

SHORT COMMUNICATIONS

CATALYTIC DEUTERIUM EXCHANGE REACTIONS WITH ORGANICS*

XXV.† CATALYTIC SELF-ACTIVATION AND E.P.R. STUDIES WITH GROUP VIII TRANSITION METAL OXIDES

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The possible relationship between catalytic self-activation in deuterium exchange reactions and e.p.r. studies of charge-transfer adsorption on platinum oxide has already been discussed.¹ The process of self-activation is "in situ" reduction of the inorganic oxide by the organic substrate.² Previous attempts to observe self-activation and e.p.r. evidence for organic interactions with other oxides of the Group VIII transition metals have been unsuccessful even after heating at 120° for many hours.³

We now wish to report for the first time (i) self-activation of palladium, rhodium, rhenium, ruthenium, and iridium oxides during exchange between benzene and heavy water, and (ii) e.p.r. evidence for interactions between these oxides and polycyclic aromatic hydrocarbons. In contrast to platinum oxide, the present oxides, with the possible exception of palladium oxide, do not exhibit self-activation at 120° with benzene, higher temperatures being necessary (Table 1). Even at 180°, benzene does not self-activate nickel oxide, this result being consistent with the high temperature (300°) required to reduce this oxide with hydrogen.

For the e.p.r. spectra of the organic/PtO₂ interactions no fine-line structure has been observed over a wide range of experimental conditions.³ The detected paramagnetism at room temperature has been attributed to a low-lying, thermally populated, triplet state of the charge-transfer complex, for which the term "diradicaloid" has been proposed.⁴ E.p.r. interactions involving catalysts other than the Group VIII transition metal oxides have previously been reported but were attributed to either radical-ion or quinone^{5,6} formation.

In the present series (Table 1), the paramagnetic species may even be peroxides or quinones as suggested for the alkylbenzene/PtO₂ spectra.^{1,7} A comparison of

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¹ Ernst, I. T., Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Catalysis*, 1964, **3**, 568.

² Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Phys. Chem.*, 1964, **68**, 436.

³ Ernst, I. T., Garnett, J. L., and Sollich-Baumgartner, W. A., *Aust. J. Chem.*, 1966, **19**, 529.

⁴ Kainer, H., Bijl, D., and Rose-Innes, A. C., *Naturwissenschaften*, 1954, **41**, 303.

⁵ Hirota, K., and Kuwata, K., *Bull. Chem. Soc. Japan*, 1963, **36**, 229.

⁶ Hirota, K., Kageyama, Y., and Kuwata, K., *Bull. Chem. Soc. Japan*, 1963, **36**, 875.

⁷ Walling, C., in "Free Radicals in Solution." p. 397. (John Wiley: New York 1957.)

e.p.r. results for the two ruthenium oxides in Table I accentuates the possibility already discussed that water of hydration is a factor in the interaction.³

The present data are of importance in structure determination and reaction mechanism studies where labelled compounds are used extensively, since no hydrogen pre-reduction of the catalyst is necessary. Thus the simplified one-step isotopic hydrogen labelling procedure involving self-activation of the oxides should be of

TABLE I
CATALYTIC SELF-ACTIVATION AND E.P.R. DATA WITH GROUP VIII TRANSITION METAL OXIDES

Catalyst	Reaction Temp. ^a	Atom % D ^b (in benzene)	E.P.R. Signal ^c		
			Sample Temp.	Time at Temp.	Signal Intensity ^d
PtO ₂ ·2H ₂ O	120° (90°)	41.8	25°	3 min	10.0
			120	30 min	25.0
			120	60 min	0.0
PdO	120 (120)	0.84	120	7 days	1.0
IrO ₂ ·2H ₂ O	140 (140)	6.16	120	30 min	0.0
Rh ₂ O ₃	140 (140)	1.05	120	30 min	0.0
RuO ₂	140 (140)	0.66	120	30 min	0.0
Rh ₂ O ₃	180	32.4	180	30 min	5.5
IrO ₂ ·2H ₂ O	180	27.8	180	30 min	16.9
RuO ₂	180	14.1	180	30 min	13.8
RuO ₂ ·H ₂ O		—	180	30 min	0.30
ReO ₂	180 (180)	0.06	180	30 min	0.30

^a Temperature in brackets is minimum necessary for appearance of self-activation. Other temperature was used for benzene exchange runs.

^b Equilibrium D = 50.0%. Reagent quantities: benzene (2.5×10^{-2} M), D₂O (7.5×10^{-2} M), oxide (0.75×10^{-4} M). Reaction vessels stood at temperature 48 hr.

^c Pyrene used as organic since this was one of the most e.p.r. active compounds previously studied.¹

^d E.p.r. intensity is an estimate of $10^{-16} \times (\text{spins/mg of oxide})$ referred to a calibrated ruby standard internal to the cavity.

value in catalytic tritiation with T₂O⁸ and also in general deuteration work.⁹ Further, each of the oxides appears to give a different isotope orientation during the deuteration of a series such as the alkylbenzenes,^{10,11} and this specificity may be of use in mass spectrometry, spin decoupling in n.m.r.,¹² and the evaluation of coupling constants in e.p.r. spectra.¹³

⁸ Garnett, J. L., *Nucleonics*, 1962, **20**, 86.

⁹ Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Phys. Chem.*, 1965, **69**, 1850.

¹⁰ Fisher, B., and Garnett, J. L., unpublished data.

¹¹ Garnett, J. L., and Rainis, A., unpublished data.

¹² Garnett, J. L., Henderson, L. J., Sollich, W. A., and Tiers, G. V. D., *Tetrahedron Lett.*, 1961, **15**, 516.

¹³ Aylward, G. H., Garnett, J. L., and Sharp, H., *Chem. Commun.*, in press.

Experimental

Details of the e.p.r. procedure have previously been described.³ Group VIII metal oxides were supplied by Johnson, Matthey, and Co. Ltd. The technique used in the catalytic exchange reactions was the same as that reported in earlier publications.^{2,12}

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