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Flectron-donor Sites of Oxides as Investigated on Oxygen-17 Exchanged CaO Surfaces

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The electron-donor properties of various oxides (BaO, SrO, CaO, MgO, γ -Al₂O₃ and SiO₂-Al₂O₃), activated under vacuum in the temperature range 1000-1273 K, have been investigated by adsorption of 9,10-dimethylanthracene (DMAN), chlorine and oxygen (90% ¹⁷O-enriched or non-enriched).

Upon adsorption of DMAN, radical anions are formed on CaO, whereas radical cations are formed on SiO₂-Al₂O₃. On oxides of intermediate base strength (MgO and γ -Al₂O₃) very low radical concentration was obtained. The data allow for a further specification of the correlation between electron acceptor-donor properties of oxides and their acid-base strength.

Upon adsorption of Cl₂, a two g-value e.s.r. signal $(g_1 = 2.002, g_2 = 2.013)$ was observed on alkaline-earth oxides. A nearly identical signal was also observed on adsorption of O₂ on the same oxides. Upon adsorption of O₂ (non-enriched) on CaO samples, previously exchanged with ¹⁷O₂, the above signal showed some relevant modifications, suggesting that the paramagnetic species contains oxygen atoms. The signal is tentatively assigned to a O₃³⁻ surface species. This species is thought to be formed on the surface of alkaline-earth oxides in the electron-donation process from low-coordination oxidic sites (O_{CUS}²) toward acceptor molecules. The O_{CUS}² sites are therefore identified as the electron-donor sites.

The work also includes a volumetric study of O_2 adsorption on the various oxides. By comparing volumetric adsorption data with the concentration of radicals (O_2^- and O_3^-), it is possible to provide a description of the O_2 adsorption mechanism on alkaline-earth oxides.

The formation of anion radicals upon adsorption of various acceptor molecules (A) on the surface of alkaline-earth oxides, previously activated under vacuum at high temperature, is a well documented phenomenon. Some typical examples can be found in ref. (1)-(6). The nature of the electron-donor sites has attracted much attention. Most authors^{1, 4, 5, 7} appear to agree on two main points: (a) the donor centres are surface O^{2-} ions in low-coordination sites and (b) the mechanism of the electron donation is

 $O_{CUS}^{2-} + A \rightarrow O^{-} + A^{\cdot -}$.

A point of some concern with respect to the above mechanism is that whereas the A^- radicals have been detected in several cases, there is as yet no experimental evidence for the simultaneous formation of O^- species. The arguments put forward to explain this result are not completely convincing since O^- species are known to be formed on the surface of alkaline-earth oxides and to possess a stability which allows their detection by e.s.r.⁸ Moreover, Garrone *et al.* have recently proposed a mechanism for anion-radical formation which does not require electron transfer from the solid.⁹

Further experimental work is therefore needed to support these suggestions as to the nature of the electron-donor sites and the electron-donation process.

In the present work, we have studied the adsorption of 9,10-dimethylanthracene, Cl_2 and O_2 (90% ¹⁷O-enriched or non-enriched) on alkaline-earth oxides, Al_2O_3 and SiO_2 - Al_2O_3 . Relying also on O_2 adsorption experiments on ¹⁷O-exchanged CaO

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surfaces, we have been able to show that: (a) surface oxygen ions of the oxide participate directly in the electron-donation step and (b) O^- species are formed in this step.

EXPERIMENTAL

MATERIALS

High surface area MgO, γ -Al₂O₃ and SiO₂-Al₂O₃ (alumina content 25%) were prepared as previously described.^{1, 10} BaO, SrO and CaO were prepared by decomposition of the carbonates (Erba, RP) at 1173 K (CaO) or at 1273 K (BaO and SrO) under vacuum. B.E.T. surface area values (m² g⁻¹), determined by Kr adsorption at 77 K, were: MgO (200), CaO (120), SrO (3.6), BaO (0.8), Al₂O₃ (120) and SiO₂-Al₂O₃ (120).

9,10-dimethylanthracene (DMAN) and n-hexane were of Reagent grade and were further purified by distillation (n-hexane) or by recrystallization (DMAN). O₂ and Cl₂ were dried before admission to the adsorption chamber. High-purity non-enriched O₂ ('Air Liquide' 99.95%), 90%¹⁷O-enriched O₂ (Yeda, Israel) and Cl₂ (Matheson) were used without further purification.

APPARATUS AND PROCEDURE

A weighed amount of specimen (*ca.* 0.1 g) was placed in a silica bulb equipped with a side e.s.r. tube. Samples were activated under vacuum for 5 h at 1173 K (MgO and CaO), at 1273 K (SrO and BaO) or at 1000 K (γ -Al₂O₃ and SiO₂-Al₂O₃) before exposure to O₂, Cl₂ or DMAN, generally at 298 K. Volumetric determinations of oxygen adsorption were performed by contacting the activated samples with O₂ at a pressure of *ca.* 50 Pa. Pressure readings were made with a differential pressure transducer (MKS, Baratron) capable of detecting variations of 0.1 Pa. The adsorption was considered complete when two successive readings at 5 min intervals did not differ by > 0.5 Pa. Total adsorption and irreversible adsorption (molecule m⁻²) were determined as described below.

Solutions of DMAN in n-hexane $(10^{-2} \text{ mol dm}^{-3})$ were evacuated at room temperature and successively contacted with the activated samples by means of a break-seal system.

¹⁷O-exchanged CaO samples were prepared by heating CaO samples, previously activated under vacuum, in the presence of 90% ¹⁷O-enriched oxygen. The extent of isotopic exchange was monitored by gas-phase analysis on a mass spectrometer (VG, Micromass 601).

The e.s.r. spectra were recorded at X-band frequencies on a Varian E-9 spectrometer. The absolute number of spins was determined from electronically integrated spectra using Varian 'strong pitch' $(3 \times 10^{17} \text{ spin m}^{-1})$ as a standard.

RESULTS

ADSORPTION OF 9,10-DIMETHYLANTHRACENE (DMAN)

Upon adsorption from a solution of n-hexane, an e.s.r. signal consisting of seven main lines with a splitting of *ca*. 7.6 G* is observed on $SiO_2-Al_2O_3$, previously activated under vacuum at 1000 K [fig. 1, spectrum (*a*)]. Each line of the spectrum is further resolved into a multiplet with a splitting of *ca*. 3 G. The signal corresponds to *ca*. 4×10^{15} spin m⁻².

CaO, activated under vacuum at 1173 K, gives, upon adsorption from the same solution as above, an e.s.r. signal [fig. 1, spectrum (b)] showing a poorly resolved sequence of lines with a splitting of ca. 2 G. The signal intensity corresponds to 1.6×10^{15} spin m⁻².

 γ -Al₂O₃, activated at 1000 K, and MgO, activated at 1173 K, give weak and structureless e.s.r. signals.

In table 1 the hyperfine proton-coupling constants of DMAN radicals chemisorbed on the surface of CaO and $SiO_2-Al_2O_3$ are compared with those of the radical cation and anion in solution. The comparison shows that an anion radical forms on the surface of CaO and a cation radical on the surface of $SiO_2-Al_2O_3$.

* 1 G = 10^{-4} T.

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FIG. 1.—E.s.r. spectra recorded at 77 K on (a) $SiO_2-Al_2O_3$ and (b) CaO after contacting the samples at 298 K with a solution of 9,10-dimethylanthracene in n-hexane.

TABLE 1.—HYPERFINE PROTON-COUPLING CONSTANTS OF 9,10-DIMETHYLANTHRACENE RADICA	LS
CHEMISORBED ON OXIDE SURFACES AND IN SOLUTION ^a	

radical	CH ₃ 9–10	H 1-4	H 2–3	H 1, 2, 3, 4	ref.
cation in solution	8.00	2.54	1.19		11
anion in solution	3.88	2.90	1.52		11
chemisorbed on SiO ₂ -Al ₂ O ₃	7.6			3.0	this work
chemisorbed on CaO	(4.0)			2.0	this work

^a Hyperfine constants are expressed in gauss (1 G = 10^{-4} T). Estimated error: ± 0.1 G.

ADSORPTION OF CHLORINE

Upon adsorption of Cl₂ at 298 K on alkaline-earth oxides, previously activated under vacuum at 1173 K, a two g-value e.s.r. signal is observed ($g_1 = 2.002$ and $g_2 = 2.010$). The e.s.r. spectra recorded at 77 K are collected in fig. 2: MgO [spectrum (a)], CaO [spectrum (b)] and SrO [spectrum (c)]. A nearly identical signal has been

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FIG. 2.—E.s.r. spectra recorded at 77 K on (a) activated MgO, (b) CaO and (c) SrO, after exposure to chlorine at 298 K.

observed by Kibblewhite and Tench¹² upon adsorption of Cl_2 on MgO. The species will be hereafter referred to as O_n^{n-} , the assignment being discussed below. The presence of an additional set of low-intensity lines in the low-field side of the spectra, clearly visible on the CaO sample [fig. 2, spectrum (b)], suggests the formation of a second paramagnetic species which probably contains chlorine atoms. Although an identification of this species is not possible, the formation of the Cl_2^- radical can be ruled out.¹³ Adsorption of Cl_2 at a lower temperature (146 K) also fails to give Cl_2^- .

OXYGEN RADICALS ON CaO

Upon adsorption of O_2 (non-enriched) at 298 K on CaO activated under vacuum at 1173 K, a two g-value signal ($g_1 = 2.0020$, $g_2 = 2.013$) was observed in the e.s.r. spectrum recorded at 77 K in the presence of 0.1 kPa of O_2 in the gas phase [fig. 3, spectrum (a)]. The signal is the same as that observed after Cl_2 adsorption on the alkaline-earth oxides and will be therefore designated as O_n^{n-} . The spectrum of this species is broadened at higher oxygen pressure. In particular, the half-height linewidth of the sharp component at $g_1 = 2.0020$ doubles when the oxygen pressure is increased



FIG. 3.—E.s.r. spectra recorded at 77 K on CaO samples, previously activated under vacuum at 1173 K, after exposure to oxygen at 298 K. Adsorption of non-enriched O₂: (a) in the presence of O₂ in the gas phase and (b) after evacuation at 298 K. Adsorption of 90% ¹⁷O-enriched oxygen: (c) in the presence of O₂ in the gas phase and (d) after evacuation at 298 K. Adsorption of non-enriched O₂ on ¹⁷O-exchanged CaO: (e) in the presence of O₂ in the gas phase and (f) after evacuation at 298 K.

from 0.1 to 1 kPa. After removal of the gas-phase O_2 by evacuation at 298 K, the e.s.r. signal becomes much more complex. The spectrum observed in these conditions was previously shown to arise from three different surface species: O_2^- , O_3^- and $O_n^{n-.14}$ The three g-value signal of the O_3^- species ($g_1 = 2.0023$, $g_2 = 2.0095$ and $g_3 = 2.0185$) is shown in fig. 3 [spectrum (b)]. As previously reported, the O_2^- and O_3^- species are not detected in the presence of oxygen in the gas phase because of the presence of well known strong broadening effects.

Upon adsorption of O₂ (90%¹⁷O-enriched) on a CaO sample, thermally activated as described above, a spectrum identical to that obtained after adsorption of non-enriched O_2 was observed in the presence of O_2 in the gas phase [fig. 3, spectrum (c)]. By contrast, after removal of O_{2} at 298 K, the spectrum appears to be drastically modified. In particular, in the central region of the spectrum [fig. 3, spectrum (d)] the three components of the O_3^- species, which dominated the spectrum after adsorption of non-enriched O_2 [spectrum (b)], are now absent. Thus, with ¹⁷O-enriched O_2 , the central parts of the spectra recorded in the presence or in the absence of oxygen differ very little: namely, only the lines of the O_n^{n-} species are clearly visible [compare spectra (c) and (d)]. This result demonstrates that the species O_n^{n-1} is also present after removal of oxygen at 298 K. The O_n^{n-} signal is not observed in spectrum (b), being obscured by the more intense signal of the O_3^- and O_2^- species. An important difference with respect to spectrum (b) is the presence in spectrum (d) of a set of six low-intensity lines with a splitting of ca. 5 G. These lines are most probably some of the hyperfine components of the O₃⁻ species. Indeed, according to the analysis made by Tench,¹⁵ the species $({}^{16}O_{s} - {}^{17}O_{b} - {}^{17}O_{c})^{-}$, where O_{s} is a lattice oxygen of the surface, should give a spectrum consisting of 36 lines centred around g_1 with $A_b^1 = 108$ G and $A_c^1 = 70$ G.



FIG. 4.—E.s.r. spectrum recorded at 77 K on CaO after exposure to 90% ¹⁷O-enriched oxygen. The details of the central part of the spectrum (out of the scale in this figure) are shown in fig. 3, spectrum (d).

These lines could not be detected because of their low intensity. However, as $A_b^2 = A_b^3 = 15$ G and $A_c^2 = A_c^3 = 10$ G around g_2 and g_3 , two sets of 24 lines should be obtained with a splitting of *ca*. 5 G.

In the spectrum recorded under vacuum, the simultaneous presence of the species O_2^- is shown by the persistence of the line at g = 2.10 (g_z -component) and by the fact that, with higher receiver gain, 11 lines centred around g_x are observed (fig. 4). The A_x -value (75 G) is in good agreement with that reported (76 G) by Che *et al.* for O_2^- on pyridine-promoted CaO.¹⁶

Adsorption of O_2 on ¹⁷O-exchanged CaO samples

Prior to oxygen adsorption, a CaO sample was exchanged with $90\%^{17}$ O-enriched oxygen. Three successive portions of enriched O_2 (2.4×10^{-4} mol) were contacted at 1173 K for 2 h with a CaO sample (oxygen content 4.9×10^{-4} mol, expressed as O_2) previously activated under vacuum for 5 h at 1173 K. The final extent of exchange was $26\%^{0}$ of the total oxygen content (surface and bulk) in the CaO sample. The CaO was further activated under vacuum at 1173 K for 1 h and then exposed to non-enriched O_2 at 298 K. The spectra recorded at 77 K in the presence of O_2 [spectrum (e)] and after removal of O_2 [spectrum (f)] are reported in fig. 3. Spectrum (e) (species O_n^{n-}), when compared with spectra (a) and (c), shows three main differences: (i) a marked broadening of the line at $g_1 = 2.0020$, (ii) the appearance of a new line at g = 2.028 and (iii) a decrease by a factor 2 of the signal intensity (from integrated spectra). The relative intensities of the three components of spectrum (e) are unaffected by varying the microwave power.* In the spectrum recorded under vacuum [spectrum (f)] the O_3^{-} signal is again visible and the component of the O_n^{n-} species at g = 2.028 is still present.

* An expanded spectrum recorded with higher receiver gain does not show additional lines.

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The ¹⁷O-exchanged CaO sample was successively contacted with a large excess of non-enriched O₂ at 1173 K for 6 h, evacuated at 1173 K for 1 h and then exposed to non-enriched O₂ at 298 K. Spectra (a) and (b) were obtained. In particular, the line at g = 2.028 disappeared and the intensity of the O_nⁿ species was restored.

OXYGEN RADICAL ON OTHER OXIDES

The formation of oxygen radicals on MgO, thermally activated under vacuum, has been investigated previously.¹⁷ The main results can be summarized as follows. After O₂ adsorption, MgO samples, activated at 1173 K, show a weak signal from the O_nⁿ⁻ species. The formation of O₂⁻ and O₃⁻ observed in some cases is strongly dependent on the previous history of the sample: pre-exposure to H₂¹⁷⁻¹⁹ and different thermal treatments in air, such as quenching or annealing of the samples after heating at high temperature.²⁰

On adsorption of O_2 at 298 K on SrO, activated *in vacuo* as for the other alkalineearth oxides, no e.s.r. signals are observed. However, if adsorption is carried out at 146 K, the signals of O_2^- and of O_3^- (the latter in trace amounts) appear. On leaving the sample for a few hours at room temperature the signals disappear, indicating a lower stability of these species on the surface of SrO as compared with MgO and CaO.

No e.s.r. signals are observed when O_2 is adsorbed on BaO, γ -Al₂O₃ and SiO_2 -Al₂O₃.

VOLUMETRIC MEASUREMENTS OF O_2 Adsorption

A measurement of more strongly bound oxygen (irreversible oxygen) was taken as follows. O₂ was first adsorbed at 298 K on samples activated under vacuum at 1023 K (γ -Al₂O₃ and SiO₂-Al₂O₃), at 1173 K (MgO and CaO) or at 1273 K (BaO and SrO).

sample	irreversible oxygen ^a $/10^{-15}$ molecule m ⁻²	oxygen radicals /10 ⁻¹⁵ spin m ⁻²	
BaO	1600	0.0	
SrO	170	1 ^{b, c}	
CaO	14	7°	
MgO	0.5	0.0^d	
$\gamma - Al_2O_3$	0.2	0.0	
SiO ₂ -Al ₂ O ₃	0.2	0.0	

TABLE 2.—OXYGEN ADSORPTION AT 298 K

^{*a*} Amount of oxygen not desorbed by evacuation for 10 min at 298 K. ^{*b*} Concentration of radicals obtained by adsorption at 146 K. No radicals were formed at 298 K. ^{*c*} Simultaneous formation of O_2^- and O_3^- ($O_2^- = 5.5 \times 10^{15}$ and $O_3^- = 1.5 \times 10^{15}$) on CaO. On SrO the species O_3^- is present in trace amounts. ^{*d*} In some cases O_2^- and O_3^- are also formed on MgO (for details see the references quoted in the text).

The amount of O_2 determined in this way will be called total oxygen. Subsequently, the samples were evacuated for 10 min at 298 K, and a seond portion of oxygen was adsorbed, always at 298 K. The amount of oxygen adsorbed in this last experiment will be called reversible oxygen. The difference between the total adsorption and the reversible amount is the irreversible oxygen reported in table 2. Table 2 also lists the concentration of oxygen radicals as determined by e.s.r.

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DISCUSSION

ELECTRON ACCEPTOR-DONOR PROPERTIES OF OXIDES

The formation of the radical cation of DMAN on the surface of $SiO_2-Al_2O_3$ and that of the radical anion on the surface of CaO provide new and definitive evidence for the existence of a correlation between electron acceptor-donor properties of oxides and their acid-base properties. In fact, previous work from our group has shown that the concentration of the negative radical of nitrobenzene (NB), formed by adsorption of NB on the surface of oxides, monotonically decreases when the oxides are taken in the order of their decreasing basicity (BaO > SrO > CaO > MgO > Al_2O_3 > SiO_2-Al_2O_3).^{10, 21} Moreover, the concentration of positive radicals of hexamethylbenzene (HMB) increases when the oxides are taken in the same order of basicity given above.²¹ Namely, the higher the basicity of an oxide, the higher its electron-donor properties on the one hand, and the lower its electron-acceptor properties on the other.

Conversely, when the concentration of the radicals of perylene (PE), anthracene (AN) and naphthalene (NA) is considered for the same oxides (again listed in the order given above), there is a minimum in the radical concentration on oxides of intermediate basicity (MgO and Al₂O₃).²¹ This behaviour may be explained using the assumption that radical anions of PE, AN and NA are formed on the surface of strongly basic oxides (BaO, SrO and CaO) whereas radical cations are formed on strongly acidic oxides (SiO₂-Al₂O₃). However, for alternant hydrocarbons, such as PE, AN and NA, the spectroscopic differences between their anion and cation radicals are small, both in the e.s.r. and electronic spectra.²² Therefore, in view of the poor resolution of powder spectra, an unambiguous assignment of the radicals cannot generally be made on the basis of spectroscopic evidence alone. The above considerations account for some difficulties encountered in the assignment of the e.s.r. spectrum of PE chemisorbed on the surface of Al₂O₃.^{23, 24} In particular it is rather difficult to decide whether the radical anion or the radical cation of PE is formed. The situation is much simpler with DMAN in view of the large difference (a factor of ca. 2) in the hyperfine coupling constants of the methyl protons for the radical anion as compared with the radical cation (table 1). Thus (i) the formation of the radical cation of DMAN on $SiO_2-Al_2O_3$, (ii) the formation of the radical anion on CaO and (iii) the lack of formation of such radicals on MgO and Al_2O_3 are in agreement with the trend observed with PE, AN and NA on the same oxide surfaces.²¹ The results also provide evidence for the general statement that radical anions are formed by adsorption of PE, AN and NA on basic oxides and radical cations on acidic surfaces.

NATURE OF THE ELECTRON-DONOR SITE

The simplest way to visualize the formation of negative radicals on the surface of oxides is to invoke a direct electron-transfer process from a surface site toward a given acceptor molecule (O_2 , Cl_2 , nitrobenzene, *etc.*). As far as the nature of the electron-donor sites on alkaline-earth oxides is concerned, most authors agree that these consist of surface O^{2^-} ions in low-coordination sites ($O^{2^-}_{CUS}$).^{1,4,5,7}

Recently, Garrone *et al.* have proposed a different mechanism to explain the formation of anion radicals on the surface of alkaline-earth oxides.⁹ According to these authors, the anion radicals can be formed without any electron transfer from the solid. In fact, an XH molecule (*e.g.* a hydrocarbon) with a large enough electron affinity can be heterolytically chemisorbed on a surface ($Me^{2+}O^{2-}$) site leading to species $Me^{2+}X^-$ and OH_s^- . Subsequently, the carbanion can transfer an electron to a second XH molecule leading to the anion radical XH⁻⁻. Note that both mechanisms require the participation of O_{CUS}^{2-} sites. These surface centres are Lewis base sites, although

they act as a source of one electron only, in the first case, and Brönsted base sites, in the second case. Accordingly, a correlation between electron-donor properties and basicity of the surface is expected in both cases.

In our opinion, the mechanism proposed by Garrone et al.⁹ might well be operating with specific molecules and satisfactorily explain the sensitizing effect of pyridine and other molecules in promoting the formation of O_2^- on alkaline-earth oxides, but the participation of O_{CUS}^2 in the electron-donor process emerges in the present study, as will be illustrated below. In particular, the species O_n^{n-} and O_3^- will be shown to originate from O⁻ species which are the first product in the oxidation of the electron-donor centre O_{CUS}^2 . It is therefore convenient to consider first the main features of the O_n^{n-} species:

1. The centre is on the surface (or very near to it), as shown by the fact that its e.s.r. signal is substantially broadened on increasing the O₂ pressure.

2. The centre contains oxygen atoms since the e.s.r. signal is different on the 'natural' CaO as compared with the ¹⁷O-exchanged sample. On this latter sample, the broadening of the signal, the appearance of a new, broad component and the decrease of intensity are thought to arise from hyperfine interactions with ¹⁷O.

3. The centre originates from an oxygen species already present on the CaO sample after activation. The same signal is in fact obtained whether O₂ or Cl₂ is adsorbed. An identical signal is obtained upon ${}^{16}O_2$ or ${}^{17}O_2$ chemisorption.

In principle, three possible species could account for the above features: O^- , O_2^{2-} and O_3^{3-} . Species O_n^{n-} with n odd and > 3, also possible in principle, do not appear likely.

The O⁻ species can be ruled out in view of the following two main points. First, the e.s.r. spectrum of the species O⁻, previously detected on alkaline-earth oxides,^{8, 25} shows features which do not agree with those of the O_n^{n-} signal. In particular, the g-values are substantially different: 2.047 and 2.0014 for O^- as compared with 2.01 and 2.0020 for O_n^{n-} . Secondly, the O⁻ species readily reacts with O₂ leading to the species O_3^- and, therefore, cannot be observed in the presence of O_2 .

The species $O_2^{2^-}$ can also be ruled out. Two possibilities must be considered: (a) the species is the diamagnetic peroxy ion and (b) the species contains two unpaired electrons $(O^- \cdots O^-)$. In the first case no e.s.r. signal should be detected, whereas in the second case the molecule is in a triplet state. However, the e.s.r. spectra of the species $O^- \cdots O^-$ (V° centres), previously observed in MgO single crystals,²⁶ are rather different from the spectrum we observe for O_n^{n-} . In particular, due to a very large D-term (> 200 G), separated e.s.r. lines are observed for the V^o centre.²⁶

In the light of the above arguments, the O_3^{3-} species appears to be the most suitable model for the centre under discussion. O_3^{a-} centres, consisting of a triangular array of O^- species, are thought to be placed either on (111) surface micro-planes, which are formed during the activation of alkaline-earth oxides under vacuum at high temperature, or more simply on the corner of the oxide particle.7, 20

A mechanism for O_2 adsorption on alkaline-earth oxides can now be considered. The following sequence of surface reactions is proposed:

$$O_{CUS}^{2-} + O_2(g) \rightarrow O_2^- + O_{CUS}^-$$
(1*a*)

$$2 O_{\rm S}^{2-} + O_2(g) \to 2 O_2^{2-} \tag{1b}$$

$$O_{CUS}^{-} + O_2(g) \to O_3^{-} \tag{2a}$$

$$2 \operatorname{O}_{\mathrm{CUS}}^{-} \to \operatorname{O}_{2}^{2^{-}} \tag{2b}$$

$$3 \operatorname{O}_{\mathrm{CUS}}^{-} \to \operatorname{O}_{3}^{3-} \tag{2c}$$

$$O_2^{2-} + O_2^{2-} \to 2 O^{2-} + O_2(g).$$
 (3)

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The mechanism is based upon the detection by the e.s.r. technique of O_2^- [step (1 a)], O_3^- [step (2a)] and O_3^{3-} species [step (2c)]. The formation of diamagnetic species, O_2^{2-} [steps (1b) and (2b)] and O^{2-} [step (3)] is inferred from a comparison of the adsorption data, as determined by the volumetric method, with the concentration of radicals (table 2). The data of table 2 also suggest that reaction (1b) is prevalent with respect to reaction (1a) on the surface of BaO and SrO, in agreement with the more pronounced tendency of these materials to give peroxides. Accordingly, O^{2-} surface ions taking part in reactions (1a) and (1b) are designated by different symbols, respectively O_{CUS}^{2-} and O_{S}^{2-} , to underline the fact that whereas a large fraction of them can participate to step (1b) (such as, for instance, on BaO), only those in lowcoordination sites are active in step (1a). Following step (1a), the electron-donation step, the O⁻ ions formed undergo surface reactions (2a), (2b) and (2c). The occurrence of these reactions accounts for the lack of O⁻ detection by e.s.r. However, the detection of O_3^- and O_3^{3-} species strongly supports the suggestion that O^- ions are formed first. Moreover, in the case of CaO, which may be studied in a more quantitative way, the concentrations of O_2^- , O_3^- and O_3^{3-} are consistent with the stoichiometry of the adsorption scheme. In particular, from step $(1a) [O_2^-] = [O^-]$ and from steps (2a) to $(2c), [O^{-}] = [O_{3}^{-}] + 2[O_{2}^{2-}] + 3[O_{3}^{3-}] (5.5 \times 10^{15} > 1.5 \times 10^{15} + 3 \times 0.6 \times 10^{15}).$ Finally, step (3) accounts for possible formation of O^{2-} species by surface migration of peroxy ions and O₂ desorption from particular sites (near to kinks, edges or corners).

	$C/10^{-15}$	spin m ⁻²	
sample	O ₂	Cl ₂	
 SrO		10	
CaO	0.6	2	
MgO	0.2	0.8	
Al ₂ O ₃	0.0	0.0	

TABLE 3.—CONCENTRATION OF SPECIES O_3^{3-} AFTER O_2 or Cl_2 adsorption at 298 K

Finally, we briefly consider the concentration of O_3^{3-} species formed on the surface of oxides after adsorption of Cl_2 or O_2 (table 3). As expected from the electron-affinity values, the concentrations obtained upon Cl_2 adsorption are higher than those obtained with O_2 . Furthermore, the concentration of O_3^{3-} is found to decrease monotonically in passing from SrO to γ -Al₂O₃. This finding is relevant in view of the fact that the O_3^{3-} concentration is expected, on the basis of the mechanism proposed here, to be proportional to the concentration of O_{CUS}^{2-} donor sites. Therefore, the concentration of O_3^{3-} can be regarded as a rough measure of the concentration of the electron-donor sites. Thus, the correlation between electron-donor properties and surface basicity, previously found to rely on the concentration of electron-donor sites.

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