

obtain complete reaction in a reasonable time. After refluxing the supernatant was intensely coloured, but evaporation to dryness showed that in fact it contained very little rhenium and the bulk of the product was formed as a black solid. After centrifuging, the solid was vacuum dried and analysis showed the material to be rhenium tetrachloride. Found: Re, 56.7; Cl, 43.3; required for ReCl_4 : Re, 56.8; Cl, 43.2.

Rhenium tetrachloride is a black solid which closely resembles the tetraiodide and tetrabromide. It is readily hydrolysed in moist air and all manipulations have to be performed in a dry box. On hydrolysis the compound forms some hydrated dioxide, but, like technetium tetrachloride, it does not completely hydrolyse to the dioxide since some colour remains in solution. Even on boiling with nitric acid and silver nitrate variable chlorine analyses were obtained, and it was found necessary to fuse the material with sodium hydroxide-sodium peroxide mixtures to obtain reproducible analytical results.

Although rhenium tetrachloride appears to be crystalline we were unable to obtain an X-ray diffraction pattern by the Guinier technique.

The magnetic properties of the compound are interesting; between 300°K and 220°K the Curie-Weiss law is obeyed but below 220°K the susceptibility rapidly increases. For the high-temperature points $\theta = 158^\circ$ and $\mu_{\text{eff}} = 1.55$ Bohr magnetons. This result may be compared with the value of 0.9 Bohr magnetons obtained for rhenium tetraiodide⁷ and probably indicates that the compounds are not magnetically dilute.

Rhenium tetrachloride is thermally unstable; gentle heating in vacuum leads to evolution of rhenium hexachloride. Rhenium metal is the final product after heating at 400° under vacuum.

These preliminary results show that rhenium tetrachloride resembles rhenium tetraiodide and tetrabromide closely, but it is quite different from its technetium analogue which is thermally stable⁸ and has quite different magnetic properties⁹.

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Shift of the Acceptor Absorption Spectrum in $n-\pi$ Charge Transfer Complexes

It has been well established¹⁻⁴ that in $n-\pi$ charge transfer complexes with iodine as the acceptor the absorption band of the free iodine at about 520 nm is shifted to shorter wave-lengths in the complexes. The magnitude of the shift can be roughly correlated with the heats of formation of the different iodine complexes⁴. It has also been shown that in $n-\pi$ complexes with chloranil as the acceptor the absorption band of free chloranil at about 285 nm is shifted to longer wave-lengths in the complexes^{5,6}. $n-\pi$ complexes with chloranil in highly polar solvents exhibit the spectrum of the chloranil negative ion⁷. It has been suggested⁸ that in these cases charge transfer is complete

in the ground-state. The principal absorption bands of the chloranil negative ion lie to the long wave-length side of the absorption bands of the chloranil, while the absorption bands of the I_2 negative ion lie to the short wave-length side of the band of the I_2 molecule. It has been shown that the I_2 negative ion has an absorption band at 400 nm^{9,10}. This appears to be the limit to which the 'Blue shift' of iodine in $n-\pi$ complexes goes⁴. The spectra of some iodine complexes could well be interpreted as due to the presence of the I_2 negative ion stabilized by complete charge transfer in the ground state.

Mulliken¹¹ has interpreted the iodine 'blue shift' as being due to the increased exchange repulsion between the iodine molecule and the donor.

A simpler explanation is suggested. In very weak complexes the acceptor molecule receives very little charge and thus exhibits the absorption bands of the free acceptor molecule. In very strong complexes charge transfer is complete in the ground-state and the acceptor is in fact a negative ion. In medium-strength complexes the acceptor has partial ionic character and thus its absorption represents an intermediate state between the molecule and the negative ion. The fractional shift of the acceptor band is thus a measure of the amount of charge transfer taking place. In terms of Mulliken's representation¹² of the ground-state of the complex by the wave-function:

$$\psi_N = a \psi_{(DA)} + b \psi_{(D^+A^-)}$$

where $\psi_{(DA)}$ is the wave-function of the donor-acceptor pair without strong interaction and $\psi_{(D^+A^-)}$ is the wave-function of the donor-acceptor pair bound by ionic forces, the fraction of charge transfer corresponds to the ratio $(b/a)^2$.

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Labilization of the α -Hydrogen Atom of Generally Labelled Tritiated L- α -Amino-acids in the Presence of Renal D-Amino-acid Oxidase

WE have found that the specific activity of L-amino-acids labelled with tritium, which were isolated after D-amino-acid oxidase treatment of the corresponding generally labelled DL-compound, was much lower than expected. The DL-amino-acids were labelled by exchange with tritiated water in the presence of a platinum catalyst¹, and reverse isotope dilution analysis with both D- and L-carriers² showed that the tritiated amino-acids were labelled in the D- and L-components to the same extent. Paper chromatographic analysis³ confirmed the radiochemical purity (>98 per cent) of the DL-amino-acids, which were afterwards treated with crude D-amino-acid oxidase (hog kidney extract) by well-established techniques⁴. The specific activity of the tritiated compounds was measured by combustion of the compounds in oxygen followed by β -liquid scintillation counting of the tritiated water produced⁵. The radiochemical purity of the isolated L-amino-acids was determined by paper chromatographic analysis and the optical purity by reverse isotope dilution