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Radical Processes in the Adsorption of Olefins on Zeolites

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The formation and reactions of radical species in the interaction of olefins with zeolites of different types are examined and the nature of the oxidation-reduction centres, the mechanism of the thermal reactions of radicals, and the possible role of radical structures in catalytic processes on zeolites are discussed.
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I. INTRODUCTION

The catalytic reactions and mechanisms of the adsorption of olefins on zeolites of different types have been the subject of numerous studies and their results have been surveyed in a number of monographs.[1-3] In the vast majority of the publications the catalytic and adsorption processes involving olefins are discussed taking into account the formation as intermediate species of carbonium ions or carbanions on Lewis or Brønsted centres.

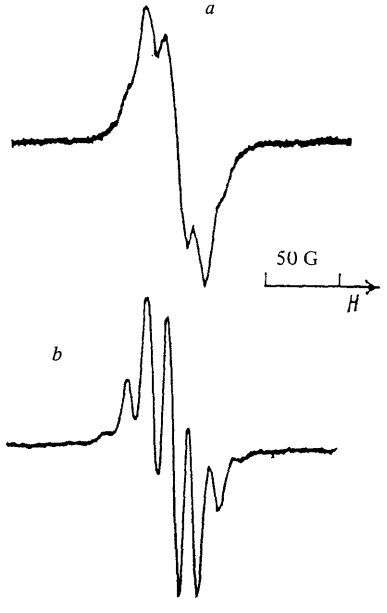


Figure 1. The EPR spectra arising in the adsorption of oct-1-ene (*a*) and pent-2-ene (*b*) from solution in CCl_4 on the lanthanide-form of the zeolite Y.[6]

Many fewer studies have been devoted to the radical species arising in the interaction of olefins with zeolites of different structure and to the nature of the centres initiating the formation of radicals, the mechanism of the thermal reactions of radicals, and their possible role in catalytic processes. This problem has acquired particular interest in recent years in connection with the discovery of the unique ability of high-silica zeolites to convert olefins into aromatic compounds.[4,5] The aim of the present review was to survey the available data concerning the mechanisms of the formation and reactions of radicals in the adsorption of olefins on zeolites and also to discuss the nature of the centres responsible for the one-electron charge transfer process.

II. THE FORMATION OF RADICALS IN THE ADSORPTION OF OLEFINS ON ZEOLITES OF THE FAUJASITE TYPE

The EPR spectra arising in the adsorption of olefins (2-methylbut-2-ene, 4-methylpent-2-ene, pent-2-ene, and oct-1-ene) on zeolites were apparently first published by Hirschler et al[6] (Fig.1): the adsorption was carried out from solutions in CCl_4 on the lanthanide-, Ca-, and Ce-forms of a type Y zeolite after their preliminary heat treatment at 500 °C in a stream of dry air. The same spectra, albeit slightly broadened owing to the high concentration of radicals, were observed in the adsorption of the pure olefins. The removal of the sorbed gases from CCl_4 (by evacuation) does not alter the EPR spectra, i.e. the oxygen contained in solution does not influence their characteristics.

The ratios of the intensities of the components of the spectrum (1 : 6 : 15 : 20 : 15 : 6 : 1) (Fig.1*b*) agree well with the EPR spectrum for the case of six equivalent protons with a hyperfine structure (HFS) constant a_H = 13.5 G. The EPR spectrum of oct-1-ene with the component intensity ratios 1 : 4 : 6 : 4 : 1 and a_H = 12.0 G corresponds to a species with four equivalent protons. The EPR spectra observed in the adsorption of 2-methylbut-2-ene and 4-methylpent-2-ene contain respectively 7 and 5 poorly resolved components with approximately binomial intensity ratios. The above values of a_H, which are approximately equal to half the corresponding values for the protons of the CH_3 group in the ethyl radicals (26.87 G), show, according to Hirschler et al,[6] that the unpaired electron in the radicals formed can be delocalised over two carbon atoms. It is fairly difficult to understand how radicals with five or six equivalent protons are formed from the adsorbed olefins mentioned above. It is believed[6] that the EPR signal produced can be associated with the olefin isomerisation or polymerisation products. At any rate, the polymer extracted from the zeolite, formed after the adsorption of pent-2-ene, gave rise to the

same EPR spectrum as that observed in the adsorption of pent-2-ene. Hirschler et al[6] do not express any views about either the nature of the centres on which the radical species are formed or the structure of the radicals formed.

Suzaki et al[7] continued the investigation of the properties of radicals arising in the adsorption of the olefin (but-1-ene) from the gas phase on the cation-substituted (Ce, Mg, Ca, Sr, Zn) zeolites Y and compared the rate of formation of the radicals with the rate of isomerisation of but-1-ene. The adsorption of but-1-ene on the CaY zeolite (degree of exchange 91.8%) at 25 °C leads to the appearance of a spectrum which is completely identical with that illustrated in Fig.1*b* with $a_H = 14.7$ G and $g = 2.002$. At temperatures from −16° to 25 °C and a but-1-ene pressure p ranging from 0.065 to 160 mmHg the steady-state concentration N of the radicals formed is expressed by the equation

$$N = N_s \frac{Kp}{1 + Kp}, \qquad (1)$$

where $N_S = 2 \times 10^{21}$ spins cm^{-2} and $K = K_0 \exp(\Delta H/RT) = 0.9$ (mmHg)$^{-1}$ (at $T = 25$ °C and for $\Delta H = 4.1$ kcal mole^{-1}); N_S amounts to 10^{-3} of the number of adsorbed but-1-ene molecules, i.e. 0.1% of the adsorbed olefin molecules are converted into radicals. A characteristic feature of the behaviour of the radicals formed is that they are stable if the gas phase contains but-1-ene molecules but recombine on evacuation (the EPR signal gradually disappears), the kinetics of this process being described by a second-order equation. If thermal desorption is carried out after the disappearance of the EPR signal, then it is possible to observe the presence of octane, octene, butane, butene, propene, and propane.

The experiments carried out by Suzaki et al[7] to investigate the influence of the zeolite dehydration temperature on the intensity of the EPR spectrum enabled them to put forward certain considerations about the mechanism of the formation of the radicals. Thus the possibility of the formation of a radical as a result of the transition of an H atom from the OH group of the zeolite to a but-1-ene molecule with formation of a 2-butyl radical is postulated†, because the intensity of the EPR spectrum increases by a factor of 15 on reducing the dehydration temperature from 600° to 250 °C. According to the authors,[7] the increase of the signal intensity after the addition of H_2O confirms the proposed mechanism and the formation of octane at temperatures above 100 °C and the decrease of the EPR signal intensity on evacuation are due to the recombination of the 2-butyl radicals. The seven equally spaced lines in the EPR spectrum have been explained by the interaction of the unpaired electron with the six equivalent hydrogen atoms of the radical formed. If this is true, then, as stated correctly by the above investigators,[7] the HFS constant should be the same as for the α- and β-protons in the butyl radical in the liquid phase, i.e. approximately twice as great as the measured value (14.7 G). The authors suggest that this contradiction cannot be eliminated by assuming the formation of the allyl radical as a result of the abstraction of a hydrogen atom from the but-1-ene molecule, because in this case it would be difficult to account for the influence of the dehydration temperature and the addition of H_2O on the EPR signal intensity.

Thus the authors[7] postulate the formation of the 2-butyl radical and suggest that the low HFS constant can be due either to the perturbation of the wave function of the unpaired electron under the influence of the electrostatic field of the zeolite lattice or to the decrease of the unpaired electron density of the carbon atom of the radical owing to the partial transfer of the electron to the zeolite, i.e. the formation of a partly charged 2-butyl radical.

Another important feature of the investigation of Suzaki et al[7] is the attempt to compare the concentration of radicals with the degree of isomerisation of but-1-ene and to show that the 2-butyl radical can behave as an intermediate in the isomerisation process. This idea is seemingly confirmed by four observations:

1. the number of radicals in different cation-substituted forms of the zeolite Y is correlated with the degree of conversion of but-1-ene (Table 1);
2. the dependence of the rate of isomerisation on the hydrocarbon pressure is of the same type as the corresponding dependence of the intensity of the EPR signal of the radical formed, which is described by Eqn.(1);
3. at a constant pressure the degree of isomerisation of but-1-ene changes following the addition of H_2O in proportion to the change in the EPR signal intensity; we may note that, when the EPR signal intensity changes by a factor of approximately 4, the degree of isomerisation is only slightly altered;
4. following the addition of O_2, the isomerisation reaction is suppressed and 2-butyl radicals are converted into peroxy-radicals.

Table 1. Dependence of the degree of conversion α of but-1-ene and the concentration of radicals N_S on the type of zeolite employed (β is the degree of exchange).[7]

Catalyst	β, %	$10^{-15} N_S$, spins/100 mg	α, %	Catalyst	β, %	$10^{-15} N_S$, spins/100 mg	α, %
CeY	91.8	200	88	ZnY	91.8	2	20
MgY	72.5	80	80	CuX	—	*	13
CeY	67.5	60	68	CoX	83.3	nil	5
CaY	93.2	10	58	MgX	96.8	nil	traces
CeX	—	10	37	ZnX	100	nil	traces
NH_4Y	90.5	9	72	TlX	100	nil	traces
SrY	97.6	4	65	NaY	100	nil	traces

*It may be that the EPR signal of the radical is not observed owing to its overlap by the signal due to the Cu^{2+} cation.

However, having measured the rate of isomerisation and the rate of formation of radicals using a mixture of deuteriated and non-deuteriated but-1-enes, the authors showed that the rate of isomerisation is higher, i.e. the 2-butyl radical is not an intermediate and is not in equilibrium with the intermediate of the isomerisation reaction. It is also assumed that a small proportion of 2-butyl radicals on the outer surface of the zeolite may be an intermediate product of the isomerisation process.

Although the authors[7] seemingly demonstrated that the radicals formed in the adsorption of but-1-ene on cation-substituted zeolites Y are not intermediates in the isomerisation reaction, this idea was again discussed by Otsuka et al.[8] They investigated the isomerisation of *cis*-but-2-ene at 25 °C on the zeolite HY (degree of exchange 86%) subjected to vacuum heat treatment in the range 400–650 °C. They studied the influence of promoting agents (CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, and HCl) on the rate of reaction and compared the latter with the concentration of the radicals formed on the initial and promoted zeolites. It was found that the rate of isomerisation on the zeolite evacuated at 650 °C increases sharply in the presence of preadsorbed CCl_4.

†Here and henceforth the radical $CH_3CH_2\dot{C}HCH_3$.

The promoting effect of CCl_4 is manifested only for zeolites heat-treated above 500 °C. An infrared spectroscopic study of the interaction of CCl_4 with the acid OH groups of the zeolite heat-treated at 650 °C showed that this interaction is weak and reversible: the entire adsorbed CCl_4 is removed by evacuation at room temperature.

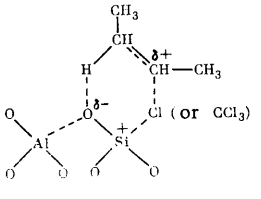
On the other hand, the data presented in Table 2 show that CCl_4 preadsorbed on the zeolite evacuated at 650 °C induces a sharp increase of the EPR signal intensity during the subsequent adsorption of *cis*-but-2-ene. The adsorption of the olefin on the clean specimen is accompanied by the appearance of only a weak EPR signal. It is noteworthy that this signal consists of a seven-component spectrum with $g = 2.003$ and $a_H = 14.5$ G and is almost identical with the signals observed by other workers;[6,7] among all the chloro-compounds investigated, only CCl_4 induces a sharp increase of the EPR signal intensity. The specimen evacuated at 400 °C is not subjected to the promoting effect of CCl_4 as regards the intensity of the EPR signal due to the adsorbed olefin and also the catalytic activity.

Table 2. The relative intensities *I* of the EPR signals of the radicals formed in the *cis*-but-2-ene + chloro-compound + zeolite HY system at 25 °C.[8]

Adsorbate	*I*, rel. units
CCl_4 + butene	17*
CCl_4 + butene	280
$SnCl_4$ + butene	21
$GeCl_4$ + butene	5
$SiCl_4$ + butene	13
HCl + butene	5
Butene	7
Butene	23**

*The temperature of the preliminary heat treatment of the zeolite was 400 °C; in the remaining cases it was 650 °C.
**After 24 h; in the remaining cases—after 1 h.

In conformity with the hypothesis put forward by Suzaki,[7] Otsuka et al. believe that the EPR spectrum observed during the adsorption of *cis*-but-2-ene is due to the formation of a partly charged 2-butyl radical, which is an intermediate in the isomerisation reaction, and the increase of the rate of the isomerisation reaction under the influence of CCl_4 is related to precisely this factor. The observed[8] increase of the rate of isomerisation under the influence of other chlorine-containing additives, which do not induce an increase of the EPR signal, has been explained by the modification of the Brønsted acid centres. The unique ability of precisely CCl_4 to promote the formation of radicals in the adsorption of the olefin is associated, according to Otsuka et al,[8] with the possibility of the dissociation of CCl_4 into the radical species CCl_3 and Cl (not detected by EPR) on centres arising in the high-temperature dehydroxylation. The CCl_3 or Cl radical species stabilised on the electron-accepting centre promote the formation of a partly charged 2-butyl radical on interaction of the olefin with the acid OH group. The proposed mechanism of the interaction is shown below:



The results of detailed studies of the interaction of various olefins with cation-substituted zeolites of the faujasite type have been described.[9-12] It is emphasised[9] that the adsorption of olefins on zeolites leads to the appearance of EPR spectra with an odd number of components, which cannot be explained, according to the author,[9] by the addition (or abstraction) of hydrogen atoms to (from) the olefin molecule, since the signal of such a radical would have had an even number of components (if all the hydrogen atoms in the molecule participate in the formation of the HFS). It is therefore suggested that the radical species arises as a result of electron transfer from the zeolite lattice to the olefin molecule. Data for the formation of the radical in the adsorption of but-1-ene on the zeolite CeX (68% exchange) are presented as an example. The EPR spectrum produced contains seven components ($g = 2.0037$, $a_H = 14$ G); the signal intensity is much greater in this case when the adsorption is carried out on a specimen activated *in vacuo* and then treated with O_2. It is suggested that an electron is transferred to the olefin molecule from the Ce^{3+} cation or from the reduction centre.

A further development of the study quoted above involved the investigation[10] of the formation of radicals in the adsorption of various olefins (propene, isobutene, *cis*- and *trans*-but-2-enes, but-1-ene, and *cis*- and *trans*-pent-2-enes). After the adsorption of the above olefins, EPR spectra containing seven and nine components and having a binomial distribution of intensity appear ($g = 2.0023 \pm 0.0005$, $a_H = 14$ G). The author[10] suggests that the radical species do not have the allyl structure, because 3,3,dimethyl-but-1-ene, which does not produce such a structure, gives rise to an identical EPR spectrum. Cyclic olefins (cyclopentene and cyclohexene) give rise to intense EPR signals with a poorly resolved HFS.

The following properties of the radical species may be noted in relation to the radicals formed in the adsorption of isobutene:

1. the radicals are stable at room temperature;
2. an increase of temperature to 50 °C entails an increase of signal intensity, which falls on further increase of temperature;
3. cooling to room temperature again results in the appearance of a signal with an HFS but with a lower intensity;
4. the radicals are stable when acted upon by O_2, CO_2, and H_2O: exposure of the specimens to air for several days does not result in the destruction of radicals;
5. the adsorption of H_2O, before the adsorption of the olefin or simultaneously with the latter, inhibits the formation of radicals.

The influence of various substituting cations in zeolites X and Y and also of the heat treatment conditions has been studied in greater detail by Krzyzanowski.[11] The appearance of a seven-component spectrum of the type described above in the adsorption of propene on zeolites X and Y containing the cerium, lanthanum, and praeseodymium cations proceeds, according to the author,[11] as a result of electron transfer from the lanthanide cation (particulary Ce^{3+}) to the propene molecule. The same mechanism of the formation of the radical has been put forward for the zeolite FeY containing Fe^{2+} cations capable of being converted into Fe^{3+}. However, zeolites containing Co^{2+} do not generate radicals following the adsorption of an olefin, like the zeolite CaX. The adsorption on the zeolite CaY results in the observation of a low-intensity EPR signal. The behaviour of zeolites AgY and AgX proved to be interesting.[11] In this case the EPR signal (an intense singlet with $g = 2.0025$ and a width $\Delta H = 7.2$–7.4 G) appeared also in the adsorption of ethylene, which had not been observed in studies involving other zeolites.

It is essential to note that for the zeolites CeX and CeY there exists a threshold degree of exchange which depends on the activation temperature and the type of zeolite and below which radicals are not formed in the adsorption of an olefin. Table 3 presents the corresponding data for the formation of radicals in the adsorption of but-1-ene. It is striking that the threshold concentration for the zeolite CeY is lower than for the zeolite CeX (particularly at low activation temperatures). This fact has been explained[11] by the lower degree of migration of cerium cations in the zeolite Y towards centres which are not readily accessible for interaction with olefinic centres (S_I in hexagonal prisms and $S_{I'}$ and $S_{II'}$ in sodalite cells).

Table 3. The influence of the degree of exchange β and the activation temperature T_a of the zeolites on their ability to form radicals.[11]

Type of zeolite	T_a, °C	β, %	n
CeX	300	40	11.3
CeX	450	45	12.7
CeX	550	56	15.8
CeY	300	15	2.8
CeY	450	20	3.7
CeY	550	55	10.3

Notation: n is the number of Ce^{3+} cations per unit cell.

The conditions of heat treatment and the atmosphere in which it is carried out exert a significant influence on the concentration of the radicals formed. For decationated zeolites and the zeolites CaY and CeY with degrees of exchange guaranteeing the localisation of the cations in the large cavities, an increase of the activation temperature from 200° to 600 °C is accompanied by an increase of the EPR signal intensity possibly as a result of the increase of the number of defects on dehydration. On the other hand, in the case of the zeolites CeX with large degrees of exchange, the activation temperature can promote the migration of the cations to inaccessible centres and can decrease the concentration of the radicals formed.

The activation of the zeolite in an O_2 atmosphere increases sharply the concentration of the radicals formed in the adsorption of an olefin[11] and the higher the activation temperature the greater the EPR signal intensity. The effect of activation increases both with increase in the degree of exchange and with increasing O_2 pressure at the given temperature. When the zeolites activated in O_2 are treated with hydrogen, the intensity of the EPR signal due to the radicals formed in the subsequent adsorption of olefins diminishes to a greater extent the higher the temperature of the treatment in H_2. For the cerium-containing zeolites, the activating influence of O_2 can be explained by the appearance of cerium cations in the highest valence states (for example, Ce^{4+}), which are involved in the one-electron transfer.

The influence of O_2 on the formation of radicals in the adsorption of butene on the zeolite CaNaX has been studied in greater detail by Krzyzanowski.[12] He was able to show that, when the treatment of the zeolite in O_2 at 200 °C is accompanied by the appearance of the O_2^- radical-anion, then the concentration of the latter diminishes in the adsorption of butene. It has been suggested that the butene molecule is converted into a radical by abstracting an electron from the oxygen radical-anion. Krzyzanowski[12] also observed the following extremely interesting effect: in the adsorption of butene on CeNaX the concentration of the O^- radical-anions initially rises sharply and then falls (Fig.2). This phenomenon was explained by the conversion of the diamagnetic forms of the oxygen anions (O^{2-} or O_2^{2-}) into the paramagnetic form O^- on interaction with butene molecule and by the subsequent decrease of the O^- concentration accompanied by the simultaneous increase of the concentration of organic radicals. Thus in the first instant of adsorption the olefin molecules behave as electron acceptors (the appearance of the paramagnetic form O^-) and are converted into radical-anions, after which the concentration of the O^- radical-anions diminishes either owing to the formation of the neutral form O and the subsequent increase of the concentration of the organic radical-anions or owing to the conversion of O^- into O^{2-}; in the latter case the olefin molecules behave as electron donors. Krzyzanowski[12] did not discuss the question which of these processes leads to a decrease of the O^- concentration.

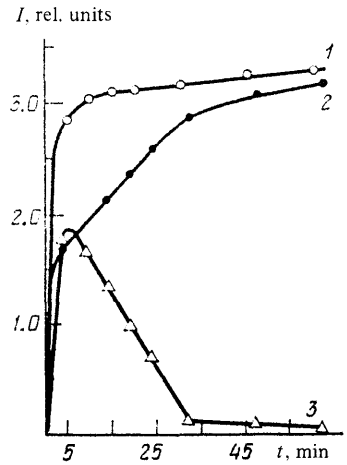


Figure 2. Variation of the intensity I of the EPR signals of radicals with the time t for the CeNaX-68 zeolite treated in N_2O at 500 °C (curves *1* and *3*) and 200 °C (curve *2*): *1*) and *2*) radicals formed in the adsorption of butene; *3*) O^- radical-ions.

Thus we have considered studies in which the formation of organic radicals was observed in the adsorption of olefins on decationated and various cationic forms of zeolites of the type of faujasite. Analysis of the results shows that at present there is not any single point of view both on the nature of the radicals formed and on the centres responsible for their appearance as well as their role in catalytic processes. We can only note the most important questions which have not yet been solved or which have received contradictory answers in studies by different investigators.

1. It has been shown that the adsorption of various olefins both from solution[6] and from the gas phase[7-12] on cationic and decationated forms of faujasites leads to the appearance of EPR signals which have virtually identical parameters. However, it is not clear whether this spectrum refers to a primary radical or an oligomeric radical or whether

it is characteristic of polymeric products which can be extracted from the zeolite surface.[6] It has been established that the heat treatment of the zeolite in O_2 increases significantly the intensity of the EPR signal during the subsequent adsorption of the olefin,[9,11,12] but data concerning the influence of O_2 and H_2O on the formation of radicals are contradictory. Thus it has been shown[6,10] that the presence of O_2 does not influence either the parameters of the EPR signal or its stability, while the adsorption of H_2O simultaneous with that of the olefin or its preliminary adsorption inhibits the formation of radicals. It has been established[7] that H_2O promotes the formation of radicals and that the form of the signal changes under the influence of O_2; this has been attributed to the formation of peroxy-radicals.

2. According to Suzaki et al.[7] and Otsuka et al.,[8] in the adsorption of olefins on faujasites alkyl radicals are formed as a result of the transfer of a hydrogen atom from the zeolite OH group to the olefin molecule and are stabilised by the partial transfer of electron density to the zeolite lattice. It is not clear whether this mechanism is sufficient for the stabilisation of the highly reactive alkyl radicals and, furthermore, on this assumption it is difficult to account for the strong activating influence of the treatment in O_2 and the appreciable increase of the EPR signal intensity on the cationic forms of zeolites (particularly the Ce-forms) compared with the H-form. The Ce^{3+} and Fe^{2+} cations cannot behave as radical-forming donor centres either,[9,11] because they are absent from the oxidised forms of zeolites. The Ce^{4+} cation functioning as an acceptor centre also cannot be regarded as responsible for the formation of radicals in the general case, because the latter are produced also on the decationated forms and on zeolites containing the Mg^{2+}, Ca^{2+}, and La^{3+} cations,[7] which do not behave as acceptor centres. The oxygen radical-anions formed under extremely specific conditions on the surfaces of faujasites[13] likewise cannot be regarded as the cause of the appearance of radicals in the adsorption of olefins, because in most cases they have not been detected either after the oxidative treatment of the zeolite or in the course of the adsorption of the olefin.

3. In our view, there is at present no convincing evidence that the above organic radicals are intermediates on faujasites, for example, in the isomerisation of olefins.[7,8] This hypothesis has been in essence rejected by Suzaki et al.,[7] although Otsuka et al.[8] later returned to it. Since the fraction of the radicals formed relative to the total number of adsorbed olefin molecules is 0.1%, it is evident that the amount of isomerisation products determined experimentally is due to the conversion of molecules which do not form radicals.

Next we shall consider the mechanisms of the formation and reactions of the radicals arising in the adsorption of olefins on high-silica zeolites, because in this case the available data permit a more detailed analysis of the nature of the radical-forming centres and of the structure of the radical species.

III. THE NATURE OF THE RADICALS FORMED IN THE ADSORPTION OF OLEFINS ON MORDENITE

The few studies devoted to the formation of radicals in the adsorption of olefins on mordenites dealt mainly with the character of the conformation and of the rotation of the radical species in the zeolite channels. Shih[14] obtained EPR spectra in the adsorption of *cis*- and *trans*-but-2-enes on the zeolite HM at low temperatures. It consists of a sextet of triplets arising owing to the interaction with the α- and β-hydrogen atoms, accompanied by the splittings a_{H_α} and a_{H_β} presented below:

Olefin	a_{H_β}, G	a_{H_α}, G	T, °C
cis-But-2-ene	16.2±0.4	8.2±0.4	−30
trans-But-2-ene	16.2±0.4	8.2±0.4	−50

Shih[14] assumes that the 16.2 G splitting is caused by the two identical CH_3 groups, while the 8.2 G splitting is due to the hydrogen atoms in the α-position, the small splitting by the α-hydrogen atoms being caused by the non-planar conformation of the alkene radical-cation.

The adsorption of tetramethylethylene on the zeolite HM at 25 °C is accompanied by the appearance of an EPR spectrum consisting of 13 equidistant components with a splitting of 17.5 G, corresponding to the interaction of the unpaired electron with the 12 equivalent protons.[15] The character of the spectrum changes little in the temperature range from −196° to 25 °C, which is due to the free rotation of the radical.

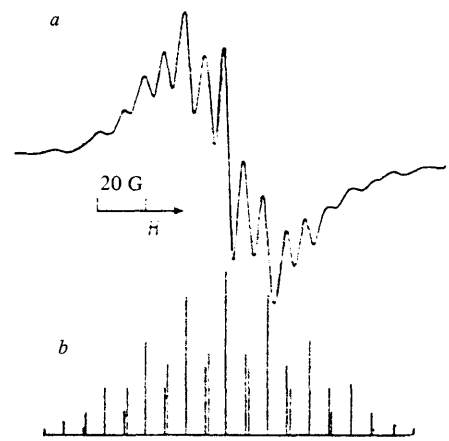


Figure 3. EPR spectrum arising in the adsorption of propene on the zeolite HM: *a*) experiment; *b*) calculation.

The EPR spectrum arising in the adsorption of a cyclic olefin (cyclopentene) on the zeolite HM was obtained in the same study.[15] A spectrum arises at −125 °C which can be accounted for by the splitting caused by the interaction with the four equivalent β-hydrogen atoms (a_{H_β} = 37 G) and two equivalent α-hydrogen atoms (a_{H_α} = 14.5 G). It is striking that in this case the splitting by the α-atoms is greater than in the case of the but-2-enes,[14] which is associated with the rigid planar conformation of cyclopentene. The observed EPR spectrum arising from the cyclopentene radical-cation[15] was accounted for on the hypothesis that the molecule rotates about an axis perpendicular to the five-membered ring. Calculation by the Hückel method showed that the unpaired electron is in a bonding π orbital and that its density is distributed equally between the two carbon atoms. Thus the splitting a_{H_α} = 14.5 G observed for cyclopentene is close to the value calculated from the McConnell relation $a_H = Q_{CH}\rho_C$ (Q_{CH} is a proportionality constant and ρ_C the π-electron spin density at the carbon atom), provided that Q_{CH} = 29.9 G (ρ_C = 0.5).

The adsorption of propene, but-1-ene, and pent-1-ene at 20 °C on the zeolite HM has been investigated by Leith.[16] All three hydrocarbons give rise to an EPR spectrum consisting of 19 lines with a_H = 8.1 G (Fig.3). The spectrum was described on the assumption that a radical of the type $CH_3-\overset{\beta}{C}H_2\overset{\alpha}{C}H=\overset{\alpha}{C}H=CHCH_3$ is formed from C_3H_6 and that the following interactions take place: (1) the interaction of one β-proton with one proton of the fixed CH_3 group (triplet with a_H = 33.6 G); (2) the interaction of one β-proton with two α-protons and with one proton of the CH_3 group (quintet with a_H = 16.8 G); (3) the interaction of the central proton with the last proton of the CH_3 group (triplet with a_H = 8.1 G). Heating to 100 °C reduces the splitting to 4.3 G and at 200 °C a broadened singlet with $\Delta H \cong 15$ G is observed. In our view Leith's description of the spectrum,[16] based on the concept of the formation of a linear dimer and of the presence of the three non-equivalent hydrogen atoms in one of the CH groups, is to some extent arbitrary. One should note that the observed spectrum is not sufficiently well resolved. However, Leith's observation[16] that the EPR spectra appearing in the adsorption of different linear olefins at 20 °C are identical is an important result.

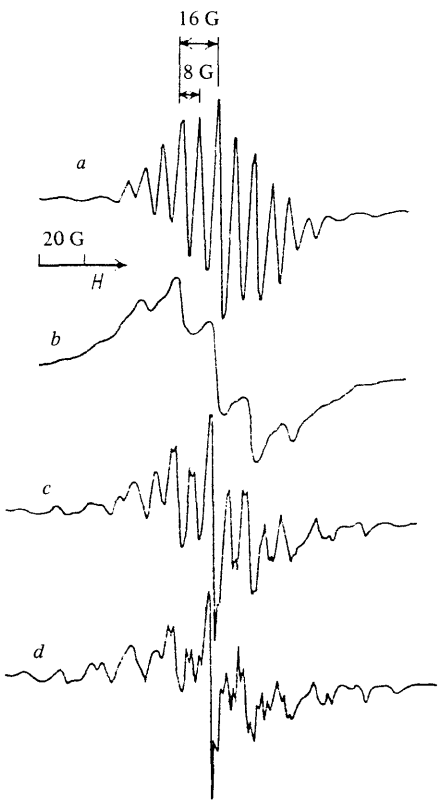


Figure 4. EPR spectra obtained 3 min (*a*), 1.5 h (*c*), and 8 h (*d*) after the adsorption of propene on the zeolite HM at 20 °C; *b*) spectrum of the specimen cooled to −196 °C after adsorption.

Unfortunately the studies of the formation of radicals in the sorption of olefins on zeolites HM examined above disregarded many important questions. (a) The nature of the primary radicals formed in the sorption of different olefins, the character of their thermal transformations, and the influence of various compounds on these processes were not analysed; (b) the structure of the centres responsible for the formation and reactions of the radical species was not discussed.

These problems were examined in greater detail in other investigations.[17-19] A study was made of the formation of radicals in the interaction of ethylene, propene, but-1-ene, isobutene, pent-1-ene, pent-2-ene, oct-1-ene, 2-methylhept-2-ene, cyclopentene, and cyclohexene with the zeolite HM. Fig.4 presents the EPR spectra observed in the adsorption of propene at 20 °C. Immediately after the adsorption of propene, an isotropic spectrum appears (Fig.4*a*); cooling the specimen to −196 °C is accompanied by the reversible conversion of this spectrum into that shown in Fig.4*b*. At 20 °C the spectrum in Fig.4*a* is slowly converted into that in Fig.4*c* (over a period of approximately 1.5 h) and further into the spectrum in Fig.4*d* (over a period of approximately 8 h). It is striking that the maximum intensity of the spectrum in Fig.4*a* is attained 5 min after adsorption, after which the signal intensity remains unaltered for approximately 6 h and corresponds to a spin concentration of 8×10^{17} spins g^{-1} (or one radical species per approximately 250 unit cells of the zeolite HM). Experiments involving the adsorption of propene on the deuteriated surface of the zeolite HM[17] showed that the hydrogen atoms of the radical species rapidly exchange with the OD groups of the zeolite HM even at −78 °C.

EPR spectra analogous to those illustrated in Fig.4 are observed in the adsorption of all the olefins investigated, except the cyclic olefins, at 20 °C. There are only some differences in the signal intensities and in the case of ethylene a spectrum with an HFS is observed against the background of a broader line.[20] These results confirm the data published earlier.[16]

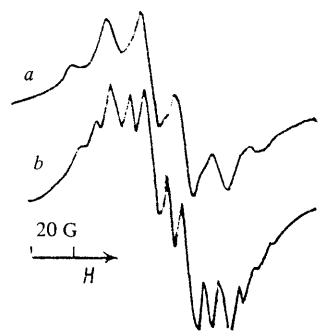


Figure 5. EPR spectra arising in the adsorption of propene on the zeolite HM at −78 °C: *a*) 2 h after adsorption; *b*) after brief warming of the specimen and recooling to −78 °C.

The identity of the EPR spectra obtained in the adsorption of various olefins shows that even at 20 °C rapid chemical reactions occur and the spectrum in Fig.4*a* is that of a radical with a secondary structure identical for different initial olefins. The data obtained in the study of the adsorption of olefins at a low temperature, where one can expect the formation of radicals from the unaltered molecules of the initial olefin, are therefore significant. For this purpose, a study was made[17] of the formation of radicals in the adsorption of ethylene, propene, but-1-ene, isobutene, pent-1-ene, and cyclopentene at −78 °C. It was noted that,

after the adsorption of ethylene on the zeolite HM at −78 °C, the EPR signal is not manifested for at least 3 h. The EPR spectrum arising in the adsorption of propene is illustrated in Fig.5*a*. Its intensity is appreciably lower than in the adsorption at 20 °C and its character remains unaltered for 5 h at −78 °C. A decrease of temperature to −196 °C is accompanied by an increase of the intensity of the broad line and the identical broadening of all the HFS components. A slow increase of temperature from −78 °C leads to an irreversible change in the EPR spectrum (Fig.5*b*), which is transformed at 20 °C into one of the type shown in Fig.4*a* and further into that in Fig.4*d*.

The adsorption of isobutene at −78 °C gives rise to the EPR spectrum shown in Fig.6*a*; cooling of the specimen to −196 °C results in the irreversible transition to the spectrum in Fig.6*b*. In this case too a gradual increase of the temperature of the specimen is accompanied by irreversible changes in the spectrum (Fig.6*c*). Fig.6*d* illustrates the spectrum obtained in the adsorption of but-1-ene at −78 °C; it coincides with that for the same olefin published by Shih.[14] The adsorption of pent-1-ene at −78 °C gives rise to the EPR spectrum of the type shown in Fig.4*a*, which is characteristic of the adsorption of propene at 20 °C. The changes in the spectrum on raising the temperature are identical with those shown in Figs.4*a*–4*d*.

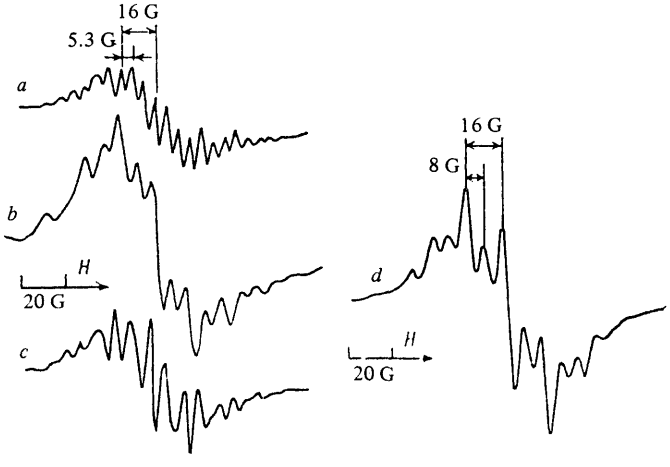


Figure 6. EPR spectra arising in the adsorption of isobutene (*a*–*c*) and but-1-ene (*d*) on the zeolite HM at −78 °C: *a*) 1 h after adsorption; *b*) after cooling to −196 °C; *c*) after brief reheating from −78 °C to 20 °C and recooling to −78 °C.

It is essential to note that the EPR spectra arising as a result of the interaction of all the olefins investigated with the zeolite HM[17] are stable only in the absence of oxygen; the introduction of O_2 at 20 °C leads to the instantaneous irreversible disappearance of the spectrum.

We shall analyse in greater detail the results of a study[17] of the first stage in the adsorption of olefins at 20 °C. The isotropic spectrum (Fig.4*a*), consisting of 11 equally spaced components with a splitting of approximately 8 G between them and non-binomial ratios of their intensities, is converted at −196 °C into the spectrum in Fig.4*b*, containing five equally spaced components with a splitting of 16 G and nearly binomial intensity ratios. Presumably, the radical species formed on adsorption contains two groups of protons: (1) a group of four equivalent protons (the interaction with these protons corresponds to a_H = 16 G), whose signal broadens slightly at −196 °C; (2) a group of two equivalent protons (giving a splitting of 8 G), whose signal broadens markedly at −196 °C. The EPR spectrum comprising eleven equidistant components, calculated on the basis of these postulates, has intensity ratios similar to those observed.

The fact that at 20 °C identical EPR spectra arise (Fig.4*a*) following the adsorption of different olefins, in which the number of substituents at the double bond varies from zero (ethylene) to three (2-methylhept-2-ene), can be explained by the formation of the same hydrocarbon radical fragment, which determines the structure of the EPR spectrum.

The set of data obtained for the adsorption of olefins at −78 °C confirm the hypothesis concerning the secondary nature of the radical giving rise to the spectrum of the type illustrated in Fig.4*a* and makes it possible to postulate the following reaction scheme and the following structure of the radical species. Evidently the EPR spectra arising in the course of the adsorption of olefins at −78 °C are due to the formation of primary radicals. The absence of the EPR signal in the adsorption of ethylene at this temperature shows that the radical-forming centre in the zeolite HM does not possess sufficient electron affinity to ionise the ethylene molecule, in view of its high ionisation potential compared with substituted olefins, and the appearance of an EPR spectrum of the type shown in Fig.4*a* when ethylene is adsorbed demonstrates ambiguously the occurrence of the oligomerisation reaction.

The EPR spectrum corresponding to the adsorption of propene at −78 °C (Fig.5*a*) indicates the formation under these conditions of a radical containing five equivalent protons. This radical, formed as a result of the abstraction of one hydrogen atom from the propene molecule, probably has an allyl structure in which all the hydrogen atoms are equivalent as a consequence of the delocalisation of the π-bond and rapid exchange. Although the hydrogen atoms in the free allyl radical are not equivalent,[21] the situation may be different for the species stabilised in the structure of the zeolite HM. As already stated above, heating of the specimen with propene adsorbed at −78 °C is accompanied by the disappearance of the spectrum shown in Fig.5*a* and the appearance of the spectrum of the type illustrated in Fig.4*a*. Formally these exchanges in the spectrum can be accounted for by the disappearance of one of the five equivalent hydrogen atoms, to which corresponds a_H = 16 G, and the appearance instead of a group of two hydrogen atoms (a_H = 8 G). From the standpoint of chemical reactions, such a change in the spectrum is probably associated with the alkylation of the allyl structure and the formation of a species in the spectrum for which a_H = 16 G is associated with the four α-protons of the allyl system and a_H = 8 G is associated with the two β-protons. The fact that the EPR spectrum of the radical formed in the adsorption of pent-1-ene at −78 °C is identical with that in Fig.4*a* apparently confirms the structure of the secondary radical species put forward above.

However, a different version of the structure cannot be ruled out either for the species giving rise to a spectrum of the type shown in Fig.4*a*, namely it can consist of an alkene radical arising without the elimination of a hydrogen atom, in the spectrum of which a_H = 8 G is due to the interaction with the two α-protons, while a_H = 16 G is due to the interaction with the four β-protons. The EPR spectra of the alkene radicals containing from four to six β-protons

differ little from one another and the distributions of the intensities of the eleven central components are similar in these three cases, while the components at the edges of the spectrum are weak.

We shall now consider the possible structure of the radicals formed in the adsorption of isobutene and but-1-ene at −78 °C. The EPR spectrum comprising 21 equidistant lines with a_H = 5.3 G (Fig.6*a*) can be interpreted if it is assumed that the adsorption of isobutene entails the formation of an alkene radical-cation in which six equivalent β-protons give rise to a septet with a_H = 16 G, while two α-protons give rise to a triplet with a_H = 5.3 G. The reduction of the temperature of the specimen to −196 °C inhibits the rotation of the radical, a_H for the α-protons increases to 8 G, and the spectrum of the type shown in Fig.6*a* degenerates into one of the type in Fig.6*b* (15 equidistant lines with a_H = 8 G). It should be noted that the spectrum of the type in Fig.6*a* cannot be accounted for by the formation of a radical species having the structure of an allyl type, i.e., in contrast to the adsorption of propene, the adsorption of isobutene involves the formation of an alkene radical-cation.

As stated above, the EPR spectrum arising in the adsorption of but-1-ene is identical with the spectra of sorbed *cis*- and *trans*-but-2-enes[14] and its HFS is due to a septet generated by the six β-protons and the triplet due to the two α-protons with a_H = 16.3 and 8.2 G respectively. It is of interest to note that the spectrum for but-1-ene (Fig.6*d*) is identical with that obtained in the adsorption of isobutene at −196 °C (Fig.6*b*), which indicates the presence in both radicals of six equivalent protons in two CH_3 groups and confirms the identical character of the radicals in these two cases.

In our view, the radical with the allyl structure is formed only in the adsorption of propene at −78 °C, while in the case of the remaining olefins the formation of radicals of the alkene type without the elimination of the hydrogen atom is probably preferred.

The set of data examined permits the conclusion that even at 20 °C, as a result of rapid reactions involving the isomerisation of the double bond, skeletal isomerisation, and oligomerisation, the primary radicals formed from different adsorbed olefins at −78 °C can give rise to oligomers of different structure and molecular weight containing a radical fragment having the same chemical structure and responsible for the appearance of identical EPR spectra. These structurally identical radical fragments are localised in sections of the mordenite lattice with a specific geometry and this constitutes the manifestation of the unusual "matrix" effect of the zeolite.

We shall attempt to carry out an analysis in order to discover the process with which the slow changes in the structure of the EPR spectra at 20 °C can be associated (Figs.4*a*, 4*c*, and 4*d*). Data for the adsorption of C_3D_6 at 20 °C show that the integral intensity of the EPR signal does not change over several hours, i.e. the changes in the HFS if the spectrum are not associated with the change in the concentration of the radical species. Analysis of the HFS of the spectra in Figs.4*c* and 4*d* suggests that they are anisotropic, i.e. the changes in them are not related to a change in the structure of the radical fragments formed. In this case the gradual transition from the isotropic (Fig.4*a*) spectrum to the anisotropic (Figs.4*c* and 4*d*) spectra can be caused by the transition from the initial disordered disposition of the radical species to an ordered arrangement of the latter in space in the geometrically regular mordenite structure. The ordering process is accompanied by the inhibition of the rotation of the radical species, which is demonstrated by the fact that, on cooling to −196 °C, the isotropic spectrum (Fig.4*a*) changes its shape markedly (Fig.4*b*), while the spectrum in Fig.4*d* hardly changes on cooling in this way. Thus presumably at 20 °C there is rapid initial formation of radical fragments, which are gradually accommodated in lattice elements with a specific geometry, distributed regularly in the mordenite structure, and produce a "sublattice" of ordered radicals.

For the adsorption of C_3H_6 on the zeolite HM at 20 °C, Leith[16] recorded an EPR spectrum identical with that shown in Fig.4*c* but less well resolved, i.e. it can be regarded as an intermediate form of a slowly changing signal.

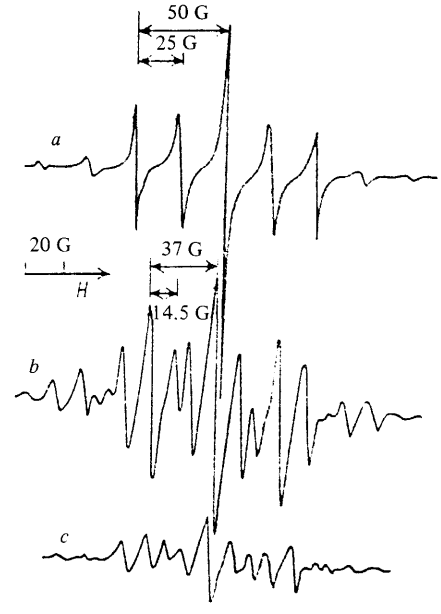


Figure 7. EPR spectra observed in the adsorption of cyclopentene on the zeolite HM: *a*) 3 min after adsorption at −78 °C; *b*) after cooling to −196 °C; *c*) at 20 °C.

Kucherov and Slinkin[17] also described unusual changes in the structure of the EPR spectra of cyclic olefins (cyclopentene and cyclohexene) as the temperature is altered. Fig.7 presents the EPR spectra arising in the adsorption of cyclopentene on the zeolite HM. Its adsorption at −78 °C is accompanied by the rapid appearance of the spectrum in Fig.7*a*, which does not vary with time. Cooling of the specimen to −196 °C leads to the reversible conversion of the signal into the spectrum shown in Fig.7*b*. An increase of the specimen temperature to 20 °C is accompanied by the irreversible transition from the spectrum in Fig.7*a* to that in Fig.7*c*, which then remains unaltered at 20 °C for at least 18 h. It is significant that the disappearance of the signal due to the adsorbed cyclopentene radical-cation on treatment with O_2 is reversible; in contrast to the radical-cations of olefins, the spectrum in Fig.7*c* is fully restored on evacuation of the system for 2–4 h at 20 °C.

The results were accounted for by Kucherov and Slinkin[17] in the following way. The nine line spectrum (Fig.7*a*) with non-binomial intensity ratios, arising in the adsorption of cyclopentene at −78 °C, is due to the formation of an alkene radical species in which there are two groups of protons: two equivalent α-protons (to which corresponds a_H = 50 G) and four equivalent β-protons (a_H = 5 G). The spectrum

in Fig.7*b* agrees well with that obtained earlier[15] for the adsorption of cyclopentene on the zeolite HM at −125 °C. This spectrum is due to an alkene radical and consists of 15 HFS components; it is possible to identify in this spectrum a quintet (a_H = 37 G) due to four β-protons and a triplet (a_H = 14.5 G) due to two α-protons. The spectrum in Fig.7*c* arising at 20 °C has an HFS which differs little from that of the spectrum in Fig.7*b*; consequently, at temperatures ranging from −196 °C to 20 °C, the chemical structure of the cyclic alkene radical-cation remains unaltered and only the degree of freedom of its rotation changes.

In order to understand the mechanism of the reactions of olefins on high-silica zeolites, it is extremely important to examine the character of the thermal transformations of the radical species formed following the adsorption of various olefins on the zeolite HM; the existing information about these reactions is discussed in the next Section.

IV. THE REACTIONS OF RADICAL SPECIES AT ELEVATED TEMPERATURES ON THE HM ZEOLITE AND OTHER ZEOLITES

The reactions of C_2–C_8 olefins, cyclopentene, cyclohexene, and also a series of compounds having a significantly different chemical structure, namely acetylene, butadiene, allyl chloride, allyl alcohol, n-hexane, cyclohexane, and methyl alcohol, have been investigated[18] on the H-forms of zeolites whose characteristics are given below:

Zeolite	SiO_2/Al_2O_3	Degree of decationation, %
HM	10	92
HM-26	26	99
HY	4.3	70
HKL	5.2	82
H-Cesite	5.2	95

The EPR spectra observed on heating an HM zeolite specimen with propene adsorbed at 20 °C are illustrated in Fig.8. The changes in the HFS shown in Fig.8 are typical for all C_2–C_8 olefins. We may note that the introduction of O_2 leads to the immediate disappearance of the spectra in Figs. 8*a*–8*c*, while the spectrum in Fig.8*d* not only does not disappear in the presence of oxygen but its intensity actually increases markedly with retention of the HFS. In the adsorption of olefins on the HM zeolite specimen heated to 300 °C the spectrum shown in Fig.8*d* appears immediately. The adsorption of olefins in air is not accompanied by the appearance of an EPR signal, but the subsequent heat treatment of the system in the presence of O_2 at 250–300 °C leads to the appearance of an intense signal of the type illustrated in Fig.8*d*. The same EPR signal appears on heating the zeolite HM with adsorbed cyclopentene and cyclohexene at 300 °C.

The adsorption of acetylene and allyl chloride on the zeolite HM at 20 °C with subsequent heat treatment at 300 °C likewise leads to the appearance of the spectrum shown in Fig.8*d*. An analogous process proceeds also when butadiene and allyl alcohol are adsorbed on the zeolite HM with subsequent heat treatment at 300 °C. It is remarkable that the EPR spectrum of the type in Fig.8*d* arises also on heating the HM zeolite specimen at 250–300 °C with saturated compounds such an n-hexane, cyclohexane, and methanol.

Thus, for all the compounds enumerated above adsorbed on the zeolite HM, heat treatment at 250–300 °C leads to the appearance of the same EPR spectrum of the type shown in Fig.8*d*: the HFS of the EPR spectra arising in the reactions of different compounds are identical and there are only insignificant differences in the resolution of the individual components.[18]

In order to understand the nature of the signal generated, a study was made of the interaction of benzene and toluene with the zeolite HM at 300 °C. In both cases intense symmetrical singlets with ΔH = 3.7 and 7 G respectively arise at this temperature.

Apart from the zeolite HM, the EPR spectra generated in the high-temperature (up to 450 °C) interaction of benzene, n-hexane, and methanol with the zeolites HY, HKL, and H-cesite have been investigated.[18] In contrast to the zeolite HM, heating of all the zeolites investigated up to high temperature produces singlet EPR spectra without any HFS. Only on mordenite with a higher modulus (the zeolite HM-26 was obtained by direct synthesis) do n-hexane and methanol give rise on heat treatment to 350 °C to the EPR spectrum of the type shown in Fig.8*d* having a somewhat poor resolution of the HFS components compared with the zeolite HM.

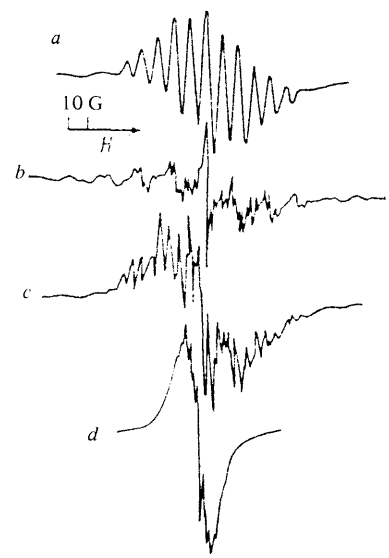


Figure 8. EPR spectra arising on heating the zeolite HM specimen containing propene adsorbed at 20 °C: *a*) at 20 °C, 5 min; *b*) at 90 °C, 50 min; *c*) at 200 °C, 15 min; *d*) at 300 °C, 20 min.

Thus only the zeolite HM possesses the unique ability to generate selectively, after the adsorption of compounds of different classes (unsaturated and saturated) at 250–300 °C, a structure giving rise to a characteristic EPR spectrum. We shall consider the nature of the radical generating this type of EPR spectrum.

It has been shown[17] that, when olefins of different types are adsorbed on the zeolite HM at 20 °C, the same radical fragment is formed rapidly and then undergoes further transformations on raising the temperature. The disappearance of the EPR signal produced on heating the specimen to 200 °C, after the addition of O_2, is probably associated with the retention by the radical formed of an alkene (or allyl) structure. However, the appearance at 250–300 °C of radical species resistant to the action of O_2 (the spectrum in Fig.8*d*) suggests that their chemical nature has changed fundamentally. It is known that radicals formed in the adsorption of aromatic compounds on zeolites are resistant

to the action of O_2.[22] In an earlier study[16] it was already suggested that the high-temperature treatment of propene adsorbed on the zeolite HM is accompanied by the formation of radicals of this kind. It has been shown[18] that, after adsorption with subsequent high-temperature treatment of all the zeolites investigated, benzene and toluene produce a singlet EPR spectrum. The EPR spectra obtained in the adsorption of isomeric xylenes on the zeolite HM at 20 °C have also been published;[18] the fact that the EPR spectrum appearing after the adsorption of *o*-xylene is identical with the spectrum Fig.8*d* arising on heat treatment of zeolite HM specimens with various compounds adsorbed on them is noteworthy. It is striking that the EPR spectrum arising following the adsorption of *o*-xylene is extremely stable at temperatures up to 300 °C in an oxidising atmosphere and fully retains its HFS. The EPR spectra for *m*- and *p*-xylenes adsorbed on the zeolite HM are converted into a spectrum of the type shown in Fig.8*d* on heating to 200 °C.

Thus it can be seen that the adsorption of compounds of different classes on the zeolite HM at 250–300 °C produces selectively adsorbed 1,2-dialkylphenylene radicals. We use by convention the term 1,2-dialkylphenylene radicals for the radicals giving a spectrum of the type in Fig.8*d*, because they are spectroscopically identical with the radicals formed in the adsorption of *o*-xylene, whose EPR spectrum does not change on raising the temperature from 20° to 300 °C. It is noteworthy that the EPR spectrum in Fig.8*d* with equally spaced components and $a_H = 1.8$ G cannot be described using the known HFS constants for the protons of the benzene ring and the CH_3 groups of the *o*-xylene radical-anions.[23] This may be caused by a change in the chemical composition of the adsorbed radical compared with the *o*-xylene molecule or by a change in the HFS constants of the hydrogen atoms for the adsorbed radical compared with the radical in the liquid phase.

The following questions arise in the analysis of the results:

1. what can be the general chemical mechanism of the reactions leading to the formation of aromatic molecules from compounds of different classes on the zeolite HM;
2. what can be the causes of the selective formation of adsorbed radicals with a specific structure on the zeolite HM at high temperatures.

The mechanism of the chemical reactions leading to the formation of aromatic compounds on the H-forms of high-silica zeolites from unsaturated and saturated hydrocarbons is still not known. It is only clear that it must be complex because hydrogenation–dehydrogenation reactions do not take place on these zeolites. Presumably the process proceeds via the complex disproportionation of the initial molecules with formation, on the one hand, of light saturated compounds and, on the other, of unsaturated compounds. As a result, a non-cyclic hydrocarbon fragment with a high degree of unsaturation, for example, tetraene, whose cyclisation leads to the formation of an alkylated aromatic compound, may be formed on the active centre on the zeolite surface. Aromatic molecules may be formed in this way not only from unsaturated but also from a series of saturated compounds, which are initially converted into olefins by the abstraction (in the form of CH_4) of the terminal group.

This idea about the character of the process agrees with the conclusions of a study[24] of the synthesis of compounds on the zeolite HM from labelled [2-^{13}C]isobutene and it has been suggested that aromatic molecules are formed via intermediate dimerisation and triene formation stages. Analysis of the reactions of n-hexane, cyclohexane, and cyclohexene when these are adsorbed on the zeolite HM also shows that the cracking and oligomerisation reactions play a decisive role in high-temperature transformations. The formation of benzene, whose heat treatment would yield products characterised by a narrow singlet ($\Delta H = 3.7$ G) in the EPR spectrum, might have been expected for the above compounds, particularly cyclohexene. However, experiments showed that these compounds form 1,2-dialkylphenylene radicals, which indicates a complex mechanism for the formation of the aromatic ring. For example, the process involving cyclohexane should proceed via ring opening with formation of an olefin and its oligomerisation followed by cracking with formation of polyenes and their ring closure to give the aromatic system.

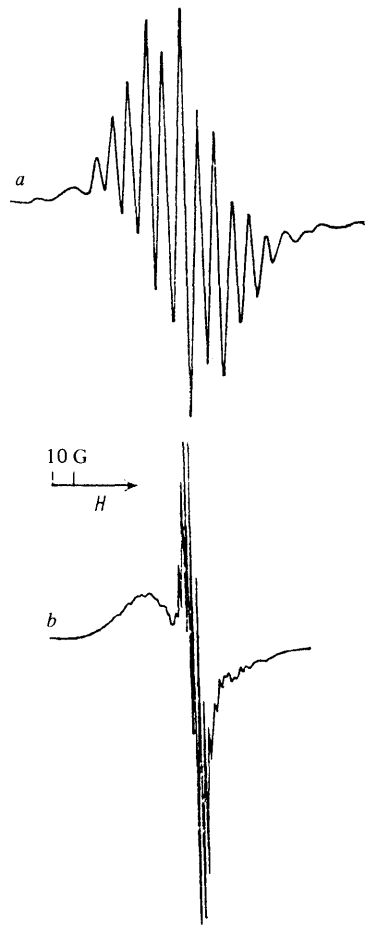


Figure 9. EPR spectra observed in the successive interaction of propene, benzene, and oxygen with the zeolite HM at 20 °C: *a*) zeolite HM + C_3H_6; *b*) (zeolite HM + C_3H_6) + C_6H_6 + O_2.

The data available do not yet permit the final conclusion that the formation of aromatic compounds from various starting materials on high-silica zeolites is a radical process, but one cannot rule out that the intermediate radical species are important participants in this process.

The understanding of the nature of the centres propagating the formation of aromatic compounds on high-silica zeolites is extremely important for the elucidation of its mechanism. An attempt to solve this problem has been undertaken.[19]

V. THE INFLUENCE OF ADDITIVES ON THE FORMATION OF RADICAL SPECIES AND THEIR HIGH-TEMPERATURE REACTIONS ON THE ZEOLITE HM

Initially we shall consider the experimental results obtained in a study[19] of the influence of added O_2, NH_3, H_2O, and SO_2 on the adsorption of an olefin (C_3H_6) and an aromatic compound (C_6H_6) on the zeolite HM.

Fig.9 presents the EPR spectra arising on consecutive interaction of C_3H_6, C_6H_6, and O_2 with the zeolite HM at 20 °C. The adsorption of C_3H_6 leads to the appearance of the 11-component signal described above. After the evacuation of the gas phase and the adsorption of C_6H_6, a signal due to the benzene-radical cation is not observed. Subsequent admission of O_2 leads to the immediate disappearance of the signal shown in Fig.9*a* and the appearance of the characteristic intense seven-component signal (Fig.9*b*) due to the benzene-radical cation.

Data[19] concerning the influence of the preliminary adsorption of NH_3 and H_2O on the concentration of the radical species formed in the interaction of C_3H_6 and C_6H_6 with the zeolite HM at 20 °C are presented in Fig.10. Evidently the adsorption of NH_3 and H_2O induces only a decrease of the intensity of the EPR signals but does not affect the HFS of the spectra arising following the adsorption of C_3H_6 and C_6H_6, i.e. it affects the amount but not the structure of the radical species; both NH_3 and H_2O inhibit the formation of radical-cations from C_6H_6 molecules at 20 °C to a much greater extent than the formation of radical species from C_3H_6.

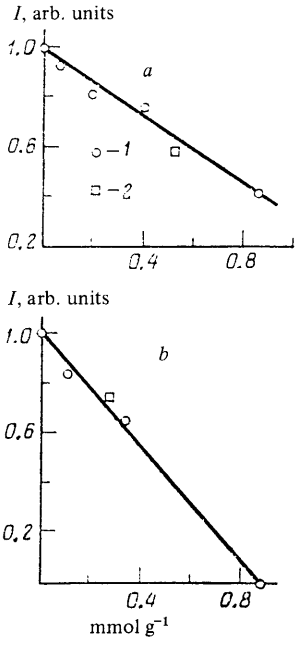


Figure 10. Dependence of the intensity I of the EPR signals in the adsorption of C_3H_6 (*a*) and C_6H_6 (*b*) at 20 °C on the amounts of NH_3 (1) and H_2O (*2*) preadsorbed on the zeolite HM

It is essential to note that at 20 °C the inhibiting effect of H_2O molecules described above is analogous to the effect of NH_3, while in the high-temperature (300 °C) heat treatment of the zeolite HM containing the chemisorbed C_3H_6 the adsorbed H_2O molecules do not prevent the formation of 1,2-dialkylphenylene radicals, while NH_3 molecules exert a powerful inhibiting effect on the process: the adsorption of 0.86 mmole of NH_3 per gramme of the zeolite HM fully suppresses the formation of 1,2-dialkylphenylene radicals.

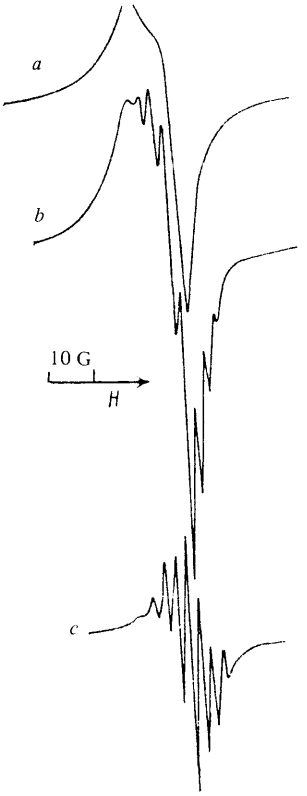


Figure 11. EPR spectra observed on interaction of the zeolite HM with SO_2 and C_6H_6 at 20 °C: *a*) zeolite HM + SO_2; *b*) (zeolite HM + SO_2) + C_6H_6; *c*) after the admission of air.

Fig.11 presents the EPR spectra[19] arising on successive interaction of SO_2 and C_6H_6 with the zeolite HM at 20 °C. The adsorption of SO_2 on the evacuated zeolite HM specimen is accompanied by the appearance of a signal (Fig.11*a*) analogous to that described by Ono and co-workers[25,26] and interpreted by them as a signal of the SO_2^- radical-anion. The adsorption of C_6H_6 on the zeolite HM specimen containing preadsorbed SO_2 is accompanied by a very rapid transition from the spectrum shown in Fig.11*a* to that in Fig.11*b*, which consists of a superposition of the spectrum in Fig.11*a* due to the SO_2^- radical-anion with unaltered intensity and the seven-component signal of the benzene radical-cation. The subsequent adsorption of O_2 leads to a transformation of the spectrum in Fig.11*b* into that in Fig.11*c*, i.e. to a marked decrease of the intensity of the signal of SO_2^- for a constant intensity of the spectrum of $C_6H_6^+$.

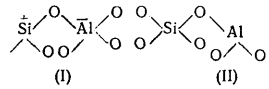
A completely different pattern arises in the successive interaction of the zeolite HM with SO_2 and C_3H_6 at 20 °C. In this case the adsorption of C_3H_6 induces a sharp increase of the intensity of the signal of the SO_2^- radical-anion (by a

factor of approximately 5) and the intensity of the 11-component spectrum is much smaller than in the interaction of the zeolite HM with C_3H_6 in the absence of SO_2.

Finally, in contrast to NH_3, the adsorption of SO_2 does not influence the formation of 1,2-dialkylphenylene radicals in the high-temperature reaction of adsorbed hydrocarbons.[19]

In order to understand the chemical nature of the centres on which the olefin and aromatic radicals are formed, it is necessary to concentrate attention in the first place on the characteristic features of the influence of O_2 on the formation of radicals from olefins and aromatic compounds. The following facts should be noted: (1) for the formation of radical-cations, it is essential that the oxidative centre in the zeolite HM should be activated by the chemisorbed O_2;[22] the presence of O_2 in the gas phase does not interfere with the formation of aromatic radical-cations and does not influence the HFS of the EPR spectra; (2) the formation of radicals from olefins hardly requires the activation of the oxidative centres on the zeolite HM surface by oxygen and the presence of O_2 in the gas phase leads to the irreversible destruction of these radicals.

It might have been supposed that radicals are formed from olefins and aromatic compounds during adsorption on two different types of oxidative centres, some of which are not activated, while others are activated by O_2, i.e. these centres can have different chemical structures. In a study of zeolites of the type of faujasite[27] it was observed that their dehydroxylation can produce Lewis centres of two types#:



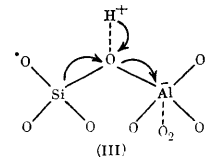
(I) (II)

We shall assume that the centres (I) and (II) are equally accessible to olefin (C_3H_6) molecules and the molecules of the aromatic hydrocarbons (C_6H_6), the aromatic molecule being adsorbed more strongly on the activated centre than the olefin molecule. Aromatic and olefin molecules are then formed respectively on the centres (I) and (II). If this were so, then, under the conditions of the experiment (Fig.9) on the successive interaction of C_3H_6, C_6H_6, and O_2 with the zeolite HM, the adsorption of C_3H_6 on the zeolite would have led to the formation of olefin radicals both on the centres (I) and (II), while in the successive adsorption of C_6H_6 its molecules would have displaced the olefin radicals from the centres (I). As a result the intensity of the EPR signal should diminish, but this effect has not been observed. It is difficult to suppose that the preservation of the intensity of the EPR signal due to the olefin radicals after the adsorption of C_6H_6 is due to the inaccessibility of the centres (I) to benzene molecules. It is more logical to assume that the olefin and aromatic radicals are formed on oxidative centres of the same type.

Before considering the nature of this centre, we shall note that it must differ from the structure of the centres (I) and (II) postulated for faujasites, because radical-cations are not formed on the zeolite HY after the adsorption of C_6H_6, while the adsorption of C_3H_6 results in the formation of a radical resistant to the action of O_2 and giving rise to a very weak five-component spectrum and a binomial distribution of intensities.[6-8] In addition it is significant that heating of the zeolite HM specimen to 450 °C is not accompanied at all by the formation of Lewis centres of types (I) and (II).[28]

The centre (II) is more characteristic of mordenite rather than zeolites of the type of faujasite.

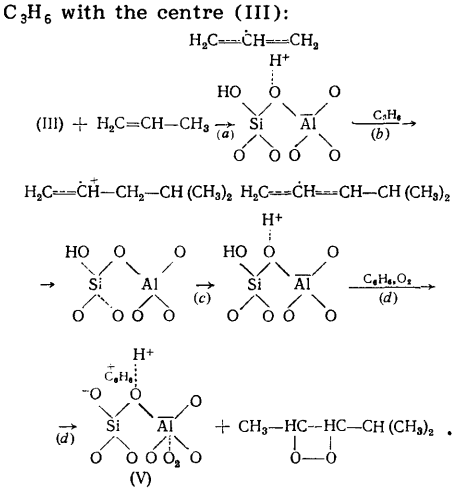
Thus it is necessary to assume the existence in the zeolite HM of active centres of a fundamentally different kind, arising at low heat-treatment temperatures (200–450 °C). In analysing the nature of the oxidative centre in the zeolite HM, the authors[19] considered the following structure:



(III)

It has a Brønsted centre, a radical acceptor centre, and an O_2 molecule chemisorbed on Al, which plays the role of an activator in the formation of aromatic radical-cations.

The possibility of the existence in SiO_2 of Si–O and Si centres and their reactivity has been investigated.[30-32] It is possible to imagine the following mechanism of the interaction of C_3H_6 with the centre (III):



An allyl radical is formed in stage (*a*) with transfer of a hydrogen atom to the radical centre, while in stages (*b*) and (*c*) dimerisation with participation of the bridging proton takes place. After the adsorption of benzene and the subsequent adsorption of O_2, the allyl radical is oxidised and destroyed [in stage (*d*)] and the benzene radical-cation is formed. It should be noted that dimerisation can precede the formation of the radical and in the case of C_2H_4 the process should proceed precisely in this sequence. It is significant that the interaction of the centre (III) with C_3H_6 is accompanied not only by the formation of an allyl radical but also probably by the removal of the activating oxygen, because otherwise the adsorption of C_6H_6 in stage (4, *d*) might have led to the formation of benzene radical-cations without the additional introduction of O_2 into the system. In the adsorption of C_6H_6 on the zeolite HM specimen containing adsorbed olefin radicals the C_6H_6 molecules are apparently localised within the zeolite channels near the centre (IV) and after the introduction of O_2 into the system are rapidly converted into radical-cations with formation of the centre (V).

The data for the inhibiting effect of NH_3 and H_2O on the formation of radicals from C_3H_6 and C_6H_6 (Fig.10) indicate a complex structure of the oxidative centre and can be readily understood if it is supposed that the centre has the structure (III). The adsorbed NH_3 molecule interacts with the bridging H^+ ion of the centre (III), which prevents the formation of an oligomeric radical [stage (*b*)]. Comparison of the data obtained with the results described by the present authors[17,18] permits a somewhat more detailed specification of the scheme presented above. Monomeric allyl

radicals [stage (*a*)] are formed in a small amount in the adsorption of C_3H_6 on the centres (III) at −78 °C. Heating of the system to 20 °C is accompanied by a sharp increase of the intensity of the EPR spectrum and a change of its HFS owing to the formation of oligomeric radicals.[17] An increase of the concentration of the radical species as a result of oligomerisation and a decrease of the ionisation potential (for example, from 9.94 eV for C_3H_6 to 8.9 eV for 3-methylbut-2-ene) makes it necessary to postulate the inhomogeneity of the centres (III) of the zeolite HM in terms of their oxidising power.

We may note that the oligomerisation process need not necessarily be associated with participation of the most acid protons. When only the strongest Brønsted centres are involved in oligomerisation, the EPR spectrum would cease to be observed after the adsorption of only approximately 0.35 mmole of NH_3 per gramme of the zeolite HM (centres for which the heat of adsorption of NH_3 is 140 kJ mol^{-1}).[33] Thus the combination of the strongest oxidising and acid properties is not obligatory for the centre (III).

The adsorption of NH_3 prevents not only the formation of radicals from the adsorbed olefin at 20 °C but also the high-temperature aromatisation of various compounds with formation of 1,2-dialkylphenylene radicals,[18] which is due to the strong interaction of the NH_3 molecules with centres of type (III) on the zeolite HM.

The mechanism of the decrease of the intensity of the EPR signal of the benzene radical-cation on adsorption of NH_3 (Fig.10*b*) is less clear, because in this case the H^+ ion is not involved directly in the formation of the radical although it can interact with the aromatic ring, causing its partial polarisation. It is significant that the decrease in the concentration of the benzene radical-cations under the influence of the adsorption of NH_3 is accompanied also by a decrease in the intensity of the singlet EPR signal arising on heating the specimens to 150–300 °C.

The adsorption of H_2O, like that of NH_3, inhibits the formation of radicals both in the adsorption of C_3H_6 and in that of C_6H_6, apparently as a result of the analogous blocking of the centre (III). It is striking that, in contrast to NH_3, H_2O is desorbed on raising the temperature and does not prevent the conversion of the adsorbed C_3H_6 into 1,2-dialkylphenylene radicals.

We shall now discuss the influence of the addition of SO_2 on the formation of radicals in the adsorption of an olefin and the aromatic compound. There are significant differences in the influence of adsorbed SO_2 on the concentrations of these radicals. On the one hand, the intensity of the EPR signal of the SO_2^- radical-anion does not change following the adsorption of C_6H_6 and the concentration of the $C_6H_6^+$ radical-cation is independent of the presence of adsorbed SO_2 molecules on the zeolite HM specimen. On the other hand, the adsorption of C_3H_6 on such a specimen containing adsorbed SO_2 molecules, some of which, as in the previous case, are in the form of SO_2^-, is accompanied by a sharp (by a factor of 5) increase of the concentration of SO_2^- and an appreciable decrease of the concentration of olefin radicals compared with their concentration on the clean zeolite HM.[19]

The results can be explained by the following processes occurring in the adsorption of C_3H_6 and C_6H_6:

$$RH + (III) \rightarrow \dot{R} + HO-Si\diagup\diagdown \qquad (2)$$

$$\dot{R} + SO_2 \rightarrow R^+ + SO_2^- \ . \qquad (3)$$

Reaction (2) proceeds in the adsorption of both C_3H_6 and C_6H_6, but reaction (3) does not occur in the case of the $C_6H_6^+$ radical-cation, because its ionisation potential (9.90 eV) is higher than that of the C_6H_6 molecule (9.24 eV);[34] the concentration of SO_2^- ions does not therefore change on adsorption of C_6H_6. On the other hand, the ionisation potential of the olefin radical is lower than that of the initial molecule and reaction (3) is in this case accompanied by an increase in the concentration of the SO_2^- radical-anions. It is significant that an electron is definitely transferred to the SO_2 molecule from the olefin radical and not from the solid, because in the latter case an increase of the intensity of the signal of SO_2^- would have been observed as a result of the adsorption of C_6H_6.

The electron transfer from the olefin radical to the acceptor molecule described above is very similar to the formation of the SO_2^- radical-ion on the MgO surface in the adsorption of C_3H_6.[35] The following reactions probably occur in this system:

$$RH \rightarrow R^- + H^+ \ , \qquad (4)$$

$$R^- + O_2 \rightarrow \dot{R} + O_2^- \ , \qquad (5)$$

$$2\dot{R} + O_2 \rightarrow R-O-O-R \ . \qquad (6)$$

The difference between this reaction sequence and the previous one consists in the fact that the adsorption of C_3H_6 on the zeolite HM leads immediately to the formation of a radical and not a carbanion, but at the same time the introduction of O_2 is accompanied by the destruction of $\dot{R}$ via reaction (6) and the signal of the O_2^- radical-ion cannot therefore be detected in the EPR spectrum.

The influence of the introduction of various cations into the zeolite HM on the formation of radical species from different compounds, including olefins, has been examined.[36] It has been shown that the introduction of Be^{2+} and Ce^{4+} hardly influences the oxidation–reduction properties of the HM zeolite centres. It has been found that, despite their localisation in the large channel and their dipole–dipole interaction with the chemisorbed radicals, the introduction of Cu^{2+} cations lowers only slightly the concentration of the radical species formed at 20 °C from both aromatic compounds and from C_3H_6. The introduction into the zeolite HM of the ions Na^+, Mg^{2+}, Ba^{2+}, and Ni^{2+}, which are localised at sites which are not readily accessible to adsorbed molecules, leads to a considerable (by a factor of 10–30) decrease of the concentration of radicals. It has been suggested[36] that the formation of the oxidation–reduction centres in the zeolite HM is associated with the rupture of highly strained Si–O–Si(Al) bonds and the cations can have a stabilising effect on the mordenite skeleton.

VI. THE FORMATION AND REACTIONS OF RADICALS ON ZEOLITES OF THE ZSM TYPE

So far only one study devoted to the formation and reactions of radicals in the adsorption of unsaturated hydrocarbons on the zeolite H-ZSM-5 has been published.[37] The zeolite specimen was subjected to a preliminary heat treatment in an atmosphere of O_2 at 500 °C for 1 h; the reaction volume was then evacuated at the same temperature for 2 h, cooled to room temperature, and the specimen was transferred *in vacuo* into the cell of the EPR spectrometer, where the alkene and alkyne vapours were adsorbed at a low temperature.

Fig.12 presents the EPR spectra obtained at a reduced temperature for the initial zeolite ZSM-5 specimen and the specimen after the adsorption of but-2-yne and 3,3-dimethylbut-1-ene. The latter spectrum is isotropic (g = 2.0028 and a_H = 17.5 G) and has been assigned to the radical of

2,3-dimethylbut-2-ene arising as a result of the intramolecular rearrangement of 3,3-dimethylbut-1-ene. The EPR signal appearing as a result of the adsorption of but-2-yne on the zeolite ZSM-5 at −123 °C consists of seven components with a_H = 10.0 G, which is due to the presence in the molecule of two equivalent CH_3 groups, which rotate almost freely within the zeolite channel. On raising the temperature above 27 °C, the spectrum in Fig.12*c* is transformed into a nine-component spectrum (g = 2.009 and a_H = 6.60 G) and does not change further on raising the temperature to 200 °C.

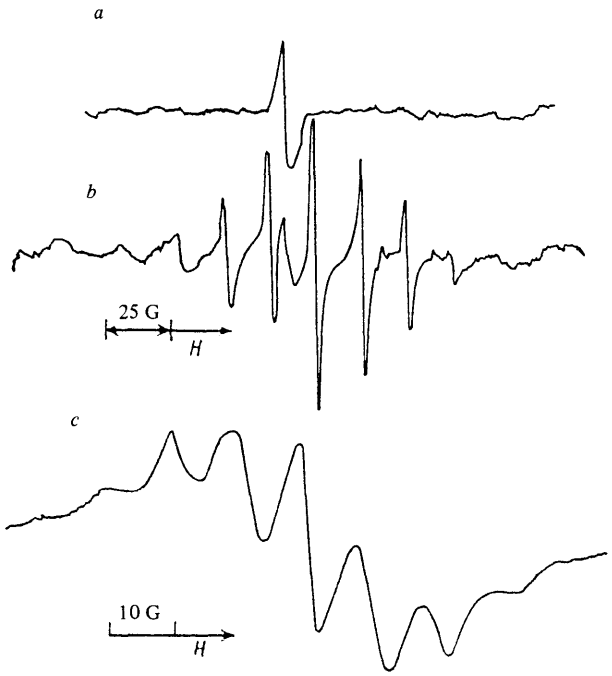
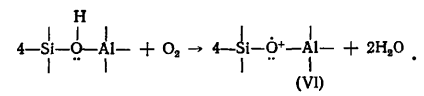
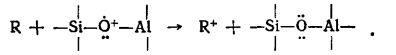


Figure 12. EPR spectrum of the lattice defects in the zeolite ZSM-5 at −150 °C (*a*) and the EPR spectra arising in the adsorption of 3,3-dimethylbut-1-ene at −150 °C (*b*) and but-2-yne at −123 °C (*c*) on the zeolite ZSM-5.

It has been suggested[37] that the spectrum in Fig.12*a* for the initial zeolite specimen is due to the appearance during the heat treatment of the zeolite in air at 500 °C of defect centres (VI) having a radical structure:

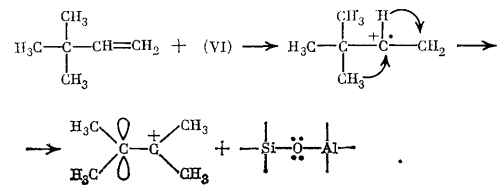


The centre (VI) obtained in this way is a hole in the oxygen atom of the zeolite lattice. According to the author,[37] the unpaired electron occupies a non-bonding molecular orbital of the oxygen atom, because at −196 °C a signal with an HFS characteristic of the reaction of the unpaired electron with the nuclear spin of the Al atom is not observed. Furthermore, the g-factor of the signal in Fig.12*a*, which is 2.0092, is equal to the g-factor of the signals due to the isoelectronic holes formed on X-irradiation of silicate and borate glasses. It has been suggested that the energy required for the appearance of such a radical centre is close to that necessary for the removal of an electron from the non-bonding orbital of the oxygen atom in the H_2O molecule, which is 12.61 eV according to photoelectron spectroscopic data. If this is true, then the positive radical centre is a powerful acceptor trap, in which the adsorbed molecule forms a radical-cation via a charge transfer mechanism:

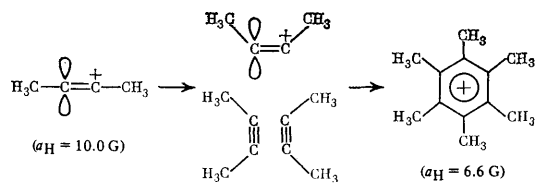


Unfortunately it is not stated in the above study[37] what is the concentration of such defect centres in the zeolite ZSM-5 and whether this concentration corresponds to the number of radical-cations formed. It is necessary to note that the nature of the centre (VI) and the character of the processes occurring on it are in essence identical to those for the centre (V) in the zeolite HM and the mechanism of the formation of radical-cations in the adsorption of olefins is the same as that discussed above.

The following mechanism has been proposed[37] for the formation of the radical and its isomerisation in the adsorption of 3,3-dimethylbut-1-ene on the centre (VI):



The change in the structure of the EPR spectrum of the adsorbed but-2-yne radical-cation on raising the temperature has been explained[37] by trimerisation accompanied by the formation of hexamethylbenzene radical-cations localised in the cylindrical channels of the zeolite ZSM-5:



Thus, in this case, as for the examples of the reactions of olefins on the zeolite HM discussed above, the final structure is an aromatic radical-cation. However, the author's hypothesis[37] that the hexamethylbenzene radical-cation is localised within the channel in the zeolite ZSM-5 is in our view erroneous, because in this zeolite the channel diameter, and not the channel radius as stated by Shih[37] is 5.8–6.0 Å; hexamethylbenzene molecules cannot be localised in such channels.

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The results of a few studies of the formation and reactions of the radicals arising in the adsorption of olefins on zeolites of types Y, HM, and ZSM-5 were examined above. Analysis of the available data shows that the adsorption of olefins of different types at room temperature on cationic and decationated forms of zeolites of the faujasite type is accompanied by the appearance of EPR spectra with virtually identical parameters. EPR spectra of identical structure also arise in the adsorption of various olefins at 20 °C on cationic, decationated, and dealuminated forms of mordenite,

but their parameters differ significantly from those observed in the adsorption of the same olefins on faujasites.

In the discussion of the results it was shown that the radicals formed in the adsorption of olefins on mordenites at 20 °C are secondary radical species arising due to oligomerisation processes and that both oxidative and Brønsted centres participate in the formation of these species. The adsorption of olefins on mordenites at low temperatures is accompanied by the formation of primary radicals characterised by individual EPR spectra. An important feature of mordenites is their ability to form selectively aromatic structures, giving rise to EPR spectra with the characteristic HFS, from compounds of different classes on zeolite lattice elements with a specific geometry.

Despite the considerable advances made, many problems still remain unsolved. The chemical nature of the radicals formed on faujasites has not been elucidated and in particular it is not known whether these radicals are primary adsorbed species or whether they are formed later as a result of subsequent chemical reactions. The mechanism of the activating influence of oxygen has not been established and its role in the formation of radicals has not been elucidated. Furthermore, the fundamental question of the nature of the oxidative centres involved in the formation of radicals still remains open, particularly for faujasites.

The solution of these problems is important not only in itself but it is also essential for the understanding of the mechanisms of the catalytic processes involving olefins and in particular on high-silica zeolites, for which one cannot rule out the possibility of an important role of reactions involving radical species.

It is noteworthy that the application of the EPR method to the elucidation of the mechanisms of the thermal transformations of compounds of different classes, including olefins, adsorbed on zeolites is important also for the analysis of the nature of the "coke" deposits formed under these conditions, which play a decisive role in the deactivation of zeolite catalysts.

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