Kirk-Othmer Encyclopedia of Chemical Technology.

OXO PROCESS

The oxo process, also known as hydroformylation, is the reaction of carbon monoxide (qv) and hydrogen (qv) with an olefinic substrate to form isomeric aldehydes (qv) as shown in equation 1. The ratio of isomeric aldehydes depends on the olefin, the catalyst, and the reaction conditions.

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + R(CH_3)CHCHO \qquad (1)$$

If a double-bond shift occurs, the number of aldehyde isomers is increased.

Synthesis gas, a mixture of CO and H_2, also known as syngas, is produced for the oxo process by partial oxidation (eq. 2) or steam reforming (eq. 3) of a carbonaceous feedstock, typically methane or naphtha. The ratio of CO to H_2 may be adjusted by cofeeding carbon dioxide (qv), CO_2, as illustrated in equation 4, the water gas shift reaction.

$$2\ CH_4 + O_2 \longrightarrow 2\ CO + 4\ H_2 \qquad (2)$$

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2 \qquad (3)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (4)$$

$$2\ CH_4 + CO_2 + O_2 \longrightarrow 3\ CO + 3\ H_2 + H_2O \qquad (5)$$

The overall process for producing a 1:1 CO to H_2 ratio by partial methane oxidation and the water gas shift reaction is represented by equation 5.

2 OXO PROCESS

1. History

The oxo reaction proceeds most frequently in the presence of a Group 8–10 (VIII) metal catalyst in the liquid phase, most particularly with members of Group 9, the Co–Rh–Ir triad. The earliest catalyst, hydrocobalt tetracarbonyl [16842-03-8], $HCo(CO)_4$, was an outgrowth of Fischer-Tropsch investigations carried out prior to World War II on the effect of olefins on hydrocarbon synthesis (1). The hydroformylation reaction, as practiced in the early days using cobalt catalysis, presented formidable requirements of high pressure, containment of the hydrogen, containment of carbon monoxide, and handling of the toxic and unstable metal carbonyls. These conditions were challenging for the experimentalist as well as for the plant operator. However, because the oxo reaction provided a direct route for converting inexpensive olefins into valuable oxygenated building blocks, widespread industrial research and usage occurred throughout Europe, Japan, and the United States.

The search for catalyst systems which could effect the oxo reaction under milder conditions and produce higher yields of the desired aldehyde resulted in processes utilizing rhodium. Oxo capacity built since the mid-1970s, both in the United States and elsewhere, has largely employed tertiary phosphine-modified rhodium catalysts. For example, over 50% of the world's butyraldehyde (qv) is produced by the LP Oxo process, technology licensed by Union Carbide Corporation and Davy Process Technology.

Propylene (qv) [115-07-1] is the predominant oxo process olefin feedstock. Ethylene (qv) [74-85-1], as well as a wide variety of terminal, internal, and mixed olefin streams, are also hydroformylated commercially. Branched-chain olefins include octenes, nonenes, and dodecenes from fractionation of oligomers of C_3–C_4 olefins as well as octenes from dimerization and codimerization of isobutylene and 1- and 2-butenes (see Butylenes).

Linear terminal olefins are the most reactive in conventional cobalt hydroformylation. Linear internal olefins react at less than one-third that rate. A single methyl branch at the olefinic carbon of a terminal olefin reduces its reaction rate by a factor of 10 (2). For rhodium hydroformylation, linear α-olefins are again the most reactive. For example, 1-butene is about 20–40 times as reactive as the 2-butenes (3) and about 100 times as reactive as isobutylene.

Oxo aldehyde products range from C_3 to C_{15}, ie, detergent range, and are employed principally as intermediates to alcohols, acids, polyols, and esters formed by the appropriate reduction, oxidation, or condensation chemistry. The oxo reaction has been the subject of various reviews (4).

The classic challenges in oxo technology are simultaneously to achieve high reaction rate, high selectivity to the desired aldehyde, and to utilize a highly stable catalyst. Since the early 1970s, considerable progress has been made using ligand-modified rhodium catalysts that address these problems. In addition, progress has been made in the development of high reactivity rhodium catalysts for the conversion of internal and mixed-olefin feed streams. These latter are considerably less reactive than simple unsubstituted α-olefins. Development of catalysts which give improved process selectivities to the straight-chain isomer, generally more valuable, and of more efficient ways to recover product from rhodium catalyst solutions, have occurred. Additionally, progress has been made in asymmetric hydroformylation by using chiral ligands as a potential route to chiral pharmaceuticals.

2. Catalysts

2.1. Unmodified Cobalt Process

Typical sources of the soluble cobalt catalyst include cobalt alkanoates, cobalt soaps, and cobalt hydroxide [1307-86-4] (see Cobalt compounds). These are converted *in situ* into the active catalyst, $HCo(CO)_4$, which is in equilibrium with dicobalt octacarbonyl [10210-68-1]:

$$Co_2(CO)_8 + H_2 \rightleftarrows 2\,HCo(CO)_4 \qquad (6)$$

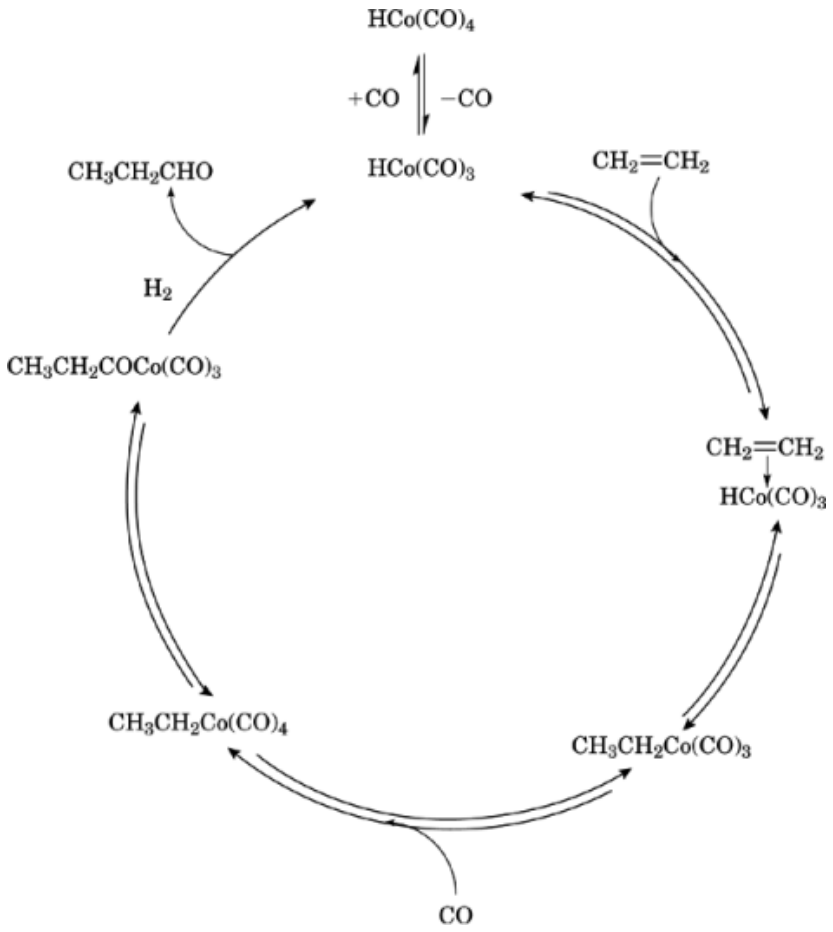


Fig. 1. Mechanism for the unmodified cobalt oxo reaction which produces propionaldehyde from ethylene.

The mechanism of the cobalt-catalyzed oxo reaction has been studied extensively. The formation of a new C—C bond by the hydroformylation reaction proceeds through an organometallic intermediate formed from cobalt hydrocarbonyl which is regenerated in the aldehyde-forming stage. The mechanism (5, 6) for the formation of propionaldehyde [123-38-6] from ethylene is illustrated in Figure 1.

The last step in this mechanism, the product forming hydrogenolysis, has been somewhat controversial. An alternative pathway (7) which involves cleavage by cobalt hydrocarbonyl to form aldehyde has been suggested. Each step in the mechanism is thought to be reversible except the final product forming step. The reverse of this reaction is so slow, it is generally neglected (8).

The rate of hydroformylation increases with increasing hydrogen and decreases with increasing carbon monoxide partial pressures (9), suggesting that rates of hydroformylation would be satisfactory at high H_2 and low CO partial pressures. In industrial practice, however, high pressures of both H_2 and CO are required in order to stabilize the $HCo(CO)_4$ catalyst at the temperatures necessary for practical rates (10). Commercial processes, for example, operate at >24 MPa (3480 psi) and $>140^{\circ}C$.

The commercially important normal to branched aldehyde isomer ratio is critically dependent on CO partial pressure which, in propylene hydroformylation, determines the rate of interconversion of the *n*-butyryl

and isobutyryl cobalt tetracarbonyl intermediates (11).

$$CH_3CH_2CH_2COCo(CO)_4 \rightleftharpoons (CH_3)_2CHCOCo(CO)_4 \qquad (7)$$

In contrast to triphenylphosphine-modified rhodium catalysis, a high aldehyde product isomer ratio via cobalt-catalyzed hydroformylation requires high CO partial pressures, eg, 9 MPa (1305 psi) and 110°C. Under such conditions alkyl isomerization is almost completely suppressed, and the 4.4:1 isomer ratio reflects the precursor mixture which contains principally the kinetically favored *n*-butyryl to isobutyryl cobalt tetracarbonyl. At lower CO partial pressures, eg, 0.25 MPa (36.25 psi) and 110°C, the rate of isomerization of the *n*-butyryl cobalt intermediate is competitive with butyryl reductive elimination to aldehyde. The product *n*/iso ratio of 1.6:1 obtained under these conditions reflects the equilibrium isomer ratio of the precursor butyryl cobalt tetracarbonyls (11).

Because of its volatility, the cobalt catalyst codistills with the product aldehyde necessitating a separate catalyst separation step known as decobalting. This is typically done by contacting the product stream with an aqueous carboxylic acid, eg, acetic acid, subsequently separating the aqueous cobalt carboxylate, and returning the cobalt to the process as active catalyst precursor (2). Alternatively, the aldehyde product stream may be decobalted by contacting it with aqueous caustic soda which converts the catalyst into the water-soluble $Co(CO)_4^-Na^+$. This stream is decanted from the product, acidified, and recycled as active $HCo(CO)_4$.

The stringency of the conditions employed in the unmodified cobalt oxo process leads to formation of heavy trimer esters and acetals (2). Although largely supplanted by low pressure ligand-modified rhodium-catalyzed processes, the unmodified cobalt oxo process is still employed in some instances for propylene to give a low, eg, $\sim 3.3 - 3.5 : 1$ isomer ratio product mix, and for low reactivity mixed and/or branched-olefin feedstocks, eg, propylene trimers from the polygas reaction, to produce isodecanol plasticizer alcohol.

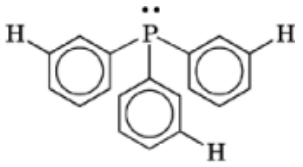
2.2. Ligand-Modified Cobalt Process

The ligand-modified cobalt process, commercialized in the early 1960s by Shell, may employ a trialkylphosphine-substituted cobalt carbonyl catalyst, $HCo(CO)_3P(n\text{-}C_4H_9)_3$ [20161-43-7], to give a significantly improved selectivity to straight-chain product. The Shell catalyst has vastly improved thermal stability over unsubstituted cobalt hydrocarbonyl and operates at 5–10 MPa (725–1450 psi) of H_2:CO and 160–200°C. The improved stability of the trialkylphosphine-substituted cobalt hydrocarbonyl, however, is offset by a lower hydroformylation activity requiring commensurately higher reaction temperatures. Thus there is a higher tendency of the olefin to undergo hydrogenation to alkane and of the aldehyde products to be hydrogenated to alcohols. Both linear and internal olefins react to yield principally linear alcohols and aldehydes. These products are a consequence of a high rate of isomerization occurring concurrently with hydroformylation and a strong preference for the α-olefinic component to undergo terminal addition with the $HCo(CO)_3P(n\text{-}C_4H_9)_3$ catalyst. C_{11}–C_{14} linear olefins, obtained from paraffin cracking or from the Shell Higher Olefins Process (SHOP), are hydroformylated to an 8:1 linear-to-branched isomer ratio, detergent range alcohol product mix in a single step. There has been large industrial usage of the Shell process since the 1960s, particularly for the preparation of detergent range alcohols (see Alcohols, higher aliphatic) (2). 2-Ethyl-1-hexanol can be produced in a single step from propylene by conducting the hydroformylation in the presence of caustic (12).

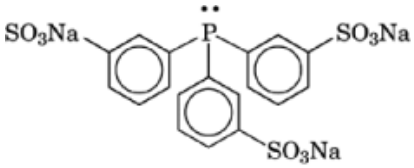
2.3. Ligand-Modified Rhodium Process

The triphenylphosphine-modified rhodium oxo process, termed the LP Oxo process, is the industry standard for the hydroformylation of ethylene and propylene as of this writing (ca 1995). It employs a triphenylphosphine [603-35-0] (TPP) **(1)** modified rhodium catalyst. The process operates at low (0.7–3 MPa (100–450 psi)) pressures and low (80–120°C) temperatures. Suitable sources of rhodium are the alkanoate, 2,4-pentanedionate, or

nitrate. A low (60–80 kPa (8.7–11.6 psi)) CO partial pressure and high (10–12%) TPP concentration are critical to obtaining a high (eg, 10:1) normal-to-branched aldehyde ratio. The process, first commercialized in 1976 by Union Carbide Corporation in Ponce, Puerto Rico, has been licensed worldwide by Union Carbide Corporation and Davy Process Technology.



(1)



(2)

The first commercial LP Oxo process flow scheme (Fig. 2) used syngas and propylene feed. Gases are fed to a pretreatment stage to remove poisons such as sulfur compounds, halides, and other harmful impurities. After purification, the gases are fed to the bottom of the reactor containing the catalyst solution consisting of the TTP-modified rhodium complex in butyraldehyde and butyraldehyde condensation products. Product and condensation by-products are removed from the reactor as vapor, a process facilitated by the superficial gas velocities of the gaseous feeds. The unreacted gases are separated from the product and recycled to the reactor. The gas recycle mode of operation may employ multireactors in parallel.

In the liquid recycle product recovery mode (Fig. 3), a modification of the initially commercialized technology, aldehyde product is separated in an external vaporizer, effectively decoupling the hydroformylation reaction from product recovery. Decoupling the oxo reaction from the separation step permits operation at milder and more favorable reaction temperatures. Lower temperatures reduce competing side reactions and extend catalyst life. A high degree of conversion is achieved by operating multireactors in series. This obviates the need for recycling unreacted gases.

2.3.1. Mechanism of LP Oxo Reaction

The LP Oxo reaction proceeds through a number of rhodium complex equilibria analogous to those in the Heck-Breslow mechanism described for the ligand-free cobalt process (see Fig. 1).

$$HRhCOL_3 \rightleftarrows {}^{CO}_{L}HRh(CO)_2L_2 \rightleftarrows {}^{CO}_{L}HRh(CO)_3L \qquad (8)$$

For example, $HRh(CO)_2L_2$, after dissociation of CO, goes on to generate *n*-butyraldehyde as shown in Figure 4 (13, 14). A similar cycle could be written for isobutyraldehyde.

The basis of the high normal to isoaldehyde selectivity obtained in the LP Oxo reaction is thought to be the anti-Markovnikov addition of olefin to $HRhCOL_2$ to give the linear alkyl, $Rh(CO)L_2CH_2CH_2CH_2CH_3$, the precursor of straight-chain aldehyde. Anti-Markovnikov addition is preferred in this instance because of fewer unfavorable steric interactions between the straight-chain, ie, less bulky, alkyl substituent and the two bulky phosphine ligands. Conversely, steric constraints are minimal in the singly substituted intermediate,

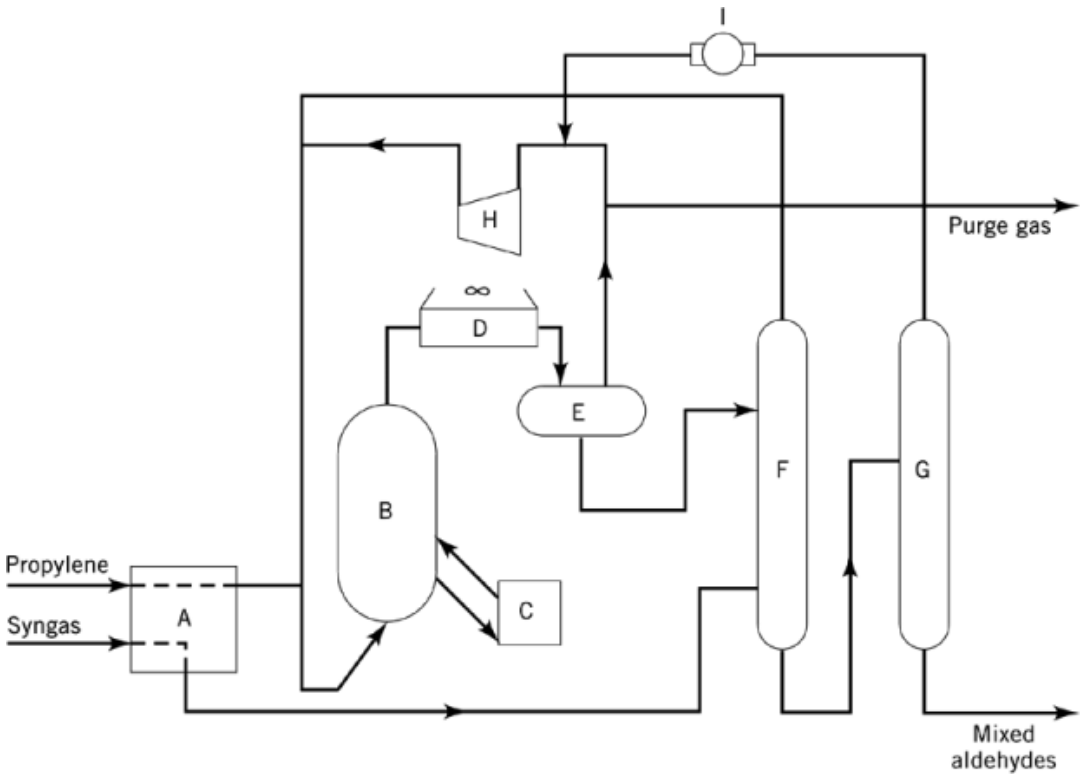


Fig. 2. LP Oxo gas recycle flow scheme: A, feedstock pretreatment; B, reactor; C, catalyst preparation and treatment systems; D, condenser; E, separator; F, stripper; G, stabilizer; H, cycle compressor; and I, stabilizer overhead gas compressor.

$HRh(CO)_2L$, resulting in a higher proportion of branched alkyl intermediate from Markovnikov addition of olefin to the rhodium hydride, and a commensurately lower selectivity to normal versus branched aldehyde product. From the equilibria depicted in equation 8, it can be seen that a high proportion of the linear aldehyde precursor, $HRhCOL_2$, is favored by a combination of high ligand concentration and low partial pressure.

2.4. Rhodium Modified with Ionic Phosphine Ligands

In 1984, Rhône-Poulenc and Ruhrchemie (now Hoechst AG) commercialized a rhodium catalyst process employing a water-soluble ligand, triphenylphosphine-*m*-trisulfonic acid trisodium salt [63995-70-0] (TPPTS) **(2)**. Product recovery is achieved by decantation from the aqueous phase containing rhodium and ligand (Fig. 5) (15). An isomer ratio of 20:1 is obtained with the TPPTS-modified rhodium catalyst, but the catalyst activity is significantly lower, so higher temperatures, higher rhodium concentrations, and higher propylene pressures are employed. Table 1 compares the operating conditions of the Hoechst/Rhône-Poulenc and LP Oxo processes. Hydroformylation reactions with a variety of other water-soluble ligands have also been reported (15).

Supported aqueous phase (SAP) catalysts (16) employ an aqueous film of TPPTS or similar ligand, deposited on a solid support, eg, controlled pore glass. Whereas these supported catalysts overcome some of the principal limitations experienced using heterogeneous catalysts, including rhodium leaching and rapid catalyst deactivation, SAP catalysts have not found commercial application as of this writing.

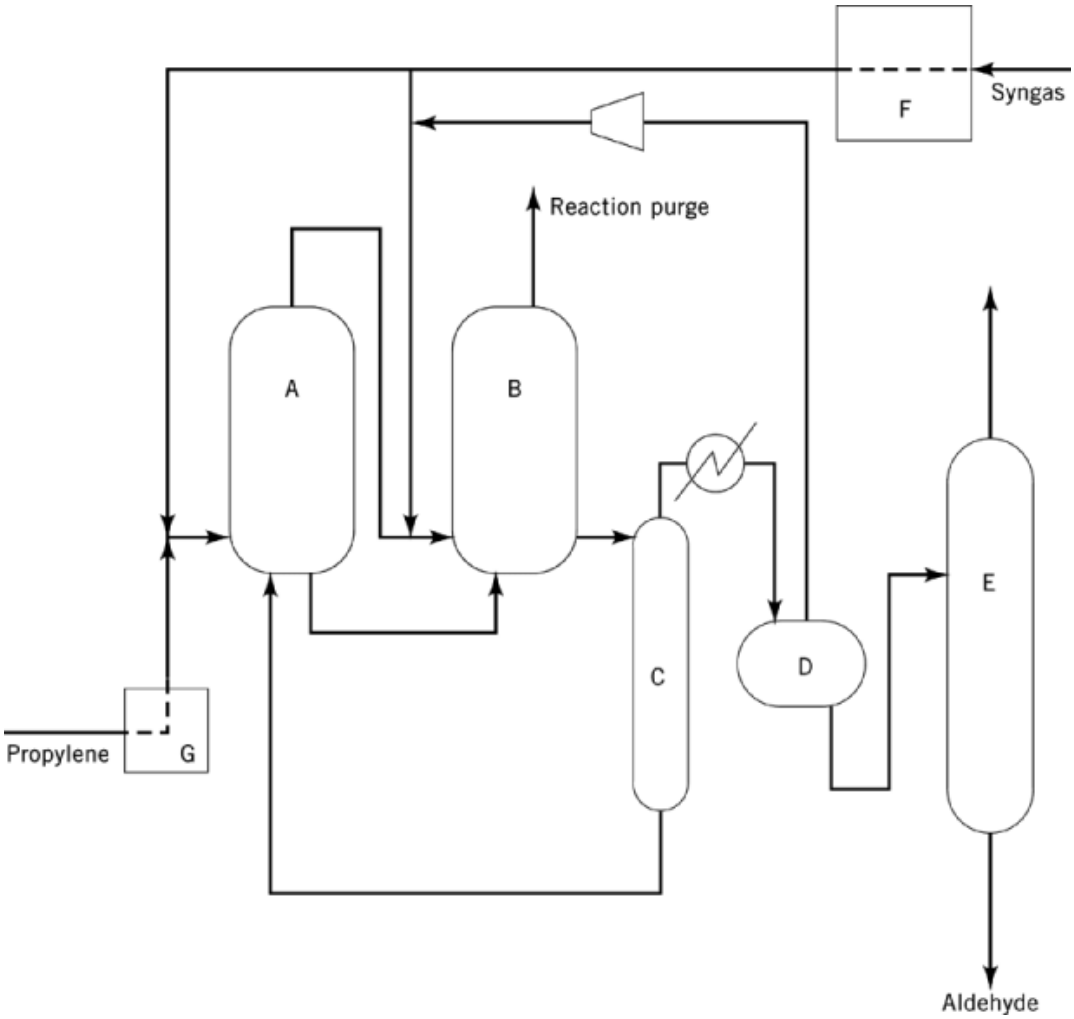


Fig. 3. LP Oxo liquid recycle flow scheme: A and B, reactors; C, vaporizer; D, catchpot; E, stabilizer; F, syngas cleanup; and G, propylene cleanup.

2.5. Other Rhodium Processes

Unmodified rhodium catalysts, eg, $Rh_4(CO)_{12}$ [19584-30-6], have high hydroformylation activity but low selectivity to normal aldehydes.

A hydroformylation process employing monosulfonated triphenylphosphine rhodium catalysts, soluble in polar organic solvents, which allows the hydroformylation of higher olefins in a single phase, has been reported. These catalysts, which have typical homogeneous catalyst reactivity, can be induced to separate after hydroformylation into nonpolar (product) and polar (catalyst) phases, thereby providing an effective means of catalyst recovery. The practical significance of this technology is that it permits the homogeneous hydroformylation of higher molecular weight and less volatile olefins such as octene, dodecene, styrene, and dienes (16). These materials tend to lose activity by transforming, particularly under acidic conditions, into the poorly soluble cluster, $Rh_6(CO)_{16}$, or under more drastic conditions, into rhodium metal. Mitsubishi Kasei has

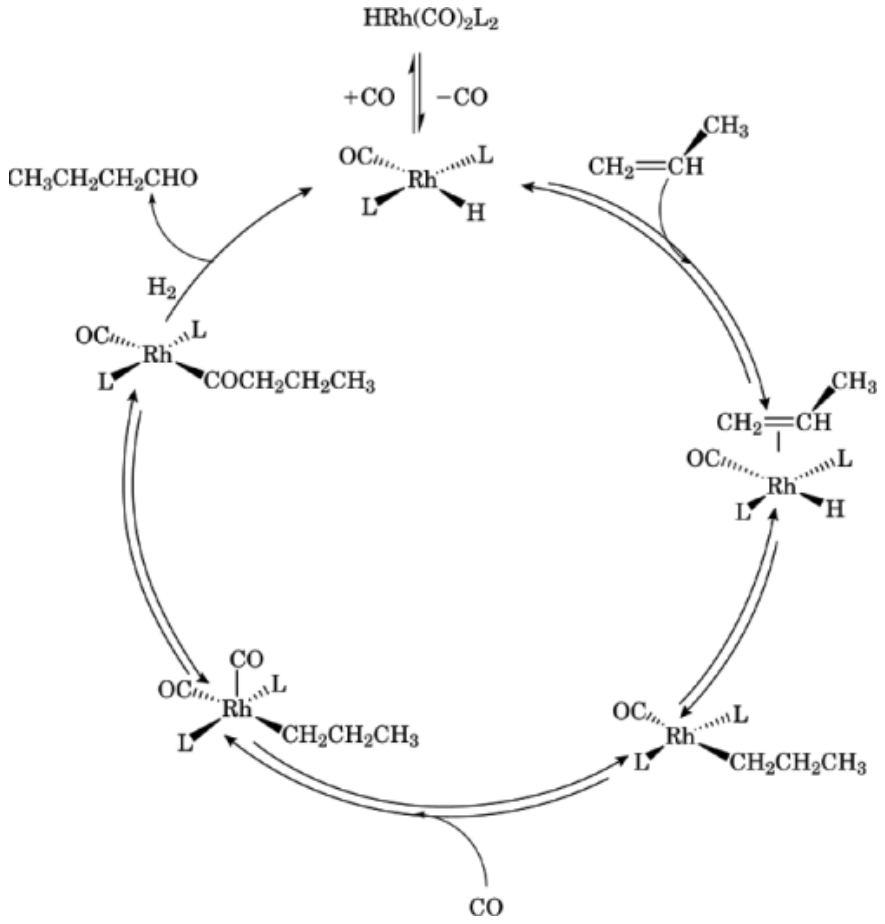


Fig. 4. Mechanism for the TPP-modified rhodium-catalyzed oxo reaction of propylene to *n*-butyraldehyde.

Table 1. Comparison of Hoechst/Rhône-Poulenc and LP Oxo Processes

	$HRh(CO)_2L_2$	
Parameter	L = TTP	L = TPPTS
temperature, °C	≥90	≥125
pressure, MPa[a]	≥1.4	≥6
Rh, ppm	200–400	300–700
C_3H_6, MPa[a]	up to 1.1	up to 4.8

[a] To convert MPa to psi, multiply by 145.

been able to take advantage of the inherent high reactivity of unmodified rhodium catalysts to convert butene dimers into branched C_9 products, ie, isononyl alcohol (17). Under hydroformylation conditions both CO and a weakly coordinating ligand, triphenylphosphine oxide $(TPPO)_{(3)}$, are available for coordination/stabilization of the metal. To provide catalyst stability during the product isolation step, small amounts of TPP are added. The TPP in the stripped catalyst solution is subsequently oxidized to TPPO prior to recycling back to the hydroformylation zone.

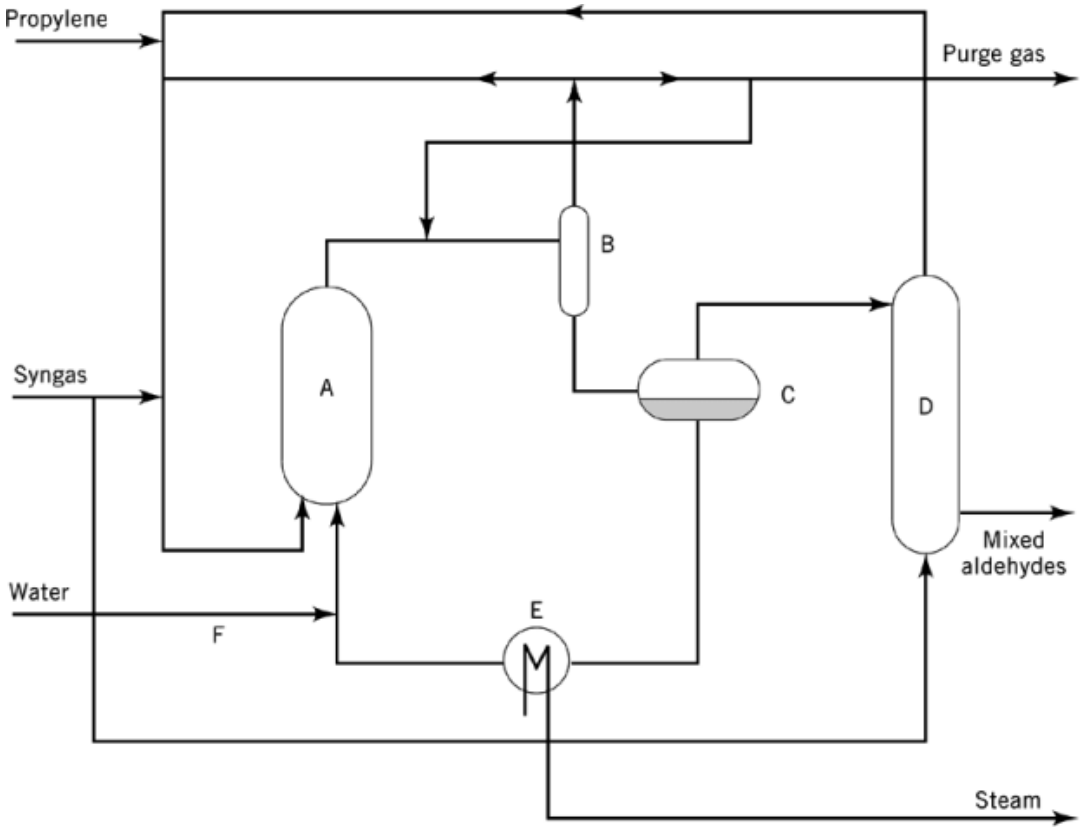
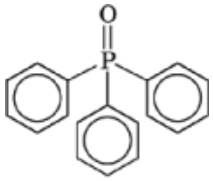


Fig. 5. Hoechst/Rhône-Poulenc oxo flow scheme: A, stirred tank reactor; B, separator; C, phase separator; D, stripping column; E, heat exchanger; and F, water inlet.



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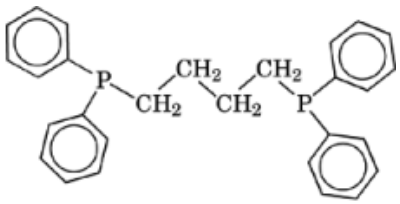
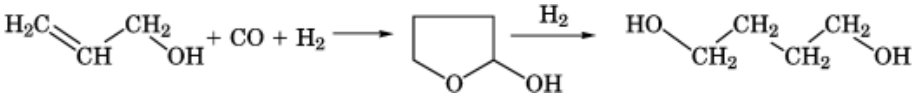


(4)

2.6. Functional Olefin Hydroformylation

There has been widespread academic (18, 19) and industrial (20) interest in functional olefin hydroformylation as a route to polyfunctional molecules, eg, diols. There are two commercially practiced oxo processes employing functionalized olefin feedstocks. Allyl alcohol hydroformylation is carried out by Arco under license from Kuraray (20, 21). 1,4-Butanediol [110-63-4] is produced by successive hydroformylation of allyl alcohol [107-18-6], aqueous extraction of the intermediate 2-hydroxytetrahydrofuran, and subsequent hydrogenation.

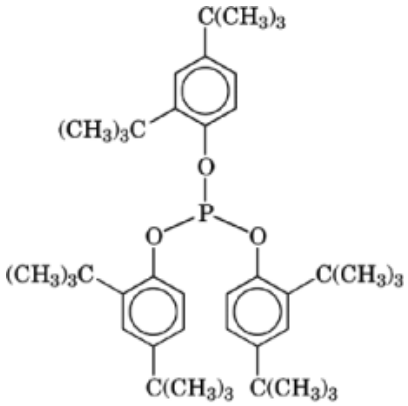


2-Methyl-1,3-propanediol is produced as a by-product. The hydroformylation reaction employs a rhodium catalyst having a large excess of TPP **(1)** and an equimolar (to rhodium) amount of 1,4-diphenylphosphinobutane (DPPB) **(4)**. Aqueous extraction/decantation is also used in this reaction as an alternative means of product/catalyst separation.

Kuraray has commercialized a process for producing 3-methyl-1,5-pentanediol [4457-71-0] from 3-methyl-3-butenol (20).

$$CH_2{=}C(CH_3)CH_2CH_2OH \xrightarrow{\text{two steps}} HOCH_2CH_2CH(CH_3)CH_2CH_2OH \qquad (10)$$

The initial hydroformylation is conducted using tris(2,4-di-*t*-butylphenyl)phosphite **(5)** as ligand.



(5)

2.7. Hydroformylation Using Other Metals

2.7.1. Ruthenium

Ruthenium, as a hydroformylation catalyst (14), has an activity significantly lower than that of rhodium and even cobalt (22). Monomeric ruthenium carbonyl triphenylphosphine species (23) yield only modest normal to branched regioselectivities under relatively forcing conditions. For example, after 22 hours at 120°C, 10 MPa (1450 psi) of carbon monoxide and hydrogen, biscarbonyltristriphenylphosphine ruthenium [61647-76-5], $Ru(TPP)_3(CO)_2$, at 2000 ppm ruthenium and 1-hexene as substrate, gives only an 86% conversion and a 2.4:1 linear-to-branched aldehyde isomer ratio. At higher temperatures reduced conversions occur. High hydrogen

partial pressures increase the reaction rate, but at the expense of increased hydrogenation to hexane. Excess triphenylphosphine improves the selectivity to linear aldehyde, but at the expense of a drastic decrease in rate.

In what may be an example of true cluster catalysis, $[HRu_3(CO)_{11}]^-$ shows good catalytic activity and high regioselectivity using propylene as substrate (24, 25). Solvent, CO partial pressure, and temperature are important variables. In monoglyme, at 80°C and starting partial pressures for C_3H_6, CO, and H_2 of 0.034, 0.022, and 0.011 MPa (4.93, 3.19, and 1.60 psi), respectively, the catalyst turnover number, product-to-catalyst ratio, is 34.3 and the *n*- to isobutyraldehyde ratio is 49.4:1. In acetonitrile solvent, all other things being equal, the turnover number drops to 25.7 and the isomer ratio to 12.1:1.

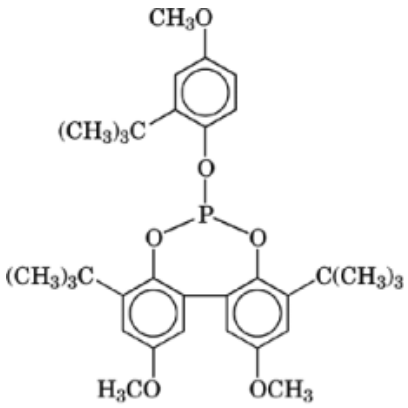
2.7.2. Platinum

Platinum catalysts that utilize both phosphine and tin(II) halide ligands give good rates and selectivities, in contrast to platinum alone, which has extremely low or nonexistent hydroformylation activity. High specificity to the linear aldehyde from 1-pentene or 1-heptene is obtained using $HPtSnCl_3CO(TTP)$ (26), active at 100°C and 20 MPa (290 psi) producing 95% *n*-hexanal from 1-pentene.

A further improvement in platinum catalysis is claimed from use of tin(II) halide and phosphine ligands which are rigid bidentates, eg, 1,2-bis(diphenylphosphinomethyl)cyclobutane (27). High rates for a product containing 99% linear aldehyde have been obtained. However, a pressure of 10 MPa (1450 psi) H_2:CO is required.

2.8. Future Trends

In addition to the commercialization of newer extraction/ decantation product/catalyst separations technology, there have been advances in the development of high reactivity oxo catalysts for the conversion of low reactivity feedstocks such as internal and α-alkyl substituted α-olefins. These catalysts contain (as ligands) ortho-*t*-butyl or similarly substituted arylphosphites, which combine high reactivity, vastly improved hydrolytic stability, and resistance to degradation by product aldehyde, which were deficiencies of earlier, unsubstituted phosphites. Diorganophosphites (28), such as structure **(6)**, have enhanced stability over similarly substituted triorganophosphites.



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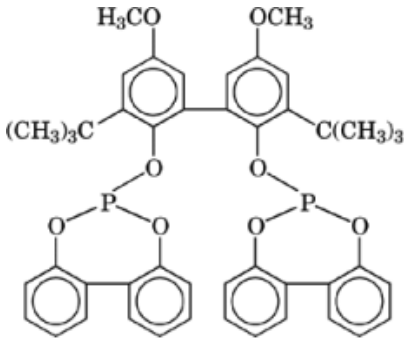
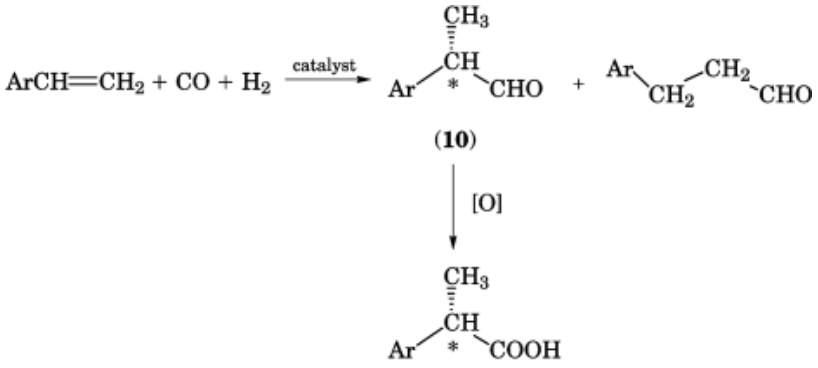


(7)

Bisphosphites such as **(7)** combine excellent reactivity, straight-chain selectivity, and high resistance to the typical phosphite degradation reactions (29). Further, the corresponding oxo catalysts are excellent olefin isomerization catalysts so that high normal-to-branched isomer ratios are obtained even from internal olefins, enabling, in certain instances, the use of inexpensive mixed isomer olefin feedstocks.

Considerable advances in asymmetric hydroformylation, a process which, among other things, provides a potential route to enantiomerically pure biologically active compounds, have occurred. Of particular interest are preparations of nonsteroidal antiinflammatory (NSAI) pharmaceuticals such as Naproxen **(8)** and Ibuprofen **(9)**, where the * represents a chiral center.



(**10**)

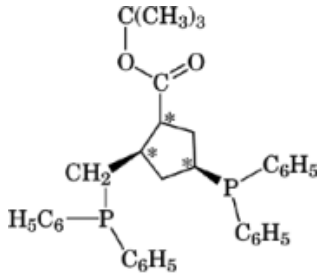
(**8**) Ar = 6-methoxy-2-naphthyl

(**9**) Ar =4-iso-butylphenyl

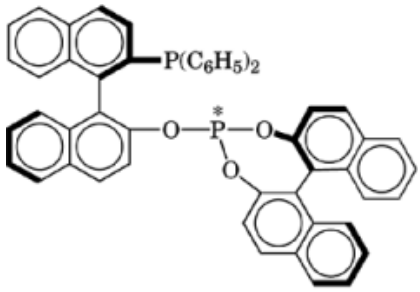
Conceptually at least, these compounds can be obtained via initial enantioselective hydroformylation of the appropriate vinyl aromatic to branched chiral aldehyde and subsequent oxidation.

For such a process to NSAI pharmaceuticals to be commercially practical requires minimally high regioselectivity and stereoselectivity to the chiral–aldehyde intermediate **(10)**, combined with retention of optical purity in the subsequent oxidation step. High optical yields ($\sim 70 - 82\%$ ee) of enantiomeric α-methylarylacetaldehydes have been obtained from styrene, *p*-isobutylstyrene, 2-vinylnaphthalene, and 2-vinyl-6-methoxynaphalene (30) employing a $PtCl(SnCl_3)L^*$ catalyst, where L* is a chiral ligand, such as **(11)**. Even higher ($>96\%$) optical yields were obtained by trapping the aldehyde as the diethyl acetal using triethylorthoformate (31). The regioselectivity of these catalysts to the branched product, eg, 0.5–3.3:1, as well as the

overall rates, however, were low. Certain chiral bisphosphite-modified rhodium catalysts (32), however, have been reported to give the desired NSAI pharmaceutical precursors at combined high regioselectivity, rate, and enantioselectivity.



(11)



(12)

High enantioselectivities and regioselectivities have been obtained using both mono- and 1,2-disubstituted prochiral olefins employing chiral phosphine phosphite (33, 34) modified rhodium catalysts. For example, *cis*-2-butene in the presence of rhodium and **(12)** (33) gave (*S*)-2-methylbutanal in an optical yield of 82% at a turnover number of $9.84\ h^{-1}$.

3. Economic Aspects

Worldwide capacity for oxo process chemicals reached 7.0×10^6 metric tons at the start of 1990 (35). Market share for oxo chemicals is divided between Western Europe (36%), the United States (30%), Eastern Europe (12%), Japan (10%), other Asian countries (8%), and South America and Mexico (4%). U.S. oxo manufacturers, products, and capacities are given in Table 2.

The propylene-based chemicals, *n*- and isobutanol and 2-ethyl-1-hexanol [104-76-7] (2-EH) dominate the product spectrum. These chemicals represent 71% of the world's total oxo chemical capacity. In much of the developed world, plasticizers (qv), long based on 2-EH, are more often and more frequently higher molecular weight, less volatile C_9 and C_{10} alcohols such as isononyl alcohol, from dimerized normal butenes; isodecanol, from propylene trimer; and 2-propyl-1-heptanol, from *n*-butenes and aldol addition. Because of the competition from the higher molecular weight plasticizer alcohols, 2-EH and dioctylphthalate [117-81-7] (DOP), its principal derviative, are expected to grow more slowly than the higher molecular weight plasticizers in the 1990s (35). Oxo products other than butyraldehydes are significant only in the United States and Western Europe, representing 41 and 38%, respectively, of these regions' total capacities.

Table 2. U.S. Oxo Manufacturers[a]

Company (plant location)	Products	Capacity, $t \times 10^3$/yr	Catalyst
Exxon (Baton Rouge, La.)	branched C_6–C_{13} alcohols; linear C_7–C_{11} and C_{13}–C_{15} alcohols	306	Co
Hoechst Celanese	propionaldehyde	30	Rh
(Bay City, Tex.)	*n*-butyraldehyde	150	
	isobutyraldehyde	16	
Aristech Chemical Corp.	*n*-butyraldehyde	113	Rh
(Pasadena, Tex.)	isobutyraldehyde	14	
BASF Corp.	*n*-butyraldehyde	107	Rh
(Freeport, Tex.)	isobutyraldehyde	25	
Eastman	propionaldehyde	59	Co
(Longview, Tex.)	*n*-butyraldehyde	315	Rh
	isobutyraldehyde	125	
Shell Oil Co.			
(Deer Park, Tex.)	*n*-butanol	102	Co–PR_3
	2-ethyl-1-hexanol		
	isobutanol		
(Geismar, La.)	C_9–C_{15} linear alcohols	295	Co–PR_3
	isononyl alcohol		
Sterling Chemicals, Inc. (Texas City, Tex.)	C_7, C_9, C_{11} linear alcohols	102	Co
Union Carbide Corp. (Texas City, Tex.)	propionaldehyde and valer-aldehyde	91	Rh
	n-butyraldehyde	329	
	isobutyraldehyde	33	

[a] Ref. 35.

The largest oxo producers in Western Europe are BASF, Hüls, and Hoechst (formerly Ruhrchemie), representing 50–51% of the total regional capacity of 2.527×10^6 metric tons. These companies have the broadest spectrum of products ranging from C_3 and C_4 adehydes to C_{13} alcohols and acids. However the primary products are *n*- and isobutyraldehyde, at combined capacities of 1.08×10^6 t. The *n*-butyraldehyde goes principally into the manufacture of 2-EH.

The spectrum of oxo products in Japan is far less diverse. Nearly 75% of Japan's total oxo capacity of 733,000 t is dedicated to the hydroformylation of propylene. 2-EH derived from *n*-butyraldehyde is by far the dominant product. Other products include linear alcohols and higher branched alcohols. Additionally, Japan is the world's principal source of branched heptyl alcohol. The three principal Japanese oxo producers having slightly more than 70% of Japan's total oxo capacity are Mitsubishi Kasei, Kyowa Yuka, and Japan Oxocol.

4. Uses

n-Propanol and *n*-propyl acetate account for about 70% of the U.S. propionaldehyde derivative market (see Propyl alcohols). These compounds are used principally in flexographic and gravure inks (qv) which require volatile solvents to prevent smearing and ink accumulation on the printing presses (see Printing processes). Some propanol is also converted into *n*-propylamines which are important pesticide intermediates (see Pesticides). *n*-Propanol is also employed as a precursor for glycol ethers, eg, Union Carbide's Propasol (propoxypropanol), having primary usage in surface coatings applications and flexographic printing inks (see Glycols). The other principal propionaldehyde derivative, propionic acid, is used principally in grain and feed preservative applications (see Feeds and feed additives). Sodium and calcium propionates are used in both food and animal feed applications (see Food additives). Some propionic acid is converted into herbicides (qv) such as

Stam (Rohm and Haas) (3′,4′-dichloropropionanilide) and into cellulose acetate propionate, a plastic sheeting and molding precursor.

The highest volume oxo chemical in the United States, *n*-butyraldehyde, is converted mainly into *n*-butanol, employed chiefly to produce butyl acrylate and methacrylate (see Acrylic acid and derivatives). In contrast, the principal *n*-butyraldehyde derivative in Europe and Japan is 2-ethylhexanol, the precursor to the poly(vinyl chloride) (PVC) plasticizer, DOP.

1,4-Butanediol [110-63-4] (BDO) goes primarily into tetrahydrofuran [109-99-9] (THF) for production of polytetramethylene ether glycol (PTMEG), used in the manufacture of polyurethane fibers, eg, Du Pont's Spandex. THF is also used as a solvent for PVC and in the production of pharmaceuticals (qv). Lesser amounts of BDO are employed in the production of polybutylene terephthalate resins and γ-butyrolactone.

The principal C_5 valeraldehyde derivatives, *n*-amyl and 2-methylbutyl alcohols, are used predominantly to make zinc diamyldithiophosphate lube oil additives (see Amyl alcohols; Lubrication and lubricants), which are employed primarily in automotive antiwear applications. Similarly, the *n*-valerate and 2-methylbutyrate esters of pentaerythritol and trimethylolpropane are used in aeromotive synlube formulations and as refrigerant lubricants.

C_7–C_9 oxo-derived acids are the principal derivatives of the C_7–C_9 oxo aldehydes, and in analogy to C_5 oxo aldehyde market applications, are used chiefly to make neopolyol esters, ie, those based on neopentyl glycol, trimethylolpropane, or pentaerythritol. These synlubes are employed almost entirely in aeromotive applications. Heptanoic acid is also employed to make tetraethylene glycol diheptanoate, a plasticizer used with poly(vinyl butyral).

Several alcohols in the C_6–C_{13} range are produced by oxo reactions and are used in both plasticizer and detergent applications. Linear C_{12}–C_{15} alcohols are employed primarily in detergent applications. Slightly more than 50% of the 540,000–590,000 t of domestic U.S. detergent alcohol capacity is produced by hydroformylation of linear olefins from *n*-paraffins or ethylene chain-growth products. The remainder is produced from natural sources. Detergent alcohols are converted principally into alcohol sulfates, ethoxylates, alcohol ether sulfates, and fatty amines. Only a small ($\sim$1%) fraction of the detergent alcohols are destined for direct consumption.

5. Safety, Health, and Environmental Concerns

Oxo plants employ mixtures of highly toxic, flammable gases under pressure at high temperatures and require strict adherence to established operating safety codes and emergency reporting procedures to local, state, and federal authorities. In the United States, carbon monoxide is classified as both an acute, fire, and sudden release hazard under the Superfund Amendments and Reauthorization Act (SARA) 311/312, requiring strictly maintained documentation of hazards and emergency procedures, eg, maintenance of appropriate Material Safety Data Sheets and reporting procedures in case of accidental release.

The carbon monoxide component of the oxo reactant gases presents the most immediate human health hazard. The OSHA exposure limit for carbon monoxide is 35 ppm (40 mg/m^3) and a ceiling of 200 ppm (229 mg/m^3). Carbon monoxide interrupts the body's normal oxygen metabolic cycle by reacting preferentially with the hemoglobin in the blood, effectively starving the body of required oxygen. The cherry red iron carbonyl heme complex formed is much brighter than the corresponding oxygen complex so that someone overcome with carbon monoxide presents a characteristic flushed appearance and bright red lips. Conventional first-aid procedures require immediate removal from the source. Appropriate fresh air equipment should be worn in the presence of high concentrations of the gas. Artificial respiration is applied if the person overcome has stopped breathing and fresh oxygen is applied to facilitate the release of CO. After initial first aid, medical attention must be sought.

Acute toxicity testing of triphenylphosphine in animals indicates a very low level of physiological activity. The oral LD_{50} for triphenylphosphine in both rats and mice is 0.8–1.6 g/kg; the intraperitoneal LD_{50} is 1.6–3.2 and 0.8–1.6 g/kg, in rats and mice, respectively (36).

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