JOURNAL OF CATALYSIS 26, 1–10 (1972)

The Catalytic Oxidation of Propylene to Benzene

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Received November 27, 1970; revised October 16, 1971

The oxidation of propylene to benzene has been found to be catalyzed by indium oxide. 1,5-Hexadiene and acrolein are produced in the early stages of the reaction, the diene oxidizing further to produce benzene. The kinetics of the reaction have been examined in some detail, and a tentative mechanism has been advanced involving the removal of hydrogen from the allylic carbons of propylene π-bonded to an In^{3+} ion as the rate-determining step.

The oxidation of olefins to unsaturated products over mixed oxide catalysts has received much attention over the last few years (*1–3*). The process has many advantages over conventional dehydrogenation reactions (*4*), not least that the latter process is reversible and the maximum yield of products is defined by the equilibrium constant at the particular conditions of reaction.

Similar drawbacks exist for acid catalyzed polymerization and cyclization reactions (*5*), but in this case no comparable oxidative process has been developed. With this in mind, attempts were initiated to identify a catalyst for the polymerization and subsequent cyclization of olefins under oxidative conditions, using the oxidation of propylene to benzene as an illustrative example.

Early experiments were based on reports from the literature: possible catalysts were found either to be active for the dimerization reaction and inactive for cyclization (e.g., thallium oxides (*6*)) or to be active for cyclization and rather inactive for dimerization (e.g., tin/antimony oxide (*2*) or bismuth molybdate (*1*): see however, Ref. (*7*)). As a result, an attempt was made to identify a new catalyst, using the analogy of oxidative dehydrogenation over molybdates as a guide (*1*). With this reaction, there is general agreement that abstraction of an allylic hydrogen by oxidic oxygen occurs after adsorption of the olefin on the catalyst surface. An electron is then transferred to the metal center, subsequent reactions leading to the formation of an unsaturated aldehyde or a diene, depending on the structure of the original fuel.

With these ideas in mind, it was thought that a similar mechanism could be proposed for the dimerization of propylene. The formation of acrolein from propylene over bismuth molybdate demands the transfer of two electrons for the overall reaction: these are, however, transferred one at a time to the catalyst. If a metal ion required two electrons effectively simultaneously (*8*), then there seemed to be a good chance that one electron could be removed from each of two adsorbate molecules. If, as a result of the electron transfer, the adsorbate–catalyst bonding became weakened, the organic fragments might be expected to dimerize. Reoxidation of the reduced metal ion would then complete the catalytic cycle. Once the concentration of hexadiene had built up, a similar reaction could occur over the same type of catalyst to give cyclization and further dehydrogenation to benzene.

A survey of possible compounds showed that indium oxide could be a suitable cata-

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lyst: the exact reasons for this are discussed in the context of the reaction mechanism. The oxide was tested experimentally and found to be a selective catalyst for the oxidation of propylene to benzene.

EXPERIMENTAL

Indium oxide was prepared by precipitating the hydroxide from a solution of indium sulfate (B.D.H.) with ammonia. The precipitate was washed, dried at 150°C and activated at 560°C in a stream of air. Supported catalyst was prepared by wet mixing fine ground oxide with 20–30 mesh pumice, the solid being dried and reactivated. Such a catalyst could be prepared containing between 14 and 70% In_2O_3 by weight.

Experiments were carried out in a conventional flow apparatus, the catalyst being placed in a glass reactor mounted in a tin bath. The temperatures at the start, middle and end of the bed could be measured, and, in the absence of a chemical reaction, were constant to within ±0.2°C.

The products of reaction were analyzed gas chromatographically using two systems. Analysis of combustible products involved a flame ionization detector associated with a column containing diethylene glycol/silver nitrate (30:70) supported on chromosorb P (15 hr:25°C). Oxygen, nitrogen and carbon monoxide were analyzed on a molecular sieve column (3 hr:20°C) while carbon dioxide and propylene were separated from other components on a silica gel column (2.5 hr:20°C): all of these gases were analyzed using a katharometer detector. Product identification was confirmed by mass spectrometric analysis and by the use of alternative columns.

RESULTS

Initial studies were completed over an unsupported indium oxide catalyst, nominally maintained at 444°C. Preliminary experiments showed that the yield of hexadiene plus benzene passed through a maximum relative to other products at a mole fraction of oxygen near to 0.2. The yield of major products was examined as a function of contact time under these conditions (Fig. 1). Traces of acrolein were observed among the initial products of reaction, but these tended to overoxidize readily. The yield of benzene passed through a well-defined maximum at a contact time of 1.2 cc/sec/cc.

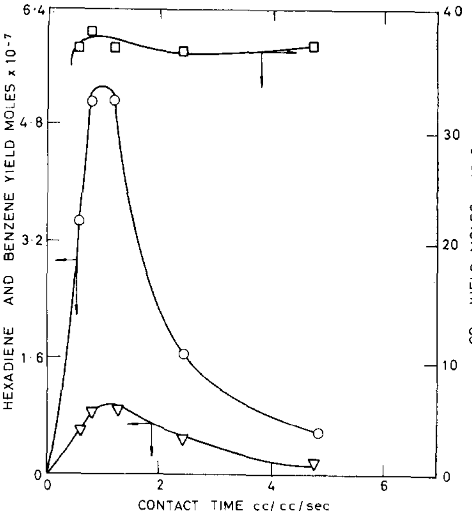


FIG. 1. Product yields as a function of contact time. $T = 445°C$; unsupported catalyst; oxygen = 0.2 mole fraction, propylene = 0.8 mole fraction. ▽ = Hexadiene; ○ = benzene; □ = carbon dioxide.

Using this value, the yield of products was examined as a function of the oxygen and fuel concentrations (Figs. 2 and 3). With no oxygen in the feed, no production of hexadiene or of benzene was apparent, but both products increased and passed through a maximum as the concentration of oxygen was increased. The yield of carbon dioxide, on the other hand, increased linearly with the proportion of oxygen. The effect of varying the concentration of propylene was then examined with the oxygen concentration maintained at $8.9 \times 10^{-3} M$ liter^{-1} (Fig. 3). The yield of hexadiene increased with the proportion of propylene while the yield of benzene passed through a maximum (and the yield of carbon dioxide through a minimum) at a mole fraction of propylene of 0.6 (corresponding to a concentration of $26.7 \times 10^{-3} M$ liter^{-1}).

The effect of temperature on the reaction was found to be more complex (Fig. 4), the

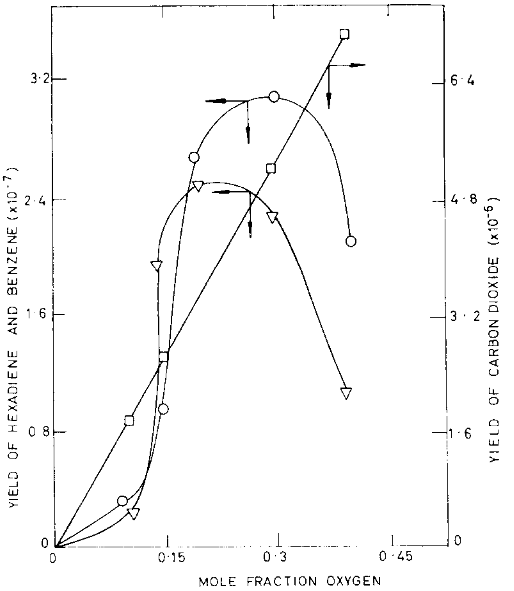


FIG. 2. The dependence of yield on oxygen. $T = 445°C$; unsupported catalyst; contact time = 1.2 cc catalyst/cc/sec; propylene concentration = 26.7×10^{-3} moles l^{-1} (0.6 mole fraction). Key as in Fig. 1.

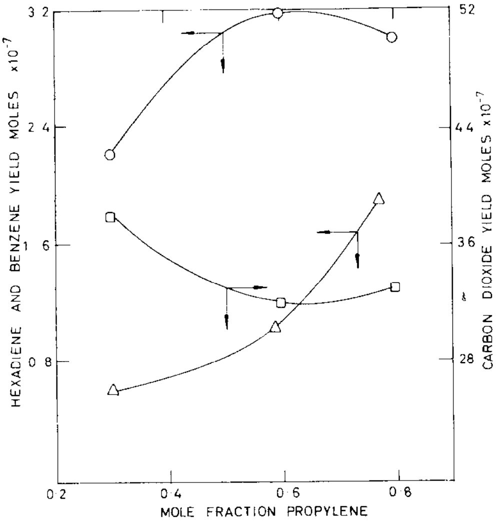


FIG. 3. The dependence of yield on propylene. $T = 445°C$; unsupported catalyst; contact time = 1.2 cc catalyst/cc/sec; oxygen concentration = 8.9×10^{-3} moles l^{-1} (0.2 mole fraction). Key as Fig. 1.

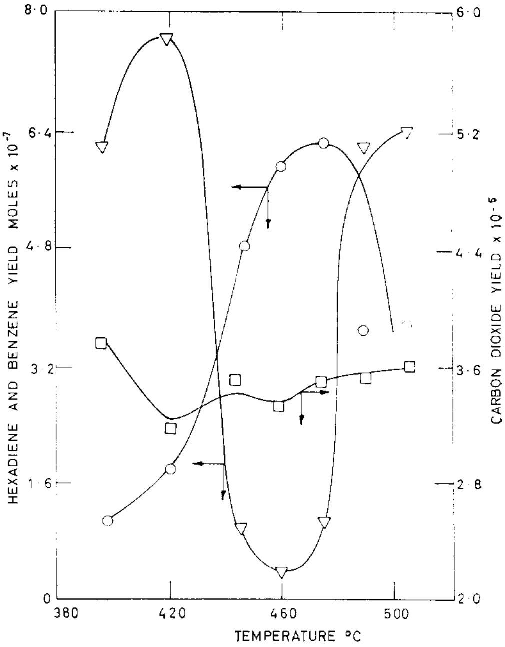


FIG. 4. The effect of temperature. Unsupported catalyst; contact time = 1.2 cc catalyst/cc/sec; [oxygen] = 8.9×10^{-3} moles l^{-1}; [propylene] = 35.6×10^{-3} moles l^{-1}. Key as Fig. 1.

amounts of hexadiene and benzene produced appearing to be inversely related. Examination of the results at higher temperatures showed that homogeneous reactions were influencing the products. The reaction was studied in a reactor filled only with support and the results were compared with those obtained from experiments over a supported indium oxide catalyst (Fig. 5). No carbon dioxide was observed in the absence of catalyst, and the overall reaction was not appreciable below 460°C. At higher temperatures, the amounts of hexadiene produced heterogeneously were much greater than homogeneously, except at very low contact times. The apparent activation energies for the homogeneous and heterogeneous reactions were calculated to be *ca.* 40 and 50 kcal/mole, respectively.

Temperature measurements made during reaction over the unsupported catalyst showed that the temperature in the bed could rise by as much at 50°C. In many cases the oxygen was found to be totally consumed during the reaction. The effect of using a supported catalyst was therefore examined: at low loadings of indium oxide, the bed was effectively isothermal and the conversion of oxygen was less than total. The dependence of products on reaction

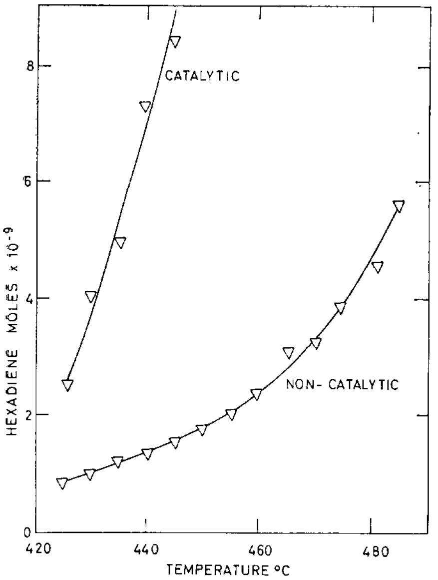


FIG. 5. The importance of the noncatalytic reaction. Supported catalyst = 0.15 wt % In_2O_3 on pumice; contact time = 0.6 cc solid/cc/sec; oxygen:propylene:nitrogen = 1:2:7. Non catalytic reaction investigated over pumice.

conditions was similar to the results obtained with the unsupported catalyst, although the yield of acrolein observed was considerably larger under isothermal conditions. No diminution in the yield of benzene (Fig. 1) could be observed when oxygen was available at all stages of reaction.

Measurements of the kinetics of the reaction were completed over dilute catalysts at isothermal conditions near to the concentrations of propylene and oxygen found to give maximum yield in the absence of any homogeneous interaction.

a. Initial rate studies. The rate of reaction was investigated as a function of reaction conditions initially at a temperature of 440°C. The homogeneous reaction was not appreciable at these temperatures, and the catalyst bed was isothermal. It was particularly important to work at low conversions to avoid inhibition of the reaction by products. Under these conditions only 1,5-hexadiene and acrolein were produced: benzene and carbon dioxide could not be identified in the exit stream from the reactor.

The variation of the yields of hexadiene and acrolein with contact time (defined as g of indium oxide/flow rate) was examined as a function of the concentration of propylene and of oxygen and as a function of temperature. Typical results are shown in Figs. 6–8. Calculation of the reaction orders and activation energies from graphs of this type showed that the initial rates of formation of hexadiene and of acrolein could be described by the equations

$$\text{Rate}_H = 1.75 \times 10^7 \exp(-45.6/RT) C_P^{0.38} C_O^{0.39}$$

and

$$\text{Rate}_A = 6.0 \times 10^4 \exp(-16.0/RT) C_P^{0.38} C_O^{1},$$

where H and A refer to hexadiene and acrolein, and C_P and C_O are the concentration in the gas phase of propylene and of oxygen, respectively. Values of energies of activation are given in kcal/mole. Standard tests for mass transfer effects (*9*) showed that these did not influence the results.

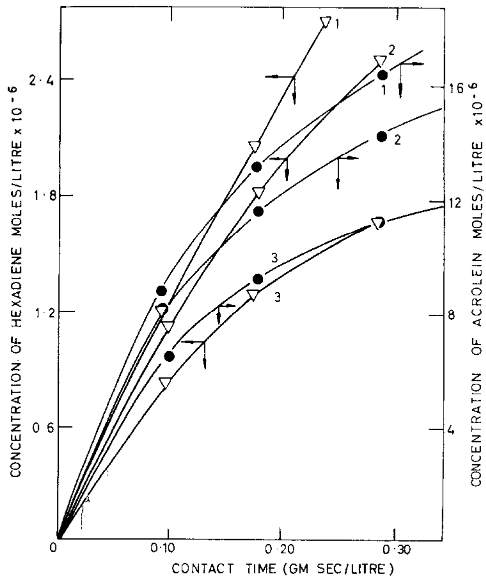


FIG. 6. The dependence of initial rate on the concentration of propylene. T = 440°C; [oxygen] = 8.9×10^{-3} moles l^{-1}; [propylene] = (1) 11.1×10^{-3}, (2) 8.9×10^{-3}, (3) 4.45×10^{-3} moles l^{-1}. ▽–▽ Hexadiene; ●–● acrolein.

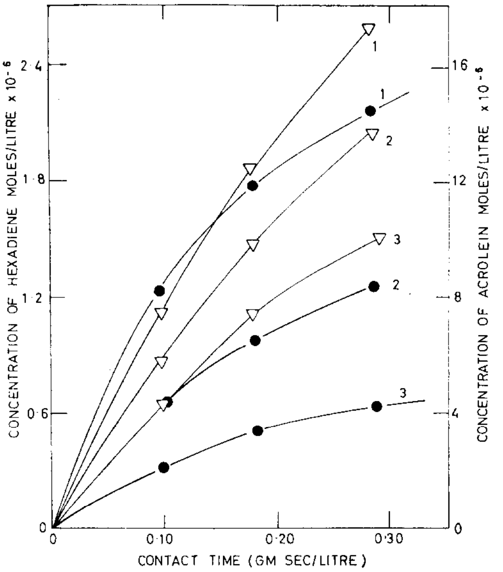


FIG. 7. The dependence of initial rate on the concentration of oxygen. $T = 440°C$; [propylene] $= 8.9 \times 10^{-3}$ moles l^{-1}; [oxygen] = (1) 8.9×10^{-3}, (2) 4.45×10^{-3}, (3) 2.23×10^{-3} moles l^{-1}.

b. Reactions at longer contact times. At longer contact times, two products appeared that had been previously observed only over the unsupported catalyst, namely carbon dioxide and benzene. Small amounts of hexatriene and 1,3-cyclohexadiene were also observed in some cases. Typical results for the behavior of the four major products are shown in Figs. 9 and 10. Several interesting trends can be noted. The yield of hexadiene was found to increase relatively rapidly with time, but to reach a steady value after ca. 50 g sec liter^{-1}. The yield of benzene, on the other hand, increased linearly and was influenced only to a very small extent by changes in the concentration of propylene or of oxygen. The yield of both products increased with increasing temperature.

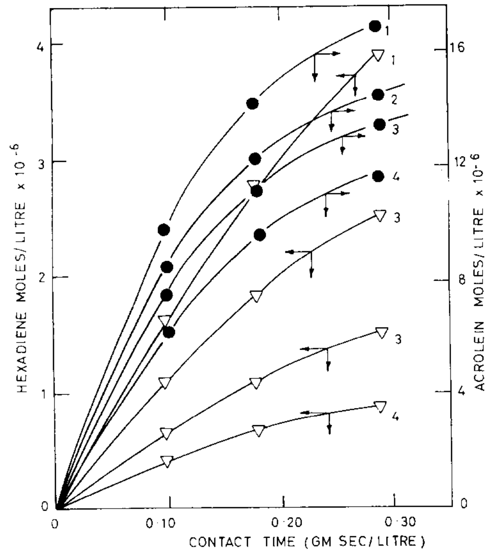


FIG. 8. The dependence of initial rate on temperature. [Propylene] = [oxygen] $= 8.9 \times 10^{-3}$ moles/liter; $T =$ (1) 450, (2) 440, (3) 430, (4) 420°C.

The yield of acrolein showed evidence of considerable overoxidation at higher temperatures and longer contact times although, surprisingly, this did not appear

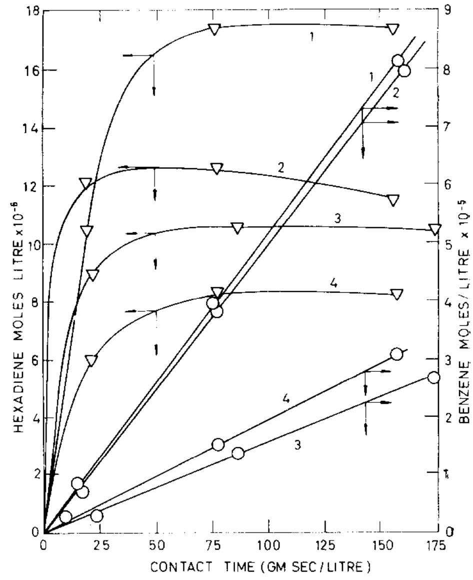


FIG. 9. The yield of benzene and hexadiene at longer contact times.

	Temperature °C	[Propylene] moles $l^{-1} \times 10^{-3}$	[Oxygen]
(1)	460	8.9	8.9
(2)	460	4.5	9.9
(3)	440	9.9	5.0
(4)	440	8.9	8.9

▽-▽ Hexadiene; ○-○ benzene; ●-● acrolein; □-□ carbon dioxide.

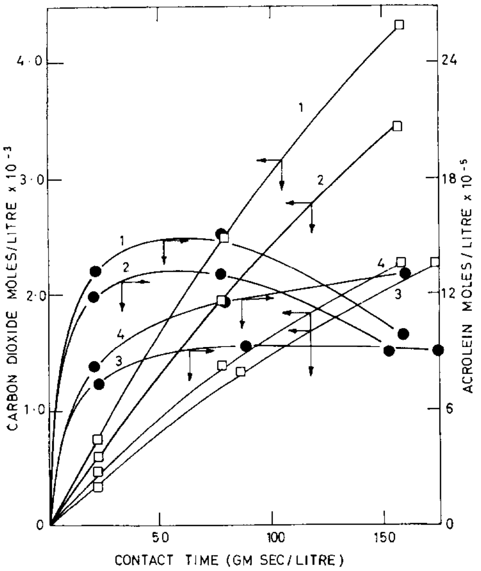


Fig. 10. The yield of oxygenated products at longer contact time. Key as in Fig. 4.

to be reflected directly by the yield of carbon dioxide.

At these long contact times, it is convenient to express the rate of production of carbon dioxide in terms of the propylene available, and of benzene (bz) in terms of the gas phase concentration of hexadiene. The rate expressions so obtained were

$$\text{Rate}_{\text{bz}} = 1.85 \times 10^{8} \exp(-45.5/RT) C_H{}^{0.08} C_O{}^{0.37}$$

$$\text{Rate}_{\text{CO}_2} = 1.0 \exp(-18.0/RT) C_P{}^{0.35} C_O{}^{0.50}.$$

Overoxidation of benzene was found to be negligible at 460°C, in that less than 3% of carbon dioxide was produced on passing a mixture of benzene ($2.23 \times 10^{-3} M$ l^{-1}) and oxygen ($4.45 \times 10^{-3} M$ l^{-1}) over the catalyst. The overoxidation of hexadiene, on the other hand, was more important and involved both a homogeneous and a heterogeneous component. Under any of the conditions used in the kinetic studies, the homogeneous oxidation produced benzene and carbon dioxide, but was some 500 times less important than the heterogeneous reaction. Subtracting these amounts from the overall yields showed that the heterogeneous reaction, giving benzene and carbon dioxide from hexadiene and oxygen, produced almost the same results with respect to benzene as mixtures of propylene and oxygen under the same conditions.

Attempts were made to characterize the overoxidation of acrolein, but the results were very irreproducible owing to polymerization of the aldehyde in the service lines to the reactor, causing irregularities in the feed.

The effect of product inhibition was examined by feeding products together with reactants to the catalyst. The addition of acrolein had a significant if irreproducible inhibitory effect on the yield of all products. The addition of benzene had no effect but the addition of hexadiene decreased the overall reaction and also the production of acrolein (Table 1). The addition of butadiene, which could be recovered unchanged from the product stream, decreased the concentration of both hexadiene and acrolein by an amount inversely proportional to the concentration of butadiene added.

TABLE 1
INHIBITION BY ADDED PRODUCTS[a]

Added hexadiene moles liter × 10^{-5}	Acrolein produced moles liter × 10^{-5}
0	3.30
0.48	2.94
0.64	2.86
3.46	2.50
17.25	1.67
23.60	1.37

[a] [Propylene] = [Oxygen] = 8.9×10^{-3} moles/liter: Supported catalyst = 0.15 wt % In_2O_3 on pumice; T = 440°C; contact time = 3 g sec liter^{-1}.

DISCUSSION

The preliminary results showed that indium oxide is a good catalyst for the oxidation of propylene to 1,5-hexadiene and to benzene. The selectivity of the catalyst, defined in terms of the number of moles of propylene converted to C_6 products compared with the number of moles totally converted, was high, even under not too carefully controlled conditions. Certainly the reaction demanded more detailed investigation under well-defined circumstances.

Some preliminary conclusions can be obtained from the results reported above. As a general trend, hexadiene and acrolein were found to be formed as initial products with benzene and carbon dioxide becoming important at later stages in the reaction. The overall process is a true oxidation involving the stoichiometric equations

$$2\,CH_3CHCH_2 + \tfrac{1}{2}\,O_2 = CH_2CHCH_2CH_2CHCH_2 + H_2O \quad (a)$$

$$CH_2CHCH_2CH_2CHCH_2 + O_2 = C_6H_6 + 2\,H_2O \quad (b)$$

$$CH_3CHCH_2 + O_2 = CH_2CHCHO + H_2O \quad (c)$$

$$CH_3CHCH_2 + 4\tfrac{1}{2}\,O_2 = 3\,CO_2 + 3\,H_2O. \quad (d)$$

No hydrogen was detected among the products and benzene does not appear to be destroyed except when the oxygen concentration drops to zero. At high oxygen concentrations, hexadiene seems more readily overoxidized than benzene.

The effect of varying the concentration of propylene is more revealing in the context of reactions on the surface. If the oxidation of propylene to hexadiene, step (a), and of hexadiene to benzene, step (b), both occur on the surface, then increasing the concentration of propylene should first favor step (a), and then, as the concentration of hexadiene builds up, step (b) should become of increasing importance. If the concentration of propylene is increased still further, hexadiene could be displaced from the surface, resulting in an increased gas phase concentration of the diene and a decreased concentration of benzene. At the same time the oxidation of hexadiene to carbon dioxide would decrease, and the oxidation of propylene to the same product should increase, resulting in a minimum in the yield of carbon dioxide as the propylene concentration is increased. All of these effects have been observed experimentally (Fig. 3).

Similar reasoning can be used to explain the dependence of products upon temperature (Fig. 4). As a result of the overheating of the unsupported catalyst, the actual temperatures in the bed are higher than the values recorded, but the trend in the isothermal system was found to be the same. The initial decrease in hexadiene and increase in benzene presumably results from the acceleration of step (b). As the temperature is increased still more, the desorption of hexadiene should become easier, and the gas phase concentration of hexadiene should increase at the expense of benzene. As is seen in Fig. 4, this overall pattern of product formation is observed experimentally.

Results obtained from kinetic experiments tend to support and to extend these observations. Hexadiene and acrolein are seen to be the initial products of reaction (Figs. 6–8), while benzene is produced only when the concentration of hexadiene is appreciable (Fig. 9). The fact that the yield of benzene produced by the oxidation of hexadiene is almost the same as from propylene when the reaction is carried out under the same conditions indicates that benzene is formed from hexadiene, as do the values of the kinetic parameters for the two reactions. The formation of acrolein appears to be concurrent with, but independent of, the reaction producing hexadiene.

Attempts were made to fit the results obtained under controlled conditions (Figs. 6–10) with a Langmuir–Hinshelwood model. The reaction was known to be inhibited by the products of reaction (Table 1) and by butadiene. The number of models generated was limited by the indication, from the observed power rate laws, that the production of hexadiene involved adsorbed propylene and oxygen and that the production of acrolein involved adsorbed propylene and gaseous oxygen. The most satisfactory Langmuir–Hinshelwood equations were found to have the form

$$r_H = [k_H(K_PC_P)^2/(1 + K_PC_P + K_HC_H + K_AC_A)^2] \times [K_OC_O/[(1 + \sqrt{K_OC_O})^2] \quad (1)$$

and

$$r_A = [k_A(K_PC_P)^2/(1 + K_PC_P + K_HC_H + K_AC_A)^2] \times C_O \quad (2)$$

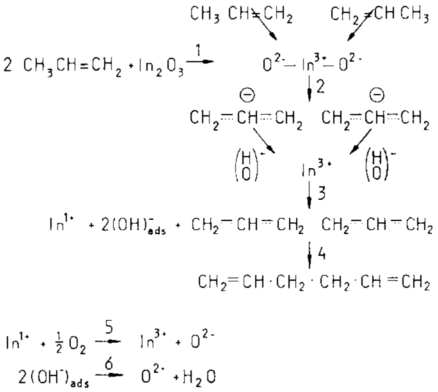
where subscripts P, H, A, O refer to propylene, hexadiene, acrolein and oxygen, respectively.

Calculated values of K_P(620 liter mole^{-1}), K_H(6.5×10^4 liter mole^{-1}), K_A(5.3×10^5 liter mole^{-1}) and K_O(560 liter mole^{-1}) were inserted into Eqs. (1) and (2), together with the appropriate experimental conditions, and used as the basis of a Runge–Kutta method of integration on an IBM 7090 digital computer (*10*). The results obtained were in good agreement with the experimental values given in Figs. 9 and 10.

These equations were based on a model in which the rate-determining reaction for the production of hexadiene involves two adsorbed propylene molecules reacting with dissociatively adsorbed oxygen. Propylene, hexadiene, and acrolein compete for the same sites, but oxygen is adsorbed at different sites. The model for the production of acrolein involves adsorbed propylene reacting with oxygen. Good agreement was not obtained between experimental results and equations based on a model involving only one propylene molecule in the rate-determining step.

It is possible to advance a tentative mechanism which satisfies many of the experimental observations. Basically the proposals rest on the possibility of adsorption of more than one olefin at an In^{3+} center (cf. indium trialkyls) and on the characteristics of the In^{3+}–In^{1+} couple. Firstly, In^{2+} has not been generally observed, and the reduction of In^{3+} appears to require two electrons effectively simultaneously (*8*). Secondly, In^{3+}, with a d^{10} electron outer shell can π-adsorb olefins, while this is not possible with In^{1+}, which has an s^2 outermost shell.

The initial step in the proposed reaction scheme involves adsorption of two olefins at an In^{3+} center (reaction 1 below). Once this has occurred, the olefin is well placed for the extraction of hydrogen ions from the allylic carbon atom by oxidic oxygen (reaction 2). The residual charged organic fragment can then transfer one electron to the In^{3+}, but the transfer of a second electron would be much more difficult. Since In^{3+} requires two electrons simultaneously, the transfer of one electron from two adsorbates would appear to be favored (reaction 3). This transfer would leave the two fragments in a position such that dimerization to 1,5-hexadiene could be expected (reaction 4). Reoxidation of In^{1+} would then complete the catalytic cycle.

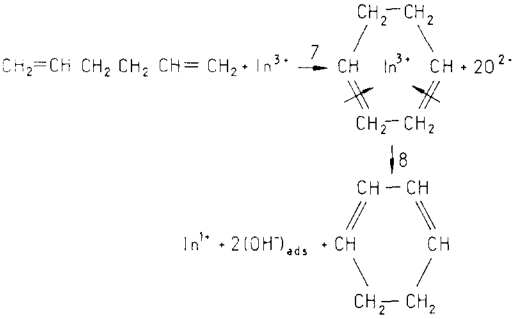


The experimental observation that the 1,5 isomer of hexadiene is produced exclusively is in agreement with this mechanism and a Langmuir–Hinshelwood model based on reaction 2 rate controlling is of the form given in Eq. (1).

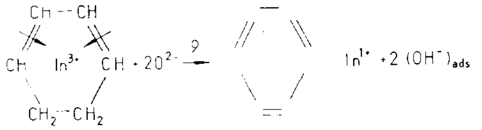
The experimental evidence obtained so far appears to be best explained by this proposed mechanism, but there are difficulties. Almost certainly reaction 1 should be represented by adsorption followed by migration of the adsorbed species to the reaction center. Chemically, it is difficult to reconcile π-adsorption of two olefins at one center, but the demands of the In^{3+} ion, together with the Langmuir–Hinshelwood model, support the postulated reactions for the data so far available. Whether or not the reaction involves, e.g., stepwise reaction on pairs of sites (*11*, *12*) demands more careful investigation.

The production of benzene could be suggested to occur subsequently to the oxidative dehydrogenation of hexadiene to hexatriene. Indium oxide has been found to catalyze such reactions, albeit in low selectivity (*13*). It is this low selectivity, compared to the high specificity of the production of benzene from hexadiene observed in the present system, that argues against this mechanism. In addition only traces of hexatriene were observed among the products of reaction. It seems preferable to propose a mechanism that has much in common with the sequence 1–6 above.

Adsorption of hexadiene on In^{3+} is probably associative and strong, since the carbon number of the diolefin is large (*14*). If adsorption is bidentate, then the molecule should be favorably located for the formation of the 1,3 isomer of cyclohexadiene via an oxidative route:



which could then migrate to a new In^{3+} center where benzene is produced:



Reactions 7–9 bear obvious resemblances to the dimerization reactions. The individual reactions and the overall scheme satisfy the requirements: a) that two electrons should be transferred simultaneously to In^{3+} at each step; b) that provided the amount of hexadiene on the surface is constant as a result of strong adsorption, the rate of production of benzene should be independent of the concentration of gas phase hexadiene but dependent on oxygen; c) that the observed energies of activation for the production of hexadiene and of benzene should be approximately the same; and d) that 1,3-cyclohexadiene is the only cyclic olefin observed among the products of the reaction.

The kinetic results for the production of acrolein would appear to support the mechanistic suggestion that the reaction involves the donation of one electron to In^{3+} from two adsorbates, the residual fragments being so placed that dimerization is impossible. Closer inspection shows, however, that this cannot be the case. If this were to be true, the same type of intermediate must be involved in the production of hexadiene as in the production of acrolein and this intermediate must be produced by the same type of reaction (i.e., reactions 1–6 above). This cannot be so since: a) the apparent orders of reaction for the production of hexadiene and acrolein are different; and b) the observed energies of activation are very different. Under these circumstances, a stepwise reaction of the type suggested by Matsuura and Schuit (*11*, *12*) would seem to offer the most likely route to acrolein.

The finding that acrolein is more strongly adsorbed than hexadiene and that both are more strongly adsorbed than propylene is typical of this type of catalyst (*14*), as is the observation that butadiene inhibits the reaction by preferential adsorption on the surface.

ACKNOWLEDGMENTS

One of the authors (L.A.D.) thanks Shell Canada for valuable financial support.

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