ION-RADICAL DECOMPOSITION OF HYDROPEROXIDES
AND PEROXIDES ON SYNTHETIC ZEOLITES

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Mechanism of formation of free radicals and their stabilization by active surface at interaction of organic peroxides with synthetic zeolites NaX and NaY is discussed. In the presence of methyl methacrylate or styrene it is possible to observe by ESR method the formation of propagating radicals of the corresponding monomers; this is, under given conditions, impossible for solution free of zeolite. It is assumed that the reaction of organic peroxides with synthetic zeolites proceeds *via* a redox mechanism, *i.e.* through the interaction of peroxides with electron-donating and electron-accepting surface centres.

It is generally assumed that most of reactions catalysed by synthetic zeolites is of ionic character[1]. In some cases also ion-radicals were experimentally found as intermediate products. *E.g.* ESR spectra of anion radicals[2] were observed when adsorbing electron-accepting compounds (tetracyanoethylene, 1,3,5-trinitrobenzene, *etc.*) on zeolites type NaY (HY) of different activity. If electron-donating compounds perylene, anthracene[3] and also unsaturated nonaromatic compounds[4,5] were adsorbed, ESR spectra of cation-radicals were observed. Therefore, Flockhart and coworkers[2] assume, besides electron-accepting centres, the presence of at least two types of electron-donating centres on the surface of zeolites namely of nonsolvated hydroxyl ions and redox centres formed at activation of zeolites at higher temperatures (over 660°C).

The oxidation effects of zeolites which manifest themselves in the formation of cation-radicals from adsorbed compounds are, for most zeolites studied, far more pronounced that reducing ones; this holds also even if zeolite activation temperature was lower than 660°C. In this case as electron-accepting centres can act Lewis' centres of tricoordinated aluminium[3], Brönstedt's centres of polarised OH groups with catalytic action of oxygen[6], adsorbed oxygen molecules with catalytic action of tricoordinated aluminium[7] and in the case of zeolites containing polyvalent ions the centres of cation localisation[8,9].

The present work deals with the decomposition of organic hydroperoxides and benzoyl peroxide adsorbed on zeolites type NaX and NaY. Mechanism of peroxide decomposition and initiation of radical processes were of main interest. We have

already found, that at the interaction of synthetic zeolites (crystalline aluminosilicates) with peroxides free radicals are formed which can be observed by ESR spectroscopy[10] or by the chemiluminescence method[11]. Both the mechanism of formation of these radicals and the explanation of their considerable thermal stability (they may be observed even at $100 - 150°C$) has not been well understood. It has been assumed that a combination of the molecular sieve effects of zeolites, chemisorption of radicals and the decompositions products, resp. together with the catalytic properties of these adsorbents are factors responsible for this phenomenon. That is why we have examined the interaction of some synthetic zeolites with certain electron--donating or electron-accepting compounds and also with some stable radicals.

EXPERIMENTAL

Chemicals

tert-Butyl hydroperoxide and α,α-dimethylbenzyl hydroperoxide were purified by the procedure due to Solomon[12]. Benzoyl peroxide was twice precipitated from a chloroform solution by ethanol. α-Methyl benzyl hydroperoxide and 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide were prepared
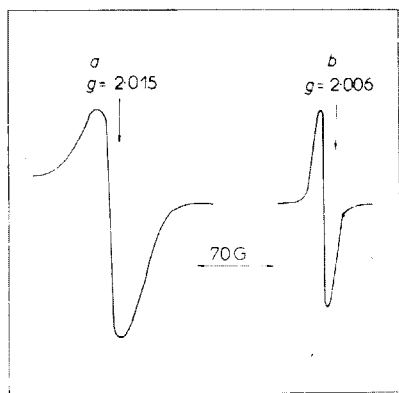

FIG. 1

ESR Spectra of Radicals Formed During the Interaction of tert Butyl Hydroperoxide (1 . . 10^{-1} mol. 1^{-1}) with NaY (a) and CoY (b) Zeolite in Benzene at Temperature 50°C
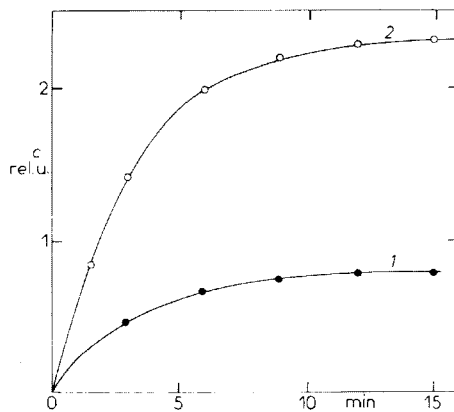
FIG. 2

The Formation of Anion Radicals of Tetracyanoethylene During the Interaction with Zeolites at 50°C in Benzene

Concentration of tetracyanoethylene 5 . . 10^{-2} mol. 1^{-1}. Curves: 1 after the adsorption to NaY zeolite, 2 simultaneous adsorption of tert-butyl hydroperoxide at concentration 1 . 10^{-1} mol. 1^{-1}.

through the photooxidation of ethyl benzene and tetralin, resp. in air, a 125 W UV lamp being a source of UV light. The concentration of hydroperoxides in solution was determined iodo-metrically.

Tetracyanoethylene and diphenylamine (Lachema, Brno, Czechoslovakia) were of analytical grade purity. N-Nitrosoacetanilide was prepared by the nitrosation of acetanilide according to Haworth and Hey[13].

Faujasite Na 13 X, Na 13 Y, NH_4Y and CoY granules or powder was kindly supplied by Research Institute for Crude Oil and Hydrocarbon Gases, Bratislava. The composition of zeolites was following: zeolite NaY: 15.1% w/w Na_2O, 21.6% Al_2O_3, 63.3% SiO_2; zeolite NaX: 18.0% Na_2O, 25.5% Al_2O_3 and 56.6% SiO_2. The zeolite samples were activated prior to each measurement by heating to 400°C at pressure $1 . 10^{-3}$ Torr. The zeolite itself did not exhibit any observable ESR signal or luminescence.

Procedure

ESR spectra were taken on the RE 1301 Spectrometer fitted with a cylindrical resonator H_{011}, the sensitivity being $1 . 10^{12}$ spin/gauss and resolving power 0.2 gauss. The concentration of radicals was expressed with regard to the carbon standard.

Chemiluminescence measurements were carried out in air using the PU SNK 7M instrument with the photomultiplier FEU-38 (Institute of Chemical Physics, Moscow). The photomultiplier voltage was 1400 V. The chemiluminescence intensity was given in relative units, one relative unit corresponding to $3.6 . 10^{-13}$ A at resistance $1 . 10^{11}$ Ω.
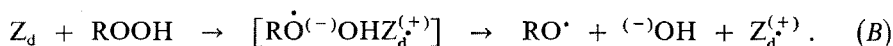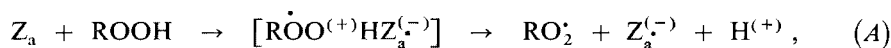
RESULTS AND DISCUSSION

The Nature of Paramagnetic Species Formed During the Interaction of Zeolites with Peroxy Compounds

Paramagnetic particles formed on the sample surface when tert-butyl hydroperoxide or α,α-dimethylbenzyl peroxide is adsorbed on zeolites of NaX or NaY type were interpreted as RO_2. radicals. This conclusion was based on the comparison of a spectrum observed with that obtained for the cobaltous acetylacetonate–tert-butyl hydroperoxide system[14]. The ESR spectrum was in both cases singlet whose line width at the first derivative was 28 gauss and $g = 2.015$. Unlike this observation, the dilute solution of α,α-dimethylbenzyl hydroperoxide or tert-butyl hydroperoxide in benzene adsorbed to zeolite CoY i.e. to the zeolite with promoted electron-donor centres $(Co^{2+}$ ions) exhibits a singlet whose line width is only 9 gauss and $g = 2.006$. This signal may be regarded as being due the presence of oxy radicals (Fig. 1).

Peroxy radicals that are formed on NaY zeolite quickly disappear at temperature above 50°C while the concentration of oxy radicals formed on the CoY zeolite is, after reaching an equilibrium level, virtually time independent up to the temperature round 90°C. It should be noted, however, that the corresponding peroxy radicals may be observed even in solution (ref.[14]) since the rate of their recombination is lower. At the same time, the rate of hydroperoxide decomposition on NaY or NaX zeolite surface should be relatively high.

The mechanism which accounts for the formation of radicals during the interaction of zeolites with peroxides (hydroperoxides), taking into account redox properties of these adsorbents, is based on the Haber–Weiss catalytic cycle known for the decomposition of hydroperoxides by transition metal ions:

$$Z_a + ROOH \rightarrow [\overset{\centerdot}{R}OO^{(+)}HZ_a^{(-)}] \rightarrow R\overset{\centerdot}{O}_2 + Z_a^{(-)} + H^{(+)}, \quad (A)$$

$$Z_d + ROOH \rightarrow [\overset{\centerdot}{R}O^{(-)}OHZ_d^{(+)}] \rightarrow RO^{\centerdot} + {}^{(-)}OH + Z_d^{(+)}. \quad (B)$$

In our case, however, the Z_a and Z_d i.e. surface electron-acceptor and electron-donor centres occur in isolated places of zeolite microstructure.

The participation of reaction (A) in the mechanism of hydroperoxide decomposition on NaX and NaY zeolites may be also confirmed by a considerable increase of tetracyanoethylene anion-radicals concentrations at temperatures above 50°C in the presence of hydroperoxides (Fig. 2). During the interaction of electron-accepting centers with hydroperoxide, electron-donating centres $Z_a^{(-)}$ are formed on the surface (reaction (A)). These centres are, at certain temperatures, capable of releasing an electron with its transfer to tetracyanoethylene (T):

$$Z_a^{(-)} + T \rightarrow Z_a + \overset{'}{T}_{\centerdot}^{(-)} \quad (C)$$
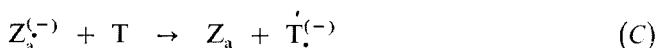
(The same reaction of hydroperoxides with tetracyanoethylene but in the absence of zeolites does not give anion-radicals of tetracyanoethylene $T_{\centerdot}^{(-)}$.) Similarly, a singlet due to cation-radicals $\left(\langle\bigcirc\rangle\right)_2$—$NH^{\centerdot(+)}$ may be seen when diphenylamine is adsorbed on the NaY zeolite; the electron $Z_a^{\centerdot(-)}$ trapped in a zeolite microstructure gives with tetracyanoethylene anion-radical. The level of cation-radicals of diphenylamine is not changing during this process (Fig. 3).

The decomposition of benzoyl peroxide on zeolite NaX or NaY is accompanied by the formation of paramagnetic species that give rise to an ESR signal. The latter is $8-11$ gauss wide (depending on temperature), the concentration being as high as $5 \cdot 10^{16}$ spins/g. When the surface concentration of electron-donor centres is considerably higher, as in the case of decationised zeolite NH_4Y activated at 550°C, the concentration of paramagnetic species, formed due to benzoyl peroxide adsorption, is also considerably higher. The radicals formed from benzoyl peroxide will be desorbed by methanol or ethanol, and the singlet's spectrum will disappear. Since benzoyloxy radicals along with benzoate anions should be formed according to reaction (B) during the interaction of benzoyl peroxide with electron-donor centres and since the cation-radical mechanism is unlikely in the view of the fact that benzoyl-peroxy radicals were not observed during benzoyl peroxide decomposition carried out under different conditions, we tend to believe that the observed spectrum reflects the presence of benzoyloxy radicals.

It is well known that benzoyloxy radicals in inert solvents easily undergo to decarboxylation:

$$R\!-\!C\!\!\overset{O}{\underset{O^{\cdot}}{\diagdown}} \longrightarrow R^{\cdot} + CO_2 \qquad\qquad (D)$$
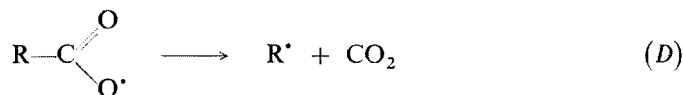
This led Wiley[15] to conclusion that during the trapping of reactive radicals from benzoyl peroxide on porous Vycor glass, only phenyl radicals can be observed at higher temperatures (up to 100°C). Such explanation of the singlet's spectrum is in controversy with the fact that no ESR spectrum could be recorded when phenyl radicals are generated on the surface in some other independent way, such as by thermal decomposition of N-nitrosoacetanilide[16]. It should also be noted that the decarboxylation of benzoyloxy radicals takes place in a cage of medium molecules. So far no information is available about the behaviour of these radicals in an isolated
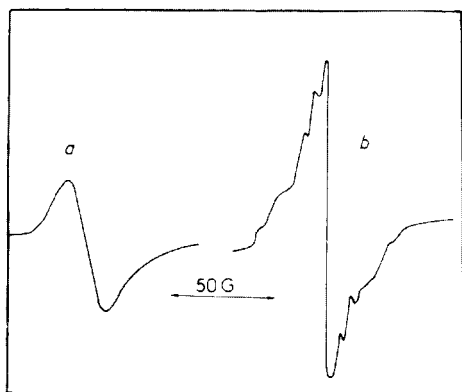

FIG. 3

ESR Spectrum of Cation Radicals Formed after the Adsorption of Diphenylamine (1 . $. 10^{-2}$ mol. 1^{-1}) to NaY Zeolite in Benzene at 50°C (system a) and ESR Spectrum of Diphenylamine Cation Radicals and Tetracyanoethylene Anion Radicals Following the Addition of Tetracyanoethylene to the System a (b)
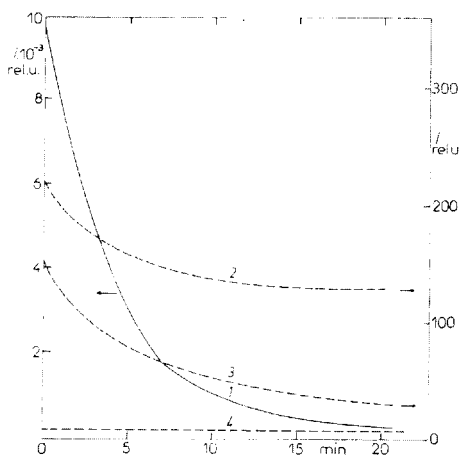

F·G. 4

Chemiluminescence Intensity Course in the System Synthetic Zeolite (35 mg)–Hydroperoxide Solution (1 ml) at 70°C

Hydroperoxides (concentration in mol. 1^{-1}): 1 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide in tetralin (1 . 10^{-2}), 2 α-methylbenzyl hydroperoxide in ethylbenzene (1 . 10^{-2}), 3 tert-butyl hydroperoxide in benzene (1 . 10^{-1}), 4 tert-butyl hydroperoxide (1 . 10^{-1}) in benzene in the absence of zeolite.

state and about the behaviour of their complexes with the zeolite surface. Finally, if the singlet indicated either the microstructural defects of adsorbent or the presence of stable radical products from low-temperature pyrolysis of benzoyl peroxide (poly-phenylene radicals) it should be possible to see it even after the washing of zeolite with methyl alcohol. This, however, is not the case.

It may be concluded that the mechanism of hydroperoxide decomposition on the surface of synthetic zeolites may be both cation and anion radical one. Benzoyl peroxide, on the other hand, will probably decompose *via* the anion radical mechanism.

The Disappearance of Primary Peroxy Radicals

The interaction of peroxides and hydroperoxides, resp., dissolved in benzene or other hydrocarbon, with synthetic zeolites gives rise to chemiluminescence radiation[11]. According to extensive work of Vasil'ev[17,18] and Schlyapintokh and coworkers[19] one of the likely sources of the chemiluminescence may be the exothermic disproportionation of peroxy radicals during which the resulting carbonyl compounds become excited. As peroxy radicals were proved to be formed during the interaction of hydroperoxides with zeolites it is plausible to apply Vasil'ev's conclusions also to these redox systems. The initial intensity of chemiluminescence (I) which is proportional to the rate of termination of peroxy radicals and to the quantum yield of chemiluminescence

$$I = \eta k_t [RO_2^{\bullet}]^2 = \eta k_i [Z][ROOH] , \qquad (1)$$

where k_t and k_i represent the corresponding rate constants, Z being the active centres concentration on the surface and η the quantum yield of chemiluminescence, increases in the following
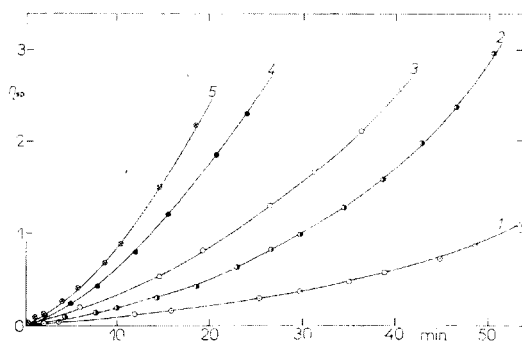

FIG. 5

Time Dependence of Methyl Methacrylate Specific Viscosity at the Interaction of Benzoyl Peroxide with Synthetic NaY Zeolite at 50°C

Amount of zeolite (mg) per 20 ml of monomer: *1* 0, *2* 400, *3* 600, *4* 1000, *5* 1200; concentration of benzoyl peroxide in monomer 1% w/w.

order: tert-butyl hydroperoxide < 2-methylbenzyl hydroperoxide < 1,2,3,4-tetrahydro-1-naph-thyl hydroperoxide (Fig. 4).

The values of initial intensity of chemiluminescence will mainly depend on chemi-luminescence quantum yields of individual termination reactions of peroxy radicals. The same conclusion may be reached when chemiluminescence experimental data are compared *e.g.* for ethylbenzene and tetralin oxidations, maintaining in both cases the same rate of initiation (*i.e.* as well as termination) of the oxidative process. The rapid decrease of chemiluminescence intensity from a maximum value is probably due to the establishement of adsorption–desorption equilibrium between the con-centration of hydroperoxides and reactive products on the surface of zeolite. On the other hand, the chemiluminescence intensity is practically zero during the simultane-ous adsorption of hydroperoxides and reactive monomers. This is caused by an ef-ficient trapping of oxy or peroxy radicals by their reaction with the monomer, the resulting radicals having a very low quantum yield of chemiluminescence in the recom-bination process.

Secondary Reactions of Radicals Following Catalytic Decomposition of Peroxy Compounds

Another experimental fact, which is in accordance with the hypothesis about the formation of reactive radicals during the reaction of benzoyl peroxide with zeolites, is the acceleration of methyl metacrylate polymerization initiated by this system instead of benzoyl peroxide itself (Fig. 5).

Unlike the benzoyl peroxide–zeolite system, no polymer insoluble in methanol is formed at half-an-hour's interaction of tert-butyl hydroperoxide with NaX or NaY
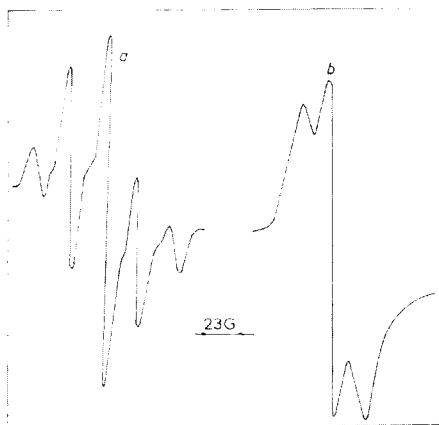

FIG. 6

ESR Spectra of Stabilised Radicals During the Polymerization of Methyl Methacrylate (*a*) and Styrene (*b*) Initiated by tert-Butyl Hydroperoxide at 70°C in the Presence of NaY Zeolite

zeolite in the presence of methyl methacrylate. The yields of paramagnetic species trapped in zeolite during the polymerization of methyl methacrylate and styrene (for ESR spectra see Fig. 6) are, however, higher when the initiation is effected by tert--butyl hydroperoxide instead of benzoyl peroxide. The experiment need not be performed in an inert atmosphere, as in the case of benzoyl peroxide; it is sufficient to cover the zeolite sample by a small volume of solvent and a corresponding monomer. This is probably due to electron acceptor centres in zeolite, responsible for hydroperoxide decomposition, whose concentration is higher than that of electron--donor centres responsible for benzoyl peroxide decomposition. It indicates that also the rate of hydroperoxide decomposition will be higher than that of benzoyl peroxide. Consequently, the number of trapped propagating radicals of a corresponding monomer will also be higher. On the other hand, oxygen which is formed during the hydroperoxide decomposition as a result of peroxy radicals interaction can simultaneously inhibit the polymerization in solution.

The similar ESR spectra have been reported by Kanazawa and Higashide[20] in their paper dealing with the interaction of methyl methacrylate with irradiated amorphous aluminosilicates whose surface was modified prior to experiments by a treatment with potassium dichromate solution. The authors assume that a corresponding ESR spectrum is due to species of anion radicals of methyl methacrylate.

$$—Al^{(-)} \quad CH_2{=}C—CH_3$$
$$\overset{|}{\underset{COOCH_3}{}}$$
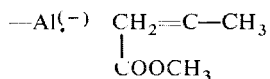
Judging from the fact that, in the case of synthetic zeolites, the paramagnetic particles cannot be desorbed from the surface by ethanol, it may be assumed that more than one or two monomer units are linked together. When polymerization propagating radicals (*e.g.* of methyl methacrylate) are prepared on the zeolite surface together with anion radicals of tetracyanoethylene then only the latter radicals (*i.e.* low molecular species) can be desorbed by ethanol (Fig. 7). The concentration of trapped propagating radicals of polymerization is practically unchanged by the desorption process.

Identical ESR spectra were observed during the thermal decomposition of 2,2′-azobis(isobutyronitrile) on zeolite in the presence of a corresponding monomer. No effect upon the decomposition reaction of 2,2′-azobis(isobutyronitrile) due to the adsorbent was found. If there are any radicals formed during the adsorption of neat, carefully purified monomer free of initiator, their concentration is well below the sensitivity threshold of the instrument. It can thus be concluded that the observed species are not anion radicals of monomer but the radicals formed through a simple addition reaction of initiator radicals to monomer.

When the compounds are added that are reactive towards the transfer reaction of free radicals formed in zeolite–hydroperoxide system then the corresponding low molecular radicals could not be trapped. The course of transfer reaction can be followed only from the decrease of primary

radicals concentration (this may be overlapped with desorption). The difference between the stability of secondary radicals formed by polyaddition and that of radicals formed by substitution is not well understood. It might be assumed, however, that during the polyaddition reaction, the radical centre diffuses, by means of a chemical reaction, away from the initiation centre. Due to a successive growth of radical length in a porous microstructure of zeolite the radical becomes immobile for translation diffusion, simultaneously leaving the active redox centre of zeolite and the probability of its recombination is thus lowered.

Low molecular radicals formed in the substitution reaction in close vicinity to catalytic centre will, with a great probability, disappear *via* a reaction with another radical or by a direct interaction with the active centre. We have found that radicals stable in solution (such as $\left(CH_3-\langle\bigcirc\rangle\right)_2 NO^{\bullet}$ or diphenylpicrylhydrazyl) disappear at the adsorption to synthetic zeolites (Fig. 8). The transfer of electron to active surface yields probably a surface paramagnetic particle whose ESR spectrum cannot be observed because of its excessive width. This apparent discrepancy with regard to the stabilising effect of zeolites upon many relatively reactive radicals is considered to be again connected with the electron-donor or electon-acceptor character of surface
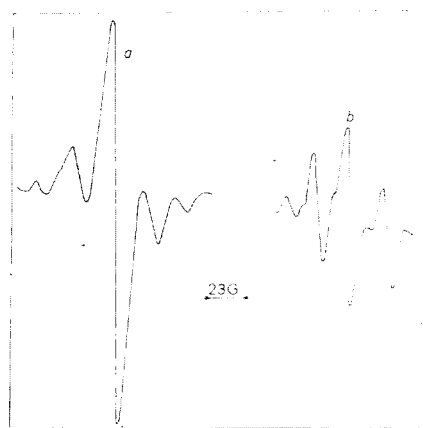

FIG. 7

ESR Spectra Measured after the Simultaneous Adsorption of Methyl Methacrylate and Tetracyanoethylene to NaY Zeolite in the Presence of $1 . 10^{-1}$ $mol.l^{-1}$ tert Butyl Hydroperoxide (*a*) and after the Addition of Ethanol (*b*)
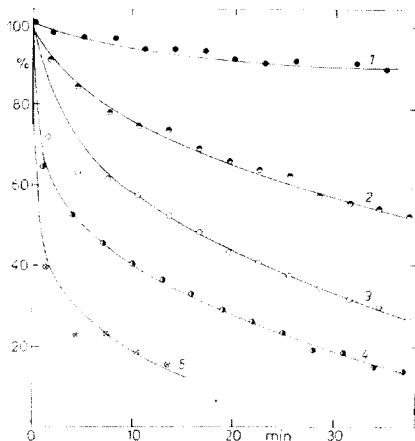

FIG. 8

The Disappearance of Stable $(CH_3O-\langle\bigcirc\rangle)_2 NO^{\bullet}$ Radicals in Benzene, the Initial Concentration being $1 . 10^{-3}$ $mol.l^{-1}$, During the Interaction with Synthetic Zeolite NaY at 60°C

Amounts of zeolite (mg) per 0·2 ml of benzene. *1* 5, *2* 9, *3* 13, *4* 18, *5* 24.

active centres *i.e.* with their oxidation or reduction properties as well as with the oxidation or reduction ability of corresponding radicals.

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