

as their permeability, to a degree associated with fully swollen polymers. The potential application of such membranes is evident in areas such as dialysis, ion-exchange, reverse osmosis and other separation processes.

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Non-dissociative Reaction of Oxygen with Metals

DURING our matrix isolation studies of the infrared spectra and structures of molecular species in metal oxide vapours¹⁻⁴, we have made some observations that are of interest in a completely different context—the primary reaction step in metallic corrosion.

Gaseous metal oxides may be formed readily as high temperature vapour species, either by heating the solid oxide or by passing oxygen gas at low pressures over the heated metal. Using both these methods we have obtained infrared spectra assignable to molecules M_xO_2 ($M=Ge, Sn, Ga, In, Tl$). Mass spectrometric evidence⁵ suggests that M_xO_2 molecules may be important components of the vapours in numerous systems. Evidence that our species contain two equivalent oxygen atoms is based, in part, on the effect of ¹⁸O-enrichment of the parent oxides, which then produce three isotopic molecules on vaporization: $M_x^{16}O^{16}O$, $M_x^{16}O^{18}O$, $M_x^{18}O^{18}O$.

When mixtures of ¹⁶O₂/¹⁸O₂ gas, containing negligible amounts of the molecule ¹⁶O¹⁸O, are passed over heated germanium, tin, gallium or indium, the spectra produced are identical with those obtained from the ¹⁸O-enriched solid oxides, and prominent infrared bands are observed for the three isotopic species. Isotope scrambling therefore takes place in the formation of the oxide molecule. When the same gaseous mixture is passed over heated thallium, however, virtually no $Tl_x^{16}O^{18}O$ is produced, although $Tl_x^{16}O^{16}O$ and $Tl_x^{18}O^{18}O$ are readily identified (Fig. 1b). When the experiment is repeated with partially equilibrated oxygen gas, containing significant amounts of ¹⁶O¹⁸O, the corresponding mixed oxide is observed (Fig. 1c). These spectra may be contrasted with that obtained from vaporization of solid thallium oxide, where complete randomization occurs (Fig. 1a).

We are therefore led to the inescapable conclusion that, in the formation of the oxide molecule Tl_xO_2 by direct oxidation of the metal, both the oxygen atoms must be derived from the same molecule of oxygen. Chemisorption of oxygen on metals is almost invariably dissociative, so that oxygen isotopes are randomized in the formation of volatile polymeric oxide species. On thallium, the initial chemisorption step seems to be non-dissociative.

Dissociative adsorption of any diatomic reactant (O₂, S₂, and so on) implies a sufficiently high energy of formation of the initial adsorption complex. Ehrlich⁶

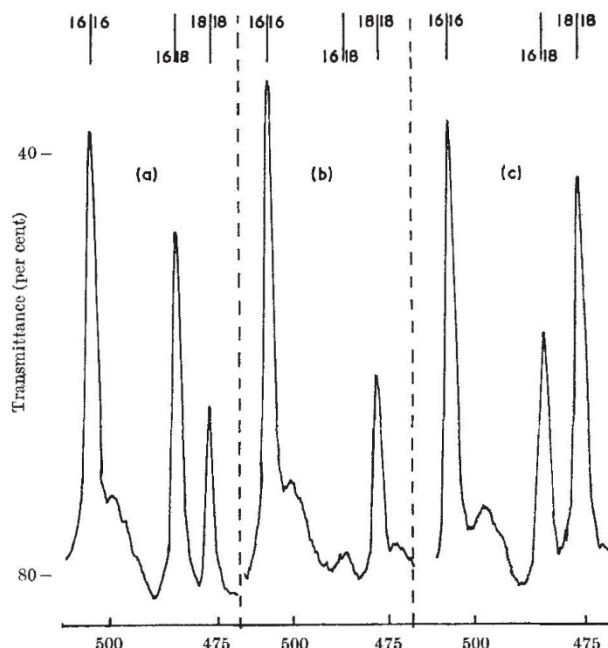


Fig. 1. Infrared spectra (cm^{-1}) of thallium oxide species obtained from (a) solid Tl_2O labelled with ^{18}O ; (b) $^{16}O_2/^{18}O_2$ mixture over heated Tl metal; (c) $^{16}O_2/^{18}O^{16}O/^{18}O_2$ mixture over heated Tl metal.

has suggested that, if the adsorption energy is great enough, one atom may be trapped at the site of primary adsorption while part of the adsorption energy is transferred, as translational energy, to the second atom. This then migrates several unit spacings across the surface before it is bound. Isotope scrambling is a necessary consequence of such a process. There is too little information about the adsorption energy of oxygen on metals to warrant any wide comparison between the elements, but it may be surmised that there must be a critical value, below which the act of chemisorption is non-dissociative. In the absence of such data, the enthalpy of formation of the oxides might be taken as a crude measure of the metal-oxygen interaction energy within any one group. For group IIIB, the ΔH_f° values (kilocalories/g atom oxygen) are

$$Ga_2O, -82; 1/3 In_2O_3, -74; Tl_2O, -42; \\ 1/3 Ga_2O_3, -86$$

On this basis it might be predicted from the thermochemical data that few other metals would show the same behaviour as thallium. It may be relevant, however, that Michell and Smith⁷ have shown that the oxidation of cadmium in air forms CdO_2 , not CdO . Here, too, the chemisorption step involves electron transfer to molecular oxygen, without dissociation. In most cases this may be a very transient precursor stage; in a few cases the reaction products reveal it.

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