ESR Spectroscopic Observation of Alkane Aggregation and of Hydrogen–Proton Transfer between Alkane Radical Cations and Alkane Molecules in CCl_3F Matrices at Cryogenic Temperatures

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Alkanes form small aggregates in CCl_3F matrices at cryogenic temperatures; upon γ-irradiation, both hole transfer to these aggregates and hydrogen–proton transfer between alkane radical cations and alkane molecules occurs.

Alkane radical cations are important reaction intermediates in the radiolysis of saturated hydrocarbons. Yet, in spite of the vast amount of work performed on the radiolysis of alkanes, fundamental questions remain about the reactivity of alkane radical cations, especially in condensed systems. Whether or not hydrogen and/or proton transfer between higher alkanes and their molecular cations widely takes place in condensed phases exemplifies such an important open question. The reaction has frequently been invoked in radiation chemical studies of higher alkanes,[1] but such studies fail to provide conclusive evidence for it.

Alkane radical cations have been studied by ESR spectroscopy in various matrices at cryogenic temperatures and thermal conversion to alkyl radicals has been observed in SF_6 and CCl_2FCF_2Cl.[2] Such studies do not clearly differentiate between ion–molecule reactions, unimolecular dissociation and neutralisation, however, nor do they provide conclusive evidence as to the identity of the reacting molecule in an ion–molecule reaction process. Isothermal concentration studies, with the alkane radical cation spectrum appearing at lower and the alkyl radical spectrum appearing at higher alkane solute concentration upon irradiation, are better suited to provide direct evidence on the hydrogen–proton transfer reaction. At present, isothermal concentration studies are limited to ethane in SF_6[3] and to C_4 to C_8 n-alkanes in a synthetic zeolite.[4]

We report that evidence for, and detailed information on, the hydrogen–proton transfer reaction between alkane radical cations and alkane molecules can be obtained in CCl_3F matrices at cryogenic temperatures. The evidence is derived from comparison of ESR spectra obtained after irradiation of alkanes at different concentrations in CCl_3F, with spectra obtained at identical concentrations in CCl_3CF_3, CCl_2FCF_2Cl and CF_2ClCCl_3. Chemical properties of these different chlorofluorocarbons are very similar. Yet, ESR spectra obtained at higher alkane concentrations differ drastically. Upon γ-irradiation of alkanes at both low and high concentration in CCl_3CF_3, CCl_2FCF_2Cl and CF_2ClCCl_3 and at low concentration in CCl_3F only the ESR spectrum of alkane radical cations is observed. At high concentration in CCl_3F, alkyl radicals also appear and the relative contribution of these alkyl radicals to the ESR spectrum increases with increasing alkane concentration. At sufficiently high concentration, alkyl radicals become the dominant radical species. From this, it is inferred that alkanes are clustered at high concentration in CCl_3F and that upon γ-irradiation alkane radical cations react with alkane molecules by hydrogen–proton transfer [eqn. (1)]. Various less plausible alternative mechanisms for alkyl radical formation may be ruled out on different grounds. The onset and extent of aggregation depends on the alkane considered. For n-alkanes, the extent of aggregation increases very markedly with chain length.

$$RH^{+\cdot} + RH \rightarrow R\cdot + RH_2^+ \qquad (1)$$

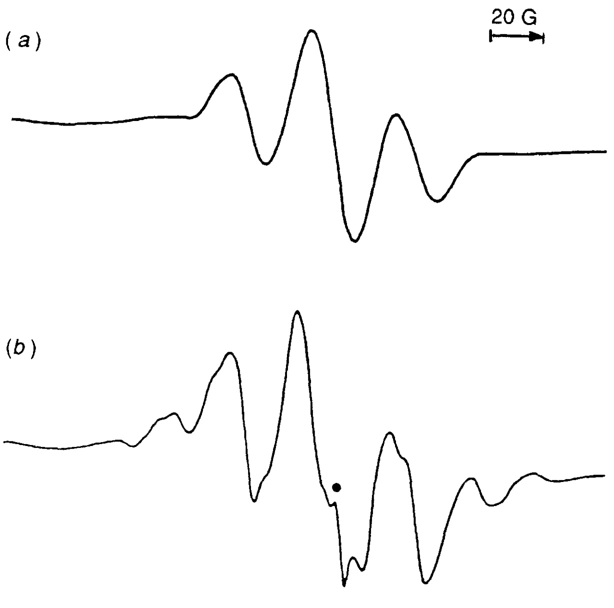

Fig. 1 First-derivative ESR spectra obtained for heptane at (*a*) 0.25 mole % and (*b*) 4 mole % in CCl_3F after irradiation with ^{60}Co γ-rays at 77 K (upper spectrum corrected for Suprasil absorption; ● indicates a background signal)

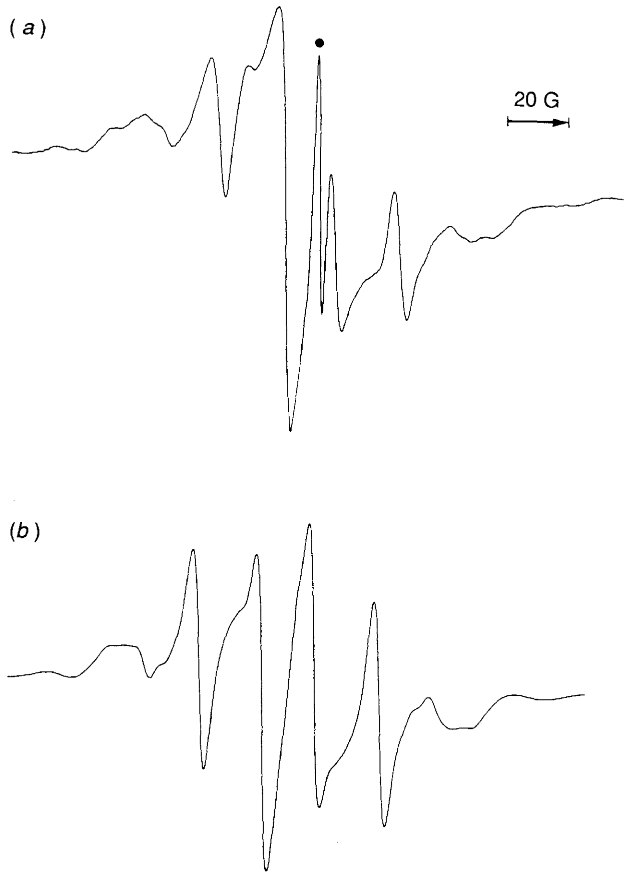

Fig. 2 First-derivative ESR spectra obtained (*a*) for CCl_3F containing 0.5 mole % tridecane and (*b*) for pure tridecane after exposure to ^{60}Co γ-rays at 77 K (● indicates a background signal)

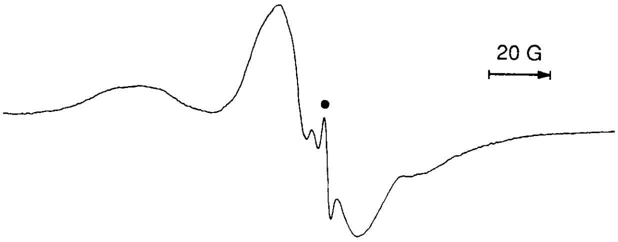

Fig. 3 First-derivative ESR spectrum obtained for CCl_3CF_3 containing 1 mole % tridecane after irradiation with ^{60}Co γ-rays at 77 K (● indicates a background signal)

Experiments conducted on heptane and tridecane are typical for the results that are being obtained. The ESR spectrum obtained after γ-irradiation of heptane at 0.25 mole % in CCl_3F consists only of a triplet with a hyperfine splitting constant of 30 G (see Fig. 1; 1 G = 10^{-4} T). This spectrum is due to heptane radical cations. In the extended structure of this cation, the unpaired electron delocalises over the carbon–carbon σ-bonds as well as the two in-plane end carbon–hydrogen bonds, resulting in a characteristic three-line spectrum with relative intensities 1:2:1, arising from coupling with the end protons.[2] The ESR spectrum obtained after γ-irradiation of heptane at 4 mole % in CCl_3F strongly differs from the low-concentration spectrum. The central triplet is distorted by the superposition of an additional spectrum, which is clearly discernible and can easily be characterised in the lateral part of the ESR spectrum. This additional spectrum corresponds quite closely to spectra of alkyl radicals obtained by γ-irradiation of C_6 to C_8 n-alkanes at 77 K[5] and can therefore be attributed to heptyl radicals. In contrast, only the heptane radical cation triplet, superimposed on some matrix absorption (*i.e.* absorption resulting from irradiation of the matrix), is present after irradiation of heptane at 4 mole % in CCl_3CF_3. Similar results are obtained in CCl_2FCF_2Cl and CF_2ClCCl_3. The extent of alkane radical cation and neutral alkyl radical formation at a particular concentration strongly depends on the alkane considered. After γ-irradiation of tridecane at 0.5 mole % in CCl_3F an ESR spectrum is obtained which corresponds quite well with the spectrum of irradiated pure tridecane (see Fig. 2). The characteristics of this spectrum, which has been attributed to alkyl radical formation, have been discussed.[5] In sharp contrast, after γ-irradiation of tridecane at the same and even higher concentrations in CCl_3CF_3 only a broad singlet, superimposed on some matrix absorption, is observed (see Fig. 3). The singlet spectrum is due to tridecane radical cations, the hyperfine splitting becoming unresolved as a result of increased delocalisation of the unpaired electron.

A detailed systematic investigation of hydrogen–proton transfer for different alkanes is currently being carried out. Both the process of alkane solute aggregation in CCl_3F at cryogenic temperatures and alkyl radical formation by hydrogen–proton transfer between alkane radical cations and alkane molecules upon γ-irradiation appear quite universal phenomena.

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