A Novel Application of Electron Spin Resonance: Selective Deuterium Exchange Using *Homogeneous* and *Heterogeneous* Metal Catalysts

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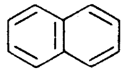
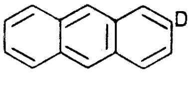
Summary E.s.r. is shown to be a unique tool for the mechanistic study of selective, stepwise deuteriation reactions, particularly in *homogeneous* and *heterogeneous* metal-catalysed isotopic hydrogen exchange in organic compounds.

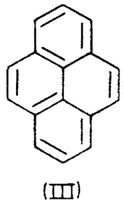
A CURRENT aspect of catalytic theory concerns the relationship which exists between homogeneous and heterogeneous metal catalysis.[1–4] We now demonstrate for the first time the unique value of e.s.r. in these reactions. There are three important problems involved in metal-catalysed isotope exchange: (i) the estimation of total deuterium incorporation, (ii) the orientation of isotope in the labelled molecule, (iii) the mechanism of isotope incorporation, *i.e.* whether stepwise or multiple. For a comparison of homogeneous and heterogeneous catalytic systems it is necessary to be able to observe positional deuteriation during initial rates of exchange, particularly in heterogeneous catalysis



(I)



(II)



(III)

where competing isotope randomisation can occur. Thus the essential requirement of the analytical method is high sensitivity for a particular deuteriated species during initial rates of exchange.

Isotope selectivity during initial exchange in polycyclic aromatics at 75°[a]

Run	Compound	Weight (g)	Reaction time (h)	Reaction volume (ml)	Deuterium distribution[b] $^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$
1	Naphthalene	0·200	0·25	8·0	73·5 (85)	22·0 (15)	4·5	
2	Naphthalene	0·250	0·50	10·0	87·5 (80)	10·4 (20)	2·1	
3	Naphthalene	0·400	1·0	16·0	66·0 (70)	26·2 (30)	7·8	
4	Anthracene	0·100	1·0	13·0	89·5 (95)	6·5 (5)	3·5	0·5
5	Anthracene	0·100	2·25	20·0	70·8 (85)	19·0 (15)	8·2	2·0
6	Pyrene	0·050	0·7	20·0	56·0 (70)	35·6 (30)	8·4	

[a] Reaction conditions involved $MeCO_2D$ (50 mole % in D_2O) containing Na_2PtCl_4 (0·015 M) except for anthracene runs where $MeCO_2D$ (67 mole % in D_2O) with Na_2PtCl_4 (0·01 M) was used.

[b] Figure in brackets is estimated approximately from e.s.r. Other distribution data obtained from low voltage mass spectrometry Orientation of isotope is predominantly in the 2-position for all compounds.

E.s.r. is unique for this work and under certain conditions is the only satisfactory method for establishing the relationship between homogeneous and heterogeneous catalysis in isotope exchange. Three critical compounds for this study are naphthalene, anthracene, and pyrene because of the importance of π-bond order in these reactions.[2,4,5] In practice it is necessary to be able to observe 5—15% of species such as (I), (II), and (III) in the presence of unlabelled parent. This has not been possible by n.m.r.; however, if the deuteriated polycyclic aromatics, after exchange, are converted into radical anions using conventional techniques such as reaction with sodium or potassium in 1,2-dimethoxyethane, deuterium analysis can be performed on these anions.

To demonstrate the use of the present e.s.r. technique, a representative range of polycyclic aromatic hydrocarbons have been catalytically deuteriated (Table), the species reported being unequivocally identified by e.s.r. and the deuteriation confirmed by mass spectrometry. A typical e.s.r. spectrum (Figure) is included for the pyrene system which shows essentially the intense $^2H_0$ anion hyperfine on which is superimposed a less intense first-order spectrum expected for the anion of species (III). From the spectrum, qualitative e.s.r. identification of the predominant $^2H_1$ species is unequivocal. More important, a reasonably quantitative confirmation of the mass spectral distribution can be made (Table) under conditions where the n.m.r. of the deuteriated species did not differ from that of the parent unlabelled molecule.

In terms of fundamental catalytic theory, the conditions suitable for the present e.s.r. applications are initial, stepwise, selective deuteriations. A further common catalytic isotope exchange situation is also amenable to e.s.r. study and this is where multiple deuteriated species are selectively formed (*e.g.* [β-$^2H_4$]naphthalene). Here, e.s.r. acts as a complementary tool to n.m.r. and m.s., since the last two techniques combine to give the same information.

In general, e.s.r. methods are experimentally time consuming, high purity aromatics are usually required, and the range of polycyclics capable of forming stable radical ions is limited. However, the e.s.r. technique is unique for certain catalytic reactions and may be applied to any deuteriation project. It may also be of value in general tritium labelling work where deuterium is used as a tracer for tritium.[6]

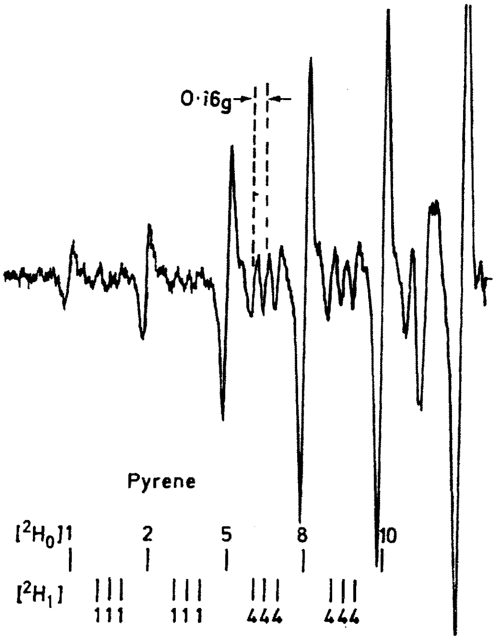


FIGURE. *E.s.r. spectrum of radical ion of* [$^2H_1$]*pyrene* (III) *in the presence of* [$^2H_0$]*pyrene.*

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[1] For preceding paper on Catalytic Deuterium Exchange Reactions with Organics, see J. L. Garnett and A. T. T. Oei, *J. Catalysis*, in the press.

[2] J. L. Garnett and W. A. Sollich-Baumgartner, *Adv. Catalysis*, 1966, **16**, 95.

[3] R. R. Fraser and R. N. Renaud, *J. Amer. Chem. Soc.*, 1966, **88**, 4365.

[4] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1969, **73**, 1525.

[5] F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, 1962, **1**, 255.

[6] E. A. Evans, "Tritium and its Compounds," Butterworths, London, 1966; J. L. Garnett, "Proceedings, Second International Conference on Methods of Preparing and Storing Labelled Compounds," EURATOM, Brussels, 1968, p. 709.