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The Polymerization of Propylene on Silica-Alumina

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The reaction of propylene on a silica-alumina catalyst was studied in a static system at 58°, 100°, 150°, and 200°C, respectively. A complex distribution of products, which were analyzed in detail in the range C_3 to C_6 by gas-liquid chromatography, was obtained at all temperatures and it was clear that polymerization was accompanied by cracking, isomerization, hydrogen transfer, and coke formation. The sequence of these reactions was partially elucidated by reacting propylene at varying contact times at 100°C and by investigating the influence on the product distribution of the prior adsorption of tetralin on fresh catalyst.

Attempts were made to define the nature and function of the active sites responsible for these reactions by using catalyst which had either been exchanged with sodium ions or had been treated with quinoline, perylene or ammonia. Two types of sites which are not readily interconverted were demonstrated, those with Brönsted acidity capable of undergoing base exchange and active in the polymerization of propylene, and those with Lewis acidity inactive for polymerization but promoting aromatization and coke-forming reactions together with saturation of olefins by hydrogen transfer.

INTRODUCTION

Several recent studies on the interaction of olefins with silica-alumina catalysts have clearly demonstrated that chemisorption takes place readily at temperatures far below those normally employed in catalytic cracking. Kemball and Rooney (*1*) investigated the reaction of cyclopentene and obtained evidence for polymerization and isomerization of the resulting complexes at 68°C. These two reactions were also found to be responsible for many of the products obtained at higher temperatures. It was suggested that the slow step in the catalytic cracking of olefins may be the breakdown of polymeric complexes or the desorption of complexes as stable molecules in agreement with the views of MacIver, Zabor, and Emmett (*2*) based on their studies of the adsorption of but-1-ene. Evidence has also been obtained for the polymeric nature of carbonium ions formed from but-1-ene at 25°C by Webb (*3*) who employed an ultraviolet spectrophotometric technique to investigate the adsorption of olefins on acidic solids.

The object of the present work was to study the nature of the polymerization reaction in detail, and propylene was chosen as a suitable reactant. It was hoped that by working at low temperatures and pressures that formation of dimers and, perhaps, trimers could be examined without too many of the complications normally encountered in the reaction of olefins at high temperatures. While several investigations of the reaction of propylene on acidic solids have been reported, most of the work was conducted at high pressures and fairly high temperatures and product analysis was not detailed. An early study by Gayer (*4*), employing a wide variety of clays and silica-alumina catalysts showed that the reaction of propylene at 300° to 400°C under atmospheric pressure was complex, resulting in products in the range C_5- to C_{23}-hydrocarbons. Johnson (*5*) investigated the kinetics of the polymerization of propylene and found that it was first order, retarded by the products. Hall, MacIver, and Weber (*6*), using a microcatalytic technique, concluded that the reaction had a zero activation energy in the temperature range 250° to 325°C.

EXPERIMENTAL

The apparatus is shown diagrammatically in Fig. 1. The reaction vessel R was thermostatically controlled by an electrically heated furnace and the temperature was measured by means of a calibrated iron-constantan thermocouple. A sample of propylene at a pressure of 482 mm of Hg in the fixed volume V (0.70 ml) was expanded into the reaction vessel (99.9 ml) containing the catalyst (1.69 g) and after reaction for 30 min desorbed during 90 min into the evacuated U-tube T and frozen at liquid air temperature. The U-tube was isolated from the reaction vessel, heated to 60°C for 20 min and the hydrocarbon vapors swept into the chromatographic column by means of a bypass in the flow line of the carrier gas. The flow of carrier gas was switched back to the main flow line after 5 min, the next dose of propylene expanded into the reaction vessel, and the isolated U-tube evacuated in readiness for the next desorption. This cycle of operations which required a total period of 145 min was repeated several times at each temperature. At some intermediate stage, the procedure was modified by carrying out three desorptions between admission of a particular dose of propylene and the next, but the interval between desorptions was the same as in the normal procedure. In some experiments, shorter periods than 30 min between the introduction of propylene to the reaction vessel and the commencement of desorption to the U-tube were used but the same total period of 145 min was allowed to elapse during each cycle.

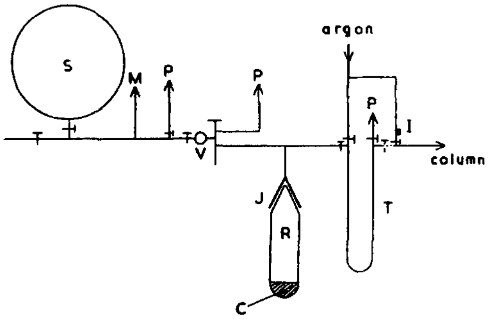


FIG. 1. Diagram of apparatus—S, propylene store; V, calibrated volume, 0.70 ml; J, water-cooled joint; R, reaction vessel; C, catalyst; T, capillary U-tube trap; P, pumping line; M, manometer; and I, serum cap.

A Pye Argon Chromatograph employing a 20-ft column of Celite (100–120 mesh B.S.S.) impregnated with 10% by weight of silicone oil and operated at 20°C and a flow rate of 33 ml/min was used for analysis. It was found that the doses of propylene which were necessary in order to obtain sufficient products for analysis were too large for the range of the ionization detector of this instrument and as a result of overloading, peak splitting, and nonlinear behavior of response made quantitative estimates of the amounts of propylene desorbed unreliable. However, satisfactory chromatograms for all the products in the range C_4 to C_6 were obtained and these were quantitatively estimated by measuring peak areas with a planimeter. As the response of this detector to different hydrocarbons is approximately the same it was assumed that the amounts of products were in the same proportions as peak areas and calibration factors for every compound were not determined. The sensitivity of the instrument was estimated by calibrating with 2,3-dimethylbutane and the total area of the peaks used to calculate the percentage recovery of carbon in the products.

The products were identified by comparing their retention volumes with those of known compounds. Qualitative analysis was considerably aided by the fact that silicone oil columns elute volatile hydrocarbons in approximately the same order as their boiling points. Identification of products as olefins or paraffins was independently checked by the removal of olefins from a sample of products by treatment with sulfuric acid. Detailed analyses were not made of the various hexenes formed because the quantities were small. The compounds listed as X and Y were nonolefinic and either heptanes or C_7 cycloalkanes.

Samples of catalyst were examined after reaction by an ESR technique, described previously (7), to detect the presence of entities with unpaired electrons.

Materials

The catalyst which was supplied by I.C.I. (Billingham Division) in pellet form (composition Al_2O_3, 10%; Fe_2O_3, 0.05 to 0.1%; Na_2O, 0.05 to 0.2%; SiO_2 remaining %) had been calcined at 695°C and had a surface area of 255 cm^2/g. After crushing and sieving, particles of 44 to 60 mesh B.S.S. were washed in hot distilled water, dried at 140°C for 24 hr and then heated at 600°C in air for 1 hr. The catalyst was stored in a vacuum desiccator over magnesium perchlorate. A fresh sample of catalyst was used for each experiment and pretreated under vacuum for 1 hr at 400°C.

Propylene was prepared by dehydration of propan-2-ol vapor under reduced pressure over activated alumina at 340°C. Water was removed by an ice trap and a tower of magnesium perchlorate and the final purification of the propylene was by distillation from a trap at —195°C. No impurities were detected by mass spectrometric or gas-liquid chromatographic analysis.

Tetralin (B.D.H.) was passed through a column of active alumina to remove oxygenated compounds and distilled. The fraction boiling between 204° and 207°C was collected and dried over magnesium perchlorate. Perylene (Rutgerswerke A.G.) was used without further purification. Quinoline (B.D.H.) was converted into the chlorozincate, hydrolyzed, and distilled under reduced pressure.

The same weight of catalyst, 1.69 g, was used in all the experiments involving special treatment of samples. A sample of base-exchanged catalyst was made by stirring for 18 hr in an aqueous solution of sodium acetate (12.2 *N*) and the amount of sodium taken up was estimated to be 0.13 meq/g by flame photometry. A sample of catalyst for use at 100°C was treated with 20 μl of tetralin and then evacuated for 24 hr at the reaction temperature. An alternative procedure was used to prepare samples for reactions at 58° or 200°C, involving the addition of only 0.2 μl and evacuation for 30 min. Treatment with quinoline was carried out by placing a sample of catalyst in a solution of 80 μl of quinoline in 3 ml of benzene, removing excess liquid by evacuation at room temperature and then continuing the evacuation for 24 hr at 200°C. Treatment with ammonia was carried out under a pressure of 68 cm for 30 min at room temperature followed by evacuation for 12 hr at 100°C. Two samples of catalyst were treated with 0.4 mg perylene in 8 ml of benzene for 30 min at room temperature. One sample was used for reaction at 200°C after evacuation for 12 hr at this temperature. The second was examined by the ESR technique and then used, after evacuation for 12 hr, at 100°C.

RESULTS

Ten consecutive desorptions were carried out for the reaction of propylene at 200°C and a selection of the results are given in Table 1. Propylene was admitted to the catalyst before each desorption except for the sixth and the seventh. The proportion of olefinic products was higher in the first desorption than in the remainder which gave more than 80% of saturated compounds. The sixth and seventh analyses, columns 5 and 6 of Table 1, corresponded to the second and third desorptions after the fifth addition of propylene. They show that a considerable amount of material was still retained on the catalyst even after two periods of desorption and the patterns of products in these two experiments were similar to the normal pattern except for slightly larger percentages of the isomeric hexanes and the compounds X and Y. Apart from the alteration in the distribution of products between the first and second desorptions, the pattern remained constant throughout the series and

TABLE 1
PRODUCT DISTRIBUTIONS EXPRESSED AS PERCENTAGES OF THE TOTAL NUMBER OF PRODUCT MOLECULES FOR REACTION OF PROPYLENE AT 200°C

Desorption number	1	2	3	6	7	9
Isobutane	21.5	25.5	26.3	17.7	24.4	26.4
Isobutene + but-1-ene	10.5	6.5	6.2	5.9	5.2	6.0
trans-But-2-ene	4.0	4.2	3.7	4.0	3.1	4.3
cis-But-2-ene	3.2	3.1	2.8	3.5	2.6	2.7
3-Methylbut-1-ene	0.3	0.2	0.2	—	—	0.2
Isopentane	21.0	26.6	29.2	24.5	21.3	29.0
2-Methylbut-1-ene	1.7	1.2	1.1	1.0	—	1.2
trans-Pent-2-ene	0.4	0.4	0.4	0.5	—	0.5
2-Methylbut-2-ene	4.6	1.8	1.6	1.3	2.0	1.5
2,3-Dimethylbutane	1.1	1.3	1.3	1.9	2.6	1.3
2-Methylpentane	10.8	10.5	9.7	15.6	14.0	10.0
3-Methylpentane	5.3	6.3	5.7	7.9	7.8	5.3
C_6-Olefins	1.2	—	0.3	—	—	—
Methylcyclopentane	2.8	2.8	2.2	2.3	2.0	2.4
X	7.5	6.4	6.1	10.4	11.4	6.2
Y	3.7	3.3	3.2	3.0	3.1	3.1
Amounts of carbon recovered in the above products relative to the first desorption						
	1.0	1.4	1.4	0.21	0.08	1.61

was not influenced by the variation in the procedure for the sixth and seventh desorptions. The total amount of products, after a sharp increase between the first and second desorptions, rose only slightly, yielding 1.8 times as much in the final desorption as in the first.

The same general features were ob-

TABLE 2
AVERAGE PRODUCT DISTRIBUTIONS EXPRESSED AS PERCENTAGES OF THE TOTAL NUMBER OF PRODUCT MOLECULES FOR REACTION OF PROPYLENE AT DIFFERENT TEMPERATURES ON CLEAN CATALYST AND ON SOME PRETREATED CATALYSTS

Temperature (°C)	58°	100°	150°	200°	100°[a]	100°[b]
Isobutane	28.9	23.2	26.4	25.0	12.1	14.9
Isobutene + but-1-ene	18.2	8.6	3.6	6.8	1.0	19.5
trans-But-2-ene		3.2	1.7	3.5	1.0	3.4
cis-But-2-ene		2.3	1.3	2.7	0.7	2.7
Isopentane	16.9	19.1	29.4	27.9	4.7	8.9
2-Methylbut-1-ene	—	1.2	0.8	1.1	—	2.0
trans-Pent-2-ene	—	0.6	0.3	0.4	—	0.9
2-Methylbut-2-ene	3.7	5.3	1.3	2.5	—	11.2
2,3-Dimethylbutane	2.5	2.6	2.2	1.7	2.6	1.0
2-Methylpentane	15.0	11.6	12.0	8.9	57.8	8.1
3-Methylpentane	3.0	3.8	5.0	4.8	19.0	2.7
C_6-Olefins	—	1.2	0.5	1.0	—	9.0
Methylcyclopentane	3.7	5.4	3.7	2.8	—	4.8
X	7.5	10.1	8.3	5.9	—	7.6
Y	—	2.5	3.3	3.5	—	2.7
Percentage recovery of carbon as products						
	1.3	8.0	23.6	35.3	17.0	6.3

[a] Reaction on catalyst treated with tetralin.

[b] Second product distribution from reaction on catalyst with adsorbed perylene.

served for reactions at the other three temperatures, 58°, 100°, and 150°C. Average distributions obtained in second and subsequent desorptions are given in Table 2 which includes details of the percentage of the propylene recovered as products at each temperature. The amount of propylene recovered unchanged fell by a factor of 4 as the temperature of reaction was increased from 58° to 200°C. Approximate activation energies for the formation of individual products were found from Arrhenius plots of the peak areas. The values ranged from 10 kcal/mole for isobutane, isopentane, and 2-methylpentane, 12 for 3-methylpentane and 2,3-dimethylbutane, to 14 kcal/mole for methylcyclopentane and X. The product distributions did not alter substantially with increase of temperature except that more isopentane was formed at the expense of the higher boiling compounds. No products containing quaternary carbon atoms or normal paraffins were observed at any temperature.

A series of experiments were carried out at 100°C with contact times shorter than the normal period of 30 min. The main differences observed were a reduction in the ratio of paraffin/olefin, particularly for C_6 products, as shown in Fig. 2. After three consecutive desorptions with contact times of 6 min, the ratios approached those found in the normal reactions with the standard contact time.

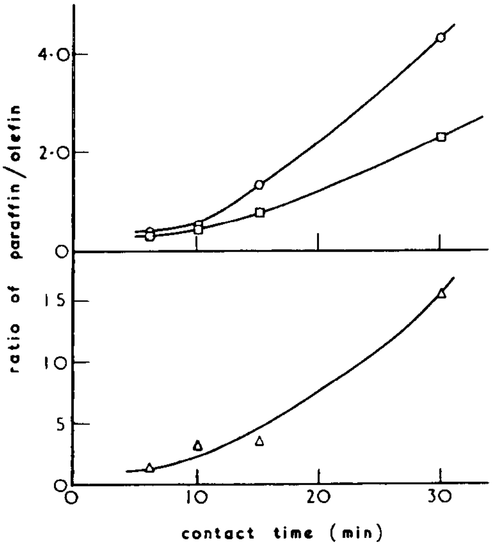


Fig. 2. Plot of paraffin/olefin ratio for different carbon numbers against contact time—□, C_4; ⊙, C_5; △, C_6.

Samples of catalyst showed a progressive color change during use, becoming yellow and finally dark brown, and radical ions were found in the more highly colored samples by the ESR technique which gave a weak unresolved signal.

A reaction was attempted with ethylene at 200°C but trace amounts of butenes were the only products.

Experiments with Treated Catalysts

The average distribution of products from a series of reactions at 100°C on the tetralin-treated sample is shown in column 6 of Table 2. This distribution was remarkable in that it contained no products above C_6 which amounted to 80% of the total products and only 3% of these were unsaturated. However, mass spectrometric analysis of the C_3 fraction showed that little of the propylene had been converted to propane. Similar results were obtained for reactions at 58° or 200° on tetralin-treated samples although the effect was not so pronounced at the higher temperature and after the initial desorption the distributions gradually reverted to those characteristic of an untreated catalyst.

The sodium-exchanged catalyst was completely inactive for the polymerization of propylene at 100°C and only gave traces of lower olefins at 200°C. However, this catalyst displayed high activity comparable to that of the unexchanged catalyst (7) for the oxidation of perylene to positive radical ions.

Reaction occurred at 200°C on the perylene-treated catalyst but the proportions of olefinic products were slightly higher than normal. After reaction, the ESR technique revealed that the signal due to the perylene cation (7) was considerably reduced and was superimposed on a second broad unresolved signal. The second perylene-treated sample showed the presence of $\sim 10^{12}$ radical ions/cm^2 of surface before it was used for reaction at 100°C and after use at this temperature, the signal was not as substantially altered as that for the first sample. The product distribution from the first desorption on this catalyst was virtually the same as that for the average distribution on an untreated catalyst but the second desorption, details of which are given in column 7 of Table 2, showed more than twice the usual proportions of olefins although the total amount of products was only slightly below the average for normal experiments. The influence of perylene was also evident but to a decreasing extent in subsequent reactions.

The sample of catalyst pretreated with quinoline was totally inactive at 200°C. No reaction occurred on the ammonia-treated catalyst at 100°C or at 200°C after outgassing for 12 hr. Some activity at 200°C was found after a further evacuation for 5 hr at 400°C and the distribution of products was similar to that shown in column 7 of Table 2 and contained more olefinic products than the normal distributions. The ammonia-treated catalyst after evacuation at 400°C was much less active for the oxidation of perylene to positive radical ions than an untreated catalyst.

Discussion

The most important feature of the reaction of propylene on silica-alumina is the number and the variety of the products even at temperatures as low as 58°C. The polymerization is accompanied by all the other reactions normally encountered in catalytic cracking, such as double-bond shift, isomerization involving the movement of methyl groups, hydrogen transfer, cyclization, aromatization, and ultimately coke formation. Although the molecular weight of the products distinguishable by the chromatographic technique was necessarily limited, the detection by the ESR technique of positive radical ions on the catalyst used established that polynuclear hydrocarbons are also formed. A scheme which summarizes the probable sequence of reactions is given in Fig. 3.

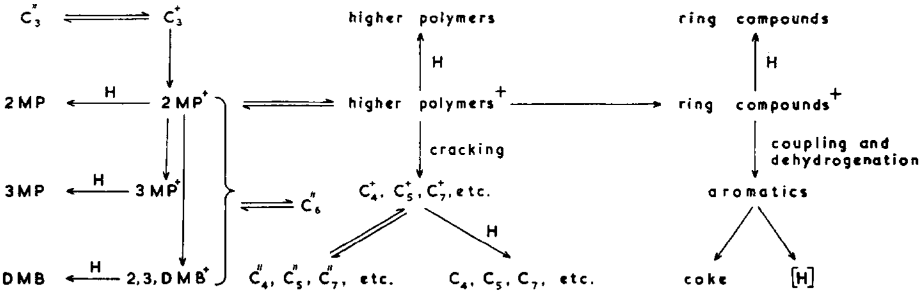


FIG. 3. Schematic representation of the reactions.

The propylene must be strongly adsorbed since it cannot be completely removed in one or two periods of desorption at 200°C. The olefinic dimers and trimers of propylene are clearly even more strongly adsorbed and more reactive than propylene itself. We believe that the main factors which control the amounts of the products recovered are the rate of desorption of olefins and the conversion of the adsorbed olefins to saturated molecules. The rate at which the latter reaction takes place depends on the availability of hydrogen on the surface which, in turn, depends on the cyclization and aromatization of polymeric species. Cyclization is probably the slow step in this transfer of hydrogen from one part of the reaction system to another and the higher activation energy for the formation of methylcyclopentane than for the other noncyclic paraffins supports this conclusion. As desorption is rate controlling, extensive polymerization, cracking, and isomerization takes place at all temperatures and so a complex array of products is obtained. Since polymerization and cracking are mutually opposing reactions, the distribution of carbonium ions on the surface approximates to an equilibrium state and thus the pattern of products obtained at different temperatures is substantially the same.

The preponderance of saturated compounds in the products indicates that the formation of these molecules by hydrogen transfer is normally easier than the desorption of olefins. However, under conditions where the supply of hydrogen is poor, more olefins are formed. This occurs during the first desorption of any experiment and in the runs with low contact times because less cyclization and aromatization take place and consequently less hydrogen is available to form saturated molecules. The decreasing amounts of olefinic products in the order $C_4 > C_5 > C_6$ is further evidence that the strength of adsorption and the tendency to react further increase with molecular weight.

The experiments with tetralin-treated catalysts provide excellent support for the suggestion that the formation of cyclic intermediates is the slow step controlling hydrogen transfer and thereby the recovery of products. Tetralin, which is known to be an active donor of hydrogen in reactions of olefins (*8*) influenced the distributions of products from the reaction of propylene in a striking, but predictable, manner. Little transfer of hydrogen occurred to propylene itself or to other normal olefins, as shown by the absence of normal paraffins in the products and thus tetralin did not inhibit dimerization of the propylene. However, the conversion of C_6-olefins to saturated products was sufficiently rapid that further polymerization and cracking of the resulting complexes was largely prevented and, in particular, no methylcyclopentane was formed. The substantial reduction in the amounts of C_4 and C_5 products with the tetralin-treated catalyst shows that these species originate mainly from the cracking of large polymeric species and not from the breakdown of C_6 entities. The plentiful supply of hydrogen from tetralin causes the products to be almost entirely saturated molecules with only traces of the butenes, which, like propylene, do not as readily undergo conversion to saturated molecules as the C_6 olefins. Finally, the substantial increase in the amount of carbon recovered as products with the tetralin-treated catalyst (cf. columns 6 and 3 of Table 2) is good evidence that the availability of hydrogen is an important controlling factor in the normal experiments.

Some useful conclusions can be obtained from a comparison of the proportions of the isomeric hexanes formed in the reaction of propylene with calculated values based on thermodynamic data, as shown in Table 3. The union of two propylene molecules might lead to the formation of a carbonium ion corresponding either to 2-methylpentane or to 2,3-dimethylbutane but 3-methylpentane cannot be formed unless a methyl-shift reaction takes place. It is clear that a 2-methylpentyl carbonium

TABLE 3

COMPARISON OF EXPERIMENTAL AND CALCULATED EQUILIBRIUM RATIOS OF THE ISOMERIC HEXANES FOR REACTION OF PROPYLENE AT DIFFERENT TEMPERATURES ON CLEAN CATALYSTS AND ON A CATALYST CONTAINING ADSORBED TETRALIN AT 100°C.

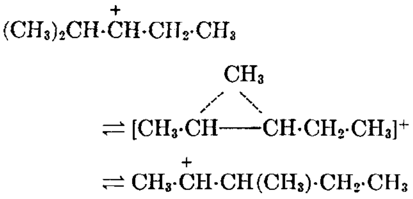
Temp. (°C)	2-Methylpentane/2,3-dimethylbutane		2-Methylpentane/3-methylpentane	
	Calc.	Exp.	Calc.	Exp.
58°	1.6	5.7	2.9	4.5
100°	2.0	4.5	2.6	3.1
100°[a]	2.0	22.2	2.6	3.0
150°	2.3	5.5	2.4	2.4
200°	2.5	4.1	2.2	1.9

[a] Reaction on catalyst containing adsorbed tetralin.

ion is the primary product as the ratio of 2-methylpentane/2,3-dimethylbutane is always greater than the equilibrium ratio, particularly at low temperatures and in the presence of the tetralin-treated catalyst. Thus, the dimerization of propylene on silica-alumina follows the Markownikoff rule and proceeds by the reaction

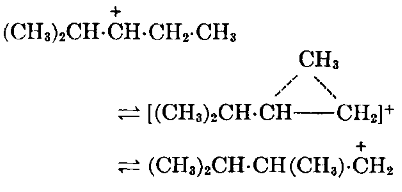
$$CH_3\cdot\overset{+}{C}H\cdot CH_3 + CH_2{=}CH\cdot CH_3 \rightarrow (CH_3)_2CH\cdot CH_2\cdot\overset{+}{C}H\cdot CH_3$$

The isomerization of 2-methylpentyl to 3-methylpentyl carbonium ions occurs fairly readily giving equilibrium ratios of the corresponding paraffins at 150°C or above and this reaction is not hindered by the presence of tetralin. On the other hand, the isomerization of 2-methylpentyl to 2,3-dimethylbutyl carbonium ions is obviously slower, and does not occur to the same extent on the tetralin-treated catalyst as on the normal catalyst at 100°C. This result with the tetralin-treated catalyst shows clearly that the distributions of C_6 compounds depend on the relative rates of the isomerization of the corresponding surface species and their conversion to saturated molecules by hydrogen transfer. The difference in rates of the two isomerizations is understandable on consideration of the carbonium ions and activated complexes involved. The first takes place by the reaction



$$(CH_3)_2CH\cdot\overset{+}{C}H\cdot CH_2\cdot CH_3 \rightleftharpoons [CH_3\cdot CH\overset{CH_3}{\text{——}}CH\cdot CH_2\cdot CH_3]^+ \rightleftharpoons CH_3\cdot\overset{+}{C}H\cdot CH(CH_3)\cdot CH_2\cdot CH_3$$

and the second by



$$(CH_3)_2CH\cdot\overset{+}{C}H\cdot CH_2\cdot CH_3 \rightleftharpoons [(CH_3)_2CH\cdot CH\overset{CH_3}{\text{——}}CH_2]^+ \rightleftharpoons (CH_3)_2CH\cdot CH(CH_3)\cdot\overset{+}{C}H_2$$

The monosubstituted cyclopropyl structure in the activated complex of the second reaction will be less easily formed than the corresponding disubstituted structure in the first and furthermore, the second reaction involves the production of a primary carbonium ion whereas only the more stable secondary ions are involved in the first. Differences in the rates of isomerization of various hydrocarbons, similar to those found in the present work, have been reported previously (*9*, *10*).

The absence of any reaction of propylene on the sodium-exchanged catalyst suggests that Brönsted sites are required for this reaction and that Lewis sites are inactive. This conclusion is in agreement with the results obtained by Holm, Bailey, and Clark (*11*) who showed that the polymerizing activity of a series of catalysts paralleled their Brönsted, but not their total acidity. The formation of perylene radical ions on the sodium-exchanged catalyst must occur on the Lewis sites and this shows that these are not readily converted to Brönsted sites under aqueous conditions as suggested by Trambouze, de Mourges, and Perrin (*12*). The reactivity of the perylene-treated catalyst for the reaction of propylene agrees with the suggestion that perylene was adsorbed only on the Lewis sites and not to any appreciable extent on the Brönsted sites. The greater proportion of olefins formed from propylene on the perylene-treated catalyst at 200°C suggests that the Lewis sites may be responsible for the reactions which supply the hydrogen required for the conversion of olefinic species and carbonium ions to saturated products. This conclusion agrees with the hypothesis that the Lewis sites are active in the build-up of aromatics and coke which was substantiated by the ESR investigations carried out by Rooney and Pink (*7*). The detailed results for the reaction of propylene at 100°C on the perylene-treated catalyst provide further confirmation of these ideas. The change in the ESR signal after reaction is consistent with the growth of aromatic structures, initiated by the coupling of perylene species (*7*), and this gives rise to a certain amount of hydrogen which cannot readily desorb from the silica-alumina as hydrogen gas (*13*). Consequently, the first desorption of products from the reaction of propylene yields as much saturated product as the normal experiments. Once this supply of hydrogen has been exhausted, the subsequent desorptions give more olefinic products than are found from untreated catalysts because the presence of the perylene blocks the Lewis sites and inhibits the generation of more hydrogen by cyclization and aromatization.

These results with the perylene-treated catalysts assist in the understanding of the role of tetralin discussed above. The tetralin is probably adsorbed at the Lewis sites and liberates hydrogen by conversion to naphthalene which may then undergo further reaction; the activity for the reaction of propylene is not affected because little adsorption of tetralin occurs on the Brönsted sites. Leftin and Hall (*14*) have shown that aromatic hydrocarbons such as cumene and triphenylmethane are adsorbed at Lewis sites by loss of a hydride ion and recently Leftin (*15*) has suggested that simple olefins may also adsorb in a similar manner to yield allylic carbonium ions. The driving force behind all these reactions at the Lewis acid sites appears to be the extension of π electron systems in positively charged complexes with consequent gain in stability by resonance.

Mapes and Eischens (*16*) concluded from infrared studies on ammonia adsorbed on silica-alumina that most of the ammonia retained after outgassing at 175°C was held on Lewis sites. We, therefore, expected ammonia-treated catalysts to show some activity for the polymerization of propylene after evacuation at 200°C, as the Brönsted sites would not be substantially covered. This was not found and so it appears that these sites remained poisoned unless a more drastic outgassing at 400°C is applied. Even after this further treatment, the Brönsted sites are still partially poisoned and so also are the Lewis sites, as shown by the poor activity of the catalyst for the formation of perylene positive radical ions and the proportion of olefins in the products from the reaction of propylene. The chemisorption of quinoline apparently takes place on both types of sites and renders the catalyst inactive.

Data on the experimental percentages of some of the C_4-olefins together with calculated equilibrium values are given in Table 4. Although we could not distinguish between isobutene and but-1-ene in our chromatographic apparatus, it is likely that very little of the latter is present because the equilibrium percentage expected at 200°C is only 2.5%. The equilibrium percentage of isobutene was obtained only with the ammonia-treated catalyst and in second or subsequent desorptions from the perylene-treated catalyst, i.e. under conditions where the supply of hydrogen was poor. The lowest percentage was found from the hydrogen-rich tetralin-treated catalyst and the normal experiments showed intermediate behavior. We believe these results arise because isobutene readily suffers desorption as isobutane if hydrogen is available and that this reaction

TABLE 4

COMPARISON OF EXPERIMENTAL AND CALCULATED EQUILIBRIUM PERCENTAGES OF THE ISOMERIC BUTENES FOR REACTION AT THREE TEMPERATURES ON CLEAN CATALYSTS AND FOR REACTION ON PRETREATED CATALYSTS AT 100°C

	100°				150°		200°	
Temperature (°C)	Calc.	Expt.	Expt.[a]	Expt.[b]	Calc.	Expt.	Calc.	Expt.
Isobutene + but-1-ene	76.3	61.0	37	76.2	70.8	55.0	65	52.3
trans-But-2-ene	16.4	22.8	37	13.3	20.0	25.5	24	27.3
cis-But-2-ene	7.3	16.2	26	10.5	9.2	19.6	11	20.4

[a] Reaction on catalyst containing adsorbed tetralin.

[b] Second product distribution from reaction on catalyst containing adsorbed perylene.

occurs more rapidly than the interconversion of the butenes involving methyl-shift reactions. The preferential formation of *cis*-but-2-ene as opposed to the *trans* compound, noticeable under all the conditions we used was observed, as long ago as 1946, by Voge and May (*17*) and more recently by others (*18, 19*). It implies that there must be some influence of a steric nature controlling the manner in which a hydrogen ion is removed from an adsorbed *sec*-butyl carbonium ion.

The marked difference in the reactivity of ethylene and propylene can be attributed to the difference in the ease of formation of ethyl and isopropyl carbonium ions which are required to initiate polymerization.

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