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Transformations of Olefins, Cyclopropanes, Diolefins and Acetylene in the Presence of Molybdenum Oxide on Alumina

MARIAN OTREMBA AND MARIAN TANIEWSKI

Department of Chemistry, Silesian Technical University, Gliwice, Poland

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The transformations of olefins from C_2 to C_6, cyclopropanes C_3 and C_4, diolefins C_3 and C_4, as well as acetylene in the presence of MoO_3/Al_2O_3 catalyst were studied in a flow system at various temperatures and contact times. All hydrocarbons underwent complex transformations and detailed analytical information about the products has been given. The reaction products contained mainly hydrogen, hydrocarbons richer in hydrogen compared with the parent molecule, isomers of the reactant, and higher and lower unsaturated hydrocarbons. A detailed reaction mechanism has been postulated involving a process of surface fragmentation and interactions between adsorbed species. Some specific features of the transformations of individual hydrocarbons and the role of secondary processes have been discussed.

INTRODUCTION

In the course of investigating the chemisorption of ethylene, its self-hydrogenation to ethane has been observed (*1, 2*). A similar reaction was noticed later with some other hydrocarbons. Until now there were reported the processes of self-hydrogenation of ethylene (*3–6*), propylene (*5, 6*), cyclopropane (*6, 7*) and acetylene (*6, 8–10*). Only metals were used as the catalysts in such processes.

The other important catalytic transformation of olefins is disproportionation, discovered by Banks and Bailey (*11*). The reaction occurs in the presence of metal oxides, such as MoO_3 on alumina, and on many other recently reported heterogeneous and homogeneous catalysts as well (*12, 13*). Disproportionation leads to equimolar quantities of the corresponding lower and higher olefins and, what is remarkable, only to some particular isomers, at least when conversion is low, such that the secondary isomerization and disproportionation reactions are still negligible.

In our previous paper (*14*) we have reported that propylene passed over molybdenum oxide on alumina undergoes a transformation yielding hydrogen, propane, butenes and a highly unsaturated surface residue. We postulated then a mechanism for this complex transformation, which included self-hydrogenation as a process responsible for the formation of hydrogen and propane, as well as some sort of redistribution of carbon atoms responsible for butenes and being quite different from disproportionation.

Carefully reviewing the published results of the studies on catalytic reactions of olefins, such as oligomerization, isomerization, disproportionation, etc., we have noticed a frequent presence among the reaction products of components suggesting the occurrence of a transformation resembling that observed by us with propylene. Little attention has been given by the authors to the origin of such by-products. Some authors do not discuss it at all, others link those by-products with cracking or disproportionation side-reactions (*15–18*).

The object of our present work was to obtain detailed analytical information about the products of transformations of olefins from C_2 to C_6, cyclopropanes C_3 and C_4, diolefins C_3 and C_4 as well as acetylene in the presence of supported molybdenum oxide. It was hoped that such abundant information would be a sufficient basis to formulate the general scheme of the mechanism of such catalytic transformations of various hydrocarbons.

EXPERIMENTAL METHODS

Materials. The catalyst used was 14.5% MoO_3 supported on γ-Al_2O_3, the same as described previously (*14*), reduced in a stream of hydrogen at 500°C. Ethylene used was pure commercially available product containing 0.03% of ethane. No other impurity was detectable. The other pure commercially available reactants were propylene (0.08% C_2H_6, 0.1% C_2H_4, 0.1% C_3H_8), acetylene (1% impurities) and butadiene-1,3 (0.2% impurities). Isobutylene (99.5% purity), pentene-1 (99.4%), 2-methylbutene-2 (99%) and hexene-1 (99%) were supplied by AG Fluka. Allene (99.5%) was obtained from Koch-Light Lab. and methylcyclopropane (99.4%) from K & K Lab. Inc. Butene-1 (0.1% C_3H_6, 0.2% *trans*-C_4H_8-2, 0.2% *cis*-C_4H_8-2) was prepared by thermal decomposition of *n*-butyl acetate (*19*). Cyclopropane (0.2% C_3H_8, 0.05% C_3H_6, 0.1% C_4H_8-2) was prepared by debromination of 1,3-dibromopropane (*20*). Commercially available nitrogen was purified and freed from traces of oxygen by passage through sodium supported on alumina.

In all experiments hydrocarbon–nitrogen mixtures of different concentrations have been used.

Apparatus and procedure. The apparatus used consisted of a steel pressure cylinder, pressure regulating devices, a gas flow regulating system, a glass tubular reaction vessel inserted into a vertical electric furnace as well as the necessary controlling devices. The outlet of the reactor was connected directly with a set of gas chromatographs. The hydrocarbon–nitrogen mixtures were prepared by admission of a strict amount of each component to a carefully evacuated pressure cylinder. The mixture was then admitted to the reaction vessel through a pressure reducing device enabling stabilization of the outgoing stream pressure independently of the pressure changes in the cylinder and then through a sensitive flow regulating system (accuracy ±1%). A glass reaction vessel was filled with a catalyst bed into which a thermocouple sheath was inserted. The temperature was measured and recorded to ±0.1°. The temperature of the furnace was maintained constant within ±0.2°. All experiments were carried out by a flow method at atmospheric pressure. After each run (1–4 hr) the catalyst was regenerated by calcining for 3 hr in a stream of dry air at 500°C, reducing for another 3 hr at 500°C with hydrogen and finally cooling to the reaction temperature with nitrogen. In this way its previous activity was practically restored.

Analysis. The gaseous reaction products were analyzed chromatographically using a set assembled from several units. The following columns and analytical conditions were applied:

I. A column (length 0.7 m, diameter 4 mm) filled with active charcoal (0.2–0.3 mm) operated at 20°C. Carrier gas, argon; detector, katharometer.

II. A column (length 1 m, diameter 4 mm) filled with bis(2-ethylhexyl) sebacate (3%) on silica gel (Perkin-Elmer) operated at 20°C. Carrier gas, hydrogen; detector, katharometer.

III. A column (length 4 m, diameter 4 mm) filled with bis-2-methoxyethyl adipate and di-2-ethylhexyl sebacate on Chromosorb P, 13.5:6.5:80 (Perkin-Elmer) operated at 20°C. Carrier gas, hydrogen; detector, katharometer.

IV. A column (length 4 m, diameter 4 mm) filled with 1,2,3-tricyanethoxypropane (27%) on alumina (*21*) operated at 25°C. Carrier gas, hydrogen; detector, katharometer.

V. A column (length 2 m, diameter 4 mm) filled with Apiezon L on Chromosorb P (Perkin-Elmer). The initial column temperature was 80°C (2 min) and then increased by 10°/min. Carrier gas, argon; detector, flame ionization.

The determination of hydrogen in the reaction products was carried out by system I. The other products of transformation of ethylene were analyzed using systems II and IV and of hexene-1 using III and V. In all other cases systems III and IV were normally used.

Calibrations were carried out using calibrant mixtures of the compositions close to those of the reaction products.

Results and Discussion

When passed over the catalyst, all the hydrocarbons studied undergo some transformations. The experimental results, however, indicated a decrease in catalytic activity with time. In order to eliminate the time-dependencies a special treatment of the experimental data analogous to that described previously (*14*) has been applied. The concentrations of the products after 40 min of the run were calculated by interpolation of the experimental values using a plot of log (concentration) against $(\text{time})^{1/2}$. In a few cases the concentrations after some other time have been calculated as well. The concentrations were then expressed as a percentage of the total reaction mixture without nitrogen. In the course of the investigation the reaction temperature and the amount of catalyst (contact time) were varied.

In Table 1 are presented only the results obtained with each hydrocarbon at such conditions where the specific features of its transformation are best exhibited. All other results, not included here, were perfectly consistent with the results presented and the conclusions drawn.

The experimental results clearly indicate that in the presence of molybdenum oxide on alumina many unsaturated hydrocarbons and cycloalkanes undergo complex transformations leading to an extensive range of products. The reactivity of hydrocarbons in such processes varies markedly from one individual hydrocarbon to another. Thus, the reactivity of olefins increases with the number of carbon atoms in the molecule. The rate of disappearance of diolefins and acetylene substantially exceeds that of olefins. Sometimes complete disappearance of reactant has been observed at the initial stage of the run, accompanied by a strong exothermic effect.

Hydrogen was detected in all cases among the reaction products. Its amount depends upon the hydrocarbon used and increases with reaction temperature and contact time. The reaction products contain also some components richer in hydrogen compared with the parent molecule, i.e., alkanes forming by transformation of olefins or cyclopropanes and olefins as well as alkanes forming from diolefins or acetylene. The amount of such products also increases with temperature and contact time. The complex transformation includes, among others, the isomerization of the reactant. In the case of cyclopropanes, a very rapid irreversible isomerization to olefins occurs. Allene isomerizes to methylacetylene, butene-1 to butenes-2; whereas pentene-1 or hexene-1 isomerize to all possible isomers. Apart from other products, there are formed also appreciable quantities of hydrocarbons with lower and higher number of carbon atoms than in the initial molecule, mostly of the same homologous series. In the most thoroughly investigated of the olefin transformation processes, all lower olefins down to ethylene and higher olefins up to dimers were identified. Also, in the case of propylene, by using a better analytical method we recently found pentenes and hexenes not identified earlier (*14*). Though the total yield of olefins formed depends on the reactant, those differing by one carbon atom from the initial alkene are usually produced preferentially. Nevertheless, as we demonstrated with hexene-1, all olefins are formed in comparable quantities, even when due to low conversion the concentrations of all newly formed olefins in the gas phase are still low.

The processes of hydrocarbon transformation were in each case accompanied by a progressive deactivation of the catalyst.

Reaction Mechanism

On the basis of all the experimental results the following reaction scheme can be postulated:

TABLE 1

Reactant	Ethylene			Propylene			Butene-1			Isobutylene	Pentene-1		
Initial conc., vol. %	49	49	49	16	50	50	40	40	40	50	13	13	13
Catalyst, g	5.0	5.0	5.0	5.0	5.0	5.0	0.13	0.80	5.0	5.0	5.0	5.0	5.0
Flow rate, $cm^3 . min.^{-1}$	20	20	20	20	20	20	20	20	20	20	10	10	10
Temperature, °C	300	350	400	200	300	350	350	350	350	350	182	250	300
Composition of reaction mixture without N_2, vol.%													
Hydrogen	2.2	4.2	7.8	0.4	3.6	6.6	0.2	1.9	12.0	12.2	2.1	18.0	32.0
Alkane[b]	3.1	6.9	14.3	2.1	6.8	10.0	0.2[c]	1.1[c]	5.8[c]	14.8	1.5	12.6[d]	16.5[e]
Ethylene	92.5	87.2	76.3	0.2	0.5	0.7	-	0.2	1.2	0.7	-	0.4	1.4
Propylene	0.4	0.4	0.6	92.1	84.6	78.2	0.1	0.7	4.1	3.7	0.6	2.0	3.6
Butenes	1.8	1.2	0.9	2.1	2.4	2.8	99.4	95.6	73.2	61.8	1.8	6.1	11.9
Pentenes				1.7	1.1	0.7	-	0.5	2.7	5.3	88.6	56.0	26.1
Hexenes				1.4	1.0	0.9	-	-	1.0	1.5	5.2	7.8	8.5
Others													
Composition of butenes, %													
Butene-1	16	19	17	3	5	8	37	22	21	4	9	10	13
trans-Butene-2	45	42	38	8	10	16	31	45	44	9	47	35	34
cis-Butene-2	35	32	32	6	8	11	32	31	30	6	23	22	21
Isobutylene	4	7	13	83	78	65	0	2	5	81	21	33	31
Composition of pentenes, %													
Pentene-1				3	3	7		5	2	2	8	5	3
trans-Pentene-2				16	15	18		10	9	9	53	23	9
cis-Pentene-2				12	10	15		10	8	6	27	19	8
2-Methylbutene-1				30	30	25		20	20	21	2	13	20
2-Methylbutene-2				38	42	35		55	60	62	10	40	58

[a] After 140 min. [b] Alkanes with the same number of carbon atoms as in the reactant. [c] Only *n*-butane. [d] *n*-Pentane, 5.6; isopentane, 7.0. [e] *n*-Pentane, 8.8; isopentane, 7.7. [f] C_7H_{14}, 9.8; C_8H_{16}, 3.1; C_9H_{18}, 1.2; C_{10}, 0.9. [g] Cyclopropane. [h] Methylcyclopropane. [i] Acetylene. [j] Butadiene-1,3. [k] Allene. [l] Methylacetylene.

1. Chemisorption and fragmentation of adsorbed species.

$$C_nH_{2m}\,(g) \longrightarrow C_nH_{2m}\,(ads) \tag{1a}$$

$$C_nH_{2m}\,(ads) \begin{cases} \rightarrow aH\,(ads) + C_nH_{2m-a}\,(ads) & \text{(1b)} \\ \quad \text{where } a = 1,2,3.\ .\ .\ . & \\ \rightarrow C_bH_{2b+1}\,(ads) + C_{n-b}H_{2m-2b-1}\,(ads) & \text{(1c)} \\ \quad \text{where } b = 1,2.\ . & \end{cases}$$

Hydrocarbons chemisorbed on the catalyst surface (1a) undergo fragmentation into chemisorbed hydrogen atoms, chemisorbed alkyl groups and adsorbed remnants of the molecules (1b) and (1c). The substantial amount of hydrogen and of self-hydrogenation products in the reaction mixtures is obvious evidence for the extensive surface dehydrogenation of the parent molecule. In our previous paper (*14*) we have postulated also fragmentation yielding methyls and now we are extending this view to higher alkyl groups as well. Evidently, with larger molecules the adsorbed reactant may fragment at more than one C–C bond.

The surface species formed in (1b) and (1c) may participate as intermediates in the numerous reactions of addition (see below) or they may undergo further fragmentation.

The relative role of the further fragmen-

TRANSFORMATION OF HYDROCARBONS

2-Methyl-butene-2	Hexene-1	Cyclopropane			Methyl-cyclo-propane	Acetylene			Allene			Butadiene-1,3		
21	6	18	18	18	20	50	50	50	47	47	47	48	48	48
5.0	5.0	5.0	0.32	5.0	5.0	1.0	5.0	5.0	1.0	5.0	5.0	1.0	5.0	5.0
10	20	20	20	20	20	20	20	20	20	20	20	20	20	20
350	250	200	250	250	250	350	350	350	350	350	350	350	350	350
								a			a			a
18.8	13.4	0.3	0.3	1.5	8.5	3.2	16.4	9.5	1.6	14.9	3.4	1.1	6.4	2.5
18.8	5.2	2.6	0.5	11.1	8.6	0.5	10.3	2.5	0.6	5.4	0.6	0.2	3.8	0.1
0.8	0.1	0.1	-	0.4	0.6	60.1	63.9	71.0	0.1	0.5	0.2	0.1	1.4	1.0
1.7	0.9	73.2	10.1	66.3	4.8	4.5	3.7	5.4	6.0	64.3	24.8	0.3	4.5	1.4
7.6	2.1	1.8	0.5	6.0	69.1	6.2	5.6	7.8	1.0	9.8	2.7	13.8	80.3	50.1
44.2	6.3	2.4	-	2.4	7.2				0.3	2.9	0.8	0.3	2.8	0.8
7.8	54.1	4.9	-	6.8	1.1				0.2	2.1	0.4			
	15.0^f	14.6^g	82.6^g	0^g	0^h	25.2^i	0^i	2.0^i	48.7^k	0^k	21.0^k	84.2^j	0.8^j	44.0^j
						0.3^j	0^j	0.5^j	41.5^l	0^l	46.0^l			
10		10		8	20	11	17	18	5	6	5	28	25	23
24		41		26	43	48	38	38	12	15	14	43	43	45
17		24		16	30	26	28	27	8	10	11	29	30	23
48		25		50	7	15	17	17	75	69	70	0	2	0
2	1	4			1					5	8		12	7
10	8	21			8					18	22		8	10
7	5	18			6					16	19		6	8
22	25	28			22					18	16		20	21
59	61	29			63					43	35		54	54

tation is substantial in establishing the final proportion between the lower and higher hydrocarbons produced by additions.

2. Addition of chemisorbed hydrogen atoms to the adsorbed species.

$$C_nH_{2m}\ (\text{ads}) \xrightarrow{\text{H(ads)}} C_nH_{2m+1}\ (\text{ads}) \xrightarrow{\text{H(ads)}} C_nH_{2m+2}\ (\text{ads}) \xrightarrow{\text{H(ads)}} \ldots \tag{2a}$$

$$\text{H(ads)} + C_nH_{2m-1}\ (\text{ads}) \rightarrow C_nH_{2m} \tag{2b}$$

$$\text{H(ads)} + C_{n-b}H_{2m-2b-1}\ (\text{ads}) \rightarrow C_{n-b}H_{2m-2b} \tag{2c}$$

$$2\text{H(ads)} \rightarrow H_2 \tag{2d}$$

$$R_1\text{—}\underset{x}{\text{CH}}\text{—}\underset{x}{\text{CH}}\text{—CH}_2\text{—}R_2 \xrightarrow{-\text{H}} R_1\text{—}\underset{x}{\text{CH}}\text{—CH}\text{=}\text{CH—}R_2 \xrightarrow{+\text{H}} R_1\text{—CH}_2\text{—CH}\text{=}\text{CH—}R_2 \tag{2e}$$

The initial hydrocarbon is hydrogenated in (2a) by addition of 2 or, if possible, 4 hydrogen atoms. In this way alkanes are produced from olefins or cyclopropanes, whereas olefins and alkanes are formed from diolefins or acetylene. The hydrogen atom may also combine (2b) and (2c) with the species formed by its previous abstraction. In (2b) the initial hydrocarbon is reproduced, though sometimes double-bond isomerization occurs, as shown in (2e).

It appears that the mechanism of a

double-bond isomerization (2e), based on a common intermediate with the fragmentation process (the species with one abstracted hydrogen atom) is the most reasonable to be assumed. One can suppose, however, that with the extent of reaction and accumulation of hydrogen an alternative route of isomerization through alkyl groups may increasingly contribute. The high rate of isomerization indicates that the first dissociative step is rapid and reversible.

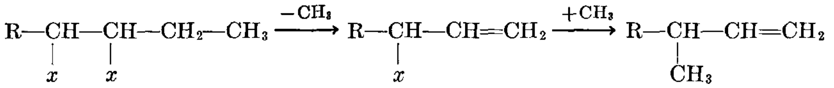
In (2c) there are formed hydrocarbons of the same homologous series but of lower molecular weight.

The surface recombination of hydrogen atoms (2d) or hydrogen abstraction by a hydrogen atom from the adsorbed species yield molecular hydrogen.

3. Addition of chemisorbed alkyl groups to the adsorbed species.

$$R_1\,(\mathrm{ads}) + R_2\,(\mathrm{ads}) \rightarrow R_1R_2 \qquad (3a)$$

$$C_bH_{2b+1}\,(\mathrm{ads}) + C_{n-b}H_{2m-2b-1}\,(\mathrm{ads}) \rightarrow C_nH_{2m} \qquad (3b)$$



$$\mathrm{R{-}}\underset{x}{\mathrm{CH}}\mathrm{{-}}\underset{x}{\mathrm{CH}}\mathrm{{-}CH_2{-}CH_3} \xrightarrow{-\mathrm{CH_3}} \mathrm{R{-}}\underset{x}{\mathrm{CH}}\mathrm{{-}CH{=}CH_2} \xrightarrow{+\mathrm{CH_3}} \mathrm{R{-}}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}CH{=}CH_2} \qquad (3c)$$

The interactions between alkyl groups formed in (1c) or (2a) and the species poorer in hydrogen, formed in (1b) or (1c) can account for higher hydrocarbons (3a). In particular, with case (3b) being the reverse of (1c) the initial hydrocarbon may be regenerated, but this may lead to a change in its initial structure and formation of the skeletal isomers, as shown in an example with methyl groups (3c).

The relative role of alkyl groups in the surface reactions depends on the ease of their formation (this being, in its turn, a function of the hydrocarbon structure, the reaction temperature, etc.), their stability, efficiency in addition reactions as well as ability to migrate on the catalyst surface.

On this model, skeletal isomerization would simply be one of the results of the general scheme based on elimination and addition of the alkyl groups. The processes of skeletal isomerization and formation of lower and higher hydrocarbons are, therefore, inseparable. Thus, relative ease of splitting off the alkyls from higher olefins is able to explain both the large amounts of skeletal isomers as well as of the products of carbon atom redistribution.

As a consequence of a higher rate of isomerization as compared with self-hydrogenation, isoalkanes are present apart from normal alkanes among the products of transformation.

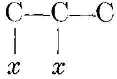
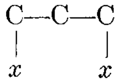
4. The secondary reactions. The primary unsaturated products formed in the consecutive processes occurring in a single residence of a molecule on the surface undergo desorption and readsorption and then the secondary transformation processes, according to the same reaction scheme. Such processes occur intensively only at higher conversions of the initial reactant, and particularly at long contact times. Because of its high rate, the isomerization of the products is the most important among the secondary reactions. Thus, the secondary isomerization of butenes is responsible for the equilibrium concentrations of *n*-butenes in the C_4 fraction of the products. Fractions C_5 and higher contain all possible isomers. The secondary transformations of olefins, being the primary products of the transformation of diolefins and acetylenes, considerably enlarge further the extensive range of primary products. By analogy, the secondary transformations of olefins, being the products of isomerization of cyclopropanes, lead to a change in the composition of the products.

5. Deactivation of the catalyst. Extensively dehydrogenated surface species form the residues remaining on the catalyst surface and responsible for the progressive decrease in the catalyst activity. Such highly unsaturated species are accumulated, as we pointed out previously (*14*), not only on the molybdenum oxide surface but on the alumina as well. By polymerization, cyclization, etc., they are rearranged into the structures comprising the final surface deposit.

The mechanism of transformation proposed above correctly accounts for all the products. The possibility of quantitative correlation is, of course, limited because of the multidirectional nature of this complex transformation.

Some Specific Features of the Transformation of Individual Hydrocarbons

Transformation of ethylene yields propylene, apart from self-hydrogenation and dimerization products. Propylene is not produced by secondary disproportionation of ethylene and butene-2, in view of the evidence that its yield falls in time with the same rate as that observed for all other products. The formation of propylene from ethylene was recently noticed also by other authors (*22*). The formation of butenes from propylene cannot be explained in terms of disproportionation, as they are produced in a great excess over ethylene and moreover, as the fraction C_4 contains considerable quantities of isobutylene, unexpected from the point of view of disproportionation mechanism. We could not exclude, however, that some part of the ethylene and normal butenes was formed by an accompanying disproportionation (*11*).

Our observation that the fraction C_4 obtained by transformation of cyclopropane at 200°C contains much less isobutylene, compared with propylene transformed under identical conditions, favors the view about the migration of methyl group. By adsorption of propylene and cyclopropane the following species are formed correspondingly:  $\underset{x}{\mathrm{C}}-\underset{x}{\mathrm{C}}-\mathrm{C}$ (I) and  $\underset{x}{\mathrm{C}}-\mathrm{C}-\underset{x}{\mathrm{C}}$ (II). The addition of methyl to (I) may proceed as α- or β-addition yielding *n*-butenes or isobutylene. The results show that β-addition is preferred. On the other hand, the addition of methyl to (II) may proceed only as an α-process producing *n*-butenes. Only subsequent isomerization of the adsorbed species leads to the composition of C_4, resembling that observed in the case of propylene. The experiments with cyclopropane at 250°C have in fact indicated that this was the case.

In the case of the butene-1 transformation we have shown that double-bond isomerization occurs very rapidly. The equilibrium is reached before the self-hydrogenation and carbon atom redistribution products are formed in reasonable amounts. Unlike pentene-1, 2-methylbutene-2 and hexene-1, in the case of butene-1 only weak skeletal isomerization has been observed (small amounts of isobutylene and a lack of isobutane).

As a result of a rapid isomerization, the composition of *n*-butenes and of pentenes formed by transformation of hydrocarbons is close to equilibrium under the experimental conditions.

The results of the experiments with cyclopropane and methylcyclopropane have shown that cyclopropanes undergo transformation not only through intermediate olefins.

In case of acetylene, allene and butadiene, where because of their structure no splitting-off of alkyl groups may proceed, there are observed at first only the self-hydrogenation products. As a consequence of the high efficiency of the catalyst towards these hydrocarbons, large amounts of primary olefins (ethylene, propylene, *n*-butenes) are produced, being next transformed into a complex mixture of reaction products. The formation of butadiene, identified among the products of transformation of acetylene, may be associated with dimerization of the latter to vinylacetylene with subsequent self-hydrogenation.

General Comments

On the grounds of our present results and taking also into account our previous report (*23*) concerning the transformation of propylene over different oxides on alumina, we believe that the transformations described are a general phenomenon. The relative rates of the individual steps of the complex transformation, and, therefore, the product distribution depend on the catalyst and the conditions.

The processes of transformation of hydrocarbons needing rather long contact with catalyst were mostly unnoticed by other authors. Under conditions where the rate of the basic process is very high, the transformations described here may play only a negligible role. On the other hand, when the basic process and the transformations discussed here proceed at comparable rates the latter become the important side-reactions accompanying many real processes using olefins, dienes, acetylenes, etc. Such processes are accompanying, among others, the reactions of disproportionation of olefins, but on the other hand one cannot exclude that the transformations described here are accompanied by disproportionation. Their relative role may depend on the proportion of full fragmentation and formation of cyclobutane intermediates on the catalyst surface.

The proposed mechanism of transformation explains the origin of the formation of all by-products observed by other authors (*15–18*). When non-equimolar ratios of corresponding products are formed, they rather than disproportionation are the processes really responsible for the products. Such transformations are often responsible not only for the formation of side-products but equally for the change of catalyst activity with time.

REFERENCES

1. BEECK, O., *Discuss. Faraday Soc.* **8,** 152 (1950).
2. JENKINS, G. I., AND RIDEAL, E. K., *J. Chem. Soc.* **1955,** 2490.
3. MCKEE, D. W., *J. Amer. Chem. Soc.* **84,** 1109 (1962).
4. HIROTA, K., AND TERETANI, S., *Z. Phys. Chem. (Frankfurt am Main)* **48,** 66 (1968).
5. POPOV, A. G., AND MARDELEISHWILI, R. E., *Vestn. Mosk. Univ., Khim.* **17,** 34 (1962).
6. TAYLOR, G., THOMSON, J., AND WEBB, G., *J. Catal.* **12,** 150 (1968).
7. MERTA, R., AND PONEC, V., *J. Catal.* **17,** 79 (1970); *Proc. Int. Congr. Catal., 4th* **2,** 53 (1971).
8. DOUGLAS, J. E., AND RABINOVITCH, B. S., *J. Amer. Chem. Soc.* **74,** 2486 (1952).
9. HANSEN, R. S., ARTHUR, J. R., MIMEAULT, V. J., AND RYE, R. R., *J. Phys. Chem.* **70,** 2789 (1966).
10. TERETANI, S., AND HIROTA, K., *Z. Phys. Chem. (Frankfurt am Main)* **69,** 271 (1970).
11. BANKS, R. L., AND BAILEY, G. C., *Ind. Eng. Chem. Prod. Res. Develop.* **3,** 170 (1964).
12. BAILEY, G. C., *Catal. Rev.* **3,** 37 (1969).
13. BANKS, R. L., *Fortschr. Chem. Forsch.* **25,** 39 (1972).
14. TANIEWSKI, M., AND OTREMBA, M., *J. Catal.* **14,** 201 (1969).
15. OZAWA, Y., AND BISCHOFF, K. B., *Ind. Eng. Chem. Process Des. Develop.* **7,** 67 (1968).
16. PANTCHENKOV, G. M., KUZNETZOV, O. I., AND SHAUKI, M. I., *Neftekhimya* **9,** 67 (1969).
17. LAPIDUS, A. L., AVETISSIAN, R. W., ISAKOV, YA. I., MINACHEV, K. M., AND EIDUS, YA. T., *Neftekhimya* **10,** 648 (1970).
18. RIASHTCHENTSEVA, M. A., AFANASIEVA, Y. A., AND MINACHEV, K. M., *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1972,** 1538.
19. TANIEWSKI, M., AND LACHOWICZ, R., *Rocz. Chem.* **44,** 329 (1970).
20. KAZANSKII, V. A., AND LUKINA, M. Y., *Khim. Prom.* **6,** 462 (1960).
21. PATEROK, N., AND KOTOWSKI, W., *Chem. Anal. (Warsaw)* **16,** 801 (1971).
22. O'NEILL, P., AND ROONEY, J., *J. Amer. Chem. Soc.* **94,** 4383 (1972).
23. TANIEWSKI, M., AND OTREMBA, M., *Tetrahedron Lett.* **1967,** 1983 (1967).