

Electron donor strength of rare earth oxides

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The adsorption of electron acceptors, viz., 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) and *p*-dinitrobenzene (PDNB) on the surface of three rare earth oxides Y_2O_3 , Nd_2O_3 and Pr_6O_{11} has been studied in acetonitrile and dioxan. From the radical concentration on the surface determined using ESR spectral data, the electron donor strength of the rare earth oxides are reported.

The utility of electron acceptor adsorption for the study of electron donor properties of metal oxides has been well established¹. Esumi *et al.*² studied the electron donor properties of some metal oxides and they found that difference in electron donor properties among metal oxide systems can be characterized by the change in electron acceptor radicals formed. Comparing the radical forming activity of metal oxides, their electron donor properties have been evaluated. The adsorption of electron acceptors on some of the rare earth oxides have been reported³⁻⁷. The present note describes an investigation of the electron donor strength of three rare earth oxides Y_2O_3 , Nd_2O_3 and Pr_6O_{11} by comparing their radical forming tendencies.

Experimental

The rare earth oxides, viz., Y_2O_3 , Nd_2O_3 and Pr_6O_{11} were prepared by hydroxide method⁵ from the salts obtained from Indian Rare Earths Ltd., Udyogamandal. The electron acceptors employed for the study are TCNQ, chloranil and PDNB. The purification of these reagents and solvents have been described elsewhere⁵.

The oxides were activated at 500°C for 2h prior to each experiment. The oxide (0.5g) was placed in a 25 ml test tube fitted with a mercury sealed stirrer and was outgassed at 10^{-5} Torr for 1h. A solution of electron acceptor in acetonitrile (20 ml) was then admitted into the tube. After the solution had subsequently been stirred for 3h at 28°C in a thermostated bath, the oxide was collected by centrifuging and dried at room temperature *in vacuo*. The reflectance spectra of the dried samples were recorded on a Hitachi 200-20

UV-visible spectrophotometer with a 200-0531 reflectance attachment. The ESR spectra were measured at room temperature using Varian E-122 X/Q band ESR spectrophotometer. The radical concentrations were calculated by comparison of areas obtained by double integration of first derivative curves for the sample and standard solutions of 1,1-diphenyl-2-picrylhydrazyl in benzene.

The amount of electron acceptor adsorbed was determined from the difference in concentration of electron acceptor in solution before and after adsorption. The absorbance of electron acceptor was measured by means of a Hitachi 200-20 UV-vis spectrophotometer at the λ_{max} of electron acceptor in the solvent: 393 and 403 nm for TCNQ, 288 and 286 nm for chloranil and 262 and 261 nm for PDNB in acetonitrile and 1,4-dioxane respectively. The infrared spectra of oxides were taken on a Perkin Elmer PE-983 Infrared spectrophotometer. The surface area of oxides was determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800.

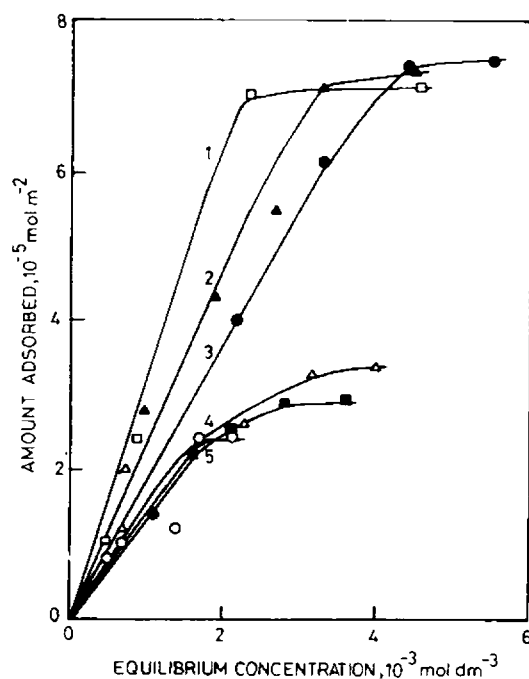


Fig. 1—Adsorption isotherms of ○ Chloranil in acetonitrile on Y_2O_3 ; □ TCNQ in acetonitrile on Y_2O_3 ; △ Chloranil in acetonitrile on Pr_6O_{11} ; ● TCNQ in acetonitrile on Pr_6O_{11} ; ■ chloranil in acetonitrile on Nd_2O_3 ; △ TCNQ in acetonitrile on Nd_2O_3

Table 1—Data of electron acceptor adsorption on rare earth oxides

Oxide	Surface area m^2g^{-1}	Electron acceptor	Colour	Limiting-amount adsorbed mol m^{-2}	Limiting-radical concentration spin m^{-2}	Radical concentration
						Amount adsorbed spin mol^{-1}
Y_2O_3	81.5	Chloranil	light pink	2.46×10^{-5}	1.38×10^{16}	5.22×10^{20}
Y_2O_3	81.5	TCNQ	green	7.21×10^{-5}	3.98×10^{18}	5.26×10^{22}
Nd_2O_3	42.4	Chloranil		2.94×10^{-5}	1.65×10^{16}	5.30×10^{20}
Nd_2O_3	42.4	TCNQ	light blue	7.36×10^{-5}	4.01×10^{18}	5.40×10^{22}
Pr_6O_{11}	11.4	Chloranil		3.39×10^{-5}	1.90×10^{16}	5.52×10^{20}
Pr_6O_{11}	11.4	TCNQ		7.44×10^{-5}	4.03×10^{18}	5.46×10^{22}

Results and discussion

The adsorption of three electron acceptors viz. TCNQ (7,7,8,8-tetracyano-quinodimethane), chloranil(2, 3, 5, 6-tetrachloro-*p*-benzoquinone) and PDNB (*p*-dinitrobenzene) were studied on Y_2O_3 , Nd_2O_3 and Pr_6O_{11} activated at 500°C . The electron affinities were 2.84, 2.40 and 1.77 eV respectively. The adsorption of PDNB was negligible on all the systems studied. In the case of TCNQ and chloranil, the adsorption isotherms obtained were of Langmuir type and the limiting amount of electron acceptors adsorbed were determined from the Langmuir plot (Fig. 1).

When the electron acceptors were adsorbed on the oxides, their surfaces acquired characteristic colouration (Table 1) owing to interaction between electron acceptor and oxide surface⁸. In the case of Pr_6O_{11} , the colourations acquired after the adsorption of TCNQ and chloranil could not be distinguished from the black colour of the oxide. The reflectance spectra of coloured samples indicated bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ², dimeric TCNQ radical⁹ and chloranil anion radical¹⁰ respectively. The electronic state of adsorbed species was studied by ESR spectroscopy which indicated the presence of radical species. The samples coloured by TCNQ and chloranil gave unresolved spectral line with a *g* value of 2.003 and 2.001 respectively with a width of approximately 30G indicating the presence of anion radicals on the surface^{11,12}. A representative plot (Fig. 2) shows the radical concentration of TCNQ adsorbed against the equilibrium concentration of electron acceptor in solution. The isotherm obtained is of the same shape as in Fig. 1. The limiting radical concentrations have also been calculated from the Langmuir plot and are given in Table 1.

It is observed that limiting amount of electron acceptor adsorbed and limiting radical concentra-

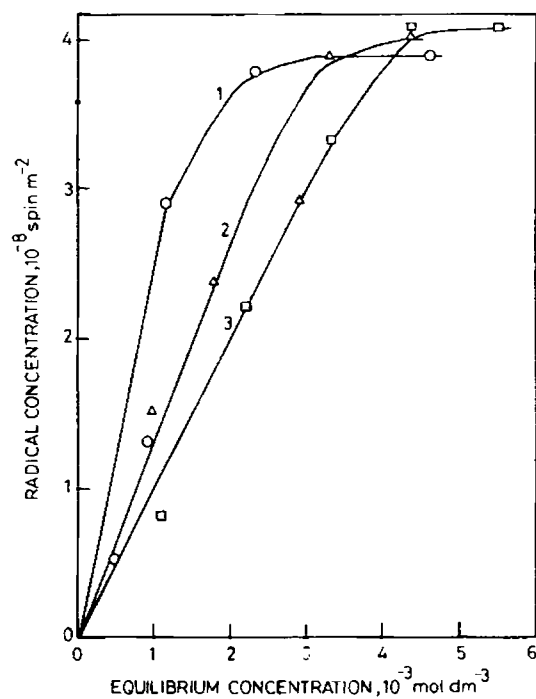


Fig. 2—Radical concentration of TCNQ adsorbed on $\circ \text{Y}_2\text{O}_3$; $\square \text{Pr}_6\text{O}_{11}$; $\triangle \text{Nd}_2\text{O}_3$

tion of electron acceptor increase with increase in electron affinity of electron acceptor and decrease with increase in basicity of solvent. A strong electron acceptor like TCNQ is capable of forming anion radicals even from weak donor sites whereas weak acceptor like PDNB is capable of forming anion radicals only at strong donor sites. Hence the limiting radical concentration of a weak acceptor is a measure of the number of strong donor sites on the surface and that for a strong acceptor is the total of all weak and strong donor sites on the surface. It is found that the limiting radical concentration and also the limiting amount of electron acceptor adsorbed decrease with decrease in electron affinity of electron acceptor. In

the case of the oxides studied, the limiting amount decreased steeply between chloranil and PDNB. Hence the limit of electron transfer (in electron affinity) from Y_2O_3 , Nd_2O_3 and Pr_6O_{11} activated at $500^\circ C$ was located between 2.40 and 1.77 eV.

It has been proposed that two types of electron donor sites are responsible for electron transfer from oxide surfaces². The electron donor sites of oxides are associated with surface hydroxyl ions at lower activation temperature and with electron defect sites at higher activation temperature. It has been observed by IR spectroscopy that the surfaces of Y_2O_3 , Nd_2O_3 and Pr_6O_{11} activated at $500^\circ C$ contain hydroxyl groups (peak near 3400 cm^{-1}).

The electron donor strength can be expressed as the conversion ratio of an electron acceptor adsorbed on the surface to its anion radical. This ratio can be estimated by dividing TCNQ radical concentration by the corresponding half value of the limiting amount of TCNQ. The values obtained for the three oxides are given in Table 1. The larger the value of this ratio, the stronger the electron donor site. This ratio is

almost constant for the three rare earth oxides studied implying a constant electron donor strength of the weak and strong donor sites.

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References

- 1 Meguro K & Esumi K, *J Adhesion Sci Technol*, 4 (1990) 393.
- 2 Esumi K, Meguro K & Meguro K, *J Colloid Interface Sci*, 141 (1991) 578.
- 3 Sugunan S, Devika Rani G & Sherly K B, *React Kinet Catal Lett*, 43 (1991) 375.
- 4 Sugunan S & Devika Rani G, *J Mat Sci Lett*, 10 (1991) 887.
- 5 Sugunan S & Devika Rani G, *J Mat Sci Lett*, 11 (1992) 1269.
- 6 Sugunan S & Sherly K B, *Indian J Chem*, (1993) (in press).
- 7 Sugunan S & Devika Rani G, *J Mat Sci*, (1993) (in press).
- 8 Meguro K & Esumi K, *J Colloid Interface Sci*, 59 (1977) 939.
- 9 Boyd R H & Philips W D, *J chem Phys*, 43 (1965) 2927.
- 10 Foster R & Thomson T J, *Trans Faraday Soc*, 58 (1962) 860.
- 11 Hosaka H, Fujiwara T & Meguro K, *Bull chem Soc Japan*, 44 (1971) 2616.
- 12 Esumi K & Meguro K, *Japan Color Material*, 48 (1975) 539.