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Catalytic Oxidation

V. Mechanisms of Olefin Oxidation Over Supported Iridium

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The reactions of ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene and the two 2-pentenes were compared over supported Ir catalysts. The rates of total oxidation decreased in the order given, while the corresponding apparent activation energies increased. With ethylene, rate maxima appeared on varying the pressure of either reactant; with propylene and 1-butene, maxima were found with oxygen only; with the other olefins, the rates increased with olefin pressure and were inhibited by oxygen over the entire range studied. About 40% of all the olefin oxidized became partial oxidation products. The most important of these were acetic acid from ethylene, propylene, the 2-butenes and the 2-pentenes, and propionic acid and acetone from 1-butene and isobutene, respectively. Smaller amounts of unsaturated aldehydes, diones and other ketones and acids were also detected. The acetic acid formed from propylene-1-^{14}C was not radioactive. A large kinetic isotope effect was found for the total oxidation of propylene labeled with deuterium in the methyl group. Possible mechanisms are discussed.

Introduction

A variety of behavior has been found in the catalytic oxidation of simple olefins. Partial oxidation products fall into classes such as ketones, aldehydes and acids, unsaturated aldehydes, dienes and epoxides. In some instances, an homologous series of compounds is produced from the corresponding olefins, while in others the products are dependent upon the molecular weight or structure of the olefin. Thus, unsaturated aldehydes are the rule over Cu_2O while acrolein is formed from C_3H_6, and dienes from higher olefins, over bismuth–molybdate (*1*). Both Pd and Ir are selective for oxidation of C_2H_4 to acetic acid and both produce acetic acid, not propionic acid, from propylene (*2*). Pt, Rh, Au, and Ru are unselective with C_2H_4, but acrolein is formed over the latter three from propylene (*3, 4*). Silver is very selective for the formation of ethylene oxide from C_2H_4, and is the only catalyst known for this reaction (*1*). With some mixed oxide systems, the product distribution is affected by the ratio of the individual oxides; e.g., the relative yields of acetic acid and acetone during C_3H_6 oxidation over SnO_2–MoO_3 can be varied in this way (*5*). The formation of acetic acid from C_3H_6 is unusual; the principal partial oxidation products from most other heterogeneous reactions contain the same number of carbon atoms as the parent olefin. The present data show that the reaction over Ir proceeds by cleavage of the olefinic double bond and is quite general for low molecular weight olefins. The mechanism may be analogous to the RuO_4 catalyzed scission of double bonds (*6*).

Experimental Methods

Catalysts and Reagents

The 5% Ir/SiO_2 catalyst was used in our previous work (*2*). The 5% Ir/α-Al_2O_3 catalyst was furnished by Englehard Industries; its support was Alcoa T-61, 14 to

20 mesh, area $\leq 0.3\ m^2/g$. The metal surface area of Ir/SiO_2 was 7.3 m^2/g of Ir; that of $Ir/\alpha\text{-}Al_2O_3$ was too small to measure.

Details concerning the purity and purification of the CP grade C_3H_6, O_2, He and H_2 are given elsewhere (*2*). The deuterated propylenes were from the same lots used earlier (*3, 4*) and the propylene-1-^{14}C was supplied by the New England Nuclear Co; 0.25 mC was diluted to 500 ml with Matheson CP C_3H_6 before use. The C_2H_4 (Lif-O-Gen) and the butenes (Phillips) were Research Grade; the 2-pentene was a mixture of the *cis-* (72%) and *trans-* (28%) isomers obtained from Matheson, Coleman and Bell.

Equipment and Procedures

The single pass flow reactor, and most of the techniques were those employed previously (*2*). A mixture of olefin (5 to 50 Torr) and O_2 (10 to 140 Torr) were diluted with He to atmospheric pressure and flowed through a 2 ml bed of catalyst. Comparisons of activity and selectivity were made at *standard conditions* (olefin, 20 Torr; O_2, 70 Torr and space velocity, 25 min^{-1}). The labeled propylenes were introduced into the reactant stream at the same pressure as the unlabeled C_3H_6, which they replaced, from a gastight syringe being driven at a constant rate (Sage Instruments Model 234). The acetic acid from the deuterated compounds was separated by GLC and analyzed with a Nuclide mass spectrometer. Products from the propylene-1-^{14}C were burned to CO_2, which was dried and its radioactivity determined. The product CO_2 and the unreacted labeled propylene were counted in the same apparatus. The validity of these methods was checked by calibration experiments.

RESULTS

Products

The partial oxidation products from the reaction of olefins over $Ir/\alpha\text{-}Al_2O_3$ under standard conditions are listed in Table 1. The results for ethylene and propylene oxidation were consistent with our earlier findings (*2*) for Ir/SiO_2 catalysts although the selectivities to acetic acid (the main product) were a little higher with the latter. Acetic acid was also the principal partial oxidation product from 2-butene and 2-pentene, while propionic acid and acetone were formed in the greatest amount from 1-butene and isobutene, respectively. The

TABLE 1
PARTIAL OXIDATION PRODUCTS FROM REACTION OF OLEFINS OVER $Ir/\alpha\text{-}Al_2O_3$[a]

	Selectivity to major products[b] (%)			
Olefin oxidized	Acetic acid	Propionic acid	Acetone	Minor products observed[c]
Ethylene	4	—	—	Acetaldehyde <0.1
Propylene	18	3	3	Acrolein, 0.5; acetaldehyde, <0.1
1-Butene	11	15	<0.1	Methyl vinyl ketone, 1–3; methyl ethyl ketone + 2,3-butanedione, 1–3
trans-2-Butene	25	<0.2	<0.1	Methyl vinyl ketone, 1–4; methyl ethyl, ketone + 2,3-butanedione, 1–3
cis-2-Butene	25	<0.2	<0.1	Methyl vinyl ketone, 2–8; methyl ethyl ketone + 2,3-butanedione, 2–6
Isobutene	10	<0.2	17	Methacrolein, 2–10; C_4 acids, >2
2-Pentenes	32	8	<0.1	Unsat. and sat. C_5 ketones[d]

[a] Olefin pressures from 14 to 24 Torr and oxygen pressures from 45 to 75 Torr. For approximate temperatures, see Table 2.
[b] Moles of product formed from each 100 moles of olefin oxidized to all products.
[c] These selectivities were very dependent on overall conversion.
[d] Identities and selectivities were not completely established.

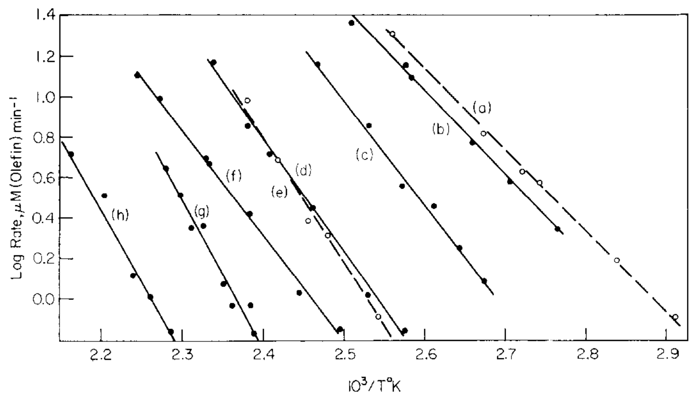


FIG. 1. Effect of temperature on rate of total oxidation of olefins over Ir/α-Al_2O_3: (a) ethylene (aged catalyst); (b) ethylene (new catalyst); (c) Propylene; (d) 1-butene; (e) cis-2-butene; (f) *trans*-2-butene; (g) isobutene; (h) 2-pentenes.

substantial amounts of acetic acid produced concomitantly in the latter oxidations may have resulted from reaction after olefin isomerization. The unreacted olefin was isomerized, e.g., with 1-butene over Ir/SiO_2 at 155°C (which gave a conversion to all products of 70%) the unreacted olefin had the composition: 1-butene 73%, *trans*-2-butene 23% and *cis*-2-butene 4%.

Minor products of olefin oxidation usually had the same number of carbon atoms as the reactant and can be divided into several classes: unsaturated aldehydes, e.g., acrolein from propylene, methacrolein from isobutene, but crotonaldehyde was not found in the products from the 2-butenes; unsaturated ketones, e.g., 1-butene-3-one from the *n*-butenes; saturated ketones, e.g., acetone from propylene, methyl ethyl ketone from the *n*-butenes; diones, e.g., 2,3-butadione from the *n*-butenes; and acids, e.g., propionic acid from propylene and C_4 acids from isobutene.

Characteristics of Total Oxidation

The data of Table 1 show that the overall selectivity to all partial oxidation products never exceeded 45% (the remaining products being CO_2 and H_2O). The effect of temperature on the rate for the several olefins is shown in Fig. 1 and the corresponding apparent activation energies are listed in Column 4, Table 2. The latter increased slightly with carbon number although the extent of the trend was obscured by the rather large uncertainties in the values for oxidation of *cis*-2-butene, isobutene and the 2-pentenes. A comparison of the relative activities for oxidation of the different olefins is made in Column 5, by specifying the temperatures required to achieve an oxidation rate of 0.5 μM (olefin) min^{-1} g^{-1} (catalyst). The data were corrected to the standard conditions (20 Torr olefin, 70 Torr O_2) from those used in the experiments (Columns 2 and 3) using the pressure dependencies described later. The two sets of data for ethylene are values obtained in two experiments separated by a 12-mo time interval, during which over 20 other oxidation experiments were carried out with the same catalyst sample. The agreement was within the experimental error, demonstrating the stability of this catalyst system. The data for the other olefins suggested an inverse relationship between the oxidation rate and the olefin chain length. The order of activity for the butenes was 1-but $\approx$ *cis* > *trans*-2-butene. The Arrhenius plots may have reflected the selectivity differences at the test conditions.

With Ir/α-Al_2O_3, the rate of C_2H_4 oxidation passed through maxima (Figs. 2A and B) with variation of the pressure of either reactant; with C_3H_6 a maximum appeared with O_2 pressure, but not with olefin pressure. (Nor were maxima found with either of these reactions in our earlier work with

TABLE 2
KINETIC PARAMETERS FOR TOTAL OXIDATION OF OLEFINS OVER Ir/α-Al_2O_3

Reactant	Olefin press. (Torr)	O_2 Press. (Torr)	Activation energy, (kcal/mole)	Temp for standard activity[a] (°C)	Olefin pressure for max rate (Torr)[b]	O_2 Pressure for max rate (Torr)[c]
Ethylene[d]	24	51	18	93	14	70
Ethylene[e]	18	73	18	92	—	—
Propylene	15	44	23	114	>40	45
1-Butene	21	73	25	137	>30	60
cis-2-Butene	78	74	30	136	>40	<15
trans-2-Butene	19	70	24	151	>50	<15
Isobutene	16	75	32	161	>40	<15
2-Pentenes	18	74	29	183	—	—

[a] Temperature at which rate of total oxidation is 0.5 μM olefin min^{-1} g^{-1} when olefin pressure = 20 Torr and oxygen pressure = 70 Torr.
[b] With oxygen pressure in range 45 to 75 Torr.
[c] With olefin pressure in range 14 to 24 Torr.
[d] Initial ethylene experiment on catalyst sample.
[e] Second ethylene experiment on same catalyst sample after intervening time interval of 12 mo during which over 20 oxidation experiments were carried out over sample.

Ir/SiO_2 catalysts.) In each case, the position of the maximum in one reactant shifted slightly to higher pressures if the pressure of the other reactant was increased. With the higher olefins, only 1-butene showed a rate maximum (at an O_2 pressure of about 60 Torr). The final columns of Table 2 show that the rates for the other butenes were always inhibited by O_2, but increased with olefin pressure, as found for C_2H_4 and C_3H_6 over Ir/SiO_2 catalysts (*2*).

Effect of Reaction Variables on Selectivity

The rates of formation of the *minor* oxidation products listed in Table 1 could not be measured with sufficient accuracy to quantitatively define their dependence on temperature and reactant pressures. The selectivities for the *major* partial oxidation products (propionic acid from 1-butene, acetone from isobutene and acetic acid from the other olefins) declined slowly with increasing temperature, suggesting that the activation energies for the formation of these were lower by 1 to 5 kcal mol^{-1} than that for the production of CO_2 and H_2O. The pressure dependencies of the rates of formation of the major partial oxidation products were generally similar to those for total oxidation, but the selectivities tended to decrease slightly with

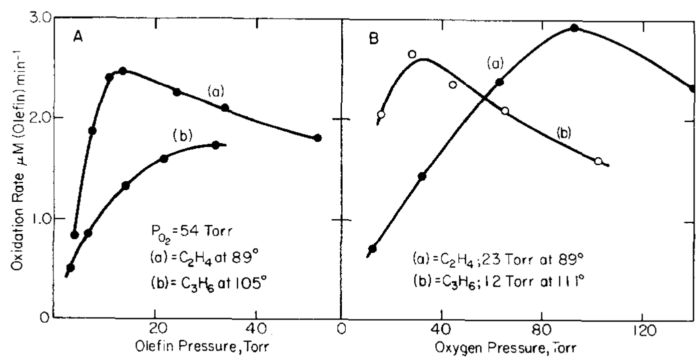


FIG. 2. Effect of reactant pressure on rate of total oxidation over Ir/α-Al_2O_3.

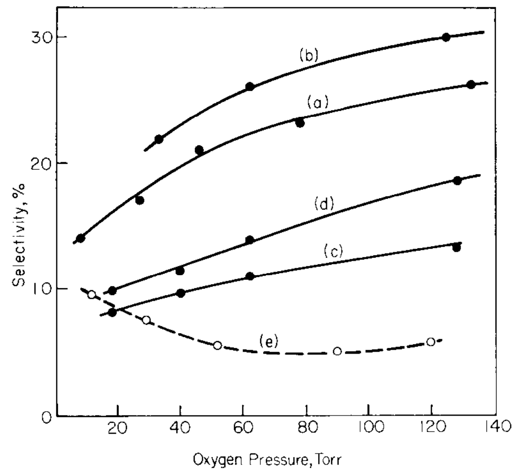


FIG. 3. Effect of oxygen pressure on selectivity of olefin oxidation over $Ir/\alpha\text{-}Al_2O_3$: (a) acetic acid from propylene; (b) acetic acid from *trans*-2-butene; (c) acetic acid from 1-butene; (d) propionic acid from 1-butene; (e) acetic acid from ethylene.

increasing olefin pressure and to increase appreciably with oxygen pressure. The latter effect is shown in Fig. 3. The single exception was acetic acid from ethylene which had the reverse dependency, reflecting a different mechanism (*2*) in this case. Partial oxidation of C_3 through C_5 olefins apparently was favored by an oxygen covered surface.

Oxidation of Deuterium-Labeled Propylenes

The results from experiments in which deuterium-labeled propylenes were oxidized are summarized in Table 3. Each determination of the rate of total oxidation, or of acetic acid formation, for a labeled compound was bracketed with measurements of the corresponding rate for unlabeled propylene. For partial oxidation, the isotope effects were small ($1.3 > k_h/k_d > 1$) and not specific to labeling in one particular position. A large isotope effect ($k_h/k_d = 3.5$) was found, however, for total oxidation of propylenes when the methyl group was labeled with deuterium. The dramatic increases in selectivity found in these cases stemmed from this effect. Values for both modes of oxidation of CH_3CDCH_2 were probably low because its pressure was

TABLE 3
RATE OF OXIDATION OF DEUTERIUM-LABELED PROPYLENES OVER $Ir/\alpha\text{-}Al_2O_3$[a]

Reactant	Rate of oxid. to: CO_2 and H_2O	Rate of oxid. to: Acetic acid	Selectivity to acetic acid, %
C_3H_6	4.46	1.78	28.5
C_3D_6	1.20	1.40	53.8
C_3H_6	4.43	1.95	30.5
C_3H_6/D_2O[b]	—	2.24	—
CD_3CHCH_2	1.36	1.61	54.2
C_3H_6	4.60	1.85	28.7
CH_3CHCD_2	4.10	1.40	25.4
C_3H_6	4.38	1.73	28.3
CH_3CDCH_2	3.08[c]	1.38[c]	30.9
C_3H_6	4.63	1.76	27.5

[a] At 140°, olefin pressure 7 Torr, oxygen pressure 120 Torr, in μM olefin min^{-1}.
[b] Oxidation of C_3H_6 in the presence of 10 Torr of D_2O.
[c] May be low because of low inlet propylene pressure.

somewhat below that of the C_3H_6 it replaced (the reaction was about first-order in olefin pressure under the experimental conditions). The rate of acetic acid formation was enhanced slightly by H_2O or D_2O. A corresponding increase in selectivity may have occurred, although the rate of total oxidation was difficult to measure accurately in these cases.

Oxidation of C_3H_6 in the presence of D_2O led to a small incorporation of deuterium into the product acetic acid (Table 4). Most of this may have occurred at the acid hydroxyl group during passage through the GLC column since the water was eluted first. The reverse process was probably responsible for the nearly complete absence of acetic acid-d_4 in the products from oxidation of C_3D_6. Therefore, it was not possible to measure with accuracy the degree of retention of deuterium in the oxidation of CD_3CHCH_2 to acetic acid, or the loss of deuterium during the reaction of CH_3CHCD_2. It was, however, qualitatively apparent that these reactions occurred with cleavage at the double bond and with minimal intramolecular hydrogen–deuterium migration. Moreover, the IR

TABLE 4
DEUTERIUM CONTENT[a] OF ACETIC ACID FROM OXIDATION OF LABELED PROPYLENES[b]

Propylene	d_0	d_1	d_2	d_3	d_4
C_3H_6/D_2O[c]	90.9	6.0	1.4	1.6	
CD_3CDCD_2	0.5	1.6	3.4	91.6	2.9
CD_3CHCH_2	1.1	3.9	8.2	83.2	3.6
CH_3CHCD_2	85.0	6.2	5.5	3.3	
CH_3CDCH_2	93.3	5.9	0.8		
C_3H_6/C_3D_6[d]	50.3	4.7	4.2	37.2	1.0

[a] Corrected for small amount of unreplaced CH_3COOH still present from prior oxidation of C_3H_6.
[b] See footnote *a* of Table 3 for conditions.
[c] C_3H_6 oxidation in the presence of 10 Torr D_2O vapor.
[d] Composition of starting mixture: d_0 = 48.4%, d_1 = 0.3%, d_5 = 1.4%, d_6 = 49.9%; unreacted material: d_0 = 46.0%, d_1 = 1.0%, d_5 = 1.6%, d_6 = 51.4%.

spectra of the unreacted propylenes from these experiments showed no evidence of isomerization. The results of an experiment in which a 1:1 mixture of C_3D_6 and C_3H_6 was reacted are presented in the final line of Table 4. These demonstrated that intermolecular exchange was also minimal and that the isotope effect in C_3D_6 oxidation to acetic acid was small. More CH_3COOH was produced than CD_3COOH and an isotope effect of about 1.4 was estimated from these data; this was in fair agreement with the value derived from the rate data (Table 3).

Oxidation of Propylene-1-^{14}C

This reaction provided a convincing demonstration that acetic acid was formed by cleavage at the double bond. The results are shown in Table 5. The specific activity of the product acetic acid was only 6% that of the starting propylene whereas that of the CO_2 was larger. The nonzero radioactivity in the acetic acid probably reflected the presence of a small propylene-3-^{14}C impurity. The CO_2 which was produced during double bond cleavage should have contained all of the labeled carbon of the propylene; the CO_2 produced in total oxidation, therefore, should be only one-

TABLE 5
SPECIFIC RADIOACTIVITIES OF PRODUCTS AND REACTANT FROM OXIDATION OF PROPYLENE-1-^{14}C OVER $Ir/\alpha\text{-}Al_2O_3$[a]

Compound	Sp act[b]
Propylene	77 ± 2
Carbon dioxide	91 ± 1
Acetic acid[c]	4.5 ± 1.0

[a] At 134°, propylene pressure, 8 Torr; oxygen pressure, 95 Torr.
[b] In counts min^{-1} $Torr^{-1}$ carbon $atom^{-1}$.
[c] Counted as carbon dioxide after combustion.

third as radioactive. Knowing that the selectivity was about 30%, the specific activity of the CO_2 formed in the experiment, where both partial and complete oxidation occurred, could be calculated. The result, 96 counts min^{-1} $Torr^{-1}$, agreed with the experimental result to within the experimental error.

Oxidation of Model Intermediates

The data from the labeled propylenes led to two conclusions. First, a large primary isotope effect lowered the rate of total oxidation of propylenes containing deuterium in the methyl group, and second, acetic acid was formed by cleavage of the double bond. The isotope effect was similar in magnitude to that found for the same reaction over Rh (*3*). With Rh, acrolein was formed in fair yield (20%) via a symmetrical intermediate and its rate of formation had a similar isotope effect. Small amounts of acrolein were formed over Ir, much less than with Rh; hence, part of the CO_2 and H_2O may have stemmed from its further rapid oxidation.

The first products of C_3H_6 double bond cleavage should be formaldehyde and acetaldehyde, neither of which were observed. This led us to suspect that: (a) formaldehyde (or formic acid) was being rapidly oxidized to CO_2 and H_2O and (b) acetaldehyde was oxidized rapidly and specifically to acetic acid. To test these predictions the experiments in Table 6 were made. The specified compounds were added under conditions such that the con-

TABLE 6
RELATIVE RATES OF OXIDATION OVER $Ir/\alpha\text{-}Al_2O_3$[a]

Reactant	Reaction rate (μm min^{-1})	Product distribution, %						
		Total oxid.	Acetaldehyde	Acrolein	Acetone	Acetic acid	Propionaldehyde	C_3 acids
CH_3CHCH_2[b]	0.5	70	<0.1	0.5	2	30	0.2	3
HCHO[c]	4	>98	—	—	—	—	—	—
HCOOH[d]	>10	>98	—	—	—	—	—	—
CH_3CHO[e]	9	<5	—	—	—	>90	—	—
CH_2CHCHO[f]	3.3	80[g]	—	—	—	—	—	10
CH_2CHCH_2OH[f]	>6	>70	—	25	—	—	—	5
C_2H_5CHO[f]	0.9	<5[g]	—	—	—	—	—	>90
C_3H_7OH[f]	1.5	<10	—	—	—	—	>90	10
$CH_3CH(OH)CH_3$[e]	0.8	<10	—	—	>90	—	—	—
CH_3COCH_3[f]	<0.1	—	no products detected					
$CH_3CH—CH_2$[f] \ / O	<0.5	—	no products detected					

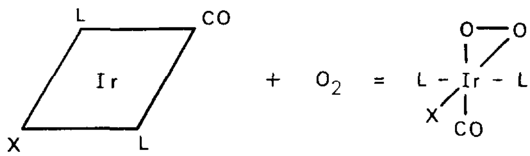
[a] At 121°, P_{O_2} = 75 Torr, over 7 g catalyst.
[b] $P_{C_3H_6}$ = 7 Torr, equivalent to 20 μm min^{-1}.
[c] Rate of addition uncertain due to some polymerization in syringe.
[d] Added at 11.8 μm min^{-1}.
[e] Added at approximately 20 μm min^{-1}.
[f] Added at approximately 6.8 μm min^{-1}.
[g] Somewhat uncertain because of competition with propylene being simultaneously oxidized.

comitant rate of propylene oxidation was low. As expected, both formaldehyde and formic acid readily formed CO_2 and H_2O while acetaldehyde, which reacted 20 times as fast as propylene, yielded mainly acetic acid. Acrolein also was oxidized much faster than propylene to CO_2 and H_2O and a small amount of acrylic acid. Allyl alcohol, another possible intermediate, was converted to acrolein, CO_2 and H_2O. Acetone and propionic acid were minor products of propylene oxidation. The data in Table 6 show that 2-propanol and 1-propanol, respectively, were possible intermediates in their formation. Propylene oxide was evidently not involved in any reaction step since it was not observed, although it was stable under reaction conditions. Acetone, acetic and propionic acids were also stable.

DISCUSSION

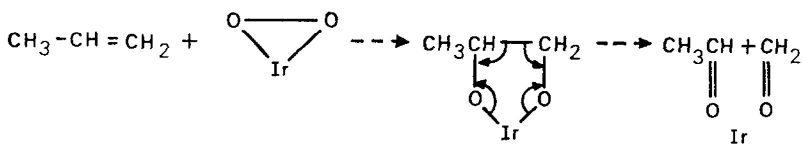
In the oxidation of simple olefins, several reactions take place simultaneously on the catalyst, and the differences which are observed among catalysts may reflect the extent to which one pathway is favored over another. When the molecule is attacked at a conjugated paraffinic carbon, the reaction passes through a symmetric (allylic) intermediate to acrolein (with C_3H_6) or to a diolefin. This reaction was favored (*3*, *4*) over Rh, Ru and Au, but acrolein appeared as only a minor product over Ir. With the latter, attack at the double bond was favored, so that any acrolein formed was rapidly reacted on to CO_2 and H_2O. Similarly, the single carbon fragment from cleavage of the double bond of α-olefins was rapidly converted to CO_2 and H_2O. Multiple carbon fragments, however, were stabilized by formation of aldehydes and acids. With C_2H_4 this possibility does not exist. Bond cleavage, or attack of the molecule simultaneously at both ends (*2*, *8*), results in total oxidation; acetic acid is formed only as fast as an intramolecular shift of hydrogen can occur to form the methyl group (*2*); epoxide formation stems from another reaction (*9*), which is important only over Ag. Finally, since equimolar quantities of acetic and propionic acids were not formed in the oxidation of the 2-pentenes, some further oxidation of the higher aldehydes must occur.

The particular activity of Ir for the cleavage reaction may be associated with its known ability (*10*) to form coordination complexes with O_2, viz,



(1)

where L represents Ph_3P and X a halide. Thus, cleavage may occur by



(2)

in which a propylene molecule adds across a coordinated oxygen molecule. If prior coordination of the olefin molecule to the same metal atom is necessary, then the scheme would be similar to that discussed by Mango and Schactschneider (*11*) for the catalysis by transition metals of addition reactions which are forbidden by the Hoffman–Woodward-rules (*12*). The direct addition of ground state (triplet) oxygen to a singlet molecule such as an olefin is unfavorable because of the difficulty of spin conservation (*13*). However, reaction (2) is not restricted in this way. Complexes such as that of Vaska (*10*) are diamagnetic and the O–O distance is relatively long (1.30 to 1.60) (*14*).

The intermediate proposed in Eq. (2) is very similar to that of the osmate esters, which function in the oxidation of olefins (*15*) by osmium tetroxide. Usually these latter reactions are carried out in such a way that hydroxylitic cleavages take place at the Os–O bonds, thus yielding cis-diols; reoxidation of the catalyst is accomplished by a suitable oxidant, which under specialized conditions can be air (*16*). The major partial oxidation products derived from the Ir-catalyzed reaction were consistent with the initial cleavage at the carbon-carbon bond according to reaction (2). Ruthenium tetroxide oxidations may operate in this same way (*6*).

The rate maxima found with both olefin and oxygen pressure would be interpreted classically in terms of a reaction between two adjacently adsorbed species competing for the same surface sites (*17*). Under some conditions our data could be fitted quite accurately by equations appropriate to this theory, but the parameters derived for one set of experimental conditions could not be carried over to a different set. As noted previously (*2–4*), the rate maxima are also suggestive of a radical chain mechanism. The presently available data simply do not warrant further speculation on kinetic interpretations.

The results shown in Fig. 1 and Table 2 show that increasing substitution at the double bond effects a decrease in oxidation rate. Similar behavior was observed for olefin hydrogenation although the data are sparce for some of these metals (*18*). However, the reasons for the similarity are probably not the same, as the apparent activation energy for hydrogenation decreases with substitution while for oxidation the opposite trend was found.

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