Such variability in behavior from animal to animal is not uncommon. Kare has reported (*4*) that some chicks showed preferences for sapid substances at concentrations which most chicks rejected. Thus when animals are treated as groups, the net result with increasing concentrations may be behavior varying from indifference to avoidance, such that any preferential trend for substances usually considered aversive might be obscured. With attention to individual differences however, preference concentrations were established for eight out of ten mice, avoidance concentrations for six, and for four, both preference and avoidance concentrations.

The evidence puts in question a generally accepted view that specific gustatory stimuli, by virtue of their primary positive or negative reinforcing values, elicit an innate consummatory or avoidance response (*5*). First, we have a bitter stimulus which is acceptable in specific concentrations in preference to water. Second, the relative acceptability is a function of concentration rather than the qualitative nature of the stimulus. And finally, maintenance of preference appears to be dependent on prior experience with the stimulus.

Since in the concentrations tested, SOA is not nutritive and has a negligible effect on osmotic pressure, the preference-avoidance function cannot be directly compared to that obtained for sugars and NaCl. However, the preference for the bitter substance as well as for sugar and salt at low concentrations may be comparable, in that all are acting as weak stimuli capable of eliciting preferential behavior. Certainly, at high concentrations detrimental osmotic effects come into play for both sugar and salt, but for SOA, even at the limit of solubility, the osmotic effects are still negligible.

The biphasic response towards the bitter substance exemplifies Schneirla's concept of orientation based on the quantitative nature of the stimulus (*6*). Accordingly, it is the degree of stimulation which determines behavior that precedes learning; a weak stimulus elicits approach, a strong stimulus withdrawal. The fact that preference or differential intake diminishes for the bitter test substance after the continuous experience of several days suggests that lack of secondary reinforcement and decrease in novelty (habituation) are responsible (*7*).

Roslyn P. Warren
Shimer College, Mount Carroll, Illinois

References and Notes

1. C. Pfaffmann, in *Handbook of Physiology*, J. Field, Ed. (Williams and Wilkins, Baltimore, 1959), vol. 1, sec. 1, p. 507.
2. R. P. Warren and C. Pfaffmann, *J. Comp. Physiol. Psychol.* **52**, 263 (1959); R. P. Warren, unpublished work; R. P. Warren and M. A. Vince, *J. Comp. Physiol. Psychol.*, in press.
3. M. W. Green, *Bull. Natl. Formulary Comm.* **10**, 131 (1942). The breakdown products of SOA, sucrose and acetic acid, would be of negligible nutritive or osmotic effect in the concentrations used. My own recent work indicates that the long-continued preference for the noncaloric "soluble saccharin" may be due to the Na^+ ion present.
4. M. R. Kare, in *The Physiological and Behavioral Aspects of Taste*, M. R. Kare and B. P. Halpern, Eds. (Univ. of Chicago Press, Chicago, Ill., 1961), p. 13.
5. C. Pfaffmann, in *Psychology: A Study of a Science*, S. Koch, Ed. (McGraw-Hill, New York, 1962), vol. 4, p. 403.
6. T. C. Schneirla, in *Nebraska Symposium on Motivation* (Univ. of Nebraska, Lincoln, 1959).
7. The experimental work was done in the Department of Zoology, Howard University.

22 March 1963

Oxygen-Carrying Properties of a Simple Synthetic System

Abstract. *An iridium compound, chloro-carbonyl-*bis*(triphenylphosphine)-iridium, in solution, takes up molecular oxygen—one molecule per metal atom —which is subsequently recovered by reducing the pressure. The adduct is photosensitive but otherwise stable at ambient temperatures. It is a monomeric molecular complex and probably contains a peroxo group with both oxygens bonded to the same metal atom.*

I wish to report an oxygen-carrying synthetic system which stands out in its simplicity and exposes new paths toward explaining and understanding the activation of molecular oxygen by metal complexes (synthetic or natural) or metals.

The oxygen carrier is a coordination compound of iridium, chloro-carbonyl-*bis*(triphenylphosphine)iridium (I), $[IrCl(CO)(Ph_3P)_2]$ (*1, 2*), with a probable molecular structure as shown in Fig. 1*A* (*1, 3*). The compound is insoluble in water and most other polar media (such as alcohols); it is soluble and stable in benzene, in which the reaction cycles have been studied. The oxygenation-deoxygenation equations are formulated in Fig. 2; conditions for the reactions, and stabilities of the reactants are summarized in Table 1.

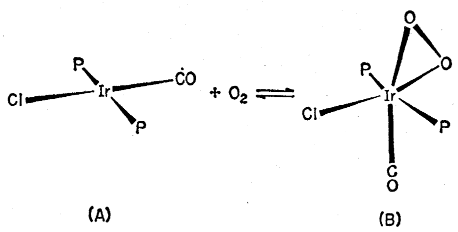


Fig. 1. Diagrams of probable molecular configurations of $[IrCl(CO)(Ph_3P)_2]$ and $[O_2\,IrCl(CO)(Ph_3P)_2]$.

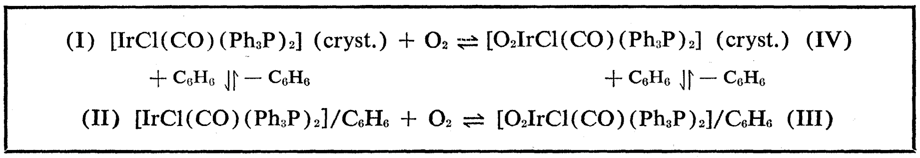
The yellow crystals of the starting complex, $[IrCl(CO)(Ph_3P)_2]$, do not react with oxygen under normal conditions (I→IV). In solution, the compound takes up one molecule of oxygen for each atom of iridium, with a color change from yellow to orange (II→III). The rates of oxygenation are moderate, that is they are considerably slower than those reported for oxygen carriers based on cobalt (*4*). The oxygen uptake has been followed volumetrically and by observing the infrared-spectral shift of the carbonyl group (*1, 5*) (Table 2).

When the oxygen pressure above the solution is reduced, the adduct reverts to the starting material (III→II). Its reappearance has been followed by infrared spectra; simultaneous evolution of molecular oxygen has been verified by gas-chromatographic analysis. Deoxygenation is fairly rapid in boiling benzene, but it is also observed at 25°C (III→II).

The oxygen adduct, $[O_2IrCl(CO)$-

Table 1. Conditions for oxygenation-deoxygenation reactions, and stabilities of the reactants. Roman numerals refer to compounds formulated in the oxygenation-deoxygenation equations.

Reaction	Ir (mole/lit.)	P_{O_2} (mm–Hg)	*T* (°C)	Time (hr)	Conversion (%)
		Oxygenation			
Crystals (I → IV)		150	25	$> 10^4$	0
Crystals (I → IV)		740	25	120	0
Solution (II → III)	10^{-2}	130	25	25	70
Solution (II → III)	10^{-2}	670	27	4	100
(In toluene) (II → III)	6×10^{-3}	740	−78	120	25
		Deoxygenation			
Solution (III → II)	2×10^{-3}	$10^{-4} \rightarrow 5$	25	< 65	20
Solution (III → II)	3×10^{-3}	(~ 0)	80	1	100
Crystals (IV → I)		10^{-5}	25	16	0
Crystals (IV → I)		$10^{-4} \rightarrow 20$	25	240	50
Crystals (IV → I)		10^{-4}	25 → 200	< 1	100



$$\begin{array}{ccc} \text{(I)}\ [\mathrm{IrCl(CO)(Ph_3P)_2}]\ \text{(cryst.)} + \mathrm{O_2} & \rightleftharpoons & [\mathrm{O_2IrCl(CO)(Ph_3P)_2}]\ \text{(cryst.)}\ \text{(IV)} \\ +\mathrm{C_6H_6} \downarrow\uparrow -\mathrm{C_6H_6} & & +\mathrm{C_6H_6} \downarrow\uparrow -\mathrm{C_6H_6} \\ \text{(II)}\ [\mathrm{IrCl(CO)(Ph_3P)_2}]/\mathrm{C_6H_6} + \mathrm{O_2} & \rightleftharpoons & [\mathrm{O_2IrCl(CO)(Ph_3P)_2}]/\mathrm{C_6H_6}\ \text{(III)} \end{array}$$

Fig. 2. Oxygenation-deoxygenation equations.

$(Ph_3P)_2]$, can be crystallized in pure form from the oxygenated solution (III→IV). At ambient temperatures the crystals are relatively resistant to deoxygenation (in vacuum); however, deoxygenation can readily be effected at elevated temperatures (IV→I).

The oxygen adduct is sensitive to light: the surface of the orange crystals slowly changes to green within days or weeks, and finally to blue-black. In the dark, samples have been stored in air unchanged over a year. The irreversible photocatalyzed reaction, observed also in solution, requires the presence of oxygen in order to become clearly observable. The identity of the product has not yet been established; it contains triphenylphosphine oxide and probably an Ir(IV) species. In the virtual absence of oxygen, that is under the conditions of deoxygenation, this photochemical side reaction is slow as compared with the dissociation of the oxygen adduct, so that only the principal reaction (III→II or IV→I) is readily perceptible (*6*).

Repeated cycling of oxygenation-deoxygenation (II←→III) has been carried out thus far only under the conditions favorable for the irreversible oxidation. An experiment of 13 cycles, extending over a period of 20 days, in light, afforded about 70 percent recovery of the starting compound. The system was exposed to oxygen at 670 mm except during brief intervals of deoxygenation at 80°C. Irreversible oxidation as a result of repeated cycling has been reported for all other carriers, but the nature of such reactions has not been established with certainty (*7*).

Table 2. Properties of $[O_2IrCl(CO)(Ph_3P)_2]$.

O	Ir	Cl	P	C	H
		Calculated			
5.9	23.7	4.4	7.6	54.7	3.7
		Found			
5.8	23.4	4.3	7.6	54.9	3.8

Molecular weight: Calculated, 812; found, 808 (in $CHCl_3$); 760 (in C_6H_6).

Conductivity: Λ_M, 0 ohm^{-1} in acetone ($1.6 \times 10^{-4}M$).

Electric dipole moment: 5.9 *D* (in C_6H_6).

Magnetism: diamagnetic (solid: χ_{Ir}, ~ 0, 77° to 367°K; in $CHCl_3$: χ_{Ir}, ~ 0, 300°K).

Infrared spectrum (*cm*$^{-1}$): ν_{IrO_2}, 857 (solid), 860 (solution); ν_{CO}, 2000 (solid), 2014 (solution). (Other bands in the spectrum result from Ph_3P.)

Perhaps the most significant aspect of the present system is that the chemical and physical characteristics of the isolated oxygen adduct can be studied in detail. Table 2 summarizes some of the important properties. Complete elemental analysis, especially direct oxygen determination, establishes the composition of the complex as formulated, substantiating the results of oxygen uptake measurements.

In considering the molecular structure and the type of bonding involving oxygen, several possibilities emerge for the given stoichiometry, but only one appears to be compatible with the available total evidence: it suggests that the oxygen adduct is best formulated as a molecular peroxide of tervalent iridium with both oxygens bonded to the same central atom as shown in Fig. 1*B*.

The presence of a peroxo group is indicated by chemical evidence (positive test for H_2O_2 on acidification). Molecular-weight data, together with conductivity measurements, show that the compound is a nonionic monomer. This eliminates polymeric peroxo-bridged structures as found in numerous cobalt complexes (*8*). The infrared spectrum reveals that the oxygen is not associated with the ligands (for example, triphenylphosphine oxide), nor is it present as a hydroxyl group. The spectrum shows a new strong absorption at 860 cm^{-1}, and this band is suggestive of a triangular metal-peroxo group such as that in some peroxo complexes of chromium (*9*) and titanium (*10*). The diamagnetism of the monomeric compound indicates tervalent iridium. The dipole moment suggests that the phosphines occupy *trans* positions as shown in Fig. 1*B* (*11*). It is interesting to note that in this structure the orientation of oxygen relative to the metal atom is analogous with that suggested by Griffith for oxyhemoglobin (*12*). The oxygenation reaction thus emerges as an oxidation of the univalent (spin-paired d^8) and four-coordinate iridium compound to a tervalent (spin-paired d^6) and six-coordinate iridium peroxo complex (*13*).

The present discovery enlarges the small group of metals (Fe, Co) known to function as oxygen carriers in some of their complexes (*7, 14*). That the present compound, $[IrCl(CO)(Ph_3P)_2]$, also reacts reversibly with molecular hydrogen (*5*) strengthens the suggestion, implicit in this report, that activated complexes in catalysis which are themselves inaccessible to direct or reliable observation may find stable models among synthetic coordination compounds of the third transition series (*15*).

L. VASKA

Mellon Institute,
Pittsburgh 13, Pennsylvania

References and Notes

1. L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.* **83**, 2784 (1961).
2. Ph_3P is $(C_6H_5)_3P$ (triphenylphosphine).
3. The crystal structure of an apparently isostructural compound, $[RhCl(CO)(Ph_3P)_2]$, is being studied by x-rays by Professor L. F. Dahl, University of Wisconsin.
4. A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds* (Prentice-Hall, New York, 1952), pp. 336–357, and references quoted therein.
5. L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.* **84**, 679 (1962).
6. For photochemical effects on other systems, see G. Englesma, A. Yamamoto, E. Markham, M. Calvin, *J. Phys. Chem.* **66**, 2517 (1962).
7. L. H. Vogt, Jr., H. M. Faigenbaum, S. E. Wiberley, *Chem. Rev.*, in press.
8. G. L. Goodman, H. G. Hecht, J. A. Weil, in *Free Radicals in Inorganic Chemistry* (American Chemical Soc., Washington, 1962), p. 90.
9. W. P. Griffith, *J. Chem. Soc.*, 3948 (1962); J. D. Swalen and J. A. Ibers, *J. Chem. Phys.* **37**, 17 (1962).
10. C. C. Patel and G. V. Jere, in *Proc. 71CCC* (Stockholm, 1962), p. 304; G. V. Jere and C. C. Patel, *Canadian J. Chem.* **40**, 1576 (1962), and references quoted.
11. This is consistent with the mechanism of analogous addition reactions; J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).
12. J. S. Griffith, *Proc. Roy. Soc. Ser. A* **235**, 23 (1956).
13. The crystal structure of the compound is being studied by Dr. J. A. Ibers of the Brookhaven National Laboratory.
14. Besides Co and Fe, Ni (*7*) and Mn (*7*) have been claimed to possess these properties.
15. I thank R. E. Rhodes for experimental assistance, Dr. J. A. Laswick for discussions, and the authors of reference 7 for permission to refer to their review paper before publication.

20 February 1963

Stomach Contraction upon Central Vagus Stimulation

After both vagus nerves in the neck of the dog are cut and their central ends are stimulated, contraction of the stomach is seen in many cases. While vago-vagal reflexes are known, this phenomenon, to the best of our knowledge, has not been described.

In acute experiments, 20 fasting male and female mongrel dogs were anesthetized with Nembutal. Both vagus nerves were sectioned high in the neck and their central stumps were stimulated with a Grass stimulator. Esopha-