Disproportionation of Propylene on a Supported Molybdenum Hexacarbonyl Catalyst

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The disproportionation of propylene has been investigated on a catalyst of molybdenum hexacarbonyl supported on alumina. A study of the kinetics of the reaction in a static system at temperatures between 290 and 350°K with propylene pressures in the range 0.5 to 20.0 kN m^{-2} is reported. Results indicate that the rate controlling step is a surface reaction between two adjacently adsorbed propylene molecules.

Various physical techniques have been used to study the factors governing the activity of the catalyst and it is suggested that the reactive complex is $Mo(CO)_xPr_{6-x}$, where x is less than six and probably between three and four, and Pr is propylene. The observed changes in catalyst activity during the activation procedure and reaction have been explained in terms of a species of this type.

INTRODUCTION

Research on the catalytic dismutation (1) or disproportionation of olefins has been reviewed by Bailey (2). Activity is found with a range of supported heterogeneous catalysts including carbonyls (1, 3) and sulphides (4) of molybdenum and tungsten, and oxides of a number of metals (1, 4-8). Much of the published work has dealt with oxides of molybdenum or tungsten, or supported cobalt molybdate, but supported hexacarbonyls have not been examined in detail.

The object of the present work was to obtain kinetic data for the disproportionation of propylene using a catalyst of molybdenum hexacarbonyl supported on alumina and to investigate some of the factors controlling the activity of the catalyst. Kinetic data have been reported for this reaction on tungsten oxide on alumina at temperatures between 589 and 728°K and interpreted by a Rideal mechanism involving attack of a gaseous propylene molecule on an adsorbed olefin molecule (9). In contrast, with supported cobalt molybdate at 394 to 478°K a

Langmuir mechanism involving the reaction between two adsorbed molecules has been proposed (10, 11).

Supported molybdenum hexacarbonyl is an interesting catalyst for study because it is active at low temperatures and pressures and the chance of interference from side reactions is small. Furthermore, the structure and composition of the active catalyst may be examined by physical techniques such as infrared spectroscopy (12). Many factors associated with the activation and the stability of the catalyst are not at present understood and we considered that some examination of these would be timely.

EXPERIMENTAL

Kinetic studies of the disproportionation reactions were carried out in a static system. The catalyst rested on the bottom of a cylindrical Pyrex reaction vessel (1.7 × 10^{-4} m³) which was part of a conventional vacuum gas handling system. The reaction vessel was connected by a gas sampling valve to a Perkin–Elmer type F11 gas chromatograph. The analysis of

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olefins from C_2 to C_6 could be carried out using a 4 m column of bis-2-methoxy ethyl adipate (20%) on Chromosorb P and a flame ionisation detector with nitrogen as the carrier gas. The column was operated at a temperature of 303°K. A temperature controller maintained the temperature of the reaction vessel to ±0.5°K as measured by a Chromel–Alumel thermocouple.

Characterization of the catalyst involved a variety of techniques. Carbon monoxide loss as the catalyst was heated was monitored using a reaction vessel linked by a capillary leak to an MS 10 mass spectrometer manufactured by G.E.C.-A.E.I. (Electronics) Ltd. Infrared spectra were obtained from nujol mulls of the crushed catalyst prepared in an inert atmosphere of dry nitrogen, and were run on a Perkin–Elmer type 457 spectrometer.

Catalysts were prepared by impregnation (3). The γ-alumina support generally used, obtained from Johnson, Matthey and Co. Ltd., was in granular form with a particle size 16–32 B.S.S. and a surface area of 2.4×10^5 m² kg⁻¹. After heating in air at 674°K for one hour the support material was contacted with a 5% by weight solution of molybdenum hexacarbonyl (British Drug Houses, Ltd.) in benzene using appropriate proportions to prepare catalysts with the required nominal compositions. Excess benzene was allowed to evaporate. The catalyst most frequently used was 5% molybdenum hexacarbonyl by weight, but catalysts containing 1% and 0.1% were also prepared, as was a catalyst comprising 5% tungsten hexacarbonyl. A sample of α-alumina (25–70 B.S.S., 1.2×10^4 m² kg⁻¹) was also tested as support material.

Propylene, ethylene, but-1-ene, cis- and trans-but-2-ene (Matheson C.P. grades) were degassed and distilled under vacuum before use, the middle third being retained. The level of impurities was less than 0.1% except for propylene which contained propane to an extent of not more than 3%. It was confirmed by experiment that the presence of saturated hydrocarbons in general, and propane in particular, had no significant effect on the nature and

kinetics of the disproportionation reaction.

A 0.5 g sample of the catalyst was normally used. Before use the catalyst was activated by heating under vacuum (1.33 $\times 10^{-4}$ N m⁻²) for one hour. The temperature of activation was varied between 323 and 423°K but the optimum activation temperature used as a standard was 373°K. The reaction vessel temperature was then adjusted to the required value in the range 273 to 373°K before admission of the reactant gas. Reactant pressures used were from 0.5 to 20.0 kN m⁻². Pressures were measured using a diaphragm vacuum gauge and in this way mercury was excluded from the dosing volume and reaction vessel. Samples, approximately 2% of the reaction mixture, were withdrawn at 8 to 15 min intervals over a period of 120 to 300 min and were analyzed immediately. Activated catalyst samples could be used for a number of experiments. After completion of a run the catalyst was evacuated overnight at 298°K before commencing a subsequent experiment.

RESULTS

Kinetics and Catalyst Activity

The molybdenum hexacarbonyl on alumina catalyst was found to be active for propylene disproportionation at temperatures between 273 and 353°K. In this temperature range conversions close to equilibrium were attained in reaction times from fifteen minutes to several hours. A typical experiment is shown in Fig. 1. The reverse reaction was studied using an equimolar mixture of ethylene and cis-but-2-ene. This reaction also approached equilibrium within four hours in the same temperature range.

The stoichiometry of the reaction

$$2C_3H_6 \rightleftharpoons C_2H_4 + C_4H_8 \qquad (1)$$
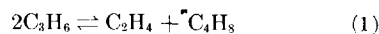
indicates that equal amounts of ethylene and butene should be formed. At temperatures in excess of 345°K equal quantities of ethylene and butenes were observed but at lower temperatures the amount of butenes detected was less than that of ethylene as shown in Table 1. All three
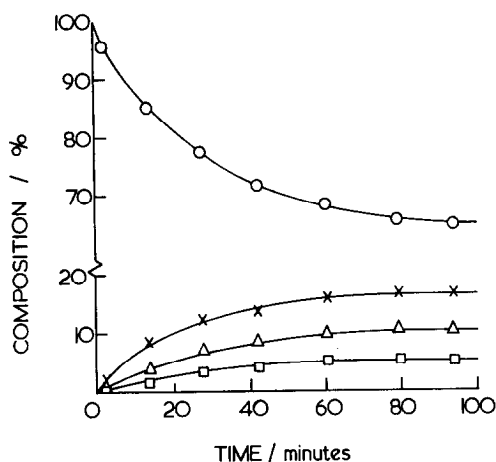
FIG. 1. The course of a propylene dispropor-tionation reaction at 342°K with an initial pro-pylene pressure of 1.3 kN m^{-2}. $\bigcirc$, propylene; $\times$, ethylene; $\triangle$, trans-but-2-ene; $\square$, cis-but-2-ene.

straight chain n-butene isomers were ob-served. But-1-ene is omitted from Fig. 1 because the amount formed was less than 1%. The experimental and calculated

TABLE 1
THE EFFECT OF TEMPERATURE ON THE C$_2$:C$_4$
PRODUCT DISTRIBUTION · % n-BUTENES
PRESENT WITH 5% ETHYLENE

Reaction Temperature (°K)	283	298	318	342	348
% n-butenes	0.7	1.6	3.0	4.2	5.0

equilibrium concentrations of ethylene, propylene and n-butenes are shown in Table 2. The ratio of n-butene concen-trations observed in the initial stages of a

TABLE 2
PRODUCT DISTRIBUTION FROM PROPYLENE
DISPROPORTIONATION

Olefin	Distribution (%)	
	Experimental[a]	Calculated equilibrium
ethylene	18.5	16.1
propylene	64.5	67.8
but-1-ene	0.8	0.8
trans-but-2-ene	11.2	11.0
cis-but-2-ene	4.9	4.3

[a] After 100 min reaction at 342°K.

TABLE 3
DISTRIBUTION ON n-BUTENE PRODUCTS FROM
A PROPYLENE DISPROPORTIONATION
REACTION AT 298°K

Time (min)	but-1-ene	trans-but-2-ene	cis-but-2-ene
1	0.0	70.1	29.9
8	0.2	69.3	30.3
15	0.5	69.9	29.6
23	1.1	70.6	28.3
73	1.4	72.0	26.6
Calculated equilibrium	2.7	73.6	23.7

reaction does not correspond to an equili-brium distribution; see Table 3. But-1-ene is not produced as quickly as the but-2-enes. In a few experiments the initial cis:trans ratio of but-2-enes differed from the equilibrium ratio, attaining values as high as 2:1. This effect is seen only in the first minute of reaction when the total concentration of products is less than 0.6%.

Attempts were made, using integrated rate equations, to determine the reaction order for the disappearance of propylene. The kinetic data were plotted according to the first-order reversible rate equation (13)

$$\ln(x_0 - x_e) - \ln(x_t - x_e) = k_1 t x_0/(x_0 - x_e) \quad (2)$$

and the second-order reversible rate equation (13)

$$\ln \frac{(x_0 - x_t)(2x_e - x_0) + x_0(x_0 - x_e)}{x_0(x_t - x_e)}$$
$$= 2k_2 t x_0 x_e/(x_0 - x_e) \quad (3)$$

as shown in Fig. 2, where x_e is the equilib-rium percentage of propylene, x_t is the percentage of propylene at time t and x_0 is the initial percentage of propylene. Non-reversible kinetic equations were also tested but were easily rejected. From these results it was impossible to determine the order of the reaction since first- and second-order plots for reversible systems were equally well obeyed. For reasons to be discussed later we assume that the reaction obeys second order kinetics.
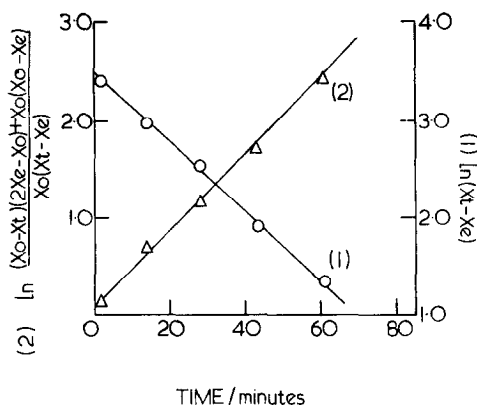
FIG. 2. (1) First-order reversible plot of a propylene disproportionation reaction, ○. (2) Second-order reversible plot of a propylene disproportionation reaction, △.

Activity of the catalyst was investigated by studying the initial rate of disappearance of propylene. The standard measurement of activity was the disproportionation of 1.3 kN m^{-2} of propylene at 298°K and the relative activities were compared on the basis of the initial rate of this reaction. The effect on catalyst activity of such factors as temperature of activation, storage time and conditions and support material were examined by studying the initial reaction on various catalyst samples. It was found that, if the time of activation was one hour, an activation temperature of 373°K produced a catalyst of maximum activity. For a first experiment performed on catalyst samples activated for one hour at 323, 373 and 403°K the initial rates were 1.1×10^{-2}, 9.3×10^{-2} and 3.5×10^{-2} % min^{-1} respectively.

The catalyst is relatively unstable when stored in air in its unactivated form. The activity of samples taken from a stock of unactivated catalyst decreases with increasing time. In Table 4 the activity displayed in initial experiments on three samples of catalyst is compared with the number of days elapsed between preparation of the catalyst and use of each sample. This loss of activity is affected not only by storage time but also by storage conditions (Table 4). The results show that the catalyst deteriorated to a greater extent in air or benzene than in nitrogen and that the

TABLE 4
CATALYST STORAGE EFFECTS

Storage conditions	Catalyst age (days)	Initial rate (% min^{-1})
In air, in subdued light	19	9.3×10^{-2}
	65	8.1×10^{-2}
	96	1.4×10^{-2}
In air, in daylight	140	No observable reaction
In air, in darkness	140	3.1×10^{-2}
In nitrogen, in subdued light	140	7.3×10^{-2}
In benzene, in subdued light	140	No observable reaction

decrease in activity was accelerated by light.

The support material generally used was γ-alumina (16–32 B.S.S., 2.4×10^5 m^2 kg^{-1}) but a catalyst was also prepared using α-alumina (25–70 B.S.S., 1.2×10^4 m^2 kg^{-1}). Identical propylene disproportionation experiments performed at 323°K on freshly prepared and activated samples of the γ-alumina supported catalyst and the α-alumina supported catalyst showed initial rates of 2.44% min^{-1} and 2×10^{-5}% min^{-1}, respectively.

The life of a sample of catalyst over a series of identical consecutive experiments was examined. For this the catalyst was activated for one hour at 373°K, cooled to 295°K and a dose of propylene, sufficient to give a pressure of 1.3 kN m^{-2} in the reaction vessel was admitted. The reaction was followed for several hours after which the catalyst was evacuated at 323°K for at least 1 hr and not more than 72 hr before use in the next experiment. The catalyst activity during a series of six runs carried out in this manner is shown in Table 5. The results indicate that the first experiment performed after catalyst activation is considerably slower than subsequent runs. After the first experiment the activity remains almost constant for identical experiments. This constant activity has been observed for as many as nine experiments after which the activity slowly decreases.

Since catalyst activity depended on many factors a run was carried out under stand-

TABLE 5

CATALYTIC ACTIVITY FOR SUCCESSIVE
EXPERIMENTS

Run No.	Initial rate (% min^{-1})
1	8.1×10^{-2}
2	0.46
3	0.46
4	0.46
5	0.43
6	0.47

ard conditions, to measure activity, between each run under new conditions. This technique may be illustrated by a series of experiments employed to measure the apparent activation energy of the propylene disproportionation reaction. The sequence of experiments, which were all carried out on the same catalyst sample is shown in Table 6. The treatment of the catalyst between each experiment was evacuation at 323°K for 16 hr. The initial rates of Runs 118, 120 and 122 were used to give the activity pattern by plotting initial rate against date of reaction and the standard 298°K activities of the catalyst when Runs 119 and 121 were performed were interpolated from this graph. Using these interpolated activities the experimental rates of Runs 119 and 121 were adjusted to a common activity level. The energy of activation calculated from these results was 30.5 kJ mol^{-1} and the frequency factor was 6×10^{-21} molecules^{-1} s^{-1} m^{-2}. (k_2 was used in this calculation.)

The effect of changing the initial pressure

TABLE 6
ARRHENIUS DATA[a]

Run No.	Date of experiment	Temperature (°K)	Initial rate (% min^{-1})	Adjusted[b] initial rate (% min^{-1})
118	23	298	1.50	
119	24	283	0.33	0.33
120	25	298	0.43	0.76
121	26	318	0.63	1.35
122	27	298	0.31	

[a] No. of molecules in reaction vessel = 4×10^{19}.
[b] k_2, second-order reversible rate constant = initial rate $\times 10^{-4}$.

of propylene on the initial rate of disproportionation was studied over the pressure range 0.5 to 20.0 kN m^{-2} at a temperature of 342°K. These results were corrected to standard catalyst activity in a similar manner to that explained previously. As may be seen from Fig. 3 the rate of reaction increased with rising pressure at low propylene pressures but at pressures greater than 6.7 kN m^{-2} the rate of reaction became independent of the initial propylene pressure.

A brief study of a catalyst prepared as 5% tungsten hexacarbonyl on γ-alumina showed it to be much less efficient for propylene disproportionation than that prepared from molybdenum hexacarbonyl. One of the more active batches of tungsten catalyst produced an initial rate of 1.3×10^{-2}% min^{-1} at 298°K for the reaction of propylene. This may be compared with results on a molybdenum catalyst under similar conditions which gave an initial rate of 9% min^{-1}.

The reactions of 1,3-butadiene and but-1-yne on the molybdenum hexacarbonyl catalyst were briefly examined. In both cases rapid disappearance of the reactant was observed but no gaseous products were detected. Exposure of an active catalyst to either of these reactants reduced the catalytic activity for subsequent reactions of propylene.

The Nature of the Catalyst

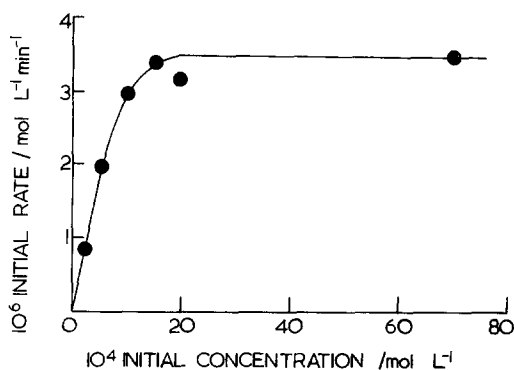During normal activation the catalyst sample changed in colour from white to

FIG. 3. Initial rates of propylene disproportionation as a function of propylene pressure.

pale lemon and then, during reaction, changed further to brown. When kept in vacuum after a reaction the samples maintained their colour but reverted to white on exposure to air. Those samples which had been activated and, either directly or after catalytic use, exposed to air were irreversibly deactivated. This poisoning effect of air was further investigated by exposing active catalysts to dry oxygen and to water vapour. Small doses of water vapour had no effect on the catalytic activity but oxygen reduced the activity considerably. Exposure to 10.6 kN m^{-2} of oxygen at 295°K for one hr lowered the initial rate of propylene disproportionation at 323°K from $3 \times 10^{-2}\%$ min^{-1} to $0.5 \times 10^{-2}\%$ min^{-1}.

Attempts were made to show that carbon monoxide was lost from the catalyst during activation using a mass spectrometric technique. A sample of fresh catalyst was placed under vacuum in a reaction vessel linked directly to a mass spectrometer by a capillary leak. As the catalyst temperature was slowly raised the peak at mass 28 was monitored. Significant differences in the spectrum were not observed until the temperature was above 523°K and quantitative measurements were not possible with this technique.

Infrared studies on catalysts of this type have already been reported (12). These showed that the unactivated catalyst had one carbonyl absorption frequency identical to that for bulk molybdenum hexacarbonyl. Spectra of the active catalyst showed two carbonyl bands, indicating the probable loss of one or more of the carbonyl groups. The dead catalyst, after exposure to air, gave no absorption in the carbonyl region. Laser Raman spectroscopy was attempted, as it was hoped that the information so obtained would augment the infrared evidence, but interference from the support and the weak absorbance of the carbonyl frequencies in Raman made it impossible to draw any conclusions from this work.

Since molybdenum hexacarbonyl is a volatile material it was considered of interest to analyse the catalysts for molybdenum before and after use. This was done by X-ray fluorescence methods. The results of this investigation on four samples of catalyst prepared with different contents of molybdenum hexacarbonyl on alumina are shown in Table 7.

Evidence so far presented suggests that on activation the catalyst loses carbon monoxide and it was hoped to measure directly the quantity of carbon present in the catalysts after activation by combustion and gas chromatographic determination of the carbon dioxide thus produced. Results indicated that, from the amount of carbon present on the catalyst before and after activation, $Mo(CO)_2$ was the likely species present. It is thought that sizeable errors are involved in this analysis because of the low concentration of carbon present and the difficulty in ensuring complete combustion.

TABLE 7

THE EFFECT OF CATALYST ACTIVATION ON MOLYBDENUM CONTENT

	% Mo	
Sample	Before activation	After activation
A	1.8	1.0
B	1.1	0.9
C	0.8	0.8
D	0.6	0.6

DISCUSSION

The Kinetics and Mechanism of Propylene Disproportionation

A comparison of the experimental and calculated equilibrium concentrations of ethylene, propylene and butenes, shown in Table 2, confirms that the retardation in rate observed during the course of propylene disproportionation is due to the attainment of thermodynamic equilibrium. Although the final distribution of the n-butene products corresponds to their equilibrium concentrations it has been established that during the initial stages of a reaction the n-butenes are not present in an equilibrium ratio. Table 3 illustrates that the proportion of but-1-ene builds up

slowly during the course of the reaction. This delay in the appearance of but-1-ene may be a consequence of the fact that a disproportionation type of mechanism (*2, 5*), in which two reactant molecules form a substituted four centre intermediate, will explain the formation of *cis-* and *trans*-but-2-ene from propylene but not the production of but-1-ene. The isomerization of the straight chain butenes on a molybdenum hexacarbonyl catalyst is presently being investigated.

It has also been observed in a few reactions that the *cis:trans* but-2-ene ratio is far from equilibrium in the first minute of reaction. This may be explained in terms of a steric influence favouring the *cis*-but-2-ene molecule which would be more readily accommodated on the catalyst surface.

As illustrated in Table 1 the butene products of the reaction of propylene were preferentially adsorbed on the catalyst support relative to ethylene. The surface area of the alumina (2.4×10^5 m^2 kg^{-1}) is sufficient to allow complete adsorption of the butene produced. Since this adsorption decreased with increasing temperature it was possible to determine a heat of adsorption of butene on the alumina support. The pressure, in percentage of butene in the gas phase necessary to give a fixed surface coverage of butene, was measured at various temperatures and plotted to a Clapeyron–Clausius equation,

$$(d \ln P / dT)\theta = Q/RT^2 \qquad (4)$$

where P is the pressure, T is the temperature, θ is the fraction of the surface covered and Q is the heat of adsorption. A linear graph was obtained which yielded 42 kJ mol^{-1} for the heat of adsorption of butene (Fig. 4).

Analysis of the kinetic data indicates the reversible nature of the reaction. The fact that equilibrium conversion in this system corresponds to only 30% reaction results in the internal kinetics being very sensitive to the choice of equilibrium concentrations and this is one of the major factors contributing to the failure of the integrated rate equations in determining
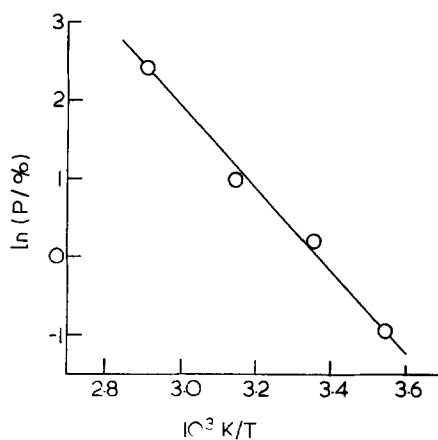

Fig. 4. Clapeyron–Clausius plot for adsorption of butene, (where surface concentration of butene is 2.4×10^{22} molecules kg^{-1}).

the reaction order. The kinetics are also distorted by the preferential adsorption of butenes, especially at lower temperatures. In systems where preferential adsorption is much less evident and where the equilibrium is approached after a longer extent of reaction, for example in the isomerization of *cis*-but-2-ene, second-order reversible kinetics are accurately obeyed (*14*). In view of this evidence second order behaviour is assumed to be more probable for propylene disproportionation.

The dependence of disproportionation rate on initial propylene pressure, as shown in Fig. 3, may be explained by a Langmuir mechanism (*15*) as proposed for this type of reaction on a cobalt molybdate on alumina catalyst by Lewis and Wills (*10*). If the rate controlling step in propylene disproportionation is postulated as being the surface reaction of two adjacently attached molecules then the appropriate expression is

$$r = \frac{k(P_P{}^2 - P_E P_B / K_{eq})}{(1 + K_E P_E + K_P P_P + K_B P_B)^2} \qquad (5)$$

where K_{eq} is the equilibrium constant, k is the reaction rate constant, K_E, K_P and K_B are the adsorption coefficients and P_E, P_P and P_B are the partial pressures of ethylene, propylene and butene, respectively. P_E and P_B may be assumed to be

near zero under the conditions in which the initial rates were measured so Eq. (5) reduces to

$$r = kP_P^2/[(1 + K_PP_P)^2] \qquad (6)$$

or

$$P_P/r^{1/2} = (1 + K_PP_P)/k^{1/2} \qquad (7)$$

The equation is tested in Fig. 5 for the data presented in Fig. 3 and the resultant straight line confirms a reaction between two adsorbed species.

The single site Rideal type of mechanism proposed by Begley and Wilson (9) would not explain the observed pressure dependence of initial rates. Also a single site mechanism is more difficult to picture if the reaction proceeds via a cyclobutane type intermediate as is now generally accepted (2). The investigations of Begley and Wilson (9) who used a tungsten oxide on silica catalyst and Lewis and Wills (10) who studied a cobalt molybdate on alumina catalyst were both conducted in flow systems and in this respect differ from the currently reported results which were obtained in a static system. The mechanistic agreement between the present results and those of Lewis and Wills may be a reflection of the fact that the temperatures and pressures used by them were more comparable to those in our static system while the results of Begley and Wilson were obtained at much higher temperatures and pressures.

The energy of activation of 30.5 kJ mol⁻¹ for the disproportionation of propylene is close to that of 32.2 kJ mol⁻¹ measured by Clarke and Cook (16) for the reaction of propylene on a cobalt molybdate on alumina catalyst.

According to the theory of absolute reaction rates (17) the appropriate equation for calculating the rate of a bimolecular surface reaction of this type is

$$v = \frac{1}{2} S \frac{C_g^2 C_s^2}{L} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_s} e^{-\epsilon_0/kT} \qquad (8)$$

where v is the rate of reaction in molecules s⁻¹ cm⁻² of surface, S is the number of possible sites adjacent to any reaction centre and L is the total number of sites per cm² of bare surface. C_g is the concentration of propylene in the gas phase in molecules cm⁻³ and C_s is the concentration of vacant sites. F_g, f_s and $f^\ddagger$ are the partition functions for gas phase propylene in unit volume, the reaction site and the activated complex, respectively. T is the reaction temperature and ϵ_0 the activation energy per molecule. Inserting the appropriate Langmuir expression for the fraction of surface covered the equation becomes

$$v = \frac{1}{2} S \frac{C_g^2 L}{(1 + AC_g)^2} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_s} e^{-\epsilon_0/kT} \qquad (9)$$

where A is the adsorption coefficient of propylene in units of cm³ molecules⁻¹. The experimentally observed pressure dependence of the disproportionation reaction rates (Fig. 5) leads to a value of 5.83 × 10³ litres mol⁻¹ for the adsorption coefficient and hence the required value of A is 9.7 × 10⁻¹⁸ cm³ molecules⁻¹. ($A = K_p/6.02 × 10^{20}$) Of the other terms in the equation C_g and F_g may be calculated; S is assumed to be unity if two olefin molecules are thought to be associated with one complex site; L is estimated as the number of molybdenum atoms per unit area; f_s is assumed to be unity and the experimentally measured activation energy is used for ϵ_0.
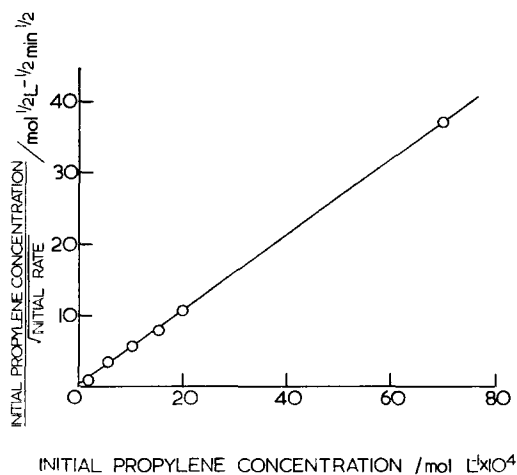
The difficulty remaining in the evalua-

FIG. 5. Langmuir plot for propylene disproportionation at 342°K.

tion of the reaction rate from Eq. (9) is the calculation of $f\ddagger$, the partition function of the activated complex. If a simple picture of the transition state is visualised in which the complex has lost all translational freedom, but retains one degree of rotational freedom and all the vibrational freedom of the gas phase, a rate of 2×10^{-4} molecules sec^{-1} cm^{-2} is obtained at 342°K and a pressure of 1.6 kN m^{-2} of propylene. The experimental rate is 5.6×10^9 which exceeds the calculated rate by a factor of some 10^{13}. It thus appears that the activated complex has considerably more freedom than is assumed in this treatment.

Another method of estimating the state of the active complex is to regard it as essentially similar to two adsorbed molecules of propylene. If the adsorption coefficient, A, is expressed in terms of the partition functions of the species involved then

$$A = (f_a/F_g f_s) \, e^{\epsilon/kT} \qquad (10)$$

where f_a is the partition function of adsorbed propylene and ϵ is the heat of adsorption. A value for the ratio f_a/F_g for adsorbed propylene based on the experimentally observed value for A can thus be calculated to be 1.5×10^9 which implies a relatively unrestricted surface species. If this value is used to calculate the partition function for the adsorbed cyclic complex the resultant reaction rate is 5×10^{11} molecules sec^{-1} cm^{-2}. The rate thus obtained, based on A, is in much closer agreement with the experimentally observed rate than that calculated on the basis of a restricted transition state.

The value of the partition functions calculated from the adsorption coefficient suggests a surprising amount of freedom in the adsorbed states of both propylene and the adsorbed complex. For the adsorbed complex this freedom involves the assumption of one degree of rotational freedom, all the normal vibrational freedom of two propylene molecules plus some very weak vibrations in place of the lost translational and rotational freedom of the gas phase

species. These weak vibrations, which would need to have frequencies in the region of 10–30 cm^{-1}, could be visualised as very gentle rocking and bending of the cyclic species.

The Nature of the Catalyst

All results attempting to elucidate the nature of the active species confirm that it is not molybdenum hexacarbonyl. The catalyst, as prepared by impregnation, is simply supported $Mo(CO)_6$ (12), but the activation procedure of heating the material to 373°K under vacuum causes loss of carbon monoxide. This carbon monoxide loss is confirmed by direct observation, and infrared spectroscopy indicated a loss of symmetry which is explained on the basis of removal of carbon monoxide. It is interesting to note (18) that solutions of molybdenum hexacarbonyl in ether and isopentane become yellow when subjected to ultraviolet irradiation. Using spectral evidence this has been explained by dissociation of the hexacarbonyl to give the species $Mo(CO)_5$. It is reasonable to assume that the yellow colouration apparent on activating the catalyst may be due to a $Mo(CO)_5$ species which again confirms that carbon monoxide is lost on activation. We believe, however, that production of the fully active catalyst involves the loss of probably two or more carbonyl groups from the hexacarbonyl molecule. Assuming that the preferred coordination number of the molybdenum is six and that the reacting olefin molecules occupy two of these positions then the maximum number of carbon monoxide ligands would be four. Note must be taken of the observation that the first run on a freshly activated catalyst is slower than subsequent runs and this could be explained by the replacement of one or more of the remaining carbon monoxide ligands by propylene. It is thus reasonable to postulate that the reactive complex is of the form $Mo(CO)_x Pr_{6-x}$ where x is less than six and probably three or four, and Pr is propylene. Once formed the active catalyst

is stable and its activity remains constant over several reactions. The decline in activity reported after nine experiments on the same catalyst may be due to the cumulative effects of small amounts of dienes, acetylenes, oxygen or other materials which would be strongly adsorbed and thus poison the catalyst.

In view of the kinetic information and these ideas about the nature of the active species the following reactive path is proposed. For the reaction of propylene we have species A, $(C_3H_6)_2Mo(CO)_x(L)_{4-x}$ formed by reversible adsorption of propylene on the active catalyst $Mo(CO)_x(L)_{4-x}$ where L may be propylene or some link with the alumina surface. The rate determining step is the rearrangement of A to species B, $(C_2H_4)(C_4H_8)Mo(CO)_x(L)_{4-x}$ through an activated complex having a similarity to a substituted cyclobutane. The reverse reaction occurs by the reversible adsorption of ethylene and butenes to form species B.

Although the activation procedure used has been a thermal one it is believed that activation could be achieved photochemically (18). The loss of potential activity when the catalyst is stored before activation is accelerated if it is stored in the presence of light. When samples of catalyst are left in strong sunlight they darken initially before becoming white and completely inactive. The possibility of photochemical activation combined with the poisoning action of oxygen could explain the ageing of the unactivated catalyst.

The quantitative analyses for molybdenum suggest that there exists a maximum coverage of the alumina with molybdenum hexacarbonyl. Catalysts prepared with a molybdenum hexacarbonyl content greater than this value will lose a fraction of it on activation so as to attain this maximum permitted coverage. A catalyst prepared as 1.8% by weight of molybdenum dropped, on activation, to 1.0%, but catalysts prepared with less than 1.0% molybdenum lost no molybdenum on activation. If the optimum level of molybdenum is accepted as $\sim$1% this gives a value of 7×10^{22} molybdenum atoms per kg of catalyst. The surface area of the γ-alumina used was 2.4×10^5 m^2 kg^{-1} so the apparent area per molybdenum atom is 340 Å^2.

The but-1-ene observed in the reaction of propylene can not be explained by a disproportionation type of mechanism. It is hoped that a current investigation of the reactions of the n-butenes on a supported molybdenum hexacarbonyl catalyst will indicate how double bond shift occurs.

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