the EPR signals of deposited chromium oxide catalysts and their catalytic activity with respect to the polymerisation of ethylene[53].

Kossee and van Reijen[53] were the first to suggest that the Cr^{4+} or Cr^{5+} ions, which give a narrow EPR signal, are the active centres of the catalyst. Recent experimental results indicate a correlation between the intensity of the narrow EPR signal of original chromium oxide–alumina–silica catalysts and their catalytic activity with respect to the polymerisation of ethylene. Kazanskii and coworkers[52] showed that the maximal catalytic activity is given by catalysts containing 2.5–4 wt.% of chromium. These are the catalysts which give the most intense narrow EPR signal (we are speaking of the original catalysts). Antuf'ev and coworkers[61] also established that the catalytic activity and intensity of the narrow EPR signal change in the same sense. In the opinion of these authors, Cr^{5+} ions are the active component of chromium catalysts for the polymerisation of ethylene. This conclusion is confirmed by data on the chemisorption of the reaction components on the catalyst. Recent work by Kazanskii and coworkers[58] has shown that the Cr^{5+} ions are the centres for the chemisorption of ethylene on the one hand and of water vapour — a poison which inhibits polymerisation — on the other.

It is significant that in the works cited the catalytic activity was compared with the intensity of the narrow signal of the original activated catalysts. At the same time, it can be seen from published data[52] that the intensity of the narrow signal has decreased by approximately one-half 3 h after the start of the reaction, reaching a steady value for the given experimental conditions.

It has been established that sexivalent chromium ions do not take part in the catalysis of the polymerisation of ethylene: disappearance of Cr^{6+} ions from the catalyst produces almost no change in its activity[52,61]. Similarly, intermediate oxides are not the active component: their presence in the catalyst has no influence on the catalytic activity of the catalyst[52]. A catalyst without carrier, containing after activation only Cr_2O_3, is inactive with respect to the polymerisation of ethylene[52,61], so that chromium sesquioxide is also inert with respect to this reaction. In accordance with this, catalysts in which the narrow EPR signal disappears after reduction by hydrogen are catalytically inert[50].

The EPR method has recently been used to study deposited molybdenum catalysts for the polymerisation of ethylene[62]. It was suggested that in this case the catalytically active component consists of quinquivalent molybdenum ions formed during the reduction of the catalysts. It should be noted that here also, as in the study of the chromium catalysts, the EPR measurements were made before catalysis. During catalysis, further reduction of the catalysts takes place, but according to the published data this additional reduction is not extensive.

The formation of Mo^{5+} ions is related to the reaction of the molybdenum oxides with the carrier, in the course of which these ions are stabilised. It is pointed out that the nature of the carrier has a significant influence on the shape of the absorption line: thus on alumina gel the signal (molybdenum concentration 8 wt.%) is symmetrical (g-factor = 1.933, ΔH = 80 G) but on an alumina–silica carrier the signal is asymmetric (ΔH = 60 G, $g_{\parallel}$ = 1.879, $g_{\perp}$ = 1.933). Asymmetric signals are also formed in catalysts based on ZrO_2 and $ZrO_2.SiO_2$.

In the case of alumina–molybdenum oxide and molybdenum oxide–alumina–silica catalysts, the catalytic activity of the catalysts and the intensity of the original EPR signal change in the same sense. Both quantities reach a maximum at a concentration of 20% MoO_3 in the catalysts.

The correlation between the intensity of the narrow EPR signal and catalytic activity was observed not only in the case of chromium and molybdenum catalysts but also in the polymerisation of ethylene on a Ziegler catalyst [$TiCl_4$ + $Al(C_2H_5)_2Cl$].[63]

The course of the reaction between $TiCl_4$ and $Al(C_2H_5)_2Cl$ was followed continuously: the reaction mixture — $TiCl_4$ + + $Al(C_2H_5)_2Cl$ in heptane at room temperature — was circulated through the resonator. After some time, a narrow EPR signal (singlet) was detected. It was established that in this system, reduction of $TiCl_4$ to $TiCl_3$ takes place and part of the $TiCl_3$ is precipitated. This precipitate does not give an EPR signal at room temperature. The authors tried to attribute this to the possible dimerisation of $TiCl_3$ in the solid phase but it is not excluded that the absence of resonance absorption by the precipitate at room temperature may also be due to the too-rapid spin–lattice relaxation of the Ti^{3+} ions. In this connection a recent paper devoted to the study of an analogous system is of interest[64]; it was established that the precipitate formed 0.5 h after the components $TiCl_4$ and $Al(C_2H_5)_2Cl$ were mixed contains no aluminium, has the composition $Ti(C_2H_5)Cl_3$, and gives no EPR signal at room temperature. At the same time, the precipitate removed 4 h after the components were mixed has the overall formula $Ti_3Cl_8Al(C_2H_5)$, contains Ti^{3+}, and gives an EPR signal at room temperature.

It is pointed out that "the curves giving the time dependence of the rate of polymerisation of ethylene and the time dependence of the concentration of unpaired electrons have identical shapes". The addition of 10% of water or oxygen (relative to the aluminium) increases the intensity of the signal by a factor of approximately 2. According to the data given in a patent[65], to which the authors refer, the same quantities of water and oxygen bring about maximal increase in the yield of polymer.

The nature of the signal was examined in subsequent work. A study of the $TiCl_4 + Al(C_2H_5)Cl_2$ system in heptane[66] ($[TiCl_4] = 0.108$ M, $[Al(C_2H_5)Cl_2] = 0.055$ M) established that here also an EPR signal (singlet) appears some time after the components are mixed (at room temperature). The intensity of this signal corresponds to approximately 2% of the concentration of alkylaluminium chloride. This signal consists of two superimposed singlets: a symmetrical singlet with $\Delta H = 22$ G and g-factor 1.925, and a weaker asymmetric signal with ΔH approximately 10 G and g-factor 1.933. After the components are mixed, the intensity of the signal increases, at first very rapidly, and then, after the precipitation of $TiCl_3$, which in this case gives an EPR signal, very slightly. After examining possible mechanisms, the authors concluded that the observed EPR signals are due to Ti^{3+} ions which are formed as a result of complex formation by $TiCl_4$ with the alkylaluminium halides and reduction of the $TiCl_4$ in this complex to Ti^{3+}. The greater the strength of the alkylaluminium halide as a Lewis acid — the acid strength increases in the order $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, $AlCl_3$ — the greater the concentration of this soluble complex and the greater the intensity of the EPR signal.

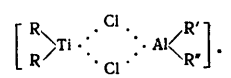
The symmetrical signal is assigned to the complex $(TiCl_3)_2.[Al(C_2H_5)Cl_2]$ and the asymmetric signal to the complex $TiCl_3.[Al(C_2H_5)Cl_2]$, obtained by the decomposition of the first complex, particularly when the ratio Al/Ti is less than unity. In a study of the closely related systems[67]

$(C_5H_5)_2TiCl_2 + Al(CH_3)_3$ [I]; $(C_5H_5)_2TiCl_2 + Al(CH_3)_2Cl$ [II];
$(C_5H_5)_2Ti(CH_3)Cl + Al(CH_3)Cl_2$ [III];
$(C_5H_5)_2TiCl_2 + Al(CH_3)Cl_2$ [IV];
$(C_5H_5)_2Ti(CH_3)Cl + AlCl_3$ [V],

however, it was shown that the analytically determined Ti^{3+} ion concentration is equal to the concentration of unpaired electrons given by measurement of the signal intensity; experimental proof is thus obtained that in these systems the EPR signal is due to Ti^{3+} ions. At a high concentration of the complex (not less than 1×10^{-1} M) the spectrum shows a singlet, but at a low concentration (less than 1×10^{-2} M) an HFS is observed (HFS in analogous systems at low concentrations of the complex was previously observed by Shilov and coworkers[68] and Maki and Rendall[69]). The conversion of the HFS into a singlet at increased concentration of the complex is accompanied by an opposite decrease in the width of the line.

An interesting phenomenon is observed in work with dilute solutions of the complex ($\leq 1 \times 10^{-2}$ M). As the Cl atoms on the aluminium are gradually replaced by CH_3 groups, the shape of the spectrum changes from one with a distinct HFS through a shape with an indistinct HFS to a broad singlet (the observed HFS, consisting of six components, indicates a high electron density at the aluminium nucleus, for which the spin is equal to 5/2). It may therefore be assumed that the localisation of the unpaired electrons on the aluminium decreases with decrease in the acidity of the complex, that is, the alkyl groups increase the delocalisation of the unpaired electrons in the complex.

From the fact that the g-factor is almost constant in the different complexes studied, it is concluded that the electron in the complex is localised to only a slight extent on R, R′, and R″, and that its density is a maximum on Ti, Al, and Cl in



A detailed investigation of the nature of the active component of the Ziegler catalyst is described by Varodi and coworkers[64], who established that the solubility in hydrocarbons shown by the above precipitates separating in the $TiCl_4 + Al(C_2H_5)_2Cl$ system is low but increases by a factor of about 1000 in the presence of $TiCl_4$. Dissolution leads to the formation of a complex of the type $(C_2H_5)TiCl_3$–$Al(C_2H_5)Cl$. This complex is found in the filtrate after separation of the precipitate.

A suspension of the precipitate in heptane is catalytically inactive. The system also remains catalytically inert after the addition of $TiCl_4$. The system formed by the precipitate + $Al(C_2H_5)_2Cl$ also has a low activity. The catalytic activity increases sharply by a factor of about 3 only after the precipitate is mixed with a filtrate containing the soluble complex compound. At the same time, the catalytic activity of the filtrate itself is also low.

The catalytic activity is thus shown by the entire precipitate–soluble complex system, the presence of $TiCl_4$ in the system playing a particularly important part and leading to the maximal formation of the soluble complex compound which is the active cocatalyst.

It can be seen that on all three types of ethylene-polymerisation catalyst studied by the EPR method, it has been possible to establish that the catalytically active component of the catalysts contains M^{n-1} ions, where n is the highest valency of the transition metal. This is probably a general feature, although it cannot be explained at present.

III. REACTIONS INVOLVING ELECTRON TRANSFER

Typical reactions of this group include the decomposition of hydrogen peroxide and dinitrogen oxide, and also oxidation by molecular oxygen. Catalysts for reactions of this type[70] exhibit a high electrical conductivity, which is necessary in order to ensure the possibility of electron transfer, through the catalyst, between the molecules reacting on the catalyst surface (from the molecule being oxidised to oxygen, or from one H_2O_2 (or N_2O) molecule to another). Paramagnetism (or ferromagnetism) is not, however, a necessary property of catalysts for this group of reactions. In recent years it has indeed been shown that there exists a whole class of catalysts for reactions involving oxidation — semiconductors containing no transition elements — which do not exhibit paramagnetism[71]. There are, moreover, a number of oxidation processes on transition metal oxides (in particular, on vanadium pentoxide), which take place without the reduction of V_2O_5, and in which paramagnetic ions (for example, V^{4+} ions) play no significant part[72]. Most oxidations, however, at any rate those involving aromatic substances and alkenes, take place in the steady state on partly reduced oxides, which contain unpaired electrons and are therefore revealed in the EPR spectrum. The study of these spectra may give

some information on the structure and properties of these catalysts. For example, Nicolau and Thom[40] made a comparative study of the EPR spectra of powdered manganese oxides (MnO_2 and Mn_2O_3) and of the same oxides deposited on γ-alumina. The conductivity electrons may lead to broadening of the paramagnetic resonance absorption lines for oxide powders which are not in the highest valency state. In actual fact, the width of the absorption spectrum of MnO_2 powder amounts to 1600 G (the signal shows HFS containing four components); with Mn_2O_3 powder, ΔH is also equal to 1600 G. Deposition of these oxides on γ-Al_2O_3 leads to a sharp decrease in the width of the EPR signals (for MnO_2/γ-Al_2O_3, ΔH = 8 G and for Mn_2O_3/γ-Al_2O_3, ΔH = 5 G), disappearance of the HFS (for MnO_2), and a decrease in the intensity of the signals (from 10^{17} to 10^{16} unpaired electrons per gramme with MnO_2, and from 10^{17} to 10^{13} unpaired electrons per gramme with Mn_2O_3). This sharp change in the signal parameters was attributed to the dispersal of the paramagnetic oxides in the form of aggregates (agglomerates) over the γ-Al_2O_3 surface. The decrease in the width of the lines is attributed to the magnetic dilution of MnO_2 by the diamagnetic γ-Al_2O_3, and the particularly sharp decrease in the intensity of the signal with Mn_2O_3 is attributed primarily to the formation of a covalent bond between the Al^{3+} and Mn^{3+} ions.

A common feature of the signals observed by Nicolau and Thom is their asymmetry. This asymmetry was attributed to the anisotropy of the crystal and also to the influence of active oxygen. Unfortunately, a comparative study of the catalytic properties of different manganese catalysts was not carried out.

1. The Decomposition of Hydrogen Peroxide and Dinitrogen Oxide

Many organic polymeric materials have a low electrical conductivity activation energy, that is, they are semiconductors with a narrow forbidden zone. They thus serve as models of a semiconducting oxide. Semiconductors, however, are effective catalysts for the decomposition of hydrogen peroxide. It is thus not surprising that organic semiconductors such as polyacenequinone (PAQ), poly(acrylonitrile) (PAN), copper polyphthalocyanine (CPP), and poly(aminoquinone)s are active catalysts for the decomposition of hydrogen peroxide[73,74]. The decomposition of dinitrogen oxide also takes place on organic semiconductors[74], the maximal activity being shown by PAN, pyrolysed at 350°C in an atmosphere of argon. PAN pyrolysed in air has an extremely low activity with respect to this process. Here, therefore, oxygen has a significant influence on the catalytic properties of this semiconductor. It is probable that as this reaction proceeds, the activity should decrease as a result of the chemisorption of oxygen, which is one of the products of the decomposition of N_2O. An interesting feature is that in the decomposition of H_2O_2 there is no indication of a difference in the activities of PAN pyrolysed in air or in an atmosphere of argon. H_2O_2 is probably sorbed on the surface no less strongly than oxygen, so that the latter cannot displace H_2O_2 from the catalyst surface.

The decomposition of N_2O also takes place intensively on poly(isoprenechloranil) (PICA) and poly(benzimidazole) (PBIA). All three polymers PAN, PICA, and PBIA, are semiconductors with a long system of conjugated double bonds and nitrogen atoms with a lone pair of electrons. Phthalocyanines (free phthalocyanine and CPP) and also polyacenequinone have almost no catalytic influence on the decomposition of N_2O. This is apparently due to the absence of a long system of conjugated double bonds in the case of phthalocyanines, and in the case of polyacenequinone to the absence of $\dot{N}$ atoms which apparently act as centres for the chemisorption of dinitrogen oxide molecules.

2. The Oxidation of Organic Substances

As already noted, the oxidation of hydrocarbons on the oxides of transition metals in their highest valency states is accompanied by partial reduction of the latter. The activity of the catalyst increases in the process and the concentration of paramagnetic centres also increases. Examples of this parallelism are familiar: for example, the maximal catalytic activity with respect to the oxidation of benzene (flow-circulation method) is shown by a vanadium–molybdenum catalyst containing 30% molybdenum, and the same catalyst also shows the maximal intensity and width for the EPR signal (singlet) observed at room temperature (ΔH = 190 G).[75] At a molybdenum concentration less than 30%, MoO_3 forms a solid solution with V_2O_5. To preserve electrical neutrality in the system, the Mo^{6+} ions must be converted into Mo^{5+} ions, or some V^{5+} ions must be converted into V^{4+} ions. At an Mo concentration less than 5%, the EPR spectrum of the catalyst shows an anisotropic HFS (two groups of lines with eight components in each, $g_\perp$ = 1.99, $g_\parallel$ = 1.90, $\Delta H_\perp$ = 50 G, $\Delta H_\parallel$ = 145 G), characteristic of the V^{4+} ion.[76] From this it was concluded that the second mechanism is involved, that is, the addition of Mo^{6+} ions to the catalyst leads to the production of V^{4+} ions in an amount which, at an MoO_3 concentration $\leq$ 30%, is approximately equal to the quantity of added Mo^{6+} ions. At a higher MoO_3 concentration, however, the latter react with V_2O_5 to form a chemical compound in which only every fifth vanadium ion is converted into V^{4+}. It is considered that the V^{4+} ions act as impurity levels which influence the electronic properties of the semiconductor (V_2O_5) and hence its catalytic activity. Ioffe and coworkers[75] consider that the results provide experimental proof of "the general influence of lattice defects on the catalytic properties of semiconducting catalysts".

Ioffe considers that the addition of ions of higher valency, for example, Mo^{6+} ions, to V_2O_5 is not necessary for the oxidation of naphthalene or *o*-xylene on V_2O_5, because here, as a result of the intensive reduction of the catalyst, there is spontaneous generation of defects (in the form of V^{4+} ions) responsible for the increase in the catalytic activity of the vanadium oxide catalyst[77].

The V^{4+} ions apparently act as centres for the activation of the molecules of the hydrocarbon being oxidised (in particular, benzene[78]). In order to bring about this activation, that is, to displace the electron density from the hydrocarbon to the catalyst, it is necessary to ensure that the Fermi level of the catalyst is sufficiently low-lying[78]. These conditions are satisfied[78] in the oxidation of benzene on a vanadium–molybdenum catalyst, which is a solid solution of MoO_3 in V_2O_5.

It is probably possible in principle, by introducing sexivalent impurity ions (for example, Mo^{6+}), to create such a high concentration of V^{4+} ions in the V_2O_5 lattice that the rate of transfer of electrons from the hydrocarbon (benzene or naphthalene) to the catalyst becomes equal to the rate of transfer of electrons from the catalyst to oxygen.

The operation of the catalyst (in the oxidation of the given hydrocarbon) will thus reach a steady state and no change will take place in its chemical and phase composition. The quantity (~30 mole %) of Mo^{6+} ions (and hence the equivalent quantity of V^{4+} ions) which can be introduced into V_2O_5 without breaking down its crystal structure is insufficient to bring about this equalisation of the rates of the donor and acceptor stages in the oxidation of aromatic hydrocarbons: this is indicated by the partial reduction of the vanadium–molybdenum catalyst in the oxidation of benzene [79], naphthalene, and xylene [77]. It is for this reason that the catalytic oxidation of benzene, xylene, naphthalene, and, apparently, other aromatic hydrocarbons, takes place in the steady state on lower oxides. The latter are thus the active components of vanadium oxide catalysts for the oxidation of aromatic compounds. This is also indicated by results obtained in a study of the oxidation of naphthalene on "sodium vanadium bronze". This "bronze" has a crystal structure close to that of vanadium pentoxide, exhibits a high electrical conductivity, contains V^{4+} ions [80], and gives an EPR spectrum with a signal analogous to the signal of a partly reduced vanadium oxide catalyst [81] and the optimal vanadium–molybdenum catalyst [75]. Nevertheless, the "sodium vanadium bronze" is quite inactive with respect to the oxidation of naphthalene (under the ordinary conditions of catalysis for this process) until partial reduction takes place with the formation of lower oxide phases on its surface [80]. It was also shown that the active component of the vanadium oxide catalyst is a mixture of the oxides V_2O_4 and V_6O_{13}, the V_2O_4 playing the leading part [82]. Of the two modifications of vanadium(IV) oxide studied — the grey crystalline form and the black form amorphous towards X-rays — the grey has the higher catalytic activity. It is the black modification, however, which exhibits intensive resonance absorption at room temperature (singlet with ΔH = = 166 G), whereas the grey modification gives no signal under analogous conditions [83]. Finally, Ioffe and coworkers [75] themselves emphasise that the line width of the EPR signal of used vanadium oxide catalysts is almost independent of the chemical composition of the catalyst. This is attributed to the fact that during catalysis, diffusion of V^{4+} ions to the surface of the catalyst takes place, with the formation of lower oxide phases on the surface.

All these facts indicate that the activity of the vanadium oxide catalyst with respect to the oxidation of naphthalene is due not simply to the presence of defects in its structure, even if these defects are V^{4+} ions, but to the formation, on the catalyst surface, of definite chemical compounds V_2O_4 and V_6O_{13} for which the "defect character" of the crystal lattice is not significant for catalysis.

It appears from published data that the nature of the EPR signals (singlets) observed at room temperature for vanadium pentoxide, partially reduced vanadium oxide catalyst, vanadium(IV) oxide amorphous towards X-rays, and "vanadium bronze", has not been finally established. Ioffe and coworkers [75] attributed the EPR signal which they observed at room temperature for vanadium–molybdenum catalysts to the presence of V^{4+} ions.

Ragle [84] considers that the EPR signals (singlets) observed at room temperature for commercial vanadium pentoxide, vanadium bronzes, and partly reduced vanadium catalysts, are due to an electron localised close to the vanadium. The absence of HFS is attributed to the mobility of these electrons. An analogous conclusion regarding the nature of the paramagnetic centres in V_2O_5 was reached by Ioffe and Patrina [85].

However, this cannot explain the difference in the behaviour of crystalline V_2O_4 and the form amorphous towards X-rays. This may be due to differences in the degree of dispersion of these modifications of V_2O_4.

Crystalline V_2O_4 is antiferromagnetic at room temperature [86]. In amorphous V_2O_4, however, because of its high degree of dispersion and the marked departure from ordering in the structure, the antiferromagnetism is probably removed to some extent and this makes it possible to observe EPR signals from V^{4+} ions at room temperature.

This interpretation explains a number of other facts. During catalysis, the surface of the vanadium oxide catalyst disintegrates, becomes amorphous, and almost doubles in area [87]. The disintegration of the catalyst surface is accompanied by an increase in the intensity of the EPR signal; at the same time, the catalyst may not be chemically reduced. For example, the intensity of the signal from V_2O_5 after catalysis of the oxidation of phthalic anhydride increases [83] by a factor of approximately 30, but no reduction of the catalyst is observed [88]. Moreover, it was established that the intensity of the EPR signal from amorphous V_2O_4 increases after catalysis by a factor of approximately 2, with the simultaneous partial oxidation of the catalyst (the experiments were carried out in gradient-free conditions and measures were taken to eliminate the possible influence of inner-diffusion retardation, which might have led to oxidation of V_2O_4 inside the granule [89]). Special experiments showed that the intensity of the V_2O_5 signal decreases after remelting: by a factor of 2 for "analytical reagent" grade V_2O_5 and by a factor of 5 for "pure" grade V_2O_5. At the same time, the concentration of V^{4+} ions in the oxides decreases by factors of only 1.5 and 2 respectively. Thus "annealing" of the defects takes place much more readily than the decrease in the concentration of V^{4+} ions. All these facts can be explained only by relating the EPR signals observed at room temperature to the presence, in the catalyst, of defects (dislocations) which are centres for the localisation of electrons.

The fact that the signal with maximal intensity is observed from amorphous V_2O_4 and not from the other oxides studied can be attributed firstly to the fact that only V_2O_4 could be obtained in the most highly dispersed state, and secondly to the fact that this oxide contains the maximal number of mobile electrons, of which a definite proportion may be localised on the dislocations in the solid.

It should be emphasised again that the nature of the signals observed at room temperature is the subject of discussion. For us, however, it is significant that the intensity of these signals is not correlated with the activity of the vanadium oxide catalysts with respect to the oxidation of aromatic hydrocarbons.

The EPR method has also been used to study the vanadium–potassium–sulphate–silica gel (VKSS) so-called "complex" catalyst for the oxidation of naphthalene to phthalic anhydride [90]. This catalyst is prepared by impregnating coarsely-porous silica gel with an aqueous solution of vanadyl sulphate and potassium sulphate with subsequent roasting at about 400°C. It was previously considered that this treatment converted the vanadyl sulphate completely into V_2O_5 [91,92] and hence that in principle any soluble vanadium salt, for example, ammonium metavanadate, could be used for the preparation of the catalyst. Vanadyl sulphate was convenient simply because it penetrates more evenly into the silica gel and ensures regular formation of V_2O_5 throughout the whole volume of the

carrier. According to these ideas, the high selectivity of the oxidation of naphthalene to phthalic anhydride on the VKSS catalyst was due to the particularly favourable distribution of the vanadium oxides in the bulk of the carrier. The vanadyl sulphate was merely the starting material for their formation.

In the study of this type of vanadium catalyst, use was made of the fact that of all the vanadium compounds whose presence might have been expected in the VKSS catalyst — vanadyl sulphate, V_2O_5, V_6O_{13}, and V_2O_4 — only vanadyl sulphate gives an intense EPR signal at room temperature[76,77,83], whereas special experiments established that the vanadium oxides deposited on silica gel are not revealed in the EPR spectrum at room temperature. It was found that the catalyst prepared by impregnating silica gel with an aqueous solution of vanadyl sulphate and potassium sulphate, with composition corresponding to that used in industry, after heating at 400°C exhibits maximal selectivity with respect to phthalic anhydride and gives an EPR spectrum with HFS. The EPR signal is also preserved after the catalysis has been carried out for a prolonged period. Moreover, contacts prepared by impregnating silica gel with vanadyl sulphate solution without potassium sulphate, which after roasting do not give a signal and hence do not contain $VOSO_4$, give an intense broad EPR signal after catalysis of the oxidation of naphthalene for several minutes. The appearance of this signal can be attributed to the regeneration of vanadyl sulphate in the catalyst during catalysis. In fact, during the oxidation of the original vanadyl sulphate to V_2O_5 on the catalyst, SO_3 is liberated and may be retained by the carrier. In the reduction of V_2O_5 during catalysis, the V_2O_4 formed reacts with the sorbed SO_3 to form vanadyl sulphate.

It was found that a catalyst prepared by impregnating silica gel with a solution of ammonium metavanadate and potassium sulphate, that is, a catalyst not containing vanadyl sulphate and hence not giving an EPR signal at room temperature either before or after catalysis, shows extremely low selectivity. After this catalyst has been treated in SO_3 vapour at room temperature, however, it begins to oxidise naphthalene much more selectively, and the concentration of the products of extensive oxidation decreases sharply. This catalyst, like that with composition corresponding to that used in industry, also gives a signal with HFS‡.

The observed facts indicate that the outstanding properties of the VKSS catalyst are due chiefly to the characteristic features of its chemical composition, namely the presence of vanadyl sulphate (which gives an EPR signal detectable at room temperature).

Since in the catalysts examined the vanadyl sulphate gives a signal with HFS, it is present in the catalyst and on its surface in the form of a dilute solid solution. The operation of a VKSS catalyst which has not been heated and which, before and after catalysis, contains an appreciable quantity of the original vanadyl sulphate, revealed in the EPR spectrum by the intense singlet characteristic of the $VOSO_4$ phase, is completely analogous to that of a previously heated catalyst in the catalysis of the oxidation of naphthalene. This can be interpreted in different ways[90]. It is possible that in order to obtain the "optimum" VKSS catalyst, the form in which the $VOSO_4$ is present — as a separate phase or in the form of a dilute solid solution — is not important and that only its presence in the system is important.

It has recently been reported that the oxidation of organic substances can also be catalysed by organic semiconductors. Thus it is stated that tetralin is oxidised by a stream of oxygen bubbles in the presence of poly(acrylonitrile)[74]. It is suggested that the action of the poly(acrylonitrile) involves the catalysis of the decomposition of hydroperoxides formed during the autoxidation of the hydrocarbon.

IV. REACTIONS INVOLVING THE DONATION AND WITHDRAWAL OF AN ELECTRON PAIR

Catalysts for this type of reaction are protonic or aprotonic acids or bases. Solid aprotonic catalysts generally show neither electrical conductivity nor paramagnetism, so that the possible applications of the EPR method in the study of catalysts of this type are extremely limited. Here also, however, its application may be useful sometimes, for example, in the examination of the influence of irradiation on the catalytic activity of silica gel and alumina–silica catalysts with respect to the reactions of cracking and isomerisation. In particular, Weisz and Swegler[93] established that pure silica gel heated for 16 h at 550°C and then irradiated with fast and slow neutrons (20 h, dose 7.5×10^{18} cm^{-2} for each type of neutron) shows no catalytic activity with respect to the cracking of isopropylbenzene (the catalytic activity was measured in a Schwab reactor at 420°C and a pressure of 1 atm). At the same time, the activity with respect to the isomerisation of hex-1-ene to hex-2-ene and hex-3-ene (measured in a flow assembly at 350°C) increases appreciably. Mikovsky and Weisz[94] also showed that irradiation with a large neutron dose (10^{20} cm^{-2}) increases the activity of silica gel in the isomerisation of but-1-ene by a factor of approximately 50, but increases the activity of an alumina–silica catalyst by a factor of 1.5–3 (the catalytic activity was measured in a flow microreactor after storage for 6 months to ensure removal of the induced radioactivity). The heat of activation on irradiated alumina–silica is 9.7 kcal mole^{-1}, whereas the value for the original catalyst is 11.4 kcal × × mole^{-1}. The selectivity of the process remains unchanged after irradiation. It is also noted that the specific surface of the irradiated catalysts is smaller by 10–20% than that of the original catalysts.

Contrary to the results of Weisz, earlier work by Lucchesi and coworkers[95,96] established a decrease in the catalytic activity of an alumina–silica catalyst (87% SiO_2), previously heated at 540°C (16 h) and 675°C (3 h), in the isomerisation of the double bond in but-1-ene after electronic irradiation (fast neutron beam 8.9×10^{18} cm^{-2}, slow neutron beam 6.1×10^{18} cm^{-2}, γ-radiation dose 1.2×10^{10} r). The catalytic activity measured 30 d after irradiation at 65°C.

We have already pointed out that the irradiation of anhydrous silica gel leads to the generation of an EPR signal which can be related to the appearance of defects in the structure of the catalyst. Panchenkov and coworkers[97] studied the cracking of isopropylbenzene in a flow assembly at 400°C on an irradiated alumina–silica catalyst with

‡ Treatment with SO_3 vapour naturally cannot alter the distribution of V_2O_5 in the bulk of the carrier, so that the high selectivity with respect to phthalic anhydride shown by the VKSS catalyst cannot be attributed entirely to the difference in the regularity of the distribution of V_2O_5 in the bulk of the carrier during its impregnation with vanadyl sulphate and metavanadate.

composition: Al_2O_3 12.8, SiO_2 87.1, Fe_2O_3 0.07%. The catalyst was irradiated with protons (energy 1.5 MeV, intensity of beam 20 μA at the temperature of liquid nitrogen) and γ-rays (dose 48 million r) at room temperature, and it was established that an EPR signal (singlet) appears after irradiation. At the same time, judging from the degree of conversion, the catalytic activity increases by 25–40% after irradiation with protons and by 77–93% after γ-irradiation.

Comparison of the results obtained by Weisz and Panchenkov shows that irradiation generates EPR signals in these catalysts and influences their activity with respect to the reactions of cracking and isomerisation. It is known that γ-Al_2O_3, which is a strong aprotonic and weak protonic acid, is a comparatively poor catalyst for the cracking reaction and that alumina–silica and silicon–zirconium catalysts, which are strong protonic and aprotonic acids, are effective catalysts for this reaction[98]. It may thus be concluded that cracking takes place actively on protonated surfaces and much less readily on aprotonic catalysts. This explains the inertness of roasted irradiated silica gel (a weak protonic acid) in the cracking of isopropylbenzene. In actual fact, irradiation creates defects in the lattice (EPR signals) but it cannot create the protonated surface necessary for cracking. The increase in the activity of roasted irradiated SiO_2 with respect to the isomerisation of hex-1-ene and but-1-ene can probably be attributed to the fact that this reaction, unlike cracking, also takes place on an aprotonic catalyst such as SiO_2. Irradiation, by producing defects in the surface, naturally leads to an increase in the number of aprotonic active centres on unit surface area of the catalyst. Similarly, as we have already seen, irradiation increases the activity of a catalyst with protonic acidity — the alumina–silica catalyst — with respect to the process catalysed by protonic surfaces, that is, the cracking process.

The decomposition of the oxygen-containing compounds formic acid and propan-2-ol involves simultaneous dehydrogenation and dehydration of the starting material. Dehydrogenation is a reaction taking place by a radical mechanism, whereas dehydration involves an acid–base reaction. It is thus natural to expect that the decomposition of the above substances should take place on catalysts of the radical type[99] which exhibit acidic properties simultaneously. For example, dehydration takes place readily on silica gel, which is a relatively strong aprotonic acid. It was shown above that irradiated silica gel gives a strong EPR signal and catalyses the dehydrogenation of cyclohexane. It was thus expected that irradiated silica gel would catalyse the decomposition of the oxygen-containing compounds in two directions — with dehydrogenation and with dehydration. It was in fact shown[100] that irradiated silica gel (Xerogel R) begins to catalyse not only the dehydration of formic acid, but also its dehydrogenation.

Slinkin and coworkers[101] studied the EPR signals of alumina–chromium oxide catalysts with a wide range of compositions (1.5–93 wt.% Cr) after roasting at 450°, 600°, and 1000°C, and after catalysis had been carried out on them. In agreement with data obtained by other authors, it was found that the original catalysts at room temperature show two signals: a narrow signal with ΔH = 40–55 G, and a broad signal with ΔH = 1000 G. After catalysis, at a chromium concentration ≤ 14%, the narrow signal (Cr^{5+} ions) disappears. With increase in the roasting temperature, the intensity of the broad line increases and its width decreases to 500 G. It was concluded that the active centres of the catalyst are not Cr^{5+} ions but a number of centres containing Cr^{6+}, Al^{3+}, and O^{2-} ions. The actual catalytic process studied is not reported, however, and an earlier paper referred to by the authors merely notes that the decomposition of propan-2-ol was studied. It is not clear from the text whether dehydrogenation, or dehydration, or both took place. It may be assumed that both processes should take place on this catalyst, which after catalysis gives an intense EPR signal and which contains a strong aprotonic acid — Al_2O_3.

The decomposition of propan-2-ol and cyclohexanol on certain organic semiconductors was recently studied[74]. On three of these — poly(benzimidazole), poly(acrylonitrile), and poly(isoprenebenzoquinone) — decomposition involves dehydration and dehydrogenation simultaneously; dehydration of the alcohols takes place almost exclusively only on the most "acidic" compound — polyacenequinone.

1. L.A.Blyumenfel'd, V.V.Voevodskii, and A.G.Semenov, "Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii" (The Use of Electron Paramagnetic Resonance in Chemistry), Izd.Sibir.Otd.Akad.Nauk SSSR, Novosibirsk, 1962, p.201.
2. D.E.O'Reilly, Adv.Catalysis, 12, 31 (1960).
3. K.Hirota, Kagaku (Kyoto), 16, 86 (1961).
4. D.J.E.Ingram, "Free Radicals as Studied by Electron Spin Resonance" (Translated into Russian), Inostr.Lit., Moscow, 1961.
5. S.A.Al'tshuler and B.M.Kozyrev, "Elektronnyi Paramagnitnyi Rezonans" (Electron Paramagnetic Resonance), Fizmatgiz, Moscow, 1961.
6. W.Low, "Paramagnetic Resonance in Solids" (Translated into Russian), Inostr.Lit., Moscow, 1962.
7. V.G.Baru, Uspekhi Khim., 32, 1340 (1963) [Russ.Chem. Rev., 590 (1963)].
8. Yu.L.Polyakin, Trudy Groznen.Neft.Inst., No 20, 14 (1958).
9. J.E.Leffler, "The Reactive Intermediates of Organic Chemistry", Interscience, New York, 1956.
10. J.Turkevich and P.W.Selwood, J.Amer.Chem.Soc., 63, 1077 (1941).
11. J.Turkevich, J.Maki, and W.J.Tomas, in "Actes du 2.Congrès Internat.de Catalyse", Edition Technip, Paris, 1961, p.1815.
12. F.F.Vol'kenshtein, Probl.Kinetiki i Kataliza, Akad.Nauk SSSR, 8, 79 (1955).
13. V.B.Kazanskii, G.B.Pariiskii, and V.V.Voevodskii, Discuss.Faraday Soc., No.31, 203 (1961).
14. Yu.N.Molin and V.V.Voevodskii, Zhur.Tekh.Fiz., 28, 143 (1958).
15. H.W.Kohn, J.Chem.Phys., 33, 1588 (1960).
16. H.W.Kohn, Nature, 184, 630 (1959).
17. H.W.Kohn and E.H.Taylor, in "Actes du 2.Congrès Internat. de Catalyse", Edition Technip, Paris, 1961, p.1461.
18. E.H.Taylor, Nucleonics, 20, 53 (1962).
19. H.W.Kohn and E.H.Taylor, J.Phys.Chem., 63, 966 (1959).
20. H.W.Kohn, J.Catalysis, 2, 208 (1963).
21. H.W.Kohn, J.Phys.Chem., 66, 1017 (1962).
22. A.V.Kiselev, Kolloid.Zhur., 2, 17 (1936).
23. E.H.Taylor and H.W.Kohn, J.Amer.Chem.Soc., 79, 252 (1957).
24. H.W.Kohn and E.H.Taylor, J.Phys.Chem., 63, 500 (1959).

25. Yu.A.Kolbanovskii, I.M.Kustanovich, L.S.Polak, and A.S.Shcherbakova, "Trudy Tashkentskoi Konferentsii po Mirnomu Ispol'zovaniyu Atomnoi Energii, Tashkent, 1959" (Proceedings of the Tashkent Conference on the Peaceful Uses of Atomic Energy, Tashkent, 1959), Izd.Akad.Nauk Uzbek.SSR, 1961, p.191.
26. V.B.Kazanskii and Yu.I.Pecherskaya, Zhur.Fiz.Khim., 34, 477 (1960) [Russ.J.Phys.Chem., 225 (1960)].
27. V.I.Vedeneev, L.V.Gurvich, V.N.Kondrat'ev, V.A.Medevdev, and E.L.Frankevich, "Energiya Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (The Energies of Chemical Bonds. Ionisation Potentials and Electron Affinity), Izd.Akad.Nauk SSSR, Moscow, 1962, pp.44, 58.
28. Ya.K.Syrkin, Uspekhi Khim., 31, 397 (1962) [Russ.Chem. Rev., 197 (1962)].
29. J.Turkevich and J.Laroche, Z.phys.Chem.(Frankfurt), 15, 399 (1958).
30. H.W.Kohn and E.H.Taylor, J.Catalysis, 2, 32 (1963).
31. E.V.Baranov, V.E.Kholmogorov, and A.N.Terenin, Dokl. Akad.Nauk SSSR, 146, 125 (1962).
32. J.Schneider and A.Rauber, Z.Naturforsch, 16a, 712 (1961).
33. Yu.A.Mishchenko, G.K.Boreskov, V.B.Kazanskii, and G.B.Pariiskii, Kinetika i Kataliz, 2, 296 (1961).
34. C.S.Nicolau, P.Wenker, and E.Pobitschka, Z.anorg. Chem., 311, 127 (1961).
35. C.S.Nicolau, H.G.Thom, and E.Pobitschka, Trans.Faraday Soc., 55, 1430 (1959).
36. D.Graham, J.Phys.Chem., 66, 510 (1962).
37. Kh.M.Minachev, M.A.Markov, and Yu.S.Khodakov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 1227 (1961).
38. T.J.Gray, C.C.McCoin, and N.G.Masse, J.Phys.Chem., 63, 472 (1959).
39. P.F.Chester, J.Appl.Phys., Suppl., 32, 2233 (1961).
40. C.S.Nicolau and H.G.Thom, in "Actes du 2.Congrès Internat. de Catalyse", Edition Technip, Paris, 1961, p.1923.
41. E.H.Taylor and J.A.Wethington, J.Amer.Chem.Soc., 76, 971 (1954).
42. T.J.Barry and R.Roberts, Nature, 184, 1061 (1959).
43. V.B.Kazanskii and G.B.Pariiskii, Kinetika i Kataliz, 2, 507 (1961).
44. Yu.I.Pecherskaya, V.B.Kazanskii, and V.V.Voevodskii, Kinetika i Kataliz, 3, 111 (1962).
45. V.I.Vladimirova, G.M.Zhabrova, B.M.Kadenatsi, V.B.Kazanskii, and G.B.Pariiskii, Dokl.Akad.Nauk SSSR, 148, 101 (1963).
46. C.S.Nicolau and K.H.Schnabel, Nature, 193, 871 (1962).
47. A.V.Topchiev, B.A.Krentsel', and A.I.Perel'man, Uspekhi Khim., 26, 1355 (1957).
48. V.V.Voevodskii, V.B.Kazanskii, and Yu.I.Pecherskaya, Kinetika i Kataliz, 1, 257 (1960).
49. Yu.I.Pecherskaya, V.B.Kazanskii, and V.V.Voevodskii, in "Actes du 2.Congrès Internat.de Catalyse", Edition Technip, Paris, 1961, p.2121.
50. G.B.Sergeev, E.K.Sharaev, K.V.Topchieva, A.I.Perel'man, and V.V.Topchiev, Neftekhimiya, 2, 18 (1962).
51. V.B.Kazanskii and Yu.I.Pecherskaya, Kinetika i Kataliz, 2, 454 (1961).
52. F.M.Bukanaeva, Yu.I.Pecherskaya, V.B.Kazanskii, and V.A.Dzis'ko, Kinetika i Kataliz, 3, 358 (1962).
53. P.Kossee and L.L.van Reijen, in "Actes du 2.Congrès Internat.de Catalyse", Edition Technip, Paris, 1961, p.1679.
54. F.M.Bukanaeva, G.K.Boreskov, and V.A.Dzis'ko, Kinetika i Kataliz, 4, 493 (1963).
55. D.E.O'Reilly and D.S.MacIver, J.Phys.Chem., 66, 276 (1962).
56. C.P.Poole, Jnr., W.L.Kehl, and D.S.MacIver, J.Catalysis, 1, 407 (1962).
57. E.P.Tronnson, D.F,Bleil, R.K.Wongness, and L.R.Maxwell, Phys.Rev., 79, 542 (1955).
58. V.B.Kazanskii and Yu.I.Pecherskaya, Kinetika i Kataliz, 4, 244 (1963).
59. C.S.Nicolau and H.G.Thom, "Hochfrequenzspektroskopie", Akademie-Verlag, Berlin, 1961, p.162.
60. D.E.O'Reilly and D.S.MacIver, Paper Presented at the Symposium on Technique on Study of Catalysis Mechanism, Boston, 5–10th April, 1959.
61. V.V.Antuf'ev, M.P.Botinov, A.G.Savin, B.I.Sazhin, A.S.Semenova, and M.I.Leitman, Kinetika i Kataliz, 3, 353 (1962).
62. G.K.Boreskov, V.A.Dzis'ko, V.M.Emel'yanova, Yu.I.Pecherskaya, and V.B.Kazanskii, Dokl.Akad.Nauk SSSR, 150, 829 (1963).
63. E.H.Adema, H.J.M.Bartelink, and J.Smidt, Rec.Trav. chim., 80, 173 (1961).
64. E.Varodi, V.I.Tsvetkova, and N.M.Chirkov, Dokl.Akad. Nauk SSSR, 152, 908 (1963).
65. German P. 1 022 382 (9th January 1958); Chem.Abs., 54, 13 740a (1960).
66. E.H.Adema, H.J.M.Bartelink, and J.Smidt, Rev.Trav. chim., 81, 73 (1962).
67. H.J.M.Bartelink, H.Bos, J.Smidt, C.H.Vrinssen, and E.H.Adema, Rev.Trav.chim., 81, 225 (1962).
68. A.E.Shilov, A.K.Zefirova, and N.I.Tikhomirova, Zhur. Fiz.Khim., 33, 310 (1959) [Russ.J.Phys.Chem., Abs., 7, (1959)].
69. A.H.Maki and E.W.Rendall, J.Amer.Chem.Soc., 82, 4109 (1960).
70. S.Z.Roginskii, Probl.Kinetiki i Kataliza, Akad.Nauk SSSR, 8, 110 (1955).
71. S.Z.Roginskii, Kinetika i Kataliz, 1, 15 (1960).
72. V.Ya.Vol'fson, Kinetika i Kataliz, 6, 553 (1965).
73. A.A.Berlin, L.A.Blyumenfel'd, and N.N.Semenov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 1689 (1959).
74. R.Sallé, J.Gallard, and P.Traynard, Compt.rend., 256, 2588 (1963).
75. V.B.Kazanskii, Z.I.Ezhkova, A.G.Lyubarskii, V.V.Voevodskii, and I.I.Ioffe, Kinetika i Kataliz, 2, 862 (1961).
76. B.M.Kozyrev, Discuss.Faraday Soc., No.19, 135 (1955).
77. I.I.Ioffe, Z.I.Ezhkova, and A.G.Lyubarskii, Zhur.Fiz. Khim., 35, 2348 (1961) [Russ.J.Phys.Chem., 1160 (1961)].
78. Z.I.Ezhkova, I.I.Ioffe, V.B.Kazanskii, A.V.Krylova, A.G.Lyubarskii, and L.Ya.Margolis, Kinetika i Kataliz, 5, 861 (1964).
79. I.I.Ioffe, Z.I.Ezhkova, and A.G.Lyubarskii, Kinetika i Kataliz, 3, 194 (1962).
80. J.Gendell, R.M.Cotts, and M.J.Sienko, J.Chem.Phys., 37, 220 (1962).
81. V.Ya.Vol'fson, L.N.Ganyuk, and E.F.Totskaya, Kinetika i Kataliz, 5, 1100 (1964).
82. V.Ya.Vol'fson, Ya.V.Zhigailo, E.F.Totskaya, and V.V.Raksha, Kinetika i Kataliz, 6, 162 (1965).
83. L.N.Ganyuk and V.Ya.Vol'fson, in Collected Papers, "Trudy Vsesoyuznoi Konferentsii po Metodam Issledovaniya Katalizatorov i Kataliticheskikh Reaktsii, Novosibirsk, 1965" (Proceedings of the All-Union Conference on Methods of Studying Catalysts and Catalytic Reactions, Novosibirsk, 1965), Vol.III, p.32.
84. J.L.Ragle, J.Chem.Phys., 38, 2020 (1963).
85. V.A.Ioffe and I.B.Patrina, Fiz.Tverd.Tela, 6, 3045 (1964).
86. I.S.Smart, Phys.Rev., 86, 986 (1952).
87. G.P.Korneichuk, V.P.Ushakova, and T.G.Skorbilina, Kinetika i Kataliz, 2, 931 (1961).
88. V.Ya.Vol'fson, G.P.Korneichuk, and V.A.Roiter, Ukrain. Khim.Zhur., 26, 306 (1960).

89. V.P.Ushakova, G.P.Korneichuk, V.A.Roiter, and Ya.V.Zhigailo, Ukrain.Khim.Zhur., 23, 191 (1957).
90. V.Ya.Vol'fson and L.N.Ganyuk, Kinetika i Kataliz, 6, 306 (1965).
91. Ota, J.Soc.Org.Syn.Chem., Japan, 15, 121 (1951).
92. H.Hoog, Chem.and Ind., 872 (1961).
93. P.B.Weisz and E.W.Swegler, J.Chem.Phys., 23, 1567 (1955).
94. R.J.Mikovsky and P.B.Weisz, J.Catalysis, 1, 345 (1962).
95. P.J.Lucchesi, D.L.Baeder, J.P.Longwell, and M.C.Schroeder, J.Chem.Phys., 31, 55 (1959).
96. P.J.Lucchesi, D.L.Baeder, and J.P.Longwell, J.Amer. Chem.Soc., 81, 3235 (1959).
97. G.M.Panchenkov, V.I.Yakovlev, L.L.Kozlov, Yu.M.Zharov, and D.A.Kuzovkin, Zhur.Fiz.Khim., 36, 1113 (1962) [Russ. J.Phys.Chem., 592 (1962)].
98. V.A.Dzis'ko, M.S.Borisova, N.S.Kotsarenko, and E.V.Kuznetsova, Kinetika i Kataliz, 3, 728 (1962).
99. E.S.Dokukina, S.Z.Roginskii, M.M.Sakharov, A.V.Topchiev, M.A.Geiderikh, B.E.Davydov, and B.A.Krentsel', Dokl.Akad.Nauk SSSR, 135, 603 (1960).
100. G.Dolmat, B.Imelik, and M.Segnin, J.Chim.phys., 58, 292 (1961).
101. A.A.Slinkin, E.A.Fedorovskaya, and A.M.Rubinshtein, Kinetika i Kataliz, 4, 230 (1963).

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