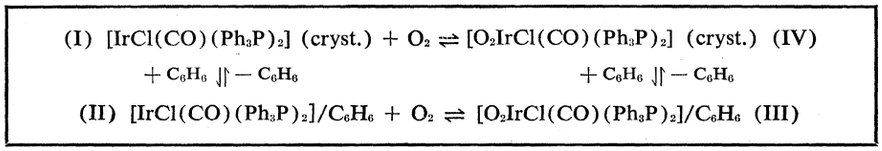

Fig. 2. Oxygenation-deoxygenation equations.

$(Ph_3P)_2]$, 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 $[O_2IrCl(CO)(Ph_3P)_2]$.

Analysis (%)					
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*).

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References and Notes

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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-

geal and gastric motility were recorded through open tubes connected to Statham pressure transducers which recorded on a dynograph; carotid pressure was recorded with the use of a Statham transducer. In 6 of the 20 dogs, stomach contractions of significant extent were seen during, or shortly after, stimulation (Fig. 1). In a number of animals which gave negative results, section of the esophagus and of the vagus nerves just above the diaphragm was followed by gastric contractions upon central-vagus stimulation. In a number of animals showing positive results, that is, gastric contractions upon central vagus stimulation, the height of the contractions increased considerably after section of the esophagus and of the vagi. There was no apparent correlation in the incidence of gastric contractions and changes in respiration or in blood pressure. In order to check the role of sympathetic impulses on gastric motility after stimulation of one or of both central ends of the vagi, the left, the right, or both stellate ganglia were excised; in two dogs, gastric contractions were abolished, while in three dogs, gastric contractions remained unaffected. It seems that pathways of impulses vary in individual animals.

The afferent and efferent pathways of this phenomenon are not known. The vagus is a mixed nerve and central stimulation travels by way of both cholinergic and adrenergic fibers. Beside nervous mechanisms, hormonal effects may play a role.

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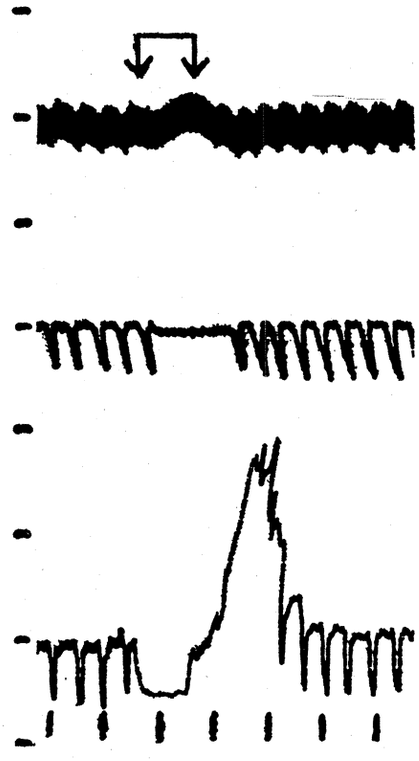

Fig. 1. Effect of stimulation of the central ends of the cut vagus nerves in the neck of a dog (cut at C_4), and esophagus and vagi cut above the diaphragm. Top, blood pressure in millimeters of mercury; center, esophageal motility, respiration is also shown; bottom, gastric motility. Arrows indicate stimulation of central ends of vagus nerves (6 v, 60 cy, 2-msec pulses). Lines on ordinate are in centimeters. Stimulation raised blood pressure 69 mm-Hg; respiration was arrested for 18 seconds; gastric tonus was depressed initially, the latent period of gastric contraction from beginning of stimulation was 18 seconds, maximum height of gastric contractions was 18.7 cm of water, and duration was approximately 20 seconds.

Note

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1 March 1963

Phosphorylase *a* Activity in Uterine Muscle: Stimulation by Ethylenediaminetetraacetic Acid

Abstract. *Injection of ethylenediaminetetraacetic acid into spayed rats or its use in phosphorylase extraction increases the activity of glycogen-phosphorylase* a *in uterine smooth muscle tissue. Since the total phosphorylase activity is not increased, the increase in phosphorylase* a *appears to result from a conversion of inactive phosphorylase* b *to the active form of the enzyme.*

Ethylenediaminetetraacetic acid (EDTA) is used in the extraction of phosphorylase from skeletal muscle since it inhibits the formation of active phosphorylase *a* from the inactive phosphorylase *b* by chelating bivalent metallic ions reported to be essential in this conversion (*1*). Our experiments show that EDTA, either administered to rats or added to the extracting medium, increases the phosphorylase *a* activity in uterine tissue (smooth muscle). Since phosphorylase *a* is believed to be the form of the enzyme that is active in vivo, the small changes in total phosphorylase (*t*) reported below do not appear to be of biological significance.

The uteri of adult spayed female rats were removed and assayed for active phosphorylase *a* and total phosphorylase (*2*). In the experimental groups 60 μmole of EDTA, the calcium or magnesium salt of EDTA, Ca, or Mg per gram of tissue were added to the 0.1*M* NaF solution used in homogenization. The free-acid form of EDTA was used; the *p*H of each solution was adjusted with NaOH to that of the glucose-1-phosphate used in the reaction (*p*H 6.1). Control uteri were homogenized in 0.1*M* NaF.

Table 1. Activity of uterine phosphorylase *a* and *t* after additions to the homogenate of 60 μmole of the materials indicated per gram of tissue, reported as micrograms of P formed from glucose-l-phosphate by 100 mg of tissue in 10 minutes at 37°C. The values given are the mean of at least four determinations with ± S.E. of mean.

Phosphorylase activity (μg P)		Ratio (a/t) × 100
a	*t*	
	Control	
85 ± 9	332 ± 9	26.1 ± 3.0
	Mg or Ca	
83 ± 8	320 ± 4	26.0 ± 6.5
	EDTA	
200* ± 11	298† ± 7	66.7* ± 1.7
	Mg or Ca salt of EDTA	
188* ± 7	298† ± 12	63.4* ± 4.0

* $P < .001$; † $P < .02$.

The effect of the different additions to the homogenate on phosphorylase activity is shown in Table 1. The phosphorylase *a* activity and the *a* to *t* ratio were significantly increased by EDTA. When the calcium or magnesium salt of EDTA was used, the percentage change in phosphorylase activity (both *a* and *t*) was the same as that produced by EDTA alone and the values are combined in Table 1. No effect on uterine phosphorylase activity was observed if $CaCl_2$ or $MgCl_2$ was added in the same concentration; these values are also combined in Table 1.

When the tissue was extracted in a medium containing 0.1*M* NaF and 60μ*M* EDTA and then dialyzed against 0.1*M* NaF, the phosphorylase *a* activity expressed as micrograms of P liberated was 115 as compared with 47 in the controls (average of two determinations). When homogenates of uteri prepared in 0.1*M* NaF were dialyzed against 0.1*M* NaF, subsequent addition of EDTA also increased phosphorylase *a* activity from 50 to 87 μg of P (average of four determinations, $P < .01$). Thus, the increase in phosphorylase *a* activity with EDTA is not dependent upon any dialyzable substance.

The blood concentration of EDTA reaches a maximum 1 hour after an intraperitoneal injection of an EDTA