

Acid–base and Electron Donor Properties of Pr_6O_{11} and Its Mixtures with Alumina

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[Manuscript received January 19, 1994, in revised form May 30, 1994]

The electron donor properties of Pr_6O_{11} activated at 300, 500 and 800°C are reported from the studies on adsorption of electron acceptors of various electron affinity (7, 7, 8, 8-tetracyanoquinodimethane, 2, 3, 5, 6-tetrachloro-1, 4-benzoquinone, *p*-dinitrobenzene, and *m*-dinitrobenzene) in three solvents (acetonitrile, 1,4-dioxan and ethyl acetate). The extent of electron transfer during adsorption is understood from magnetic measurements and ESR spectral data. The corresponding data on mixed oxides of Pr and Al are reported for various compositions. The acid / base properties of these oxides are determined using a set of Hammett indicators.

1. Introduction

Rare earth oxides have been used as promoter and supporter in catalytic reactions [1,2] and the catalytic properties of rare earth oxides have been correlated with their basicities [3,4]. But relatively few details have been reported about the surface electron properties of rare earth oxides and nature of their interactions with adsorbed molecules. In our earlier papers we have reported the electron donor properties of Y_2O_3 , Nd_2O_3 and their mixtures with alumina [5–7]. The surface properties of oxides are influenced by the method of preparation. In this paper we report the electron donicity of Pr_6O_{11} prepared by different routes and its mixtures with alumina as a function of basicity of medium.

2. Experimental

Pr_6O_{11} was prepared by hydroxide method from sulphate / nitrate obtained from Indian Rare Earths Ltd. Udyogamandal [5]. Mixed oxides of Pr and Al were prepared by cohydrolysis from their nitrate and sulphate solutions [8,9]. 5, 10, 15, 20 and 60 wt-% of Pr_6O_{11} in alumina were prepared. The following electron acceptors (EA) were used 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ) (2.84), 2, 3, 5, 6-tetrachloro-1, 4-benzoquinone (chloranil) (2.40), *p*-dinitrobenzene (PDNB) (1.77) and *m*-dinitrobenzene (MDNB) (1.26) (the electron affinity values in eV are given in brackets).

Purification of EA and solvents for adsorption and the methods of adsorption have been described elsewhere [7]. The Hammett indicators used were as follows: methyl red (4.8), dimethyl yellow (3.3), crystal violet (0.8), neutral red (6.8), bromothymol blue (7.2), thymol blue (2.6) and 4-nitroaniline (18.4) (the pK_a values are given in brackets). In each experiment 0.1 wt-% of the indicator in benzene was used.

The reflectance spectra of 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–112 X/Q band ESR spectrophotometer. Radical concentrations were calculated by comparison of area obtained by double integration of first derivative curve for the sample and standard solutions of 1, 1-diphenyl-2-picryl-hydrazyl in benzene.

The amount of EA adsorbed was determined from the difference in concentration of EA before and after adsorption. Infrared spectra of oxides were taken on a Perkin Elmer PE–983 infrared spectrophotometer.

Surface area of oxides were determined by BET method using Carlo Erba Strumentazione Sorptomatic series 1800. The values in m^2g^{-1} for Pr_6O_{11} activated at 300, 500 and 800°C were 8.6, 11.4 and 9.2 respectively. Mixed oxides were activated at 500°C and their surface areas were determined. For mixed oxides prepared from sulphates the values were 134.6, 141.55, 136.81 and 132.5 for 5, 10, 15 and 20 wt-% of Pr_6O_{11} . For oxides prepared from nitrates the values were 168.2, 171.5,

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Table 1 Limiting amounts of electron acceptors adsorbed

Electron acceptor	Solvent	Activation temperature, °C	Limiting amount adsorbed, $10^{-5} \text{ mol} \cdot \text{m}^{-2}$
chloranil	acetonitrile	300	2.22
TCNQ	"	300	6.44
chloranil	dioxan	300	2.00
TCNQ	"	300	4.65
chloranil	ethylacetate	300	2.18
TCNQ	"	300	4.96
chloranil	acetonitrile	500	3.39
TCNQ	"	500	7.44
chloranil	dioxan	500	2.71
TCNQ	"	500	5.21
chloranil	ethylacetate	500	2.98
TCNQ	"	500	5.71
chloranil	acetonitrile	800	4.54
TCNQ	"	800	9.96
chloranil	dioxan	800	3.81
TCNQ	"	800	7.71
chloranil	ethylacetate	800	4.01
TCNQ	"	800	8.48

174.8 and 178.22 for 5, 10, 20 and 60 wt-% respectively.

Tanabe's method was used for measurement of acid/base strength of oxides [10]. In the case of dark coloured samples, 0.1 g of oxide mixed with 0.15 g basic Al_2O_3 was used [11]. Magnetic susceptibility measurements were done at room temperature on a simple Guoy type balance.

3. Results and Discussion

The adsorption of *p*-dinitrobenzene (PDNB) and *m*-dinitrobenzene (MDNB) were negligible on all the systems studied. The adsorption isotherms obtained are of Langmuir type and from these isotherms the limiting amount of electron acceptor adsorbed was determined. The data are given in Table 1. The formation of anion radicals on the oxide surface as a result of electron transfer from oxide surface to adsorbed electron acceptor was confirmed by electronic and ESR spectroscopy. The reflectance spectra of adsorbed sample show bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ [12], dimeric TCNQ radical [13] and chloranil anion radical [14]. In the case of the oxides studied these assignments do not hold completely since these oxides have characteristic bands in the same region. When EA

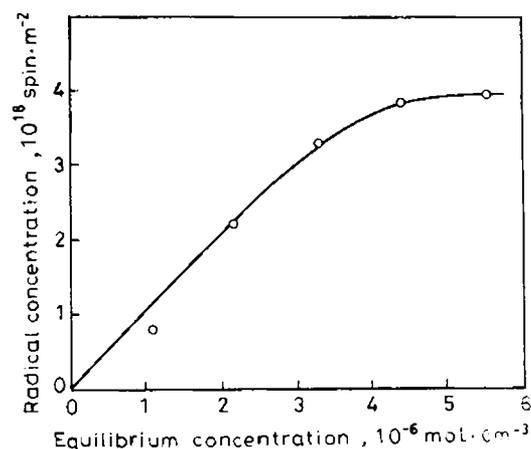


Fig.1 Radical concentration of TCNQ adsorbed on Pr_6O_{11} at 500°C

were adsorbed on the surfaces of these oxides, surfaces developed remarkable coloration like bluish green for TCNQ and pink for chloranil. In the case of pure Pr_6O_{11} the coloration could not be distinguished from black colour of oxide.

The radical concentrations of EA adsorbed on the oxides were determined from ESR spectra. The

Table 2 Acid-base parameters

(a) TCNQ: $C_A = 1.51$, $E_A = 1.68$

Solvent	C_B	E_B	C_A	E_A	$-\Delta H^{ab}$ with TCNQ, $\text{kJ} \cdot \text{mol}^{-1}$
acetonitrile	1.34	0.88			14.74
ethyl acetate	1.74	0.97			17.90
dioxan	2.38	1.09	21.90

(b) Chloranil: $C_A = 2.39$, $E_A = 2.56$

Solvent	C_B	E_B	C_A	E_A	$-\Delta H^{ab}$ with chloranil, $\text{kJ} \cdot \text{mol}^{-1}$
acetonitrile	2.74	1.81			11.19
ethyl acetate	3.56	2.33			13.61
dioxan	4.87	2.23	17.35

samples coloured by TCNQ adsorption gave an unresolved ESR spectra with a g value of 2.003 and those by chloranil gave an unresolved spectra with a g value of 2.001. These values are in agreement with those reported earlier [15,16]. Figure 1 shows radical concentration of TCNQ adsorbed against equilibrium concentration of TCNQ in solution for Pr_6O_{11} activated at 500°C . Two possible electron sources exist on oxide surface responsible for electron transfer [17]. At lower activation temperatures, surface sites are associated with the presence of unsolvated hydroxyl ions and at higher temperatures electron defect site is responsible for electron transfer. The presence of hydroxyl group on Pr_6O_{11} activated at 300 and 500°C was confirmed from IR spectral data (peak near 3400 cm^{-1}). Since concentration of surface hydroxyl ions decreases with increase in activation temperature and concentration of trapped ions increases with increase in temperature, it might be expected that trapped electrons are solely responsible for adsorption of electron acceptors on Pr_6O_{11} activated at higher temperatures. Since the concentration of trapped ions increases with increase in activation temperature, the adsorption of electron acceptor in the three solvents increases with increase in activation temperature.

The amount of EA adsorbed is found to decrease with increase in basicity of solvent. The mixing heats of substances with acid-base interaction are expressed by Drago equation

$$-\Delta H^{ab} = C_A C_B + E_A E_B$$

where E and C are Drago constants for acidic compound (A) and basic compound (B) [18]. When

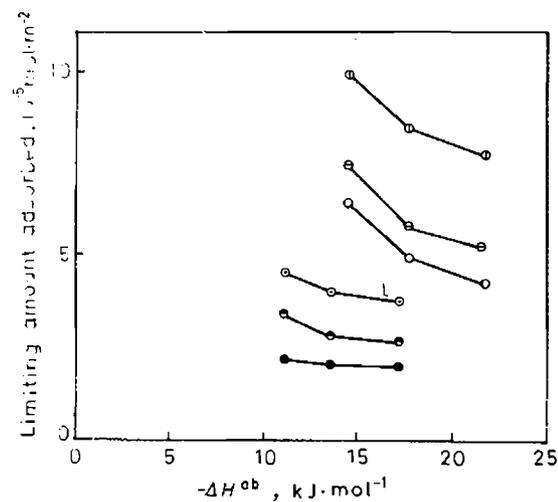


Fig.2 Limiting amount of EA adsorbed as a function of acid-base interaction enthalpy

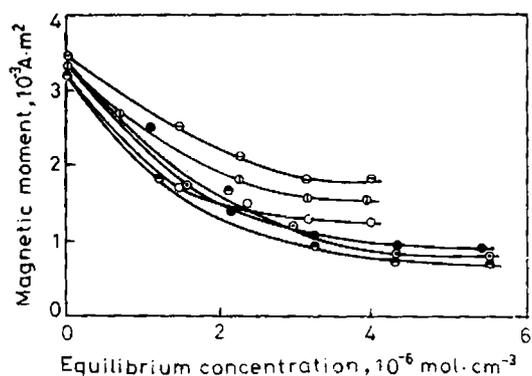
- TCNQ at 300°C , ◻ TCNQ at 500°C
- ◻ TCNQ at 800°C , ● chloranil at 300°C
- chloranil at 500°C , ◻ chloranil at 800°C

Drago equation is applied to present systems, basic compound corresponds to solvents (acetonitrile, ethyl acetate and dioxan) and acidic compound to EA. The basicity of solvent was estimated by the heat of interaction with EA and the values are listed in Table 2.

The saturated amounts of EA adsorbed on to Pr_6O_{11} activated at 300 , 500 and 800°C are plotted as a function of basicity of solvents in Fig.2. The limiting amount decreases with an increase in acid-base interactions between basic solvents and

Table 3 Basicity and $H_{o,max}$ of Pr_6O_{11} and mixed oxides

Oxide	Method of preparation	Activation temperature, C	Basicity, 10^{-3} meq · m ²				
			H_o	$H_{o,max}$	>3.3	>4.8	>6.8
Pr_6O_{11}	sulphate	300	3.68	2.41	1.14	0.65	7.5
Pr_6O_{11}	sulphate	500	4.21	2.88	1.42	0.82	7.6
Pr_6O_{11}	sulphate	800	5.12	3.84	1.81	1.21	7.8
Pr_6O_{11}	nitrate	500	3.92	2.69	1.21	0.72	7.3
Al_2O_3	sulphate	500	0.58	0.82	0.17	—	7.4
Al_2O_3	nitrate	500	0.97	0.62	0.48	0.31	7.6
5% Pr_6O_{11}	sulphate	500	1.48	0.72	0.21	0.11	7.2
10% Pr_6O_{11}	sulphate	500	1.72	0.90	0.38	0.18	7.4
15% Pr_6O_{11}	sulphate	500	1.91	1.17	0.53	0.21	7.5
20% Pr_6O_{11}	sulphate	500	2.18	1.38	0.71	0.35	7.5
5% Pr_6O_{11}	nitrate	500	2.14	1.32	0.97	0.64	8.0
10% Pr_6O_{11}	nitrate	500	2.31	1.51	0.98	0.66	8.1
20% Pr_6O_{11}	nitrate	500	2.48	1.62	1.02	0.68	8.2
60% Pr_6O_{11}	nitrate	500	2.28	1.48	0.97	0.65	8.1

Fig.3 Magnetic moment of Pr_6O_{11} as a function of equilibrium concentration of EA

- chloranil in acetonitrile at 300°C
- TCNQ in acetonitrile at 300°C
- ◐ chloranil in acetonitrile at 500°C
- ⊙ TCNQ in acetonitrile at 500°C
- chloranil in acetonitrile at 800°C
- ⊙ TCNQ in acetonitrile at 800°C

EA. The decrease is in order of acetonitrile > ethyl acetate > dioxan, the order of decreasing basicity of solvents. This shows the competition between basic solvents and basic sites of oxide for EA.

When surface acidity/basicity were determined, visible colour change was obtained for the following indicators: *p*-dimethyl aminoazo-

benzene, methyl red, neutral red and bromothymol blue. Data are given in Table 3. From the plots of acidity/basicity vs H_o of indicator the parameter $H_{o,max}$ was determined from the point of intersection of acid/base distribution curves with abscissa. As the activation temperature increases, $H_{o,max}$ value also increases. This shows the increase in basicity of oxide, which in turn accounts for the increase in limiting amount of EA adsorbed with the increase in temperature. The basic strength of a surface is considered as ability of surface site possessing an electron lone pair to transfer it to an acceptor molecule. Figure 3 shows the change in magnetic moment of Pr_6O_{11} as a function of equilibrium concentration of EA in solution. The magnetic moment of Pr_6O_{11} decreases and reaches a limiting value at the same concentration corresponding to the limiting amount of EA adsorbed. The decrease in magnetic moment on adsorption of EA shows the extent of electron transfer from oxide surface to electron acceptor.

The limiting amounts of EA adsorbed on mixed oxides of various compositions determined from the Langmuir plots are shown as a function of composition of mixed oxide in Fig.4. The electron donicity increases with increase in concentration of Pr_6O_{11} in mixed oxide and decrease with increase in basicity of solvent. On the other hand, the mixed oxide prepared from nitrate solution show greater electron donicity than Pr_6O_{11} . For mixed oxides the electron donor property increases with increase

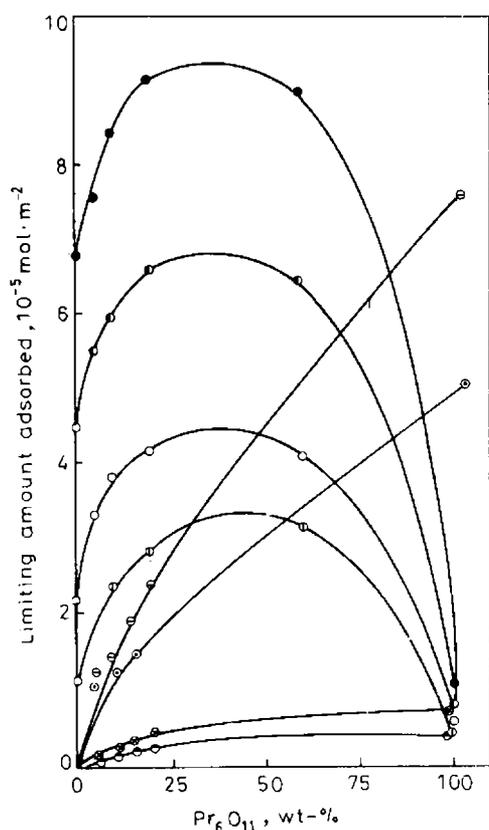


Fig.4 Limiting amount of EA adsorbed as a function of composition of $\text{Pr}_6\text{O}_{11}-\text{Al}_2\text{O}_3$

From nitrate solution

○ chloranil in acetonitrile, ● TCNQ in acetonitrile

⊙ chloranil in dioxan, ⊙ TCNQ in dioxan

From sulphate solution

⊗ chloranil in acetonitrile, ⊖ TCNQ in acetonitrile

● chloranil in dioxan, ⊙ TCNQ in dioxan

in concentration of Pr_6O_{11} as a consequence of increase in Al-O-Pr bonds without changing the limit of electron transfer. But there is not much variation of H_o_{\max} with Pr_6O_{11} content in the mixed oxide. Strong electron acceptors like TCNQ are capable of forming anions even from weak donor sites and the limiting radical concentration of a strong acceptor is the sum of the contributions from all weak and strong donor sites on the surface. Very weak sites on the surface of oxide can not be determined by titration using Hammett indicators. The maximum in the plot for mixed oxides prepared by nitrate method can be understood

from the lower electron donicity of pure Pr_6O_{11} prepared by nitrate method.

Acknowledgement

The authors wish to express their sincere gratitude to the Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship to GDR.

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