Isotopically Selective Electron Transfer between Free Radical Cations and their Parent Molecules Enables Isotope Enrichment

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Electron transfer between the thianthrene radical cation and its neutral molecule precursor shows a significant H/D equilibrium isotope effect which may be used for isotopic enrichment.

The importance of isotope separation due to the wide use of isotopes in a variety of technical and scientific applications, coupled with the observation[1-3] that electron exchange between some radical anions and their parent molecules is isotopically selective, led us to investigate the isotope effect in electron transfer reactions of radical cations and their neutral molecule precursors and the possibility of isotope enrichment *via* the electron exchange equilibrium. Here we report the preliminary result of the isotope effect in the electron transfer reaction between a thianthrene radical cation and its parent molecule.

Thianthrene radical cation perchlorate ($Th^{+\bullet}ClO_4^-$) can be easily prepared by oxidizing thianthrene (Th; $S_2C_{12}H_8$) with perchloric acid in acetic anhydride.[4] $Th^{+\bullet}$ in 5% trifluoroacetic acid (TFA)–5% trifluoroacetic anhydride (TFAn)–methylene chloride mixed solvent showed a well-resolved EPR spectrum of a quintet with hyperfine splitting constant of 0.1228 mT. On the other hand, perdeuteriated thianthrene radical cation $[^2H_8](Th^{+\bullet})$ appeared as an unresolved singlet in the same solvent. When perdeuteriated thianthrene $[^2H_8](Th)$ was added into the TFA–TFAn–CH_2Cl_2 solution of $Th^{+\bullet}$ the unique EPR spectrum of $Th^{+\bullet}$ was replaced by a superimposed spectrum of $Th^{+\bullet}$ and $[^2H_8]Th^{+\bullet}$ as illustrated in Fig. 1(*a*) as a result from the electron transfer between $Th^{+\bullet}$ and $[^2H_8]Th$ [eqn. (1)].

$$Th + [^2H_8]Th^{+\bullet} \overset{K_{eq}}{\rightleftharpoons} Th^{+\bullet} + [^2H_8]Th \qquad (1)$$

The relative contribution of $Th^{+\bullet}$ and $[^2H_8]Th^{+\bullet}$ in the spectrum can be obtained by computer simulation of the spectrum [Fig. 1(*b*)]. It reveals that the equilibrium constant of eqn. (1) is well deviated from unity, demonstrating a significant equilibrium isotope effect (EIE) in this electron transfer equilibrium. Six independent experiments with the initial concentration ratio of $Th^{+\bullet}:[^2H_8]Th$ ranging from 1 : 2 to 1 : 4 gave: $K_{eq} = 0.62 \pm 0.12$

It implies that the electron transfers preferentially to the thianthrene radical cation or, in other words, it is easier for the neutral perdeuteriated thianthrene molecule to lose an electron than it is for the protonated thianthrene to form the corresponding radical cation. A similar phenomenon has been found in electron exchange equilibrium of some radical anion–neutral molecule systems in which heavy isotope substituted molecules showed diminished electron affinity for forming radical anions in solution.[1,2,5]

Since the EIE of eqn. (1) is significant and, further, thianthrene and its radical cation are very different in their chemical and physical properties thus making them easy to separate, this isotopically selective electron transfer may be used to develop a facile method for isotope enrichment. Thus, a 1 : 1 mixture of a carefully measured quantity of Th and $[^2H_8]Th$ in TFA–TFAn–CH_2Cl_2 solvent was oxidized by a 0.5 stoichiometric amount of perchloric acid followed by addition of an excess of carbon tetrachloride. Both $Th^{+\bullet}$ and $[^2H_8]Th^{+\bullet}$ were completely precipitated and separated by filtration from their parent molecules, which remained in solution. Removal of the solvent by distillation recovered the unoxidized neutral thianthrenes for ^{13}C NMR and mass spectrometry analysis. The proton decoupled ^{13}C NMR spectrum of $[^2H_8]Th$ showed two triplets with coupling constant of 24.8 Hz which were separated from the singlet of Th. Comparison of the spectrum of the original 1 : 1 mixture of Th and $[^2H_8]Th$ with the recovered one demonstrates an apparent increase in the intensity of Th and decrease in the intensity of $[^2H_8]Th$ in the recovered sample (Fig. 2). Four independent determinations

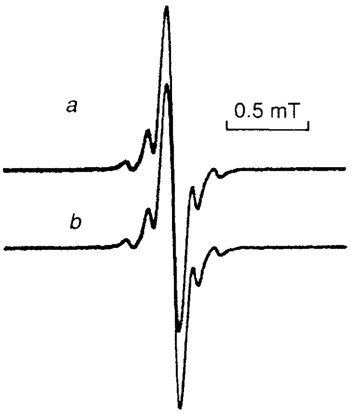

Fig. 1 Superimposed EPR spectrum of $Th^{+\bullet}$ and $[^2H_8]Th^{+\bullet}$. (*a*) Experimental spectrum recorded in 5% TFA–5% TFAn–CH_2Cl_2 mixed solvent at 25 °C. The initial concentrations of the substrates were $[Th^{+\bullet}ClO_4^-]_0 = 1.00 \times 10^{-4}$ mol dm^{-3}, $[[^2H_8]Th]_0 = 2.19 \times 10^{-4}$ mol dm^{-3}. (*b*) A computer simulated spectrum. This best simulation was obtained using a ratio of $[[^2H_8]Th^{+\bullet}]:[Th^{+\bullet}] = 2.75$ taking into account of the line-broadening owing to the electron exchange.

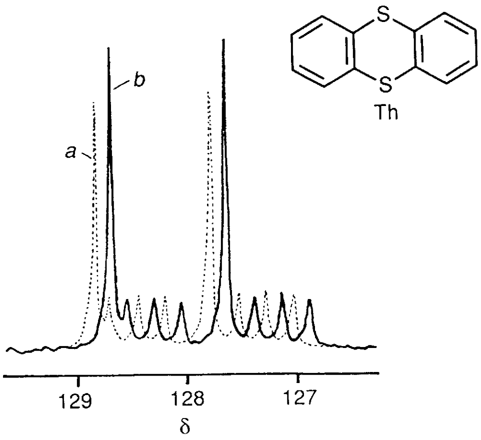

Fig. 2 Proton-decoupled ^{13}C NMR spectra of the α- and β-carbons of Th and $[^2H_8]Th$ taken in $CDCl_3$ from: (*a*) a mixture consisting of $[[^2H_8]Th]:[Th] = 1.00$; (*b*) the same mixture after 50% oxidation with perchloric acid and removal of the radical cations formed. Both spectra were recorded on a Bruker AM 400 NMR spectrometer at 100.6 MHz under identical conditions and a very long pulse delay was used to ensure the complete relaxation of the deuterium attached carbons (9.2 μs pulse width, 20 s pulse delay, same decoupling and lock power).

gave the ratio of [[$^2H_8$]Th] : [Th] being 0.80 ± 0.10 for the recovered sample that corresponds to a K_{eq} of 0.64 ± 0.08 for eqn. (1), which is in good accordance with the value obtained by EPR spectroscopy. Obviously, the radical cation must be enriched in deuterium. The same sample was subject to mass spectral analysis. The ratio of [$^2H_8$]Th] : [Th] was obtained by comparing the relative intensities of the molecular ion peak of 224 for [$^2H_8$]Th and 216 for Th. Because [$^2H_8$]Th and Th may have different ionization potentials in the ion source a series of standard samples, which contained exactly measured amounts of [$^2H_8$]Th and Th with the ratio of [[$^2H_8$]Th] : [Th] ranging from 0.5 to 2 were determined under the same experimental conditions to calibrate the result. The K_{eq} thus obtained was 0.76 ± 0.06 which is in reasonable agreement with the EPR and NMR spectroscopy results.

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