JOURNAL OF CATALYSIS 55, 299–313 (1978)

Surface Complexes of Propylene and Their Role in Catalytic Oxidation

A. A. DAVYDOV, V. G. MIKHALTCHENKO, V. D. SOKOLOVSKII,
AND G. K. BORESKOV

*Institute of Catalysis, Siberian Branch of the USSR, Academy of Sciences,
Novosibirsk 630090, USSR*

Received November 25, 1977; revised May 9, 1978

Infrared (ir) spectroscopy and thermodesorption studies of propylene adsorption on CuO, Cu_2O, Cr_2O_3, CuO–MgO, gallium molybdate, MoO_3/SiO_2, and MoO_3/Al_2O_3 have shown that propylene is adsorbed in reversible (π-allyl and σ-allyl) and irreversible (π-complexes, carboxylate, carbonate, and formate) forms. It emerges that both symmetric and asymmetric allyl complexes of propylene may participate in acrolein formation. The conversion of the surface π-allyl complexes into the Me–O–CH_2–CH=CH_2 type compound takes place on a gallium molybdate catalyst. π-Complexes, carboxylates, carbonates, and formates yield the products of complete oxidation, CO_2 and H_2O. This may occur with surface carboxylate–formate complexes either by a stepwise mechanism involving catalyst oxygen or by a concerted mechanism with the participation of molecular oxygen.

INTRODUCTION

Formation of intermediate complexes on a catalytic surface is the most important stage of a catalytic reaction. For complex catalytic reactions which occur through various paths we may anticipate several varieties of chemisorption on the catalyst surface. These lead to different products. Specifically, in the catalytic oxidation of hydrocarbons involving complete and selective oxidation, the different products result from these various forms of chemisorption. The adsorbed forms of propylene on oxide catalysts have already been studied (*1–4*). Dent and Kokes (*1*) were the first to observe the formation of π-allylic complexes on zinc oxide using ir spectroscopy.

The aim of this work is to elucidate the nature of adsorbed propylene forms which appear on the surfaces of oxide catalysts and to determine the role of these forms in the formation of products of complete and selective oxidation. This study was carried out using ir spectroscopy and thermodesorption.

EXPERIMENTAL

Cupric oxide was prepared by thermal decomposition of the hydroxide in an oxygen stream. The hydroxide was precipitated from cupric nitrate solution with ammonia. Cuprous oxide was prepared by reducing the divalent oxide at 400°C. Copper–magnesium catalysts of differing compositions were obtained via simultaneous precipitation of copper and magnesium hydroxides from a solution of their nitrates, using aqueous NaOH. Samples containing 5, 10, 20, 50, 75, and 100% cupric oxide were used. According to

0021-9517/78/0553-0299$02.00/0

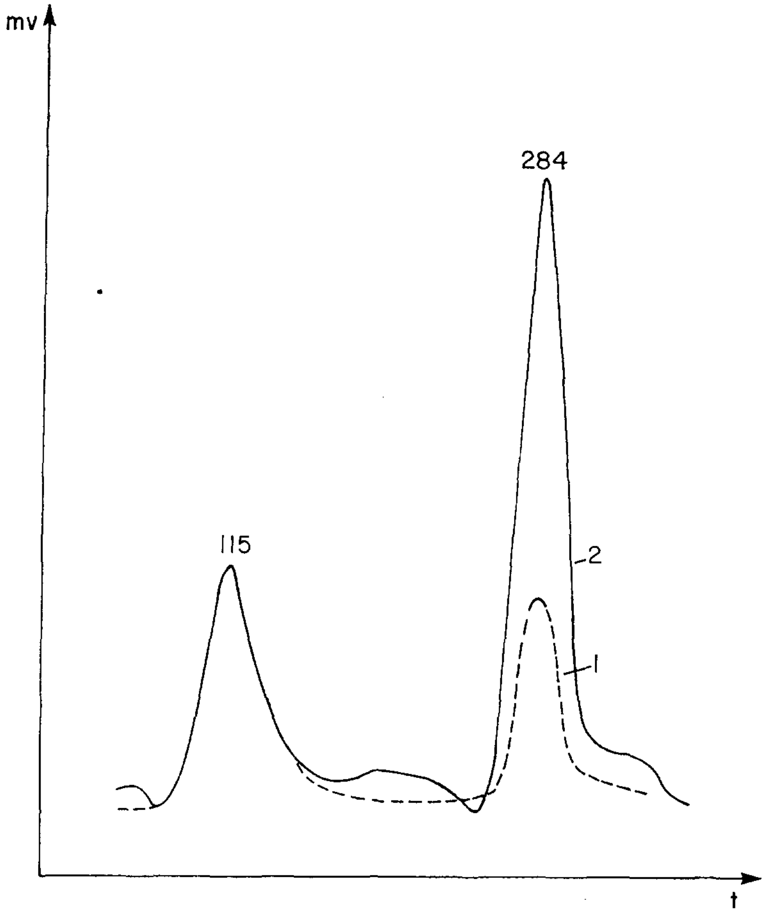


FIG. 1. Propylene desorption from the surface of Cu_2O [1] and CuO [2].

Maksimov *et al.* (*5*) samples containing 20% or less copper are solid substitution solutions of copper for magnesium in the magnesium oxide lattice, with somewhat higher copper content in the surface layers.

Chromium oxide was prepared by thermal decomposition of ammonium dichromate. Molybdenum oxide catalysts (4% MoO_3/Al_2O_3) were prepared by supporting tetrakis(π-allyl)molybdenum from pentane on alumina followed by catalyst calcination in oxygen at 450°C. Molybdenum and nickel complexes were prepared by supporting bis(π-allyl)nickel and tetrakis(allyl)-molybdenum on dehydroxylated silica. The silica was treated with a pentane solution of the complex *in vacuo*.

A vacuum chromatographic apparatus with programmed sample heating was used to study the thermodesorption (*6*). For ir studies the catalyst was pressed into 20 to 40-mg/cm^2 tablets. The ir spectra were recorded using a modified UR-10 spectrometer which permitted operation at elevated temperatures (*7*). Slit width at 1000 cm^{-1} was 1.08 mm.

RESULTS

Copper-Containing Catalysts

Chromatographic study of thermodesorption from cuprous and cupric oxides (Fig. 1) and solid solutions of CuO–MgO showed that there are two forms of propylene

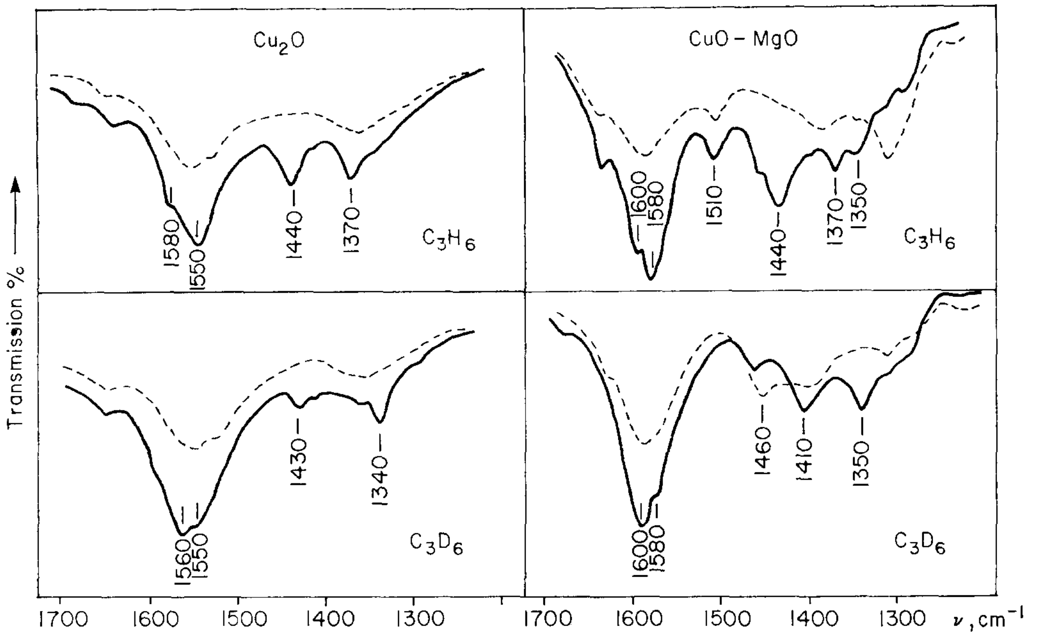


FIG. 2. The ir-spectra of propylene adsorbed on Cu$_2$O and CuO–MgO (20% Cu); propylene adsorption and evacuation at 20°C indicated by solid line; desorption at 200°C indicated by broken line.

adsorption of the catalyst surface: (a) a weakly bound, reversibly adsorbed form with a peak maximum in the desorption spectrum at ~110 ± 20°C, the rate of heating being 17°C/min; and (b) a strongly bound form which desorbs only with decomposition, beginning at ~200°C, with a peak maximum at 280°C. This peak represents propylene decomposition products, mainly carbon dioxide and a trace of water. Two similar forms of propylene adsorption were found on chromium oxide and on the oxide aluminum–molybdenum catalyst. It is interesting to point out the ratio between the absorbed propylene forms on catalysts for complete oxidation (CuO, Cr$_2$O$_3$) compared to catalysts for selective oxidation (Cu$_2$O, MoO$_3$/Al$_2$O$_3$). Propylene is primarily adsorbed irreversibly on catalysts for complete oxidation. On catalysts for selective oxidation adsorption is largely reversible.

The structures formed during adsorption were studied by means of ir spectroscopy. Propylene adsorption on Cu$_2$O and copper–magnesium catalysts produces a series of discrete maxima in the 1200 to 1800-cm^{-1} region (Fig. 2). By thermodesorption analysis reversibly bound propylene has been shown to leave the surface below 200°C. Therefore, the disappearance of a series of maxima from the spectra of adsorbed propylene below this temperature (Fig. 2) may be ascribed to the desorption of propylene molecules whose structures have not undergone decomposition. The spectra of the adsorbed propylene show that a certain portion of molecules are adsorbed on the surface without breaking the double bond. The existence of a double bond is demonstrated by the following spectral evidence (Fig. 3): the presence of ir bands due to stretching, ν =C–H (3095 cm^{-1}) and ν =C–D, of out-of-plane deformation vibrations β CH at 950 and 995 cm^{-1} in CH$_2$ and correspondingly in CD$_2$ groups, and also the appearance of a series of intense absorption bands in the region of

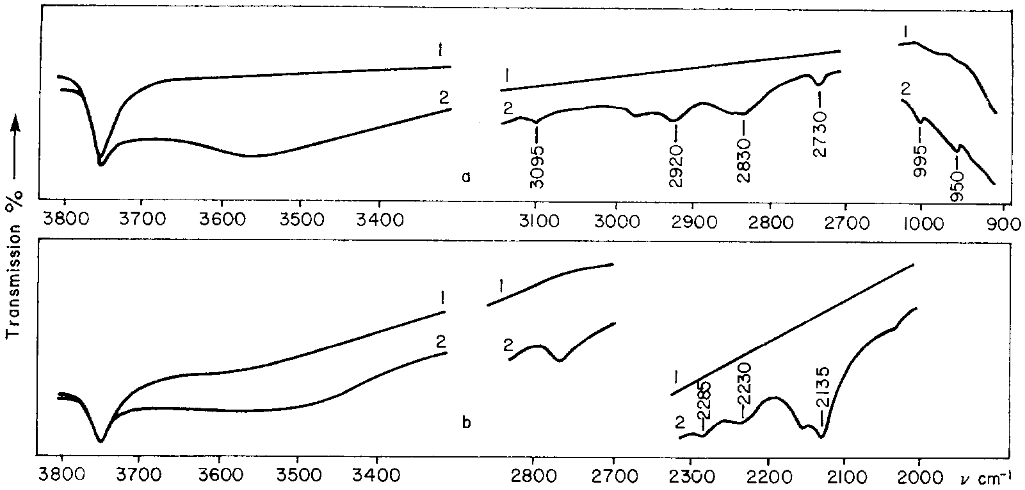


FIG. 3. The ir-spectra of CuO–MgO [1] after adsorption of C_3H_6 [2a] and C_3D_6 [2b] at 20°C, subsequently evacuated.

the asymmetric stretching of ν_{as} C=C bonds. Taking into account the comparison of spectra within a wide spectral region with those of the individual propylene complexes (*1–4, 6–13*) and the thermostability of the surface compounds, as well as the isotope shifts of the ν_{as} C=C absorption bands during C_3D_6 adsorption (Fig. 2), the following interpretation is offered for the maxima observed (Table 1). It has been shown by spectral analysis of individual propylene complexes (*10–15*) that it is most difficult to elucidate differences between various complexes via ν C–H stretching and deformation vibrations because of the overlap of the frequency ranges. Therefore, significant characteristics can be found only with the C=C vibrations. This leads to major uncertainty in identification of the surface compounds.

An absorption band at 1510 cm^{-1} which, to our knowledge, has been observed only on copper–magnesium catalysts, is within the range of frequencies characteristic of the vibrations of a greatly weakened ν C=C bond in π-complexes of propylene with metals (*10*). The surface π-complexes are rather stable thermally and can be completely removed from the surface only within the temperature range 250 to 300°C. During C_3D_6 adsorption two maxima are observed at 1410 and 1460 cm^{-1} in the region characteristic of ν C=C in π-C_3D_6 (Fig. 2). The maximum at 1410 cm^{-1} may be ascribed to C=C in π-C_3D_6 because it behaves similarly to the maximum at 1510 cm^{-1} in the desorption cycles; futhermore the observed isotope shift is close to those known in the literature for the ν C=C bond in π-complexes (*15*). A band at 1460 cm^{-1} is ascribed to ν_s C=O in an oxidized structure because during C_3D_6 adsorption an absorption band was also observed within the indicated spectral region (near 1450 cm^{-1}).

There can be no doubt about the assignment of the 1510 cm^{-1} band to a weakend C=C bond. At the same time, the assignment of the 1440-cm^{-1} maximum to ν_{as} C=C (*10, 19*) in a π-allylic complex is not unambiguous because this band is within the frequency range characteristic of C–H deformation vibrations. However, as proven by a comparison of the absorption band intensities of the stretching and deformation C–H vibrations for gaseous propylene (in this case they are similar) and for the adsorbed complex (in this case

TABLE 1

Assignment of Absorption Bands Observed in the ir Spectra of Copper–Magnesium Catalyst after Propylene Adsorption

$C_3H_{6(ads.)}$[a]	Type of vibration[b]	$C_3D_{6(ads.)}$	Type of vibration[b]
950	β CH		
995	β CH_2		
1285	ν_s C–O	1285	ν_s C–O
1320	ν_s C=O	1320	ν_s C–O
1350 (weak)	δ C–H	1350 (strong)	ν_{as} C=C=C in π-allyl
1370	ν_s C=O	1380	ν_s C=O
1400 (weak)	δ C–H	1410 (strong)	ν C=C in π-complex
1440	ν_{as} C=C=C in π-allyl	—	
1450	ν_s C=O	1460	ν_s C=O
1510	ν C=C in π-complex	—	—
1580	ν_{as} C=O	1580	ν C=C in σ-complex
1600	ν C=C in σ-complex	1600	ν_{as} C=O
1640	ν_{as} C–O	1660	ν_{as} C=O
1680	ν C=O in aldehyde	1700	ν C=O
2730	ν C–H		
2830	ν C–H	2135	ν C–D
2860	ν CH_3	2160	ν C–D
2920	ν CH_3	2230	ν C–D
2950	ν CH_3		
3095	ν =CH_2	2285	ν =C–D
3570	ν OH	2765	ν OD

[a] The adsorption bands are given observed in spectra after the gas phase was evacuated.

[b] ν, stretching; δ, deformation vibrations; β, out-of-plane deformation vibrations.

the 1440 cm^{-1} maximum is several times greater than the band intensities of C–H stretching), the assignment of 1440-cm^{-1} band to C–H deformation vibrations in one of the surface structures is impossible. The shift of the maximum from 1440 to 1350 cm^{-1} (Fig. 2) during adsorption of C_3H_6 supports the idea that the 1440-cm^{-1} band cannot be assigned to C–H deformation vibrations. According to the value of the isotopic shift, 90 cm^{-1}, this band may be assigned to ν_{as} C=C in a π-allylic complex (*1*). Figure 2 (broken lines) shows that the desorption at 200°C *in vacuo* apparently results in complete removal of π-allylic complex from the surface. Spectra of adsorbed allylbromide also lend support to the validity of the interpretation of this complex as being of the π-allylic type. Formation of allylic complexes during propylene chemisorption requries separation of one of the hydrogen atoms from the methyl group. We may expect an increase in the surface concentration of allylic structures as the energy of bond breaking during formation of the allylic complex is decreased. The substitution of bromine for hydrogen in the methyl group results in a considerable decrease in the binding energy to ~30 kcal/mol. Therefore a molecule of allylbromide must form allylic complexes on the catalyst surface more easily than propylene. The comparison of the ir spectra of adsorbed allylbromide and adsorbed propylene on the copper-containing catalysts (Fig. 4) leads to the conclusion that allyl halides and propylene generally form the same surface structures. However, it follows from a comparison of spectral intensities of the absorption bands that the

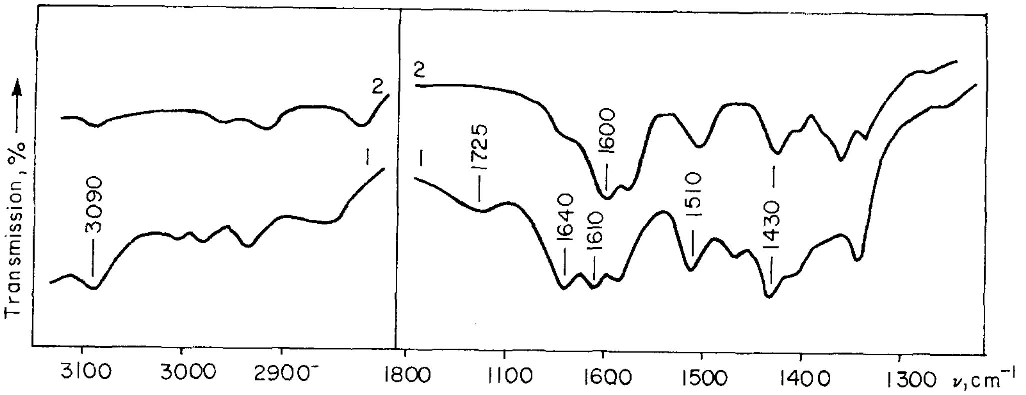


FIG. 4. The ir-spectra of allylbromide [1] and propylene [2] adsorbed at 20°C on CuO-MgO.

concentration of the surface π-allylic complexes increases considerably in the case of allylbromide adsorption.

Taking into account the position of the ν C=C double bond in σ-complexes (*11*) the intensive maximum in the 1580 to 1600-cm^{-1} region can be ascribed to the C=C stretching in the propylene surface

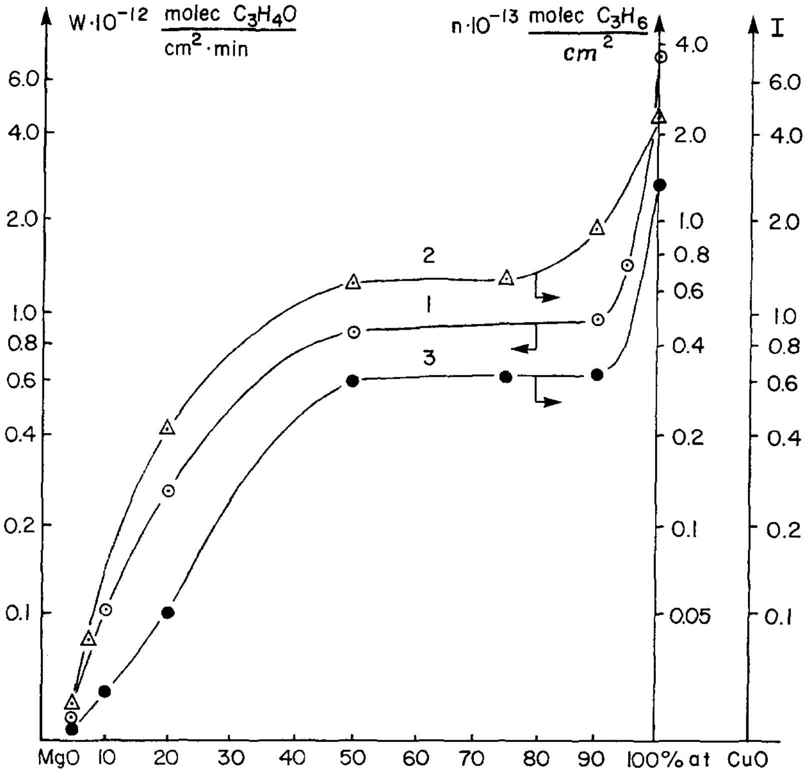


FIG. 5. Plot of rate with respect to acrolein [1] of the adsorption value of propylene in the reversible form [2] and band intensity of a π-allylic complex [3] vs catalyst composition.

complex of σ-complex type. This surface complex is less stable and begins to desorb from the surface at 100°C.

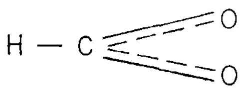
Formation of π-allylic and σ-complexes on the surface must occur with hydrogen separation. Study of the ir spectra of copper–magnesium catalysts after propylene adsorption shows that this process is really accompanied by hydrogen separation and the formation of hydroxyl groups. The spectra show the ν O–H band at 3570 cm^{-1} (interaction with C_3H_6, Fig. 3a) and the O–D band at 2765 cm^{-1} (interaction with C_3D_6, Fig. 3b). The appearance of the band of the O–D groups cannot be a result of the exchange of surface O–H groups with propylene because the intensity of the absorption bands of surface O–H groups does not vary during propylene adsorption. Furthermore the intensity of the O–D group absorbance does not vary with time.

Thus the ir spectra of propylene adsorbed at 20°C on copper–magnesium catalysts and copper oxides show that π-allylic and σ-complexes are desorbed from the surface at temperatures below 200°C with propylene formation. π-Complexes are apparently stable below about 300°C. When the temperature of desorption is more than 200°C, in addition to the decomposition of the π-complexes, there appear on the surface of the copper–magnesium catalysts new more-oxidized structures. These are formed from π-complexes. Thermodesorption data also show that the products of complete oxidation are formed from propylene at elevated temperatures. This is evidenced by the appearance of a peak not seen during adsorption.

Since propylene does not adsorb at 20°C on magnesium oxide, the main influence on the surface properties and the nature of adsorption complexes on copper–magnesium catalysts is attributed to copper ions. Therefore it is interesting to compare structures of the surface complexes on copper oxides and on copper–magnesium catalysts. Study of the ir spectra of propylene adsorbed at 20°C shows that π-allylic complexes are observed on all copper–magnesium catalysts and copper oxides. As the copper concentration in the catalysts is increased, the absorption band intensities characteristic of ν_{as} C=C in such complexes also increase (Fig. 5, curve 3). If we assume that the absorption coefficient of this band does not vary with different samples, then we may postulate that the observed intensity increase is related to the increase in concentration of π-allylic complexes per unit of surface. The π-complexes form only on the surface of copper–magnesium catalysts.

Fundamental changes occur in the σ-complex accompanying separation from a solid solution of copper oxides. The σ-complex is characterized by a 1600-cm^{-1} band for copper–magnesium catalysts and by a 1580-cm^{-1} band for copper oxides. Consequently it is difficult to estimate with any certainty the change of intensity for a given change of composition. In a series of copper–magnesium catalysts an increase in concentration of this structure on the surface is observed with increasing copper content.

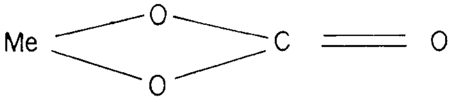
The absorption bands in the spectra of the adsorbed propylene after desorption at 200°C (Fig. 2) are characteristic of irreversibly adsorbed complexes. Analysis of the spectra shows the following relationships between structure and absorption bands:



ν_sC ═══ O 1370 cm^{-1}

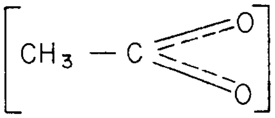
ν_{as}C ═══ O 1560 cm^{-1}

The presence of these structures on the surface is supported by the appearance of δ and ν CH (1350 and 2870 cm^{-1}) absorption bands, which shift during adsorption of deuterated propylene. 'In addition to these structures, the formation of the completely oxidized structures of the carbonate type (characterized by bands at 1280 and 1640 cm^{-1}) is observed on the surface of copper oxides:



In addition, on cupric oxide structures of carboxylate type are formed at 20°C:

$\nu_s COO^-$	1450 cm^{-1}
$\nu_{as} COO^-$	1560 cm^{-1}



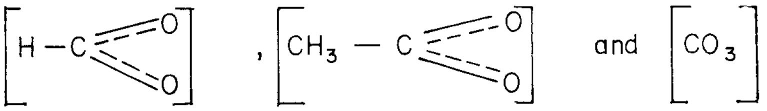
The irreversible forms of propylene adsorbed at 20°C (in addition to the π-complex) on copper–magnesium catalysts of various compositions are formate (1380 and 1560–1580 cm^{-1}), carbonate (1280–1320 and 1620–1660 cm^{-1}), and carboxylate structures of two types, stabilized on magnesium ions (1415 and 1560–1580 cm^{-1}) and on copper ions (1450 and 1560–1580 cm^{-1}). The latter structure is observed only with samples of high copper content (*20*). Such an interpretation of the observed absorption bands is supported by the spectra of adsorbed deuterated propylene (vibrations of C=O bonds shift almost not at all, i.e., 10–20 cm^{-1}). Further support is provided by study of the spectra of propylene adsorbed at high temperatures. Under these conditions only the formation of irreversible forms is observed (*21*).

MoO_3/Al_2O_3

In the ir spectra of propylene adsorbed at 20°C on MoO_3/Al_2O_3 only a single absorption band is found in the region of C=C bond vibrations (near 1600 cm^{-1}) which may be ascribed to the σ-bond between propylene and the catalyst surface. This complex is weakly bound to the surface and is easily removed *in vacuo.*

Cr_2O_3

Comparison of the adsorbed forms of hydrocarbons on catalysts for complete and for selective oxidation is useful to ascertain the roles of various adsorbed forms of propylene in the catalytic oxidation. According to ir data, propylene undergoes primarily a destructive oxidation on the surface of chromium oxide to the species



These complexes are retained on the surface up to 400°C. Only a small portion of propylene is bound reversibly via the σ-bond.

DISCUSSION

Several conclusions may be reached in consequence of comparing thermodesorption results with ir data for propylene chemisorbed on oxide systems. The chemisorption of olefins in a weakly bound reversible form is accompanied by the formation of complexes of σ- and π-allylic types. Propylene chemisorption on oxide aluminum–molybdenum catalysts and on chromium oxide does not produce π-allylic structures. Obviously, the only reversible form of the adsorbed propylene on these catalysts is a σ-allylic complex.

Absorption bands which appear in ir spectra of adsorbed propylene on catalysts of selective and complete oxidation serve partially to characterize the oxidized carbonate–carboxylate structures. These structures possess considerable thermostability, and their desorption from the catalyst surface is accompanied by the appearance of CO_2 in the gas phase. Therefore the formation of oxidized compounds of the carbonate–carboxylate type may be attributed to the irreversible form of propylene adsorption. Thermodesorption and ir data indicate that these compounds are decomposed at temperatures above 200°C. Such is accompanied by the formation of CO_2 and water. It should be noted that the presence of oxygen facilitates the decomposition of these structures and that carbon dioxide appears at or below 200°C. On copper–magnesium catalysts olefin π-complexes are formed. They decompose at 250 to 300°C. Apparently they arise from the irreversible form of propylene adsorption.

The formation of reaction products was studied during oxidation of adsorbed hydrocarbons to elucidate the possible paths of conversion of the surface propylene forms. With this aim the samples of cupric oxide and copper–magnesium catalysts were preliminary reduced to the stage where no acrolein appeared during propylene thermodesorption. In the subsequent experiments oxygen was introduced at 20°C to samples of pre-adsorbed propylene. In 5 to 10 min oxygen was removed, and thermodesorption was carried out. Oxygen was introduced (i) when two forms of propylene adsorption (reversible and irreversible) were present on the surface, and (ii) when one of these forms had been removed from the catalyst surface before oxygen admission. Acrolein formation takes place during desorption of propylene oxidized forms only when a reversible chemisorbed form of propylene is present. If the reversible adsorption form had been removed before oxygen was introduced, the subsequent desorption would not have led to the formation of acrolein.

During consecutive adsorption of propylene and oxygen at 20°C the desorption spectrum shows a peak at 200°C which is ascribed to CO_2. In the presence of oxygen, the decomposition of the irreversible form of adsorbed propylene is facilitated. This peak is in the same region as a peak of individually adsorbed CO_2. The appearance of CO_2 peak at lower temperatures in the presence of oxygen is attributed to the the decomposition of strongly adsorbed propylene.

Thus, the results obtained provide evidence for the participation of a strongly adsorbed propylene form of a carbonate–carboxylate type in the formation of products of complete oxidation. A thermostable π-complex is apparently converted into the same products.

Complexes of allylic type which are weakly adsorbed on the catalyst surface take part in the formation of products of selective oxidation as shown by a comparison of data on identification of the surface structures by ir spectroscopy and the study of desorption and oxidation of the reversible propylene form. However, it is not yet clear whether both the observed σ- and π-allylic complexes, or only one of them, participate in the formation of products of selective oxidation.

It is rather widely believed that oxidation of propylene to acrolein takes place via participation of a π-allylic complex of the olefin. Our results also support this idea. Also isotope studies indirectly indicate the possibility of acrolein formation by participation of an asymmetric surface complex. This complex was observed by us during adsorption of C_3H_6 on copper-containing catalysts, on chromium and molybdenum oxides.

The thermodesorption of individual supported molybdenum σ-allylic complexes and nickel π-allylic complexes, as well as the desorption and ir spectra of allylbromide were studied to elucidate the possible participation of the surface allylic complexes in the formation of selective products. As noted, the concentration of π-allylic complexes (intensity ν_{as} C=C, 1430 cm^{-1}) is higher in the adsorption of allylbromide than in the case of adsorbed propylene (Fig. 4). If π-allylic complexes are converted to acrolein then an increase in their surface concentration must lead to an increase in acrolein yield accompanying the thermodesorption of allylbromide. Indeed, we have found that the yield of acrolein during thermodesorption of allylbromide from CuO–MgO catalyst is 30 to 40 times greater than that formed during propylene desorption under similar conditions. It is noteworthy that the observed increase in acrolein yield is much greater than indicated by the variations in the band intensity characteristic of π-allylic complexes. It seems likely that during adsorption of allylbromide a considerable quantity of allylic complex is converted to acrolein almost immediately. In fact, in ir spectra (Fig. 4) taken during adsorption of allylbromide, an intensive band at 1725 cm^{-1} was observed. This is ascribed to ν C=O in acrolein.

Experiments on the conversion of supported nickel π-allylic complexes provide more evidence of the conversion of π-allylic surface compounds to acrolein. The surface complexes containing π-allylic groups are formed as bis(π-allylic) nickel supported on silica (*22*). In desorption acrolein, propylene, carbon dioxide, water and oil-like products have been found whose desorption occurs at 300 to 400°C. In the 20 to 200°C temperature region, as well as in desorption of propylene and allylbromide, propylene and acrolein are desorbed. As noted previously, π-allylic complexes are not formed on chromium oxide and on molybdenum oxide supported on Al_2O_3; a weakly adsorbed propylene is present as a σ-complex. Nevertheless acrolein formation was observed on these catalysts under other conditions which indicates the formation of acrolein in the presence of asymmetric σ-complex.

The ability of σ-complexes to be converted into acrolein is supported by data on immediate decomposition of individual σ-allylic complexes of molybdenum. These were obtained by supporting tetrakis(allyl)-molybdenum on SiO_2. As in the case of surface π-allylic complexes of nickel, during thermodesorption of σ-allylic complexes of molybdenum, acrolein and propylene appear with maxima at ~170°C. Thus propylene conversion into acrolein may proceed via the intermediate formation of symmetric π-allylic complexes as well as asymmetric σ-complexes. It is noteworthy that the results of the study of the thermodesorption of supported molybdenum and nickel complexes provide independent support for the above interpretation.

These conclusions are obviously drawn from adsorption studies. Thus it becomes desirable to demonstrate that during catalytic oxidation of propylene the formation of reaction products takes place via the same surface forms.

According to thermodesorption data, acrolein is formed from a weakly chemisorbed propylene and desorbs at 30 to 130°C. On this basis one may anticipate that the catalytic oxidation of propylene to acrolein will occur in the same temperature region. Total selectivity with respect to acrolein formation should be observed because strongly adsorbed propylene has no reactivity under these conditions. When pulses of reaction mixture (50 vol% of C_3H_6, 50 vol% of O_2) were contacted with copper oxide, copper–magnesium, and chromium oxide catalysts at 80 to 120°C, oxidation of propylene to acrolein was observed with selectivity of almost 100%. It is noteworthy that catalyst activity decreases with time, apparently as a result of blocking the surface with reaction products. The catalyst activity is reduced after it has been heated in a helium stream up to 200 to 250°C. These experiments show that oxidation of propylene to acrolein at low temperatures does proceed selectively and with catalysts of complete oxidation (CuO, Cr_2O_3). This is in agreement with the thermodesorption and ir data which show on these catalysts the the same intermediate surface compounds as found on the catalysts of selective oxidation.

A comparative study of thermodesorption, ir spectra, and catalytic activity of copper–magnesium catalysts of various composition in the oxidation of propylene to acrolein was carried out to elucidate the role of weakly adsorbed propylene in the catalytic process. If a reversible form of propylene participates in the catalytic process, the formation rate of acrolein must depend on the surface concentration of this form. Catalytic oxidation was carried out in a pulse installation at 200°C with a reaction mixture of composition: 10% C_3H_6, 10% O_2, and 80% He. Figure 5 is a plot of the rate of formation of acrolein, the amount of a weakly adsorbed propylene (band at 1440 cm^{-1}, i.e., π-allylic complex) vs catalyst composition. It is seen in Fig. 5 that the same dependence is observed between the rate of propylene conversion to acrolein and the concentrations of reversible forms of propylene and the π-allylic complex. This supports the idea that these forms of adsorbed propylene take part in the formation of acrolein and its catalytic oxidation.

Of particular interest are the data on the interaction between C_3H_6 and molybdates which are usually more selective toward propylene transformation to acrolein. However, the literature is almost devoid of such information because of technical difficulties (small specific surface area, etc.) arising in the course of the ir spectroscopic study of molybdates. We have studied propylene adsorption on gallium–molybdenum catalysts. The experimental technique and characteristics of samples have been reported previously by Davydov *et al.* (*27*).

Table 2 shows (a) frequencies observed in the ir spectra of C_3H_6 (values for C_3D_6 in parentheses) after adsorption at 20°C with further evacuation of the gas phase, and (b) variations in the absorption bands after desorption at different temperatures indicating the thermostability of complexes characterized by these maxima.

As is shown by thermodesorption up to 200°C with chromatographic analysis of the desorption products, reversibly bonded propylene and partial oxidation products are desorbed from the catalyst surface. Therefore, the maxima at 1100, 1400, 1600, and 1680 cm^{-1} observed in the spectra of adsorbed propylene and vanishing from the spectra upon desorption of the species up to 200°C may be associated with bond vibrations in the propylene molecule not subjected to destructive decomposition. The presence of weakened double bonds in the adsorbed complexes is indicated by the presence of adsorption bands at 2260 cm^{-1} (ν =CD) and at 2220 cm^{-1} (ν =CD_2).[2]

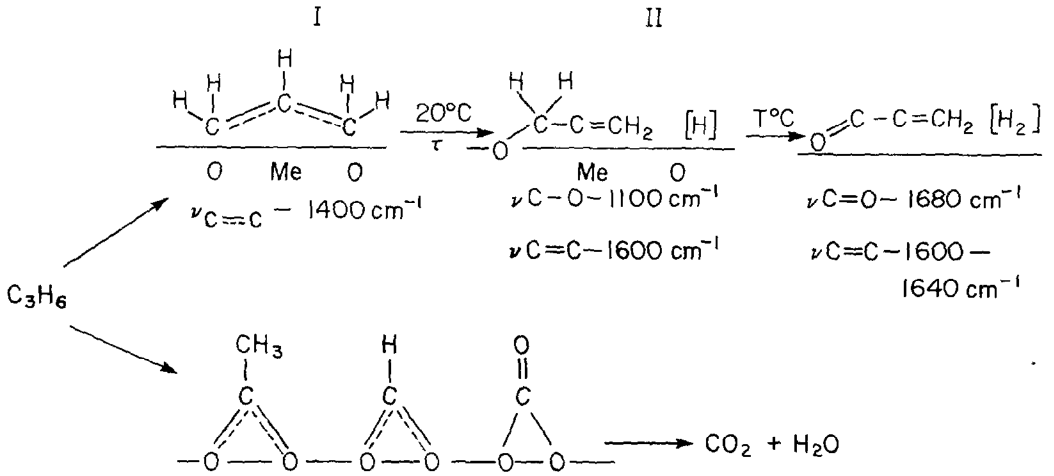
Our interpretation of the bands observed in the ir spectra of propylene adsorbed on Ga/Mo catalyst is given in Table 2. The complexes obtained were identified from the thermodesorption data and by comparison of the ir spectra with those of propylene complexes. It was necessary to take into account the thermodesorption of surface compounds and the difference in the isotopic shifts of absorption bands ascribed to the C=C, C=O, and C=H bonds in C_3D_6 adsorption.

We also wish to clarify the mechanism of conversion of allyl complex to the reaction product. Veis *et al.* (*23*) and Germen *et al.* (*24*) assume that a complex of type II is formed from that of the allyl type, as a result of interaction of the latter with the surface oxygen. To test this assumption the following experiments were carried out. Immediately after the introduction of propylene, the spectrum was recorded in the region from 1050 to 1500 cm^{-1} (recording speed, 150 cm^{-1}/min). During the first 10–15 min required to achieve equilibrium, a simultaneous decrease in the

---

[2] The ν C–H vibrations in the adsorbed complexes are obscured by the strong adsorption of the catalyst in this region.

concentration of the π-allyl complex and an increase in the concentration of complex II were observed. From the results obtained we suggest the following scheme of propylene interaction with the surface of gallium–molybdenum catalyst:



The formation of compound II probably requires the presence of a specific oxygen on the catalyst surface. This may be provided by the oxygen of the molybdenum bond, since on other catalysts not containing such bonds, the formation of these complexes was not observed.

The interaction between propylene and MoO_3/MgO, and MoO_3/Al_2O_3 catalysts has been studied to elucidate the role of molybdenum ions. Propylene adsorption at 20°C on the reduced surface of MoO_3/MgO (10 at% Mo), treated with H_2 at 450°C, followed by further treatment *in vacuo* at the same temperature for 2 hr leads to the appearance of an absorption maximum at 1600 cm^{-1} (in addition to the absorption bands of gaseous propylene). According to Mikhaltchenko *et al.* (*25*) this maximum may be ascribed to ν C=C in the surface σ-complex. Simultaneously with the appearance of this maximum, a shift of the band ascribed to the Mo=O bond from 972 to 965 cm^{-1} is observed. The measurement of ESR spectra in the course of propylene adsorption indicates propylene stabilization on the oxygen ion of the Mo=O bond (*26*). Increasing the time of propylene contact with a catalyst results in the appearance of additional maxima at 1050 and 1100 cm^{-1} in the spectrum. These may only be ascribed to the ν C–C bond vibrations. From the above results the following scheme of the formation and transformation of σ-complex is proposed:

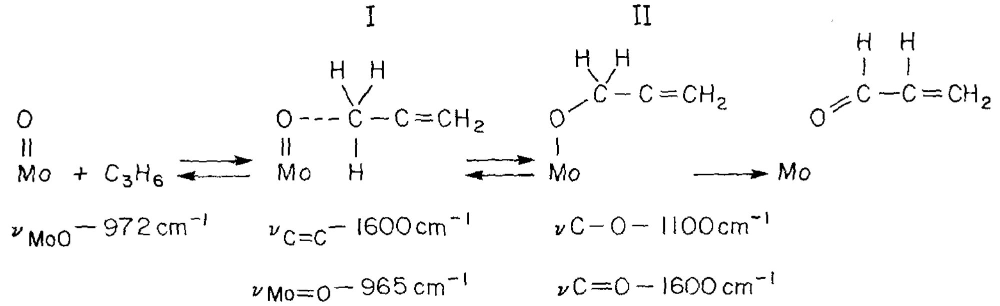
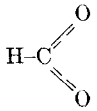
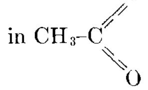
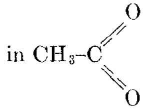
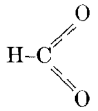


TABLE 2

Frequencies Observed and Interpretations: ir Spectra of $C_3H_6(C_3D_6)$ Adsorbed on Gallium Molybdate

Frequency (cm^{-1})	Interpretation[a]	Adsorption[b]		Desorption[b]		
		20°C	100°C	200°C	300°C	400°C
1100 (1065)	ν C–O in C=C–C–O–Me	+(+)	+↓(+↓)	+↓(−)	−(−)	−(−)
1260–1320 (1260)	ν_s C–O in CO_3	+(−)[c]	+(−)[c]	+(−)[c]	+(+)	+(+)
1350–1375 (1330–	δ C–H; ν C=O in 					
1350, 1380)	ν_s C–O in CO_3	+(+)	+(+)	−(−)	−(−)	−(−)
1400 (1300)	ν_{as} C=C=C in π-allyl–I	+(+)	+↓(+↓)	−(−)	−(−)	−(−)
1460 (1450)	ν_s C=O in 	+(+)	+↑(+↑)	+↑(+↑)	+↑(+)	+(+)
1520 (1520)	ν_{as} C–O in CO_3	+(+)	+(+)	+(+)	+(+)	+(+)
1560 (1560)	ν_{as} C=O in  and 	+(+)	+↑(+↑)	+↑(+↑)	+↑(+↑)	+(+)
1600 (1590)	ν C=C in C=C–C–O–Me–II	+(+)	+↓(+↓)	+↓(−)	−(−)	−(−)
1640, 1615 (1625)	ν C=O in CO_3	+(+)	+(+)	+(+)	+(+)	+(+)
1680 (1660)	ν C=O in ads. acrolein	+(−)	+↑(+)	+↓(+↓)	−(−)	−(−)
2100	ν C–D	(+)	(+)	(+↓)	(+)	(+)
2160	ν C–D	(+)	(+)	(+↓)	(−)	(−)
2220	ν =C–D_2	(+)	(+)	(−)	(−)	(−)
2260	ν =C–D	(+)	(+)	(−)	(−)	(−)

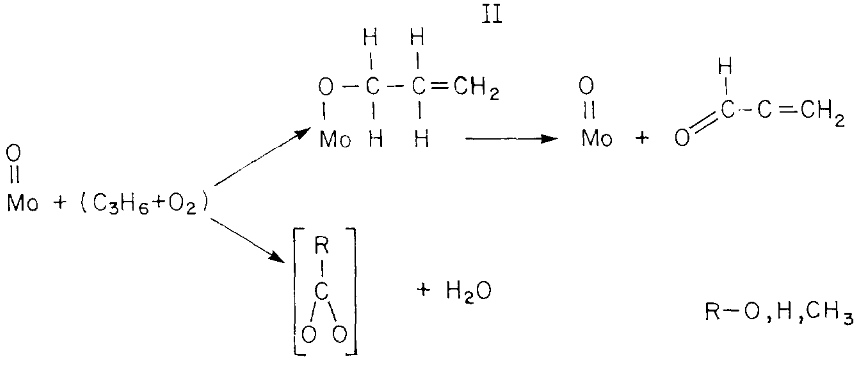
[a] ν and δ represent stretching and bending vibrations.

[b] + or −, a band is present or absent; ↓ or ↑, an increase or decrease in intensity, respectively.

[c] Not observed because of coincidence with intense band at 1300 cm^{-1}.

Interaction between the $C_3H_6 + O_2$ mixture and MoO_3/MgO catalyst at 20°C is also accompanied by the formation of a weakly adsorbed σ-complex, shift of the 972-cm^{-1} band into the low-frequency region, and the appearance of maxima at 1050 and 1100 cm^{-1}. An increase in the time of $C_3H_6 + O_2$ contact with a catalyst results in the disappearance of the 1600-cm^{-1} band of a weakly adsorbed σ-complex and the appearance of the 1700-cm^{-1} band of C=O bond stretching. Temperature increase up to 300°C does not affect the shape of the spectrum. After the catalyst sample has been heated in the $C_3H_6 + O_2$ mixture at 300°C, new bands appear in the 1300 to 1700-cm^{-1} region of the ir spectrum. These indicate the formation of surface carbonate–carboxylate structures; i.e., on the surface the following reactions take place:

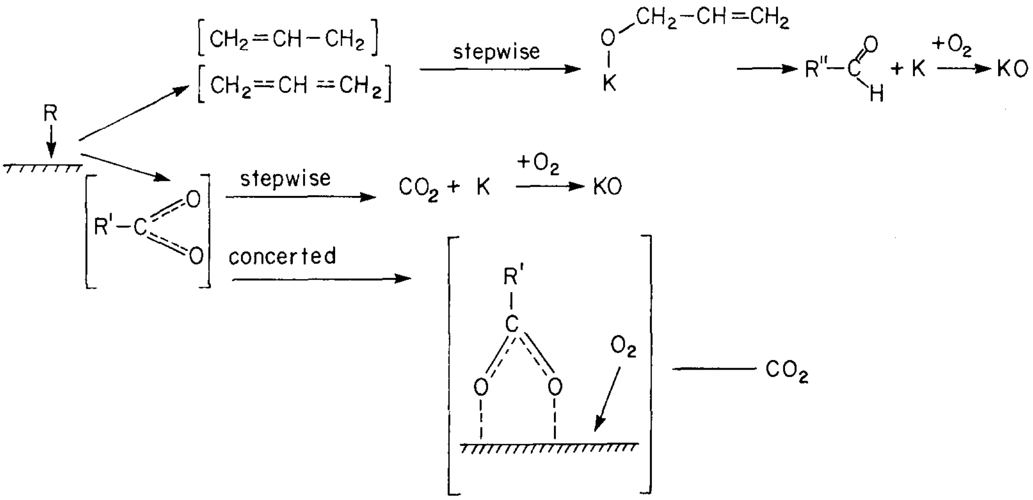
II



As a comparison of the results of propylene adsorption on gallium molybdate and copper-containing catalysts shows, a new structure II appears. This is an intermediate stage of the π-allyl complex transformation to acrolein. Since many reactions of unsaturated hydrocarbons may proceed through a π-allyl complex (e.g., polymerization, cyclization, and isomerization), it is precisely the conversion of the allyl complex to structure II that determines the course of its conversion to acrolein.

CONCLUSION

Therefore, the results obtained and measurements of the rates of individual steps lead us to suggest the following general scheme for the reaction mechanism of propylene oxidation on oxide catalysts (*28*):



In this mechanism of selective and complete oxidation of propylene, K and KO represent reduced and oxidized catalyst forms, respectively.

REFERENCES

1. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92**, 6709 (1970).
2. Krylov, O. V., *Kinet. Katal.* **14**, 35 (1973).
3. Tabasaranskaya, T. Z., and Kadushin, A. A., *Kinet. Katal.* **13**, 167 (1972).
4. Gerei, S. V., Rozhkova, E. V., and Gorokhovatskii, Ya. B., *J. Catal.* **28**, 341 (1973).
5. Maksimov, N. G., Chigrina, V. A., Boreskov, G. K., Anufrienko, V. F., and Yurieva, T. M., *Kinet. Katal.* **13**, 446 (1972).
6. Mikhaltchenko, V. G., Sokolovskii, V. D., and Boreskov, G. K., *Kinet. Katal.* **14**, 1253 (1973)
7. Tarasevich, Yu. S., and Schekochikhin, Yu. M., *J. Prikl. Spektrosk.* **19**, 963 (1973).
8. Mikhaltchenko, V. G., Sokolovskii, V. D., Boreskov, G. K., Davydov, A. A., Filippova, A. A., and Yurieva, T. M., *React. Kinet. Catal. Lett.* **2**, 215 (1974).
9. Mikhaltchenko, V. G., Sokolovskii, V. D., Filippova, A. A., and Davydov, A. A., *Kinet. Katal.* **14**, 1253 (1973).
10. Fisher, E., and Verner, G., "π-Complexes of Metals," Mir, Moscow, 1968.
11. McCellan, W. A., Hoehen, H. H., Gripps, H. N., Muetterties, E. L., and Howk, B. W., *J. Amer. Chem. Soc.* **83**, 1601 (1961).
12. Green, M. L. H., and Nagy, P., *Proc. Chem. Soc.* 378 (1961).
13. Chatt, J., and Duncanson, L. A., *J. Chem. Soc.* 2938 (1953).
14. Huggins, D. K., and Kaesz, H. D., "Progress in Solid-State Chemistry," Vol. 1, p. 417. Pergamon Press, Long Island City, New York, 1964.
15. Adams, D. M., and Chatt, J., *J. Chem. Soc.*, 2621 (1962).
16. Tabasaranskaya, T. Z., and Kadushin, A. A., *Kinet. Katal.* **12**, 1507 (1971).

17. Sverdlov, L. M., Kovner, M. A., and Krainov, E. N., Kolebatel'nye Spektry Mnogoatomnykh Molekul, "Nauka," Moscow, 1970.
18. Meyer, R., and Günthard, H., *Spectrochim. Acta* **A23**, 2341 (1967).
19. Shopov, S., and Palazov, A., *Dokl. Bol. Akad. Nauk.* 22, 181 (1969).
20. Davydov, A. A., and Budneva, A. A., *Kinet. Katal.* **15**, 1557 (1974).
21. Budneva, A. A., Davydov, A. A., and Mikhaltchenko, V. G., *Kinet. Katal.* **16**, 486 (1975).
22. Yermakov, Yu. I., Kuznetsov, B. N., Karakchiev, L. G., and Derbeneva, S. S., *Kinet. Katal.* **14**, 709 (1973).
23. Veis, F., Marion, Zh., Matzger, Zh., and Konyon, J. M., *Kinet. Katal.* **14**, 45 (1973).
24. Germen, K., Grzybowska, B., and Haber, J., *Bull. Acad. Pol. Sci. Ser. Sci. Chem.* **21**, 319 (1973).
25. Mikhaltchenko, V. G., Davydov, A. A., Budneva, A. A., Kuznetsov, B. N., and Sokolovskii, V. D., *React. Kinet. Catal. Lett.* 2, 163 (1975).
26. Maksimov, N. G., Ismailov, E. G., Anufrienko, V. F., and Davydov, A. A., *Teor. Eksp. Khim.* 11, 260 (1975).
27. Davydov, A. A., Tichy, J., and Efremov, A. A., *React. Kinet. Catal. Lett.* **5**, 353 (1976).
28. Sokolovskii, V. D., Dokt. Dissertatsiya, Novosibirsk, 1975, Boreskov, G. K., Sokolovskii, V. D., Izv. Sib. Otd. AN SSSR. ser. Khim., No. 4, v. 2, p. 46, 1976.