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Title

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Permalink

<https://escholarship.org/uc/item/4zj8s0t0>

Journal

Science, 155(3763)

ISSN

0036-8075

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Publication Date

1967-02-10

DOI

10.1126/science.155.3763.709

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Source: *Science*, New Series, Vol. 155, No. 3763 (Feb. 10, 1967), pp. 709-710

Published by: American Association for the Advancement of Science

Stable URL: <http://www.jstor.org/stable/1720573>

Accessed: 13-08-2015 18:42 UTC

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Structural Aspects of Reversible Molecular Oxygen Uptake

Abstract. The system $\text{IrX}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in benzene solution adds molecular oxygen reversibly if X is chlorine and irreversibly if X is iodine. The crystal structure of the complex $\text{IrIO}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2 \cdot \text{CH}_2\text{Cl}_2$ is reported here and compared with a previous study of the structure of $\text{IrClO}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$. The O—O bond length is 1.47 ± 0.02 angstroms in the irreversibly oxygenated iodo-compound and 1.30 ± 0.03 angstroms in the reversibly oxygenated chloro-compound.

One advantage of studying synthetic molecular-oxygen carriers is that simple chemical changes can be made and the effects of these changes on the binding of the oxygen molecule can be studied. Perhaps the best-characterized reversible synthetic molecular-oxygen carrier is $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (the Ph stands for C_6H_5) (1), and the structure of the oxygen adduct has been determined (2). A straightforward chemical change is to replace the chlorine in this system with another halogen or pseudohalogen. It turns out that substitution of iodine for chlorine results in a nonreversible molecular oxygen carrier, and here we present the first definitive data on the differences in the geometry of the oxygen molecule when it is bound reversibly and irreversibly to a transition metal.

The reversibility of oxygen uptake of the chloro-compound is readily demonstrated qualitatively. The parent compound in benzene changes color from yellow to orange when oxygen is bubbled through the solution and the oxygen adduct $\text{IrClO}_2(\text{CO})(\text{PPh}_3)_2$ can be crystallized (1). If an inert gas is bubbled through a solution of the oxygen adduct, then the color reverts to yellow and the parent compound can be crystallized. By comparison, a solution of the parent iodo-compound reacts with oxygen about ten times faster (3) than does the chloro-compound and the reaction is irreversible; that is, no color change occurs upon bubbling an inert gas through the solution, and once oxygen has been bubbled through, only the oxygen adduct may be crystallized. It appears that the lower electronegativity of the iodine atom results in the oxygen molecule being bound more strongly. Having discovered this, we thought it of interest to see if these differences in reversibility and strength of bonding would be manifested in detectable structural changes.

The oxygenated iodo-compound, $\text{IrIO}_2(\text{CO})(\text{PPh}_3)_2$, was obtained as a powder from benzene solution. It was recrystallized from methylene chloride as dark-brown, thick needles containing one molar equivalent of methylene

chloride of crystallization. This material crystallizes in space group $\text{P}2_1/n$ of the monoclinic system with four molecules in a cell of dimensions $a = 10.69$, $b = 22.86$, $c = 15.00$ Å, $\beta = 93.1^\circ$. In all, 5987 nonindependent intensities were measured at room temperature with the use of $\text{CuK}\alpha$ radiation on a Picker automatic diffractometer, by procedures previously described (4). The crystal had been ground to spherical shape and absorption corrections were applied. The structure was solved by a combination of Patterson, Fourier, and least-squares techniques. The final agreement factor $R(= \sum ||F_o| - |F_c|| / \sum |F_o|)$ for the 1573 independent reflections is 7.5 percent.

The inner coordination sphere around iridium is shown in Fig. 1. The coordination is directly analogous to that found in the oxygenated chloro-compound and may be considered to be trigonal bipyramidal if O_2 is considered as a single ligand. As in the chloro-compound, disorder between the halogen and the carbonyl occurs, although because the CH_2Cl_2 molecule is in a position unsymmetrical with respect to the iridium complex, the "half-carbonyl" and "half-iodine" ligands were resolved. (Figure 1, for the sake of simplicity, does not illustrate the disorder.) As in the chloro-compound, the two oxygen atoms are equidistant from the iridium

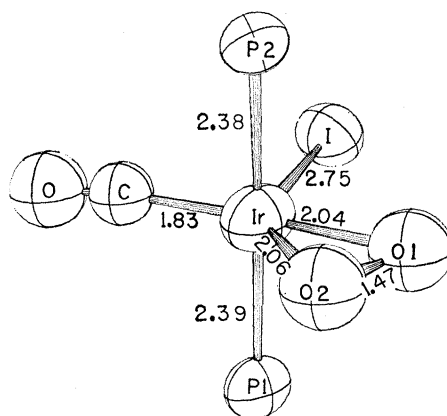


Fig. 1. The inner coordination sphere of $\text{IrIO}_2(\text{CO})(\text{PPh}_3)_2$. The errors of the distances are 0.02 Å or less.

atom, and the distance of iridium to the center of the oxygen molecule does not differ much in the two compounds (1.91 ± 0.02 Å in the iodo-compound, 1.96 ± 0.03 Å in the chloro-compound). However, the O—O distance is distinctly different in the two compounds. It is 1.30 ± 0.03 Å in the reversibly oxygenated chloro-compound; it is 1.47 ± 0.02 Å in the irreversibly oxygenated iodo-compound. The O—O bond length in the oxygenated chloro-compound resembles O_2^- , the superoxide ion, whereas that in the oxygenated iodo-compound resembles O_2^{2-} , the peroxide ion.

The position of the infrared absorption band previously assigned (3) to the O—O stretch is not sensitive to the O—O bond length, in that the band maximum in the chloro-compound occurs at 858 cm^{-1} , compared with 862 cm^{-1} in the iodo-compound, and yet the O—O distances differ by 0.17 Å. This assignment of the band as a pure O—O stretch cannot be correct.

Since practical chemical theory is very much less sophisticated than modern chemical experimentation, the important results of this work must be the demonstration of chemical and structural differences of reversible and irreversible oxygen uptake. Nevertheless, it is of interest to find a model of chemical bonding that can rationalize the observations that oxygen is bound more strongly to the iodo- than to the chloro-compound and that the O—O bond distance in the oxygen molecule is shorter for reversible than for irreversible binding to the metal. Two schemes may be used to describe the bonding between O_2 and iridium in these systems.

The first is directly analogous to that proposed by Griffith (5) for oxygenated heme. The oxygen molecule is considered in an excited singlet state similar to ethylene, and bonding (in this theoretical model) proceeds by donation of electrons from the π -orbital to a vacant orbital on the central metal ion; this sets up a dipole which reduces the extent of the donation. This dipole is simultaneously reduced by back-donation from the central metal ion, using its filled d -orbitals, to the π^* -orbitals of the O_2 group. Thus the strength of attachment of oxygen to the carrier is dependent upon the availability of electrons at the central metal ion, and this suggests that the iodo-compound should bind oxygen more strongly than the chloro-compound. This model predicts that the O—O bond

length should increase, the more strongly bound is the O_2 group, since electrons are being removed from a bonding orbital of O_2 and replaced in an anti-bonding orbital.

The second bonding model that could be applied to this system is that proposed by Parshall (6) for fluoro-alkene derivatives of $IrCl(CO)(PPh_3)_2$. The oxygen species would be O_2^{2-} and this would bond to Ir^{3+} by means of two σ -bonds and no π -bonds. Without further modifications this model does not explain the stronger bonding in the iodo-compound, nor does it predict a change in the O-O bond length on change of ligands to the metal. It appears to us that the first model is more useful in this particular case, and it can be used to make simple predictions: for example, $RhCl(CO)(PPh_3)_2$ does not add oxygen, but perhaps the iodo-compound would. Further experiments are needed to provide more information on bonding schemes and their applicability to different complexes. Specifically, both C_2F_4 (6) and $C_2(CN)_4$ (7)

add to these parent iridium systems, and the structures of these derivatives are under study. In particular, the deviations of the olefin groups from planarity should provide additional insight into the bonding of various ligands, including molecular oxygen, in these complexes.

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25 November 1966

Visual Adaptation to Gradual Change of Intensity

Abstract. *The eye can adapt to the rate of change of brightness. After exposure of the eye to a light that grows gradually brighter, a steady light appears to grow gradually dimmer, and vice versa. A field containing shading gives larger after-effects than a spatially uniform field.*

In the well-known processes of light and dark adaptation, the eye adjusts its sensitivity to the prevailing intensity of illumination. In a new effect reported here, the eye adapts, not to the intensity, but to the rate of change of illumination.

The eye was first adapted by fixating a light which grew gradually brighter. Then the light was switched to a steady intensity, and an aftereffect was seen that appeared to grow gradually dimmer. Conversely, after the eye was adapted to a light that grew gradually dimmer, a light of steady intensity ap-

peared to grow gradually brighter. The effect was confined to the stimulated areas of the retina. The aftereffect from a 30-second adaptation lasted from 1 to 10 seconds.

In practice, it is convenient to vary the intensity in an oscillating, sawtooth wave, so that it brightens or dims repetitively. A single cycle can produce a small aftereffect; many cycles produce a larger one. The brightening or dimming aftereffect is opposite in direction from the slow phase of the sawtooth waveform, and does not itself include any perceived oscillation

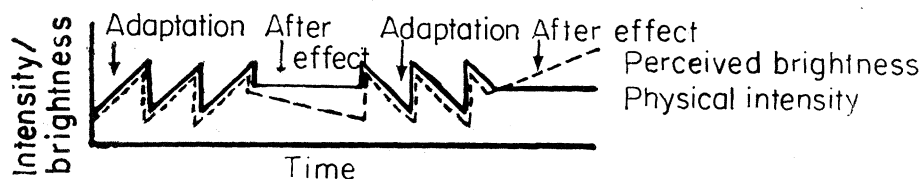


Fig. 1. Adapting light brightens repetitively (solid line, rising sawtooth wave); then, when held at steady intensity (solid horizontal line), it apparently dims (dashed falling line). Or, it dims repetitively (solid line, falling sawtooth wave); then, when it is held steady, it apparently brightens (dashed rising line).

in brightness (Fig. 1). The effect occurs with white light, and with any visible, monochromatic light. Almost any light source can produce the effect. I used Ferranti R1130B glow modulator neon lamps.

The frequency and intensity of the stimulus, and the area stimulated, are not critical. A cycling rate of 1 cycle/sec and an intensity range of 100 to 1 (2 log units) were about optimum. A pinhole source in a dark room caused a minimum effect in some subjects and no effect in others. The same was true for the entire visual field, secured when half a table tennis ball was fitted over each eye and the subject looked straight into the beam of an intensity-modulated projector. With either the pinhole or the entire visual field, the intensity modulation of the stimulus itself was inconspicuous to the subject.

Different parts of the retina can be differently adapted at the same time. A disc was divided into two halves, and each half was lit uniformly and independently by a separate neon lamp. When the two halves varied in intensity in the same direction (both brightening, or both dimming), but out of phase by any angle, then each half of the retina had an aftereffect in the appropriate direction (both dimming, or both brightening). When the two halves varied in phase, but in opposite directions (left half dimming, right half brightening), then each half had an aftereffect in the appropriate direction (left half brightening, right half dimming).

A checkerboard of 1-inch squares (12 by 12) of Polaroid was fixated through a piece of Polaroid which turned steadily through 90° , then returned sharply to 0° , so that the white squares gradually turned black, and vice versa. The appropriate aftereffects were observed in each square.

Contrast can influence the effect. A square subtending a visual angle of 4° and held at a steady intensity, was centered in a square adapting field subtending a visual angle of 45° . The intensity of this field continually increased, following an oscillating, sawtooth waveform. Owing to the contrast in brightness, the steady central square appeared to be continually dimming, in contrast to the surrounding square. After 30 seconds the intensities of both the central square and the adapting, surrounding area were held steady. The surrounding area now appeared to grow dimmer for 10 to 15 seconds, and the