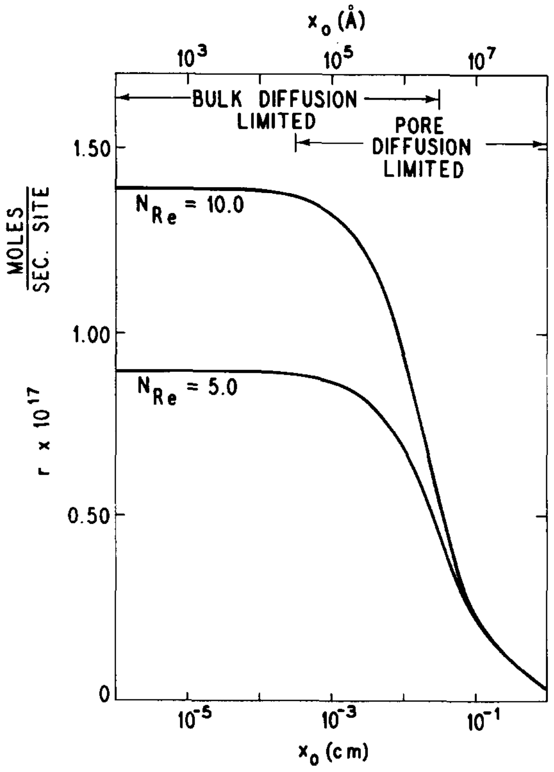

FIG. 2. Activity in one active pore as a function of x_0 and N_{Re}.

eral orders of magnitude lower (10^2–10^4) than where such limitation should occur, according to classical calculations (*5*). A site localized diffusional limitation at very active, but widely separated sites, was used to explain these unusual results.

It is concluded that perhaps more attention should be given to the possible existence of site-localized diffusional effects. This is particularly important since active site densities may be several orders of magnitude less than usually supposed (*3*) and, hence, site activities may be several orders of magnitude higher than usually supposed. Site-localized diffusion limitations may occur even at low bulk reaction rates where classical calculations predict no limitation. Perhaps diffusional effects should be excluded on the basis of experimentation rather than calculation, and even then the possibility of a surface reaction being limited by site-localized diffusion should be considered.

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A. J. MOFFAT

Phillips Petroleum Company
Research & Development Department
Bartlesville, OK 74004

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Catalytic Oxidation of Olefins over Metallic Palladium Suspended in Water

Since the development of the Wacker process, catalytic reactions of olefins using palladium salts have been studied by many workers (*1*). However, little is known about the catalytic activity of palladium metal in the selective oxidation of olefins. Patterson and Kemball (*2*) reported that the main reaction in the catalytic oxidation of olefins over palladium film was complete oxidation, but that small amounts of acetone were produced in the oxidation of propylene and higher olefins. The authors have previously found that propylene is oxidized by molecular oxygen to acrylic acid and acrolein over palladium black suspended in water (*3*). This reaction is presumably an allylic type oxidation and is of interest in that it reveals a novel and unique catalytic property of metallic palladium. In the present study the catalytic oxidation of butenes under the same conditions has been examined for the purpose of obtaining further information on the possible participation of π-allylic species in the reaction. The catalytic activities of other group VIII metals were also tested to find out which metal is the most active in the reaction.

Experimental Methods

Palladium black was prepared by reducing palladium chloride with propylene in an aqueous solution acidified by sulfuric acid (pH 1.5) in the presence of sodium perchlorate (0.05 moles/liter), which acts as a regulator of the particle size of palladium black; the product was washed thoroughly with water. The preparation of other catalysts is mentioned with the experimental results. The oxidation reaction was carried out in a closed reactor by contacting a gaseous mixture (ca. 300 ml) of olefin (50%) and oxygen (50%) with an aqueous suspension (100 ml) of the catalyst (0.1 g) with sufficient stirring. The reaction was followed by measuring the decrease of the gas volume. Products were identified by infrared and mass spectroscopy, and analyzed quantitatively by gas chromatography or neutralization titration.

Results and Discussion

Oxidation of Butenes

Results of the oxidation of various butenes and propylene are summarized in Table 1, where the gas consumption for reaction times of 70 ~ 100 min, the oxidation products and their selectivities are recorded. The main products were methacrolein and methacrylic acid from isobutene, and crotonic acid, crotonaldehyde, and methyl vinyl ketone from *n*-butenes. In every case, complete oxidation to carbon dioxide was confined to a few percent. Acetaldehyde and acetic acid were detected only in trace quantities and are omitted from Table 1.

For crotonic acid, the yields presented in

TABLE 1

Catalytic Oxidation of Propylene and Butenes Over Palladium Black Suspended in Water

Catalyst amount 0.1 g; 50°C; 1 atm.

Olefin	Reaction time (min)	Amount of gas consumption (10^{-4} mole)	Products and their selectivities[a] (%)			
			$CH_2{=}CHCOOH$	$CH_2{=}CHCHO$		CO_2
Propylene[b]	90	21.2	83	15		2
			$CH_2{=}C(CH_3)COOH$	$CH_2{=}C(CH_3)CHO$		
Isobutene	90	26.6	29	66		5
	90	25.2	25	69		6
			$CH_3CH{=}CHCOOH$	$CH_3CH{=}CHCHO$	$CH_3COCH{=}CH_2$	
rans-2-Butene	100	33.6	35	11	52	2
	100	28.6	42	9	48	1
cis-2-Butene	100	23.9	42	17	39	2
	70	28.1	45	19	34	2
1-Butene	90	29.8	30	20	49	1
	90	28.8	27	20	51	2

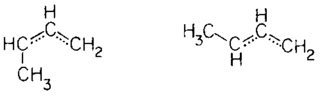
[a] On a olefin basis.

[b] Reaction temperature was 55°C.

Table 1, which were obtained by neutralization titration analysis, are the sum of the geometric isomers. In the gas chromatogram, a component was eluted just before *trans*-crotonic acid, and this peak was attributed to the *cis*-isomer. The *trans*/*cis* isomer ratios so obtained were different from each other in the three *n*-butene oxidations, having the values 1.7, 8.2, and 1.2 in the oxidations of 1-butene, *trans*-2-butene, and *cis*-2-butene, respectively. With the 2-butenes, the geometry of the reactant olefin was inherited by the product acid to a considerable extent. Separation of the two isomers of crotonaldehyde was unsuccessful.

The reactivity of the olefins was in the order of 1-butene > isobutene ≃ *cis*-2-butene ≃ *trans*-2-butene > propylene, though the comparison was approximate because of poor reproducibility of the rate. As the reaction advanced, the gas consumption rate gradually decreased, probably due to the change of the gas composition.

It is observed that (i) the active site of olefin is either an allylic carbon or a vinylic carbon apart from the allylic carbon, and (ii) no significant difference appears between α-olefin and β-olefin oxidations except the geometric isomer distribution in crotonic acid. These facts suggest that the formation of a π-allylic complex from olefin is the initial step in the oxidation reaction on the palladium metal surface. The reactivity order of the olefins appears to correspond to the reactivity order of the α-hydrogens of the olefins in abstraction reactions, as calculated by Kato *et al.* (*4*). Moreover, the *trans*/*cis* ratio in crotonic acid is reasonably accounted for by involving π-allylic species. It is known that the π-allyl (π-methyl-allyl) radical derived from *n*-butene takes either the *syn*- or the *anti*-configuration because free rotation between these conformers is prohibited (*5*).

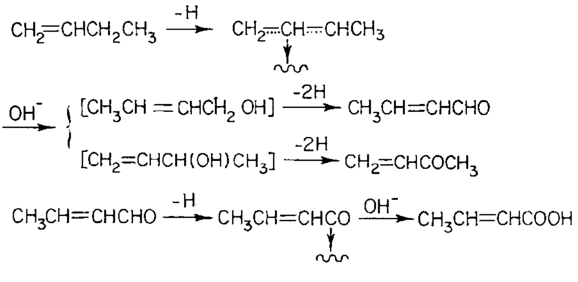


anti-Conformation *syn*-Conformation

It is expected, therefore, that if isomerization is restricted completely, *trans*- or *cis*-2-butene is converted only into the *syn*- or the *anti*-conformer, respectively, which in turn gives only *trans*- or *cis*-crotonic acid in the succeeding reaction, whereas 1-butene is converted into an isomeric mixture of crotonic acid via the two π-allylic intermediates. Accordingly, the observed *trans*/*cis* ratio can be explained as a result of such a situation, complicated a little by some isomerization of the *cis*- to the thermodynamically-favored *trans*-configuration during the oxidation.

Thus it is concluded that the olefin oxidation over palladium black proceeds via the π-allylic complex and this distinguishes it clearly from the Wacker type oxidation by palladium salts where the essential process is claimed to be the decomposition of hydroxo olefin π-complexes (oxypalladation) (*6*). A similar example is seen in the vinylation of olefin. In the propylene vinylation, for example, it was reported that allyl ester is obtained preferentially over palladium metal catalyst (*7*, *8*) while enol ester is obtained in catalysis by palladium acetate (*9*).

The reaction path after the formation of the π-allyl in the present reaction is considered to comprise the two steps illustrated below in the case of 1-butene oxidation,



$$CH_2{=}CHCH_2CH_3 \xrightarrow{-H} CH_2{\cdots}CH{\cdots}CHCH_3$$

$$\xrightarrow{OH^-} \left\{ \begin{array}{l} [CH_3CH{=}CHCH_2OH] \xrightarrow{-2H} CH_3CH{=}CHCHO \\ [CH_2{=}CHCH(OH)CH_3] \xrightarrow{-2H} CH_2{=}CHCOCH_3 \end{array} \right.$$

$$CH_3CH{=}CHCHO \xrightarrow{-H} CH_3CH{=}CHCO \xrightarrow{OH^-} CH_3CH{=}CHCOOH$$

though the detailed mechanism is not clear. The first step is the formation of aldehyde or ketone by the nucleophilic attack of OH^- or H_2O on the π-allyl, followed by oxidative dehydrogenation. The second step is the consecutive oxidation of aldehyde to acid. This process presumably proceeds by OH^- or H_2O addition coupled with the oxidative dehydrogenation, considering that the oxidation of acrolein with oxygen in methanol suspension of palladium black provides methyl acrylate as a primary product (*10*). The reaction mechanism is receiving further study.

Activities of Other Catalysts

The catalytic activities of other group VIII metals for the olefin oxidation were tested using propylene. Results are listed in Table 2, where the rate of the gas consumption per g of catalyst metal is shown as a measure of the catalytic activity.

In the case of palladium, both supported catalysts on carbon (Pd–carbon) and on tin oxide (Pd–SnO_2) showed nearly the same activities as palladium black. However, the selectivity for acrolein formation became small and that for CO_2 or acetic acid increased considerably. The formation of acetone over Pd–carbon, which is a prominent feature of the Wacker type oxidation, was probably facilitated by a small amount of Cl^- remaining in the catalyst; the amount of acetone decreased run by run when the same catalyst was used repeatedly. Pd–Al_2O_3 showed almost no activity. Platinum black and Pt–carbon had high activities, but the preferential reaction was oxidation to CO_2 or acetic acid. Rhodium or ruthenium showed no activity for the selective oxidation and only low activity for complete oxidation.

Thus, the activities of the metals decreased in the sequences $Pd > Pt \gg Ru \simeq Rh$. However, it is difficult to discuss the activity-controlling factor from this sequence because there is no guarantee that the reaction mechanism is same for all the metals studied, as shown by the marked fact that of these metals only palladium has high activity and selectivity in the oxidation to acrylic acid or acrolein. It is merely pointed out at present that Pt and Pd are known as the most active catalysts in the vapor-phase complete oxidation of olefin (*2*, *11*). Further experiments in this direction are now being carried out.

TABLE 2

CATALYTIC ACTIVITIES OF SOME GROUP VIII METALS IN THE LIQUID PHASE OXIDATION OF PROPYLENE

60°C, 1 atm.

Catalyst[a]	Activity[b]	Products and their selectivities (%)				
		$CH_2{=}CHCOOH$	$CH_2{=}CHCHO$	CH_3COCH_3	CH_3COCH	CO_2
Pd black[c]	14.1	83	15	Trace	Trace	2
Pd(5%)–carbon	26.8	76	Trace	4	8	12
Pd(10%)–SnO_2	23.8	89	3	Trace	2	6
Pd(5%)–Al_2O_3	0.79					
Pt black	9.3	3	Trace	2	14	81
Pt(5%)–carbon	15.4	6	Trace	5	10	79
Rh black	0.53					100
Rh(5%)–carbon	0.36					100
Ru(5%)–carbon	0.80					100

[a] Pt black and Rh black were prepared by reducing the salts with formaldehyde, and Pd–SnO_2 by reducing $PdCl_2$ in an aq soln containing suspended SnO_2; other supported catalysts were commercial meterials of Nippon Engelhard.

[b] Expressed as the rate of the gas consumption (10^{-3} moles/g of catalyst metal·hr).

[c] Reaction temperature was 55°C.

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TETSURO SEIYAMA
NOBORU YAMAZOE
JUN-ICHI HOJO
MASANORI HAYAKAWA

Department of Applied Chemistry
Faculty of Engineering
Kyushu University
Fukuoka, Japan

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The Catalytic Activity of α- and β-Aluminum Fluoride

The catalytic properties of aluminum fluoride have been studied relatively little up to now, partly as a consequence of negative results of experiments in the period in which the extreme activity of the other aluminum halides found widespread attention and application (*1*).

It was not until 1962 that Kaiser, Moore, and Odioso (*2*) described the isomerization of pentenes and hexenes, using aluminum fluoride catalysts prepared by prolonged treatment of alumina with concentrated HF solutions. In Russia, Chernov and Antipina (*3*) studied the cracking of isopropyl benzene with a BF_3-activated alumina catalyst; in later experiments (*4*), they also investigated the activity of aluminum fluoride catalysts prepared according to different methods, and found a relation between the activity of these catalysts and their acidity.

The first indications of the existence of two modifications of aluminum fluoride are already relatively old. Thilo (*5*) described, in 1938, the formation of AlF_3 by thermal decomposition of NH_4AlF_4 at 500°C, which compound was formed by heating of $(NH_4)_3AlF_6$ at temperatures below 350°C. Biltz and Rahlfs (*6*) had reported already in 1927 without comment the remarkably low density of AlF_3 obtained in this way, from which it is clear now that it concerned the low density hexagonal β-modification. It was not before 1962, however, that Christoph, Elkton, and Teufer (*7*) clearly distinguished between rhombic α- and hexagonal β-aluminum fluoride by means of X-ray diffraction measurements; the authors claimed the use of the β modification (prepared by dehydration of α-aluminum fluoride trihydrate at relatively low temperatures) as an active and highly selective catalyst for the hydrofluorination of acetylene.

In a recent patent application (*8*), an industrial process for the manufacture of pure anhydrous β-AlF_3 from ammonium fluoride, a by-product of the manufacture of phosphoric acid from fluorine containing phosphate ores, is described (compare Fig. 1).

In the first reaction step an aqueous so-