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Effect of Irradiation Temperatures on Hydrogen Atom Reactions in Neopentane and Its Mixtures Irradiated at 4.2 and 77 K as Studied by Electron Spin Resonance

Machio Iwasaki,* Kazumi Toriyama, Keichi Nunome, Mitsuharu Fukaya, and Hachizo Muto

Government Industrial Research Institute, Nagoya, Hirate, Kita, Nagoya, Japan *(Received February 25, 1977)*

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It has been found that the behavior of hydrogen atoms produced by the homolitic scission of the C–H bond is quite different at 4.2 and 77 K. Neopentane–isobutene (2 mol %) mixtures irradiated at 77 K show that *tert*-butyl radicals are formed by hydrogen atom scavenging in addition to neopentyl radicals. The scavengeable hydrogen atoms are estimated to be about 60–70% of the hydrogen atoms produced in the system. However, the same mixture irradiated at 4.2 K gives only neopentyl radicals which amount to the same as the total radical yield in the mixture irradiated at 77 K. This indicates that the hydrogen atoms which are scavengeable at 77 K are not scavenged at 4.2 K and they reacted with neopentane forming neopentyl radicals. The ESR line width of the neopentyl radicals, their pairwise trapping, and microwave power saturation behavior indicate that the hydrogen atoms reacted with neopentane by a rather short-range reaction at 4.2 K while some of them reacted with solutes via long-range migration at 77 K. Similar effects of irradiation temperature have been also found in neopentane–cyclohexane (2 mol %) mixtures as well as in neopentane containing a small amount of impurity. It is suggested that short-range hot abstraction from neopentane takes place at 4.2 K while a long-range tunneling reaction of thermal hydrogen atoms with solutes takes place at 77 K other than hot abstraction. The results are discussed in relation to guest radical formation in mixed crystals of n-decane-d_{22} and n-decane-h_{22} previously reported.

To elucidate the mechanisms of solid state radiation-induced reactions, information on the transient reaction intermediates has been compiled mainly at liquid nitrogen temperature (77 K) but little is known at temperatures below 77 K. The mechanisms involved have been discussed based on the information obtained at 77 K. Recently we have found that the mode of radical formation in irradiated saturated hydrocarbons is quite different at liquid helium temperature.[1] The electron spin resonance (ESR) spectra of single crystals of n-decane-d_{22} irradiated at 4.2 K indicate that most of alkyl radicals are formed in pairs with random separations distributed from 2.5 to $\simeq$25 Å, while the crystals irradiated at 77 K give spectra mainly attributable to isolated alkyl radicals. When the mixed crystals of n-decane-d_{22} containing a small amount of n-decane-h_{22} are irradiated at 77 K, guest alkyl radicals are formed with a much higher yield than that expected from the concentration. Irradiation at 4.2 K suppressed the formation of guest radicals giving essentially the same spectra as that obtained from the pure crystals at 4.2 K. What is most unusual in these experiments is that the spectra observed at 77 K after irradiation at 4.2 K are entirely different from those obtained from crystals irradiated at 77 K. Most of the distant radical pairs produced at 4.2 K remain even at 77 K and the spectra of radical pairs change into those of isolated radicals at 200 K. During the change at 200 K the appearance of the guest radical spectra is observed when mixed crystals are used. Similar results have been reported by Gillbro and Lund.[2] These results suggest that the radiation effect is dependent on irradiation temperatures and unknown phenomena might be involved in solid state radiolysis. Assuming homolytic scission of the carbon–hydrogen bonds forming alkyl radicals and hydrogen atoms followed by hydrogen abstraction from the neighboring molecules forming counter alkyl radicals, we have tentatively interpreted the irradiation temperature effect in terms of the difference in the range of hydrogen atom migration which becomes shorter at lower irradiation temperatures.

In relation to these problems, unusual hydrogen atom migration has been recently suggested by Miyazaki et al.[3] in some hydrocarbon mixtures irradiated at 77 K. According to their experiments, when neopentane containing a small amount of cyclohexane is γ irradiated at 77 K, the highly selective formation of cyclohexyl radicals takes place. They have also observed a similar selective formation of solute alkyl radicals in the photolysis of the same mixtures with HI at 77 K. From this similarity, they have suggested that hydrogen atoms produced either by radiolysis or photolysis migrate through the host crystals and selectively react with guest alkane molecules forming predominantly guest radicals. Very recently Willard et al.[4] have also pointed out that thermal deuterium atoms produced by photolysis of 3-methylpentane-d_{14}–DI selectively abstract hydrogen atoms from the impurity C–H bonds with an extremely low activation energy.

In the present studies, we have examined if such a selective formation of guest radicals in irradiated neo-

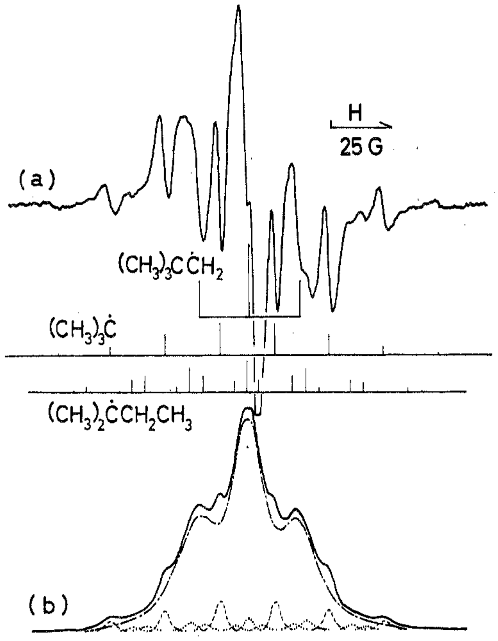


Figure 1. (a) First derivative and (b) integrated ESR spectra of neopentane x irradiated and measured at 77 K. The stick diagram indicates the hyperfine line positions of the three constituent radicals. The dotted curves in (b) indicate the decomposition of the integrated spectrum: microwave power 40 μW; modulation 2.5 G.

pentane mixtures takes place at quite low irradiation temperatures, in relation to our results obtained from n-decane-d_{22} and its mixtures with n-decane-h_{22}. In addition to 99.9% neopentane and neopentane–cyclohexane mixtures, we have studied neopentane–isobutene mixtures to determine if hydrogen atom reaction with the solute is involved. Analogous to the observation in n-decane mixtures, all samples gave solute radicals at 77 K with a higher yield than that expected from the concentration, while at 4.2 K the excess formation of solute radicals was almost completely suppressed. The results seem to be consistent with our previous suggestion that the range of hydrogen atom migration is shorter at 4.2 K.

Experimental Section

Samples of neopentane (99.9%) obtained from Tokyo Kagaku Seiki Co. were distilled by a trap-to-trap method in a vacuum line and then treated with a sodium mirror before transferring into ESR tubes. Samples of cyclohexane (guaranteed reagent) obtained from Wako Junyaku Co. were distilled two times and passed through a 30-cm column of active alumina. Samples of isobutene (guaranteed reagent) obtained from Tokyo Kasei Co. were used without further purification. The samples were irradiated with x-rays (45 kV, 40 mA) to a dose of about 0.3 Mrad. The details of our low temperature irradiation apparatus is described in our previous paper.[5] For quantitative measurements to determine the total radical yield, the samples were irradiated with ^{60}Co γ rays to a dose of 0.5 Mrad at a dose rate of 1.6 Mrad/h. Both x and γ irradiations gave essentially the same ESR spectra. The spectra were measured with a Varian E-12 spectrometer at X-band using 100-kHz field modulation. Double integration of the first derivative ESR spectra was carried out using an on-line computer (Nicolet 1070 spectrum analyzer).

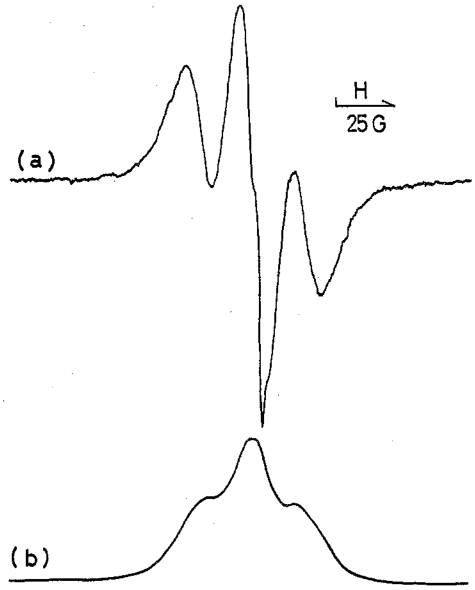


Figure 2. (a) First derivative and (b) integrated ESR spectra of neopentane x irradiated at 4.2 K and measured at 77 K: microwave power 40 μW; modulation 2.5 G.

TABLE I: Relative Amounts (%) of Solute Radicals to the Total Radicals Determined from Spectral Decomposition

Sample irrad temp, K	neo-C_5H_{12}		neo-C_5H_{12}-c-C_6H_{12}		neo-C_5H_{12}-i-C_4H_8	
	77 K	4.2 K	77 K	4.2 K	77 K	4.2 K
t-Bu	~8	<1	~3		36 ± 7	~2
t-Pen	~6		<1			
c-Hex			32 ± 7	3~5		

Results

Neopentane (99.9%). Shown in Figures 1 and 2 are the first derivative ESR spectrum (a) and its integrated spectrum (b) for neopentane (99.9%) irradiated at 77 and 4.2 K, respectively. All these spectra are measured at 77 K. The three-line spectrum with a separation of 21 G obtained from the sample irradiated at 4.2 K (Figure 2) is quite simple and is attributable to neopentyl radical I.

$$\underset{\text{I}}{(CH_3)_3C\dot{C}H_2}$$

As is shown by the stick diagram, the complicated spectrum obtained from the sample irradiated at 77 K consists of three components: a three-line spectrum of I, a ten-line spectrum with a separation of 22.4 G which is attributable to *tert*-butyl radical II, and a spectrum which is attributable to *tert*-pentyl radical III.

$$\underset{\text{II}}{(CH_3)_3C\cdot} \qquad \underset{\text{III}}{(CH_3)_2\dot{C}CH_2CH_3}$$

The identification of the *tert*-pentyl radical has been recently made by Fujimura et al.[6] using their well-resolved spectra obtained by in-situ irradiation of plastic phase neopentane at −121 °C. The CH_3 and CH_2 proton couplings are estimated to be ~24 and ~18.5 G, respectively, for our crystalline phase neopentane using the second derivative spectrum.

From the decomposition of the integrated spectrum (Figure 1b), it was found that the major species is the neopentyl radical which amounts to about 86%. The amounts of *tert*-butyl and *tert*-pentyl radicals are about 8 and 6%, respectively (Table I). Since the line width of the three-line spectrum of I is extremely broader than those of the two other species, the profile of the first derivative ESR spectrum is greatly modulated by the narrower components, resulting in a quite different profile from the three-line spectrum shown in Figure 2. However, the profiles of the integrated spectra are not very much different from each other.

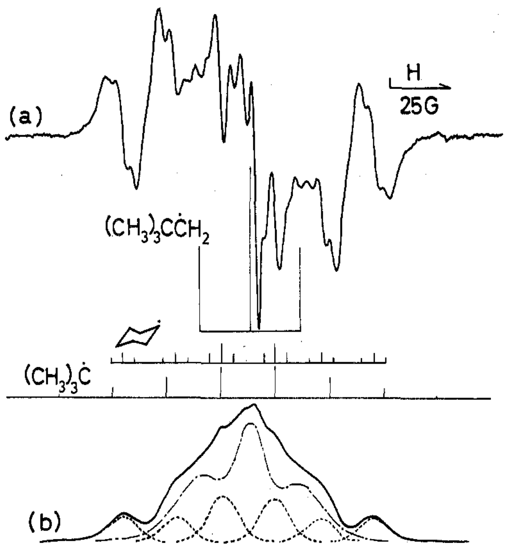


Figure 3. (a) First derivative and (b) integrated ESR spectra of a neopentane-cyclohexane (2 mol %) mixture x-irradiated and measured at 77 K. Other remarks are the same as those in Figure 1.

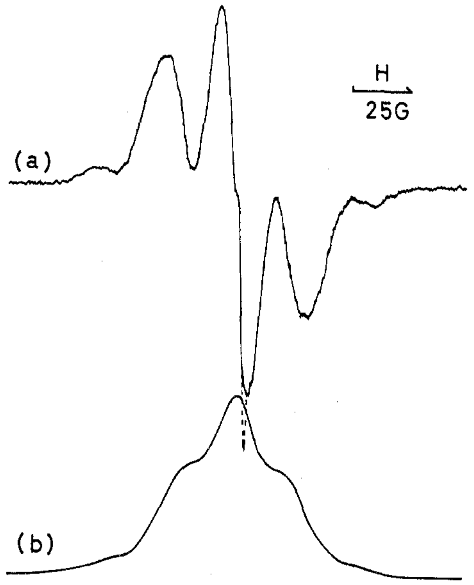


Figure 4. (a) First derivative and (b) integrated ESR spectra of a neopentane-cyclohexane (2 mol %) mixture x-irradiated at 4.2 K and measured at 77 K: microwave power 40 μW; modulation 2.5 G.

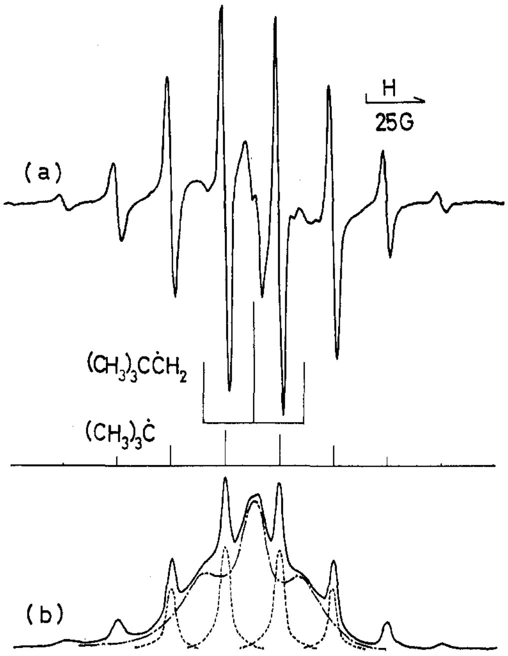


Figure 5. (a) First derivative and (b) integrated ESR spectra of a neopentane-isobutene (2 mol %) mixture x-irradiated and measured at 77 K. Other remarks are the same as those in Figure 1.

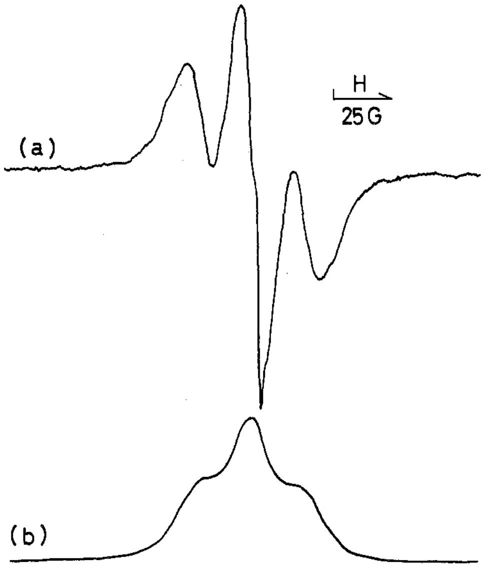
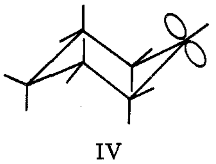


Figure 6. (a) First derivative and (b) integrated ESR spectra of neopentane-isobutene (2 mol %) mixture x-irradiated at 4.2 K and measured at 77 K: microwave power 40 μW; modulation 2.5 G.

Neopentane-Cyclohexane (2 mol %) Mixtures. Shown in Figures 3 and 4 are the spectra obtained at two different irradiation temperatures. The spectrum obtained from the sample irradiated at 4.2 K (Figure 4) is essentially the same as that of 99.9% neopentane irradiated at 4.2 K. It is clear that the main species formed at 4.2 K is the neopentyl radical I. On the other hand, the spectrum obtained from the sample irradiated at 77 K shows the formation of cyclohexyl radicals (IV) as is reported by Miyazaki et al.[3]



IV

The stick diagrams in Figure 3 illustrate the overlapping of the spectrum arising from cyclohexyl and *tert*-butyl radicals with that of neopentyl radicals. The hyperfine coupling values for cyclohexyl radicals estimated using the second derivative spectrum are $a_{\alpha H} = 22$ G, $a_{\beta H} = 41$ G, and $a_{\beta H'} = 5$ G in agreement with the values reported by Ogawa and Fessenden.[7]

From the decomposition of the integrated spectrum (Figure 3b) the amount of cyclohexyl radicals is estimated to be 32%. The amount of *tert*-butyl radicals is estimated to be about 3% from the peak height of the first derivative spectrum in referring to the spectrum obtained from the neopentane-isobutene mixtures which will be described in the next section. The amount of cyclohexyl radicals formed at 4.2 K is estimated to be about 3–5% (Table I).

Neopentane-Isobutene (2 mol %) Mixtures. Shown in Figures 5 and 6 are the spectra obtained at two different irradiation temperatures. The spectrum obtained from the sample irradiated at 4.2 K (Figure 6) is essentially the one arising from neopentyl radicals. On the other hand, the first derivative spectrum obtained from the sample irradiated at 77 K (Figure 5a) is essentially the one arising from *tert*-butyl radicals at a glance. However, the inte-

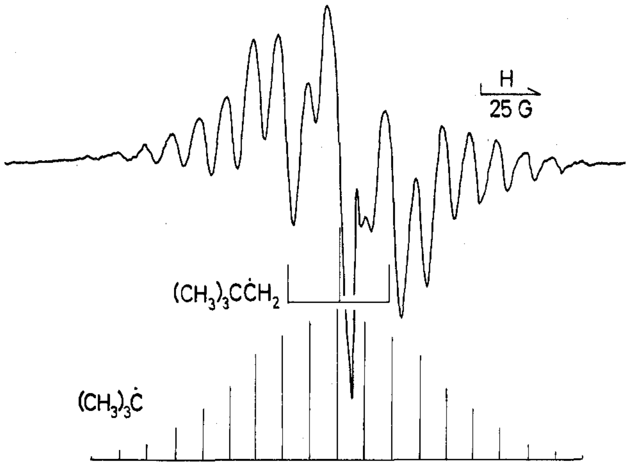


Figure 7. First derivative ESR spectrum of a neopentane–isobutene (2 mol %) mixture x-irradiated at 77 K and measured at 4.2 K. The stick diagram indicates the theoretical line spectra expected from *tert*-butyl radicals in which three methyl groups undergo tunneling rotation: microwave power 1 μW; modulation 2.5 G.

grated spectrum (Figure 5b) clearly shows a major contribution from neopentyl radicals. The amount of *tert*-butyl radicals is estimated to be 36%. A simulation of the first derivative spectrum was also performed and a similar result was obtained. The amount of *tert*-butyl radicals formed at 4.2 K is estimated to be about 2% from the peak height of the first derivative spectrum (Table I).

It is mentioned that careful analysis of the overlapping first derivative spectra of the broad and sharp components is necessary for estimating the relative abundance of the sharp component. Unless otherwise, unusually high selective formation of the radicals giving a sharp component would result.

It may be worthwhile to note here that the spectrum of *tert*-butyl radicals observed at 4.2 K changes from a 10-line spectrum with a binomial intensity ratio into a 19-line spectrum with a half-spacing and intensity ratio which is expected from the tunneling rotation of the three methyl groups (see Figure 7). As is well known, a tunneling methyl group shows a seven-line spectrum with an intensity ratio of 1:1:1:2:1:1:1 when the population of the lowest torsional level is predominant and the tunneling splitting is sufficiently smaller than kT.[8] The stick diagram in Figure 7 is the theoretical spectrum expected from *tert*-butyl radicals in which all three methyl groups undergo tunneling rotation.

Spatial Distribution of the Neopentyl Radicals. As shown in Figure 8, the spectrum measured at 4.2 K for 99.9% neopentane immediately after x irradiation at 4.2 K is much broader than that measured at 4.2 K after annealing at 77 K for 30 min. During annealing at 77 K the total radical amount decreased by about 20%. If the pairwise trapping of neopentyl radicals takes place, it is expected that the spin–spin interaction greatly contributes to the line width. Therefore, the intensity ratio, I_2/I_1, of the $\Delta M_s = \pm 2$ and the $\Delta M_s = \pm 1$ transitions was measured at 4.2 K before and after annealing at 77 K as a crude measure of the pairwise trapping of radicals.[1] The value of I_2/I_1 for 99.9% neopentane decreased from 1.8×10^{-4} to 0.95×10^{-4}, consistent with line width narrowing. It is to be noted that the I_2/I_1 value is comparable with that of n-decane-d_{22} in which alkyl radicals are formed in pairs. On the other hand, the I_2/I_1 value for samples irradiated at 77 K was less than 0.5×10^{-4}. The spectra obtained from the neopentane–cyclohexane (2 mol %) and the neopentane–isobutene (2 mol %) mixtures irradiated at 4.2 K behave essentially in the same manner. The I_2/I_1 ratios for all the samples are tabulated in Table II.

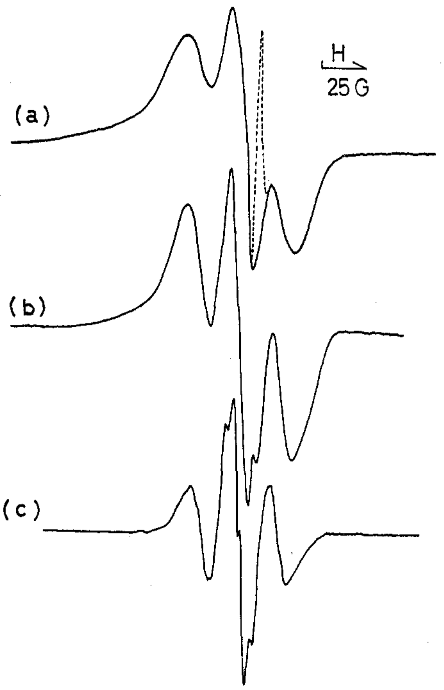


Figure 8. First derivative ESR spectra of neopentane (a) irradiated and measured at 4.2 K, (b) measured at 4.2 K after annealing at 77 K for 30 min, and (c) measured at 77 K after annealing at 145 K for 10 min. The microwave power was 4 μW for (a) and (b), 40 μW for (c); the modulation was 5 G for (a) and (b), 2.5 G for (c).

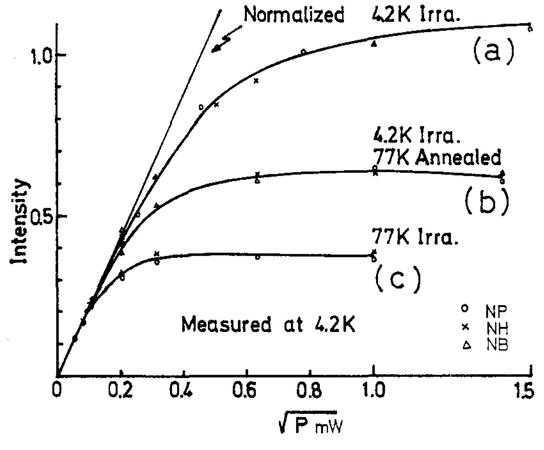


Figure 9. Microwave power saturation curves measured at 4.2 K for (O) neopentane, (X) neopentane–cyclohexane (2 mol %), and (Δ) neopentane–isobutene (2 mol %) mixtures (a) immediately after irradiation at 4.2 K, (b) after annealing at 77 K for 30 min, and (c) immediately after irradiation at 77 K. The ordinates for all the saturation curves are normalized to give the linear portion of the curves the same slope.

TABLE II: I_2/I_1 Ratios and Relative $(T_1T_2)^{1/2}$ for x Irradiated Neopentane (99.9%), Neopentane-Cyclohexane (2 mol %), and Neopentane-Isobutene (2 mol %) Mixtures

Irrad temp, K	I_2/I_1 ($\times 10^4$)[a]	$(T_1T_2)^{1/2}$[a]
4.2	~2.1	1.00
4.2 → 77	~1.3	1.64
77	<0.5	2.56

[a] Since the three samples gave a similar value if the irradiation conditions were the same, the averaged values are given.

In order to check the difference in the spatial distribution of radicals, the microwave power saturation was also measured at 4.2 K. Since the stronger spin–spin interaction decreases T_2 and thus $(T_1T_2)^{1/2}$, it is expected that

TABLE III: Radical Yields in γ Irradiated Neopentane (99.9%), Neopentane-Cyclohexane (2 mol %), Neopentane-Isobutene (2 mol %) Mixtures

Sample irrad temp, K	neo-C_5H_{12}		neo-C_5H_{12}-c-C_6H_{12}		neo-C_5H_{12}-i-C_4H_8	
	4.2 K	77 K	4.2 K	77 K	4.2 K	77 K
Total yield	1.00[a]	0.74	1.1_0	0.97	0.96	0.91
neo-Pen[b]	>0.99	0.64	1.0_6	0.66	0.94	0.58
Solute radicals[b]	<0.01	0.10	0.04_4	0.31	0.02	0.33

[a] The total radical yield for neo-C_5H_{12} irradiated at 4.2 K is taken as 1.00, to which other radical yields are referred. [b] The relative amounts of the solvent and solute radicals are assumed to be the same as those determined from the samples irradiated by x rays (see Table I).

samples with a higher local concentration of radicals exhibit a microwave power saturation behavior which is less saturated than samples with a lower local concentration.[5,9] As shown in Figure 9, all samples irradiated at 4.2 K exhibit the least saturated behavior reflecting the highest local concentration of radicals. After annealing at 77 K, all samples become more easily saturated suggesting a decrease of local concentration. This is consistent with the narrowing of the line width and the decrease of I_2/I_1. Samples irradiated at 77 K exhibit the most saturated behavior, consistent with the lowest I_2/I_1 value. The relative $(T_1T_2)^{1/2}$ values obtained from the saturation curves are tabulated in Table II.

From these results it is concluded that neopentyl radicals are formed in pairs with a much higher local concentration at 4.2 K as is the case for *n*-decane previously reported,[1] while solute radicals are formed as isolated radicals at 77 K.

Annealing above 77 K. The relative abundance of the guest to host radicals in samples x-irradiated at 4.2 K slightly increased after annealing at 77 K. Since the total amount of radicals decreased about 20%, the apparent increase of the guest radical is probably due to a decrease of host radicals which are formed in pairs. Further spectral changes were examined at 77 K after repeating successive annealing at temperatures above 77 K. Although the total amount of radicals gradually decreased, an appreciable change in the relative abundance of the guest to host radicals was not observed at annealing temperatures lower than 145 K. However, during annealing notable line width narrowing of the neopentyl radical spectrum was observed suggesting a decrease of the local concentration of radicals. With this narrowing the substructures which are attributed to γ-proton coupling by Lin and Williams[10] gradually appeared on the central line. Figure 8c shows the spectrum obtained after annealing at 145 K for 10 min for neopentane irradiated at 4.2 K. The mixtures irradiated at 4.2 K gave essentially the same spectra. From these results, it is concluded that an efficient radical conversion from the host to guest radicals does not take place in neopentane mixtures.

Total Radical Yields. The total radical yields of samples γ irradiated at 4.2 K with a dose of 0.5 Mrad were measured at 77 K and compared with those of samples γ irradiated at 77 K with the same dose. The results are summarized in Table III. The results indicate that the total radical yields in all the samples irradiated at 4.2 K are nearly the same. On the other hand, when the samples are irradiated at 77 K, the neopentane–cyclohexane and neopentane–isobutene mixtures give nearly the same total radical yield as that in samples irradiated at 4.2 K while 99.9% neopentane gives considerably smaller yields than the others. It is, however, to be noted that the yield of neopentyl radicals in samples irradiated at 77 K is nearly the same and the difference derives from the yield of radicals other than neopentyl radicals. This difference will be discussed in a later section.

It is mentioned that these measurements are made at 77 K so that some of radicals initially produced in samples irradiated at 4.2 K may be lost upon warming to 77 K. Similarly radicals produced in samples irradiated at 77 K may also be reduced during irradiation at 77 K. The samples x irradiated and measured at 4.2 K show that about 20% of the radicals initially trapped at 4.2 K are lost upon warming to 77 K when the radical amount is remeasured at 4.2 K again. However, because of spectral distortion at 4.2 K due to mixing of the dispersion mode quantitative measurements at 4.2 K are less reliable than those at 77 K. In any event, since it is not possible to estimate the radical yield produced during irradiation at 77 K if some of radicals are lost, the total radical yield was compared at 77 K.

Discussion

What is most remarkable is that irradiation at 4.2 K gives entirely different spectra from those obtained from irradiation at 77 K even after annealing at 77 K as is the case for *n*-decane irradiated at 4.2 K.[1] The formation of radicals other than neopentyl radicals is almost completely suppressed at 4.2 K for all samples examined.

Our results obtained from neopentane–isobutene (2 mol %) suggest that hydrogen atoms produced by the homolytic scission of the C–H bond of neopentane react efficiently with isobutene to form hydrogen addition radicals, that is, *tert*-butyl radicals when irradiation occurs at 77 K. An equal number of hydrogen atoms (0.5) and neopentyl radicals (0.5) must be initially formed (reaction 1). If one assumes that some of the hydrogen atoms react

$$\text{neo-}C_5H_{12} \rightsquigarrow C_5H_{11}\cdot + H\cdot \quad (1)$$

$$H\cdot + \text{neo-}C_5H_{12} \rightarrow C_5H_{11}\cdot + H_2 \quad (2)$$

$$H\cdot + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_3C\cdot \quad (3)$$

with neopentane (reaction 2) and the rest react with isobutene (reaction 3), our analyses suggest that the number of hydrogen atoms reacted with neopentane and isobutene is 0.14 and 0.36, respectively. On the other hand, the reaction of hydrogen atoms with isobutene is greatly suppressed at 4.2 K. The difference in the spatial distribution of neopentyl radicals at both irradiation temperatures strongly suggests that hydrogen atom migration to the guest molecule is suppressed at 4.2 K and that the rather short-range reaction with host molecules is predominated at 4.2 K. In other words, hydrogen atoms produced at 4.2 K cannot be scavenged by isobutene.

Positive hole trapping by isobutene followed by hydrogen abstraction from the neighboring molecule might also produce *tert*-butyl radicals. However, it is hard to believe that positive hole migration is suppressed at 4.2 K. Our preliminary results obtained from neopentane–tetramethylethylene (hole scavenger[11]) indicate that hole scavenging by tetramethylethylene is not suppressed at 4.2 K.

The behavior of guest radical formation in neopentane–cyclohexane (2 mol %) mixtures at both irradiation temperatures is quite similar to that in neopentane–isobutene (2 mol %) mixtures. This suggests that the reaction of migrating hydrogen atoms with cyclohexane forms cyclohexyl radicals by hydrogen abstraction (reaction 4) at 77 K while hydrogen atom migration is suppressed

$$H\cdot + \text{c-}C_6H_{12} \rightarrow \text{c-}C_6H_{11}\cdot + H_2 \quad (4)$$

at 4.2 K. If this is the case, our results obtained at 77 K indicate that the relative amount of hydrogen atoms which react with neopentane is 0.18 and those with cyclohexane is 0.32, neglecting a minor contribution from *tert*-butyl radical formation. Miyazaki and Hirayama[3d] reported that the formation of cyclohexyl radicals is 86%. This exceeds the number of hydrogen atoms produced in the system. This peculiarity is eliminated by our analyses.

Miyazaki and Hirayama[3d] also reported that the formation of *tert*-butyl and *tert*-pentyl (unidentified by them) radicals in 99.9% neopentane irradiated at 77 K to a dose of 0.5 Mrad is about 50%. They suggested that *tert*-butyl radicals are formed by the reaction of hydrogen atoms with radiation-produced impurities and that *tert*-pentyl radicals are formed by the reaction of hydrogen atoms with initially existing impurities, based on their experiments of the effect of preirradiation dose and sample purity. Although our analyses of the ESR spectra reduced the amount of *tert*-butyl and *tert*-pentyl radicals to about 14% from their value of 50%, this still seems to be unusually higher than expected from the concentration of impurities. However, our experiments indicate that the formation of these radicals is also suppressed at 4.2 K suggesting that both species are formed from the reaction of migrating hydrogen atoms with impurities with high efficiency at 77 K.

$$\mathrm{H\cdot + impurities \rightarrow (CH_3)_3C\cdot + (CH_3)_2\dot{C}CH_2CH_3} \qquad (5)$$

Now, as mentioned before, the total radical yield in 99.9% neopentane irradiated at 77 K is considerably smaller than those in the mixtures although the yield of neopentyl radicals is nearly the same for all samples irradiated at 77 K. This suggests that scavenging of hydrogen atoms by solutes and impurities resulted in the excess formation of radicals other than neopentyl radicals and that some of scavengeable hydrogen atoms are lost in 99.9% neopentane by recombination (reaction 6) forming

$$\mathrm{2H\cdot \rightarrow H_2} \qquad (6)$$

hydrogen molecules, since the amount of impurities is not sufficient to react with all the scavengeable hydrogen atoms produced in the system. If this is the case, the lost of hydrogen atoms by reaction 6 without forming radicals is about 0.2–0.3.

It is to be noted that reaction 5 produces one H_2 molecule from one H·, while reaction 6 produces one H_2 molecule from two H·. As a result, the hydrogen yield, $G(H_2)$, should increase upon the addition of cyclohexane. If the hydrogen yield by unimolecular detachment is neglected, the above assumptions predict that $G(H_2)$ in neopentane–cyclohexane (2 mol %) is higher by a factor of 1.25–1.43. According to the product analyses by Miyazaki et al.[3a] $G(H_2)$ in neopentane–cyclopentane mixtures irradiated at 77 K sharply increases upon the addition of a small amount of cyclopentane (see Figure 4 in ref 3a). For example, $G(H_2)$ in neopentane without solutes is about 1.6, while it increases to about 2.1, 2.3, and 2.4 with solute concentrations of 2, 5, and 10 mol %, respectively. $G(H_2)$ in the 2 mol % mixture is higher by a factor of 1.31. This agrees with the above-mentioned prediction for neopentane–cyclohexane (2 mol %) mixtures.

For these reasons, it may be concluded that the scavengeable hydrogen atoms by isobutene reacted with cyclohexane forming cyclohexyl radicals and the amount of scavengeable hydrogen atoms is about 70–72%, the rest reacting with neopentane forming neopentyl radicals at 77 K. Although this estimate assumes that all the radicals initially produced are trapped at 77 K, if it is assumed that neopentyl radicals trapped at 77 K are reduced by a factor of 0.8 and all the solute radicals are trapped without decay, as is suggested from the samples x irradiated at 4.2 K, the amount of scavengeable hydrogen atoms is about 60–62%.

TABLE IV: Relative Rate Constants and Reactivity Ratios of Tunneling Abstraction by Thermal Hydrogen Atoms from Neopentane and Cyclohexane Estimated from the Unsymmetrical Eckart Potential[a]

	Relative rate constants[b]		Reactivity ratios	
T, K	neo-C_5H_{12}[c]	c-C_6H_{12}[d]	k_{CHX}/k_{NP}	Obsd[e]
300	4291	87162 (990)	20.3	(6.6)[f]
77	1	88 (1)	88	$\gtrsim 87$
4.2	0.018	1.83 (0.021)	100	$\gtrsim 3$

[a] $\overline{V}(x) = -\Delta Hy/(1-y) - [(E_A - \Delta H)^{1/2} + E_A{}^{1/2}]^2 y/(1-y)^2$ with $y = -\exp(2x/a)$, where E_A, ΔH, a, and x are the activation energy, the heat of reaction, the potential width parameter, and the reaction coordinate, respectively. [b] $k = BT^{1/2}\Gamma(T)\exp(-E_A/RT)$ is assumed, where $\Gamma(T)$ is the tunneling correction factor. B is assumed to be the same for the two compounds. If $B = 10^{13}$ cm^3 mol^{-1} s^{-1} is assumed, the absolute rate constant for neopentane becomes 0.7×10^9 cm^3 mol^{-1} s^{-1} at 300 K in agreement with 1×10^9 cm^3 mol^{-1} s^{-1} estimated by Hardwick.[14c] [c] $E_A = 8.6$ kcal/mol, $\Delta H = -9.8$ kcal/mol, and $a = 0.56$ Å are assumed. [d] $E_a = 6.65$ kcal/mol, $\Delta H = -19.2$ kcal/mol, and $a = 0.56$ Å are assumed. [e] Assuming a simple competition, the reactivity ratios are obtained from the relative radical yield determined from experiments. [f] Calculated value by Hardwick[14c] using the rate constants for the reaction of hydrogen atoms with hydrocarbon structural groups at room temperature.

The results obtained from all samples irradiated at 4.2 K indicate that the total radical yield is nearly the same as those in mixtures irradiated at 77 K. This means that all hydrogen atoms which are scavengeable at 77 K reacted with neopentane forming neopentyl radicals at 4.2 K. The higher local concentration of neopentyl radicals at 4.2 K is consistent with this conclusion if the hydrogen atoms scavengeable at 77 K reacted with neopentane by a rather short-range reaction.

It is quite interesting that the hydrogen atoms produced by homolytic scission behave quite differently at 4.2 and 77 K. Recently Wilkey and Willard[4] have suggested that thermal deuterium atoms can abstract H atoms from the C–H bond at 77 K with a low activation energy. Wang and Williams[12] have reported that an apparent activation energy for the hydrogen abstraction reaction from the C–H bond by $\dot{C}H_3$ radicals in CH_3CN is 1.4 kcal/mol at 90 K. Le Roy, Sprague, and Williams[13a] have explained this by a tunneling mechanism. We have examined the possibility of tunneling abstraction by thermal hydrogen atoms using the unsymmetrical Eckart potential and the analytical expression for permiability.[13b] The results indicate that the fast reaction of thermal hydrogen atoms can occur at 77 K by tunneling through a potential barrier of 6–9 kcal/mol with a potential wall thickness parameter in the reasonable range. It was also found that the difference in activation energies and heat of reactions for the primary C–H bonds of neopentane and for the secondary C–H bonds of cyclohexane leads to a reactivity ratio which is consistent with the selective reaction observed at 77 K. Although the details will be given elsewhere, some of the results are shown in Table IV. It is noted that the reactivity ratio at 77 K becomes larger than that at 300 K. This means that the selectivity is higher at 77 K in agreement with the temperature dependence of the selectivity reported by Miyazaki and Hirayama.[3d] It is well known that the relative reactivity of the hydrogen abstraction reaction from the C–H bond at ordinary temperature increases with decreasing number of C–H bonds at the group which is attacked by atoms or radicals.[14] The importance of the tunneling correction for proton and hydrogen atom reactions even at ordinary temperature is pointed out by many workers.[15] If a tunneling mechanism is involved, the selective reaction at 77 K seems to be an analogous situation observed at ordinary temperatures, including the higher reactivity of hydrogen addition to the double bond. However, it is mentioned that Miyazaki et al.[3c,16] reported some other selective reactions of hydrogen atoms which do not seem to be explained by this simple relation of relative reactivity at ordinary temperatures.

On the other hand, our experiments at 4.2 K show that the reactivity of hydrogen atoms with neopentane becomes comparable with that of cyclohexane at 4.2 K, if the effect of irradiation temperature originates from the change in reactivity ratio of thermal hydrogen atoms at 77 and 4.2 K. However, as shown in Table IV the trial estimation of the tunneling correction factor at 4.2 K shows that the situation is not very much different at 4.2 K. If one assumes that the potential barrier and width change at 4.2 K, it may be possible to explain the change in the reactivity ratio. However, there seems to be no a priori reason for the potential energy surface changes at 4.2 K. It seems difficult to explain the irradiation temperature effect by a change in the reactivity ratio of thermal hydrogen atoms for solute and solvent molecules.

Another possibility that must be taken into consideration is that irradiation at 4.2 K suppresses the migration of hydrogen atoms or the formation of hydrogen atoms which would migrate to the solutes at 77 K. The difference in the kinetic energy distribution of hydrogen atoms produced and in some matrix effects on hydrogen atom migration in the solid at the two irradiation temperatures might be related to the range of the hydrogen atoms. Suppose that there are two different pathways of dissociative excitation which produce two kinds of hydrogen atoms having different average kinetic energies. For example, Ito et al.[17] have recently observed the formation of two kinds of hydrogen atoms with different average kinetic energies by measuring the Doppler profile of the emission spectra of Balmer α radiation induced by electron impact on H_2. If the formation of two kinds of hydrogen atoms is dependent on irradiation temperatures, there is a possibility that the formation of hydrogen atoms favorable for long-range migration is suppressed at 4.2 K. A sort of cage effects at 4.2 K may preclude escape of hydrogen atoms to react with solutes and may result in a rather short-range reaction. The radiation-induced deformation of the lattice which may not be relaxed and may be accumulated during irradiation at 4.2 K might also hinder hydrogen atom migration. To reach a proper understanding of the problem, consideration of atomic collisions in solids may be required.

Timm and Willard[18] reported that hydrogen atoms produced in radiolysis of CH_4 can be trapped at 4.2 K but they are not scavenged by the addition of 0.3 mol % of isobutene at 4.2 K. They have explained this by low reactivity of thermal hydrogen atoms with isobutene at 4.2 K. However, if hydrogen atoms produced are thermalized before migrating a long distance to reach solute molecules and thermal hydrogen atoms cannot react with CH_4, the implication of their observation is similar to that of the present work, except that hydrogen atoms can react with solvent molecules in our case. Our preliminary calculation of tunneling correction factors indicates that the reactivity of thermal hydrogen atoms at 4.2 K is extremely low for CH_4 having the highest bond dissociation energy among simple saturated hydrocarbons. The formation of radical pairs between $\dot{C}H_3$ and H· in irradiated CH_4[19] also suggests that the thermalization distance of hydrogen atoms in CH_4 is short at 4.2 K. In solvents in which even thermal hydrogen atoms can react with solvent at 4.2 K, the range of hydrogen atom migration may be shorter than that in CH_4.

Taking the initial kinetic energy of hydrogen atoms into consideration, it may be concluded that short-range hot abstraction by hydrogen atoms from the matrix takes place at 4.2 K while long-range tunneling abstraction by hydrogen atoms with low kinetic energy takes place at 77 K other than by hot abstraction.

Guest Radical Formation in Mixed Crystals of n-Decane. Gillbro and Lund[2] have explained the selective formation of protiated radicals at 77 K in mixed crystals of *n*-decane-d_{22} and *n*-decane-h_{22} by excitation transfer to guest molecules. However, similarity in the irradiation temperature effect to that observed for neopentane mixtures suggests that a similar mechanism is involved in both mixtures. The observation by Wilkey and Willard[4] in 3-methylpentane-d_{14} containing a small amount of protiated impurity is also quite similar to that in decane mixtures especially in the marked mass effect. It is suggested that deuterium atom migration to guest molecules is the main cause of the selective formation of protiated radicals as proposed in our previous paper.[1] The mass effect of hydrogen abstraction from C–H and C–D bonds is expected to be quite large for tunneling reactions.[12,13] In addition, it is noted that guest radicals are also selectively formed at the C_2 atom, that is, $CH_3\dot{C}HCH_2$– is predominant rather than –CH_2–$\dot{C}H$–CH_2– and $\dot{C}H_2$–CH_2–.[2] This is also understandable from the difference in the reactivity of hydrogen atoms with hydrocarbon structural groups.[14]

Since we have observed radical site transfer in the irradiated crystals of *n*-decane-d_{22} at low temperatures and thermal radical conversion at 200 K from the host to guest radicals in mixed crystals irradiated at 4.2 K,[1] the possibility of radical site transfer to guest molecules during irradiation at 77 K might not be neglected. However, our recent study on mixed crystals of *n*-decane-d_{22} and *n*-decylbromide-h_{21} suggested that the contribution from radical site transfer to selective formation of guest radicals during irradiation is not appreciable.

NOTE ADDED IN PROOF: After completing the manuscript, the authors have received a preprint of a paper from Dr. Miyazaki.[20] He has performed product analysis of the hydrogen produced in mixed crystals of *n*-decane-d_{22} and *n*-decane-h_{22} irradiated at 77 K. It was found that DH increased while D_2 decreased with increasing addition of *n*-decane-h_{22}. In addition, DH formation is parallel to the formation guest radicals. From these results it was concluded that deuterium atoms abstract hydrogen atoms from guest molecules in agreement with our previous suggestion.[1]

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Electron Spin Resonance Characterization of Superoxide Ions in Some Oxygenated Apatites

J. Dugas*

Département de physique, Université Mohammed V, Faculté des Sciences, Rabat, Morocco

and C. Rey

Laboratoire de Physico-Chimie des Solides et des Hautes Températures, 31078, Toulouse, France

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Electron spin resonance studies of calcium, strontium, and barium phosphate and arsenate oxygenated apatites containing superoxide ions were used to determine the position and the orientation of these ions in the channels of the apatite lattice. The angle between the O_2^- bond and the c axis was studied in the different compounds.

Introduction

The apatites constitute a large family of isomorphous compounds which may be found in phosphate rocks and in calcified tissues. They correspond to the general formula

$$Me_{10}(XO_4)_6Y_2$$

$Me^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, \ldots$
$XO_4^{3-} = PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}, \ldots$
$Y_2^{2-} = 2F^-, 2Cl^-, 2Br^-, 2OH^-, CO_3^{2-}, O^{2-}, O_2^{2-}, \ldots$

The apatites generally crystallize in a hexagonal system (spatial group $P_{6_3/m}$). The structure of calcium hydroxylapatite, for instance, was described by Kay et al.[1]

The most important feature in this structure is the presence of channels running along the c (6_3) axis. These channels may be empty, or partially or completely filled with Y ions which form linear chains. They also may be partially occupied by molecular oxygen, as shown recently.[2] These apatites are referred to as oxygenated apatites. Moreover their channels contain OH^-, O_2^{2-}, O_2^-, . . .,[3] the latter being observed by ESR.[4]

In this paper electron paramagnetic resonance studies of O_2^- superoxide ions in the channels of calcium, strontium, and barium phosphate and arsenate oxygenated apatites are presented. For the sake of simplification we shall henceforth call (P,Ca)Ap the oxygenated apatite whose skeleton is built with phosphate and calcium, (As,Ba)Ap the one built with arsenate and barium, etc.

The superoxide ion has been intensively studied either in single crystals of alkali halides[5-7] and alkaline earth fluoride[8] or absorbed at the surface of powdered samples of MgO,[9] ZnO, and TiO_2[10] as implied by catalytic processes. In every case it was ascertained that the axial molecular symmetry was lowered by the crystalline environment.

Sample Preparation

Oxygenated apatites were precipitated by dropwise addition of an alkaline earth nitrate solution (70 mL, 0.125 M) into a stirred solution of diammonium hydrogen phosphate (or arsenate) (700 mL; 0.010 M) containing hydrogen peroxide (10%). All reagents were analytical grade. Precipitations were performed at 80 °C with pH values of 11.8. The products were separated by filtration or centrifugation, washed, and dried at room temperature.

X-ray analysis has shown the precipitates to be pure apatites. Hexagonal a and c parameters were determined using NaCl (a = 5.6402 Å) as an internal standard. The values thus obtained are reported in Table I.

Experimental Results

The difficulty of obtaining, till now, sufficiently large single crystals of these apatites has lead us to study ESR spectra of powdered samples and thus there is a great loss of information. Such averaged spectra, without hyperfine structure, present only lines corresponding to the "**g** tensor" principal components and thus give only some pictures of the symmetry of the defect.

In this work the ESR spectra were obtained with a conventional X-band homodyne spectrometer built in the Laboratoire de Physique des Solides, Toulouse. The frequency of the magnetic field modulation was 100 kHz. Measurements have been achieved either at room temperature or at liquid nitrogen temperature using a Varian variable temperature accessory. In this last case, the intensity of spectra was strongly enhanced. For both the barium apatites (P,Ba)Ap and (As,Ba)Ap spectra are observable only at liquid nitrogen temperature.

All spectra are characteristic of an anisotropic g factor with two generally well-resolved components, except for (As,Ca)Ap. g values are given in Table I also. We shall see later that with such g values so close to the free electron one, there may exist two distinct values for g_x and g_y, but they are not resolved. The low field line (corresponding to g_z) is generally anomalously broader and flatter than those attributable to the perpendicular (g_x and g_y) component. Moreover, in the (As,Ca)Ap spectra, the main line is widened on its low field side and it is very difficult to determine a correct g_z value. For the apatites the spectra are very intense, especially at low temperature, indicating

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* On leave from Laboratoire de Physique des Solides, Université Paul Sabatier, Toulouse, France.