Electron Spin Resonance Absorption of Hexane/Silica Gel Systems γ-Irradiated at Low Temperatures

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The system hexane/silica gel and the pure components have been irradiated at 77°K with ⁶⁰Co γ-rays at a dose rate of 8 krad/h to a total dose of about 0.7 ± 0.15 Mrad. Before irradiation the samples were carefully degassed. ESR spectra were recorded at 3 cm wavelength in the temperature range 77°K to 300°K. The absorption intensities at different compositions were measured at 77°K.

Of the silica gel resonance lines, one at $g = 2.0080$ vanishes at very low hydrocarbon contents, while another component at $g = 2.0008$ which shows ²⁹Si hyperfine structure is not influenced by the presence of the hydrocarbon. In the hydrocarbon phase the spectrum changes with the composition of the system and evidence have been found for the existence of ethyl radicals. No hydrogen atoms have been found in pure silica gel and only very small amounts in the composite systems.

The dependence of the free radical yields on the hydrocarbon content has been discussed in terms of two simple models. The yields of paramagnetic species in the two phases imply an interaction between the components and the magnitudes of the yields strongly suggest an energy transfer from the silica gel in the formation of free radicals. A saturation effect occurs at a hydrocarbon electron fraction of 0.02. This corresponds to a coverage of 5 % of the BET surface. In a model where radicals are produced at active centers, the number of these is found to be about 10^{17} per m² BET surface. It is estimated that 5—25 % of the radiation energy released in the silica gel is transferred to the hydrocarbon.

The temperature dependence shows the ethyl radicals to be more stable than the other hydrocarbon radicals. The radicals formed at the lowest hexane contents are less stable than the radicals formed in the pure substance contrary to previously reported results for methane and ethane.

During the last few years attention has been drawn to the action of ionizing radiation on heterogeneous systems consisting of one solid, inorganic phase, mostly an oxide, and one liquid or gaseous phase. Investigations in this field proceed along two lines. The one is concerned with the chemical activity of solids irradiated before they are brought into contact with the second phase, the other studies the action of radiation on the entire heterogeneous system. A review of recent work has been given by Coekelbergs et al.[1] The importance of the field lies in the possibility that some contribution can be made to the elucidation of the mechanism of chemical catalysis. One of the main problems is the role played by the solid as a possible transducer for passing the energy of the ionizing radiation to the liquid or gaseous phase.

Irradiated heterogeneous systems with hydrocarbon as one component e.g. pentane/silica gel (Caffrey and Allen,[2] Sutherland and Allen[3]) and isopropyl-benzene/silica-alumina (Hentz[4-6]) have been analyzed for hydrocarbon products. The conversion of hydrocarbons on silica gel was investigated by Barter and Wagner.[7] Electron spin resonance measurements on similar systems have been reported by Kazansky et al,[8,9] who studied ethane and methane on silica gel, and by Topchiev[10] and Kolbanovskii et al.[11]

The electron spin resonance studies hitherto reported have so far only been of a qualitative nature. They have indicated that an interaction occurs between the two phases. However, the energy transfer process has not been discussed on the basis of the data obtained. Therefore a more complete investigation was initiated in order to study in detail both the structure of the radicals formed and their yields at different compositions of the system. For the present work the system hexane/silica gel was chosen and it has been investigated for paramagnetic species after γ-irradiation at low temperature. The intention was to get information about the interaction mechanism at an earlier stage of the process than can be obtained by the analysis of the final products (a report on these products as studied by gas chromatography will be given elsewhere[12]).

EXPERIMENTAL AND SAMPLE PREPARATION

Materials. Silica gel for chromatographic purpose, 100—200 mesh, (AB Kebo, Stockholm), was used. The specific surface area (BET) was determined as 1110 ± 90 m^2/g. After irradiation with γ-rays to a dose of 10 Mrad the value 1160 ± 80 m^2/g was found showing that no change of the BET surface had occurred (we are indebted to Messrs. Svenska Ackumulator AB Jungner, Oskarshamn, Sweden, for performing these measurements). The gel contained some black particles which could not be removed by oxidation at high temperature for several hours. These impurities are responsible for weak ESR signals which occasionally have been obtained from nonirradiated silica gel samples.

The hexane (Philips Petroleum Co) was 99.96 mole % pure with methylcyclopentane as the most probable impurity.

Small quantities of carefully degassed hexane were vacuum distilled on to weighed amounts of silica gel which had been kept at 500°C and 10^{-5} mm Hg for about 10 h. The hexane fraction was determined from the weight of the ampoules before and after adsorption. It was checked after completed measurements from the weight loss of the ampoule content upon heating. The maximum content of hexane corresponded to an electron fraction of 0.45. More hexane gave a moist appearance to the silica gel powder.

Irradiation. The samples were irradiated with γ-rays from ^{60}Co under vacuum (10^{-5} mm Hg) in ampoules similar to those described earlier.[13] However, the present ampoules used suprasil quartz for the tube adapted for the microwave cavity. In most experiments

the samples were kept in this tube also during the irradiation. The radiation source [14] gave 8 krad/h and the doses were 0.7 ± 0.15 Mrad (in one case 10 Mrad at about 350 krad/h, cf. Fig. 3). The irradiation temperature was 77°K.

ESR-spectrometer. The electron spin resonance spectra were recorded on a Varian V-4500 spectrometer working at a wavelength of 3 cm and utilizing 100 kc/s magnetic field modulation.

Absorption intensities. The absorption intensities of the signals were determined relative to pure hexane irradiated under the same conditions. The first moments were calculated after separation of the signals in the central part as indicated in Fig. 4 c. The G-value used [10] for hexane was 4.7. In a specific experiment the relative spectrometer sensitivity was checked with non-irradiated samples of pure hexane and pure silica gel in the cavity. The signal from a small glass capillary with solid DPPH (1,1-diphenyl-2-picrylhydrazyl) centered in a sample tube containing either of the two substances at 77°K was observed. No difference in the absorption from DPPH could be seen showing that the sensitivity did not depend on the dielectric properties of the sample.

<div align="center">RESULTS</div>

Silica gel. The first derivative spectrum at 77°K of irradiated silica gel contains a number of components (Fig. 1). The strong component has $g = 2.0080 \pm 0.0005$ and a line width $\Delta H = 9$ gauss. This line is difficult to saturate as is the broad wing on the low field side. Of the other components the one centered around $g = 2.0008 \pm 0.0005$ with $\Delta H = 2 - 2.5$ gauss is more easily saturated. If the sample is kept at 168°K for one minute the resolution of the spectrum recorded at 77°K increases but the number of components is the same. At room temperature very little of the signal remains.

Contrary to results from other investigations (cf. Kazansky et al.[8]) no signals from hydrogen atoms could be observed.

Hexane. The spectrum of hexane irradiated at 77°K consists of seven main lines having an additional structure (Fig. 2). The separation of the main lines is 25—30 gauss. The same spectrum is obtained after a dose of 10 Mrad at 350 krad/h. The radicals are stable for a couple of minutes up to temperatures 2—3 degrees below the melting point. At 178°K — one degree below the melting point of hexane — the spectrum is essentially the same but better resolved (Fig. 3). The total splitting is 176 ± 2 gauss and the line width about 4 gauss. Most of the hydrocarbon radicals in the sample of Fig. 3 have decayed and therefore the narrow line in the centre originating from the ampoule appears comparatively strong. In all other spectra reported here the signal from the ampoule is very weak and of no significance.
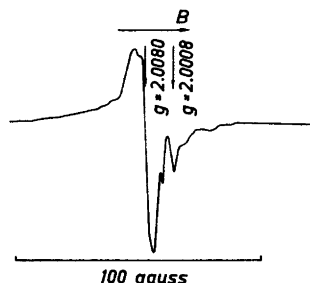

Fig. 1. ESR derivative spectrum at 3 cm wavelength and 77°K of silica gel irradiated with γ-rays at 77°K. Dose rate 8 krad/h and total dose about 0.7 Mrad.
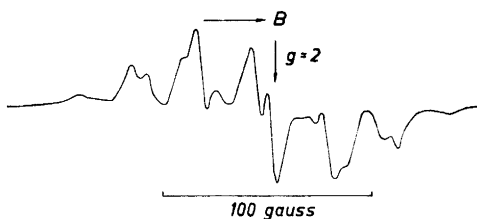
Fig. 2. ESR spectrum at 77°K of hexane irradiated under the same conditions as in Fig. 1.
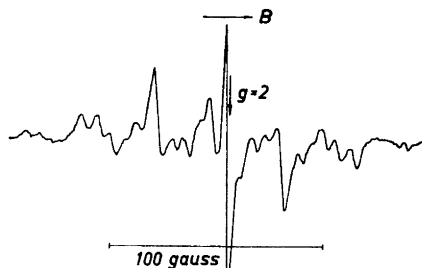
Fig. 3. ESR spectrum at 178°K of hexane irradiated at 77°K and at a dose rate of 350 krad/h to a total dose of about 10 Mrad. The strong narrow line in the center originates from the ampoule.

Hexane/silica gel two-phase system. The appearance of the spectra from the composite system varies with the relative contents of the two components. The structure is complicated and a model based on simple superposition of the spectra from the pure components must be rejected.

In Fig. 4a the spectrum at a hydrocarbon electron fraction $x_1 = 0.45$ is shown. In the range $x_1 = 0.05 - 0.20$ an additional pair of lines appears (Fig. 4b) with a splitting of 26.7 ± 0.4 gauss and a line width of only 1.5 gauss. Possibly these lines
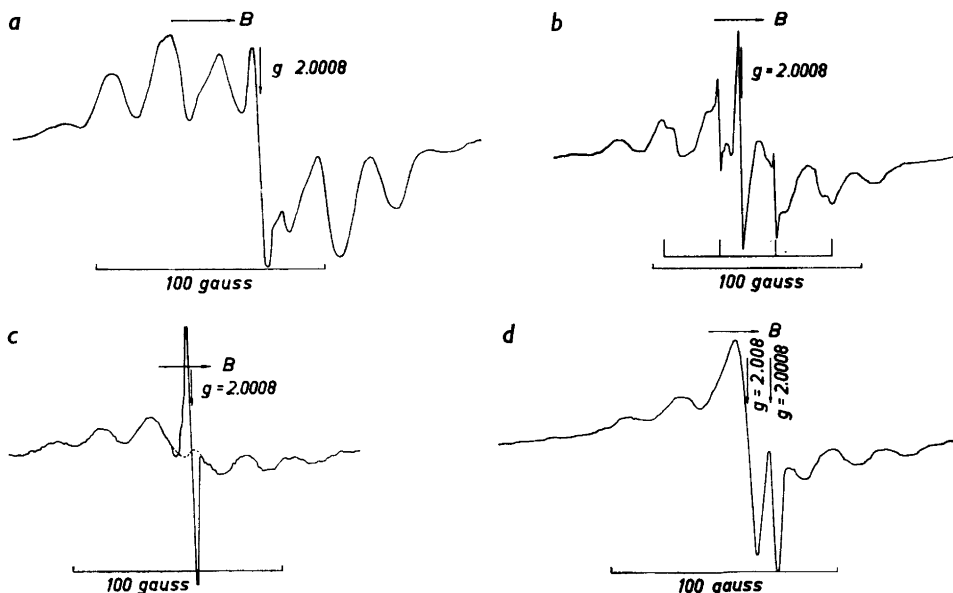

Fig. 4. ESR spectrum at 77°K of hexane + silica gel irradiated under the conditions of Fig. 1. The electron fractions x_1 are in a) $x_1 = 0.45$, b) $x_1 = 0.18$, c) $x_1 = 0.02$ and in d) $x_1 = 0.01$.
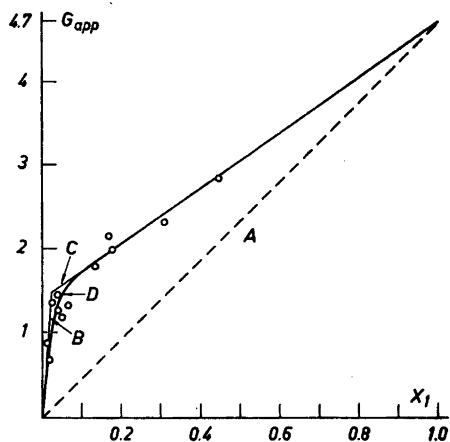
Fig. 5. Apparent hydrocarbon radical G-values (number of radicals per 100 eV absorbed by the entire system) as function of the hydrocarbon electron fraction x_1. The dotted line (A) represents no interaction. The solid lines (B, C, and D) are obtained from equations given in the text with $G_{ads} = 75$ and $x_1{}^s = 0.020$.

are the central part of a quartet as indicated in the figure. At electron fractions less than 0.05 the narrow lines are absent as exemplified from Fig. 4c ($x_1 = 0.02$) and Fig. 4d ($x_1 = 0.01$). Signals from hydrogen atoms have been found, but with a very small intensity as compared to the intensity of the hydrocarbon radicals. Only one of the components ($g = 2.0008$) from the pure silica gel spectrum persists at all compositions. In addition to this, one of the broad components ($g = 2.0080$) can be seen at the lowest hexane concentration used ($x_1 = 0.01$, Fig. 4d).

The temperature dependence has been studied qualitatively. The hydrocarbon signal from samples at lower x_1 decays with a half life of the order of half an hour at 130°K and less than 30 seconds at 168°K. The additional narrow lines in Fig. 4b persist at higher temperatures than the other hydrocarbon signal. At 178°K their decay time seems to be at least 15 min.

Two weak satellites associated to the narrow silica gel signal in Fig. 4b could be detected at 130°K from a sample in which the hydrocarbon radicals had decayed. Their amplitudes are about 2 % of the amplitude of the main line and their separation is 10 gauss.

Yields of paramagnetic species. The number of hydrocarbon free radicals produced by 100 eV radiation energy absorbed by the entire system (G_{app}) is given in Fig. 5 as a function of the hydrocarbon electron fraction x_1.

A rough estimate shows that the yield of centers in pure silica gel is about twice the yield of radicals in pure hexane.

The intensity of the silica gel signal has at $x_1 = 0.01$ decreased to 5—10 % of the pure silica gel value and is for higher x_1 values less than 5 %.

DISCUSSION

Energy transfer. Energy transfer mechanisms in heterogeneous systems have been discussed earlier [2,4] from an analysis of the yield of final products. In our case the yields of paramagnetic species from both phases should give information about possible energy transfer. Since most data have been obtained

from the hydrocarbon phase, an extensive discussion will be given only for this phase.

The yield of free radicals in hexane G_{app} (Fig. 5), would follow the straight line (line A in Fig. 5)

$$G_{app} = G_{hom} \times x_1$$

if the silica gel acted as an inert diluent. G_{hom} is the yield in a pure hexane phase. As the experimental points deviate from line A we conclude that the free radical production is dependent on some interaction between the two phases.

For a discussion of the experimental results we suggest two simple models for the adsorption mechanism. In both models it is assumed that the silica gel has an active surface on which molecules can be adsorbed. The yields of free radicals, G_{ads}, formed on this surface are calculated per 100 eV of energy released in the adsorbed hydrocarbon. This yield does not take any possible energy transfer into account and the energy distribution between the phases is thus obtained from the density of electrons in these phases (for a similar concept G_{gas} see Ref. 1, pp. 60—61). Hexane molecules not situated on the active surface are assumed to give free radicals with the yield G_{hom}. For the total yield we get

$$G = \alpha_{ads} \times G_{ads} + (1 - \alpha_{ads}) \, G_{hom}$$

where α_{ads} is the fraction of the total number of hexane molecules that are adsorbed on the active surface.

In the first model we further assume that molecules selectively enter the active surface until this becomes completely saturated. This occurs at the hexane electron fraction x_1^s. G_{app} as defined above is then given by (line B in Fig. 5)

$$G_{app} = G_{ads} \times x_1$$

For concentrations beyond x_1^s a similar reasoning gives (line C in Fig. 5)

$$G_{app} = G_{hom} \times x_1 + (G_{ads} - G_{hom}) \frac{x_1^s}{1 - x_1^s} (1 - x_1)$$

In the other model the probablity for an added molecule to be adsorbed somewhere on the active surface equals the ratio non-occupied active surface/total active surface. This means, for example, that only when one molecule has been adsorbed on the active surface there is a small but definite probability to find another molecule adsorbed on the inactive surface. This model has the advantage of leading to simple expressions. Less idealized models will contain more parameters than can reasonably be determined from the experimental data. With our assumptions we have

$$dN_a = \frac{A - A_a}{A} \, dN$$

where A and A_a are the total and occupied active surface, respectively, and where N is the total number of hexane molecules adsorbed and N_a the number

adsorbed on the active surface. Assuming that every molecule adsorbed on the active surface occupies the same area, we get

$$G_{app} = G_{hom} \times x_1 + (G_{ads} - G_{hom}) \frac{x_1{}^s}{1 - x_1{}^s} (1 - x_1)$$

$$\times \left[1 - \exp \left(- \frac{1 - x_1{}^s}{x_1{}^s} \times \frac{x_1}{1 - x_1} \right) \right]$$

This equation is represented by line D in Fig. 5.

In Fig. 5 G_{app} as a function of x_1 is given for both models with the same values of G_{ads} and $x_1{}^s$. The difference between the models is small but the second model (line D) gives the better fit with the experimental points. From this we get $G_{ads} = 75$ and $x_1{}^s = 0.020$.

In the way we have defined G_{ads}, the obtained value would imply that on the average only 1.3 eV are required for the free radical formation. These must be formed through rupture of carbon-hydrogen or carbon-carbon bonds. The dissociation energies of these bonds in n-alkanes are 4.4 and 3.4 eV, respectively.[15] These values are significantly larger than the value (1.3 eV) obtained from G_{ads}. Polarisation effects in the adsorbed phase are expected to be quite small (cf. Ref. 9). Therefore, we infer that energy transfer from the silica gel to the hexane is very likely involved prior to or in connection with the free radical formation even at the low temperature used. The alternative explanation of a better energy utilization in the adsorbed phase must be rejected. The energy necessary for free radical formation, 21 eV in pure hexane, can in that case at most be reduced to a value corresponding to the bond dissociation energy.

The broad line at $g = 2.0080$ from silica gel gradually disappears when the hydrocarbon concentrations is increased up to saturation. This constitutes a further piece of evidence for energy transfer between the two phases. It is also very likely that the paramagnetic center responsible for this signal is localized near the surface of the silica gel. From the free radical yields one can estimate that up to saturation the production of these centers is reduced with roughly 10 centers for each hydrocarbon radical formed. This decrease can be due to either a reaction between the centers and the hexane molecules or a failure to form the centers in the presence of the adsorbed phase. At present it is not possible to decide between these possibilities.

The gel surface occupied by each adsorbed molecule can be estimated from the X-ray data of crystalline hexane [16] to be about 40 Å^2. From this figure and the observed $x_1{}^s$-value one finds that only about 5 % of the total BET surface is active. The reasons for this low value may be several. Part of the total surface can be inaccessible to hexane molecules because of too small pore radii. Alternatively, free radical formation may only occur at a limited number of active sites, which then in our case is about 10^{17} per m^2 BET surface. Similar values were found by Hentz [4] from data on the final products in the system isopropylbenzene/silica-alumina. However, the active sites might be produced by the radiation in which case their number depends on the total dose. This possibility has not been investigated here.

Assuming that there is no difference in the energy for hydrocarbon free radical formation in the adsorbed state and in the pure phase one can estimate the fraction of the energy released in the silica gel that is transferred (*cf.* Ref. 10) at or above the saturation point. If all the energy transferred is used in free radical formation, this fraction is about 5 %. Alternatively, if the transferred energy is used with the same efficiency as in the homogeneous phase (about 0.2) the fraction is as much as 25 %. The last value is not unreasonably high as the specific surface area is very large. The average thickness of the silica gel layer is only of the order of 10 Å.

Structure of centers in silica gel. Relatively little is known about the electronic structure of defects in fused quarts and silica gel. This is partly due to difficulties in getting samples of a high purity. Silica gel has been studied by Kazansky *et al.*[8,9] and by Kohn.[17] In certain respects their results are contradictory (influence of oxygen). Their low temperature results are essentially the same as those obtained in the present work.

In accordance with the findings by Kohn [17] no resonances due to hydrogen atoms have been found in samples irradiated at 77°K. Thus formation of the radicals in the two-phase systems through reactions involving hydrogen atoms abstracted from surface hydroxyl groups [8] can be disregarded.

The line at $g = 2.0008$ does not seem to be influenced by the presence of hexane. The resonance has the characteristics of a trapped electron and the satellite lines might be interpreted as due to hyperfine interaction with one neighbouring nucleus of ^{29}Si (*cf.* Weeks and Nelson [18]). It seems likely that this signal is localized in the interior of the silica gel.

The main difference between spectra from pure silica gel and gel with an adsorbed layer of hexane is found in the broad line at $g = 2.0080$. The center giving this signal is localized on the gel surface as discussed above. The signal is similar to a line with $g = 2.0068$ found in fused silica [19] and thought to be due to a positive hole. A signal with high g-value has also been discussed by van Wieringen and Kats [20] who found that the presence of water in fused silica reduces the signal intensity. Similar observations by Weeks and Lell [21] were explained to be due to localization of some fragments from water molecules at these centers.

Structure and life time of hydrocarbon radicals. The different radicals that can be produced in hexane are likely to have different lifetimes. Therefore the spectrum of pure hexane seems to contain essentially one type of radical since annealing does not change the general appearance of the spectrum (Figs. 2 and 3). An interpretation based on isotropic couplings has not been successful. Further studies of the line shapes are expected to show on which carbon atom the unpaired electron is localized.

The hexane spectrum at low electron fractions as shown in Fig. 4c and d is less resolved than the spectrum from the pure hydrocarbon. There is no obvious explanation for this effect but fixation of the radicals to the silica gel surface might give rise to variations in the hyperfine couplings due to differences in orientations on the surface. This in turn would broaden the lines.

The two narrow lines found in spectra from samples of intermediate hydrocarbon contents are thought to be due to ethyl radicals for the following reasons. Narrow lines appear in spectra from a polycrystalline sample when

all hyperfine interactions involved have negligible anisotropy. In hydrocarbons this would be the case for radicals with β-protons only and no α-protons. However, such species are not likely to be formed in the present system and they are thus excluded from this discussion. Another possibility is that the radicals produced have anisotropic hyperfine interactions with one or more α-protons, but that the anisotropy is averaged out through rapid tumbling of the complex. At low temperatures this effect has been noticed only for small species such as the methyl radical. The observed splitting 26.7 gauss differs considerably from that found for this radical (23 gauss both in the solid,[22] liquid,[23] and adsorbed states [9]). This excludes the methyl radical as a possible source for the observed lines. The motions of larger radicals are restricted to internal rotations. Secondary radicals will have broad lines only, even if the $>\dot{C}H$ fragment is allowed to rotate around an axis. This rotation is also more restricted than that for end groups of radicals like $R-\dot{C}H_2$. Here the rotation around the bond axis can average out the anisotropy for lines corresponding to opposing nuclear spins of the two α-hydrogens. The other lines are still broad (cf. Ref. 24). This motion also results in equal isotropic hyperfine couplings to the β-protons. To get an even number of sharp lines, as observed, one must have an odd number of β-protons. Thus, the narrow lines must be due to ethyl radicals. Furthermore, ethyl radicals have been observed in the solid state under various conditions, (Cochran et al.,[24] Sullivan and Koski,[25] Kazansky and Pariisky [9]) and in all cases a pronounced sharp central doublet with a separation of about 27 gauss is observed in good agreement with our observed splitting of 26.7 gauss. The other two lines of the same quartet (Fig. 4b) are considerably reduced in amplitude (cf. Ref. 9) and can very well be hidden under the main spectrum. There seems to be little evidence for the presence of other normal alkyl radicals with a freely rotating CH_2 group in any of the samples. These radicals should give an easily recognizable sharp central line which we do not observe.

The reason for the existence of the ethyl radicals in a limited hexane concentration range is not fully understood. At the lower electron fractions they may be present but not visible as sharp lines due to restricted rotation as a consequence of stronger fixation to the silica gel surface. At the higher electron fractions the mechanism giving these radicals may not be very effective due to competing formation of other radicals.

According to models given above the number of free radicals with the yields G_{hom} and G_{ads} will be formed in approximately the ratio 3:1 at the electron fraction 0.45. Then one would expect the spectra in Figs. 4a and 2 to be quite similar. The explanation for the differences must be that the radicals, produced in the composite system with the assumed yield G_{hom}, are not identical with the radicals formed in the pure hexane. This is not quite unexpected since the hydrocarbon layer even at x_1-values well above $x_1{}^s$ is probably quite thin. This layer will evidently have a structure different from solid hexane. Therefore, the radicals may have different conformation even when they are formed with the same yield.

The temperature dependence shows that the ethyl radical is more stabilized on the surface of the silica gel than the other hydrocarbon radicals. This is in agreement with the results obtained by Kazansky and Pariisky [9] who found that

radicals from ethane and methane are stabilized up to temperatures more than a hundred degrees above the melting points of the hydrocarbons. It seems remarkable that the other radicals from hexane on the surface start to decay at a temperature below the melting point of the pure hydrocarbon. The length of the hydrocarbon chain and the degree of coverage of the surface may influence the lifetimes but no systematic study of this has been performed as yet.

Conclusions. The electron spin resonance technique gives information about paramagnetic species at a rather early stage of the processes leading to the final products. However, even at the low temperatures that were used in our investigation, diamagnetic products may well be formed and thus escape detection. For example, hydrogen molecules are formed with a high yield in the system studied here (*cf.* Kinell and Adolfsson [12]) although very few precursors in the form of hydrogen atoms have been found by means of the electron spin resonance method. Nevertheless, the changes in the appearance of the spectra of both components of the two-phase system and the quantitative results strongly suggest that an energy transfer process is active prior to or at the stage of free radical formation. We also find that under certain assumptions 5—25 % of the energy released in the silica gel may be transferred to the hydrocarbon. The saturation effect of the yields observed at very low hydrocarbon content, might be interpreted as a nonaccessibility of the major part of the surface or as a consumption of certain active sites for radical production on the adsorbent. The number of these sites per m^2 silica gel surface has been estimated. It is also shown that various types of radicals in the hydrocarbon phase of the composite system are present, of which one, the ethyl radical, has been positively identified. The structure of the other radicals found in the adsorbed state are as yet left unexplained, as is their relatively low stability. A more detailed knowledge of the influence of the adsorbent is required, and we hope that further experiments with other hydrocarbons will help to elucidate these problems.

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