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Isomerization of Butenes on Bismuth Molybdate

Recirculation and Pulse Reactions of Butenes on Koechlinite

PH. A. BATIST, P. C. M. VAN DER HEIJDEN, AND G. C. A. SCHUIT

Department of Inorganic Chemistry and Catalysis, University of Technology, Eindhoven, The Netherlands

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The kinetics of the isomerization of butenes over the Bi_2O_3–MoO_3 (Koechlinite) catalyst were investigated in recirculation and in pulse experiments. At temperatures between 150–250°C, isomerization prevails over the oxidation to butadiene. In the recirculation experiments, isomerization proved strongly inhibited by butadiene, and the apparent activation energies for isomerization were high (17–19 $kcal \cdot mole^{-1}$). In the pulse experiments where diene inhibition is nonoperative, low activation energies (2–4 $kcal \cdot mole^{-1}$) for isomerization were observed. It is concluded that isomerization and oxidation occur on similar combination of the B and A centers as postulated by Matsuura. This was confirmed by the action of NH_3 in a temperature range where isomerization and oxidation are of comparable rate. Both reactions proved to be strongly inhibited.

INTRODUCTION

Isomerization of butenes as a secondary reaction during oxidation of butenes over bismuth molybdate has been observed by many workers who studied the mechanism of oxidation (see Adams *et al.* (*1*) and Schuit *et al.* (*2*)). Little attention has been paid so far to the elucidation of the mechanism of isomerization apart from the suggestion that isomerization can be understood as the reverse of allyl formation (*2*). Recently a new model for the oxidation of butene was published by Matsuura and Schuit (*3*), which was derived from kinetical studies of Batist *et al.* (*4*) and from adsorption measurements performed by Matsuura. According to this model, the catalyst plays a bifunctional role. It possesses adsorption sites (B centers) as well as special lattice oxygen ions (A centers) which are involved in the oxidation and which under certain circumstances can be blocked by the product butadiene. The B center (a three center site) is considered as a vacancy on Mo^{6+} ion surrounded by corner-sharing oxygen ions (O_B^{2-}) of the Mo layer. The A center is an oxygen ion from another layer. The vacancy interacts with the double bond of the olefin after which an allyl carbonium ion and a proton become attached to O_B. It is the A center oxygen which is split off in the form of water. Here the catalyst is reduced and also here a new O_A^{2-} ion appears either by O^{2-} diffusion from the bulk or by reoxidation with gaseous oxygen. The important question now arises as to what extent the isomerization can be brought into relation with this model. The possibility remains that for this reaction one does not need a combined action of the two different centers. If isomerization can be understood as the reverse of allyl formation on the B center, then A centers are not necessary for isomerization. On the other hand, the possibility cannot be neglected that also here both centers are involved. It was the intention of this work to find out what actually happens during isomerization. Therefore, we choose to study the reaction under such conditions (relatively low temperatures) that isomerization is the main reaction and oxidation a secondary reaction.

This could not be realized with continuous flow reactions. A slow reaction, however, measured according to the recirculation method, was suitable for this purpose. At low temperatures indeed isomerization was favored and oxidation surpressed. Another system applicable for the study of the isomerization is the pulse method at low temperatures, which was also applied.

The necessity for the presence of an A site in the reaction site was demonstrated for the oxidative dehydrogenation of 1-butene by the presence of a strong inhibition by butadiene. Whether or not the reactive site for the isomerization contains an A site could be demonstrated by investigating the influence of the presence of butadiene on the isomerization reaction. Another possibility is given by the action of NH_3: Does this compound act in a similar way on the reactions?

Experimental Procedure

The technique of recirculation is already described in our previous paper (*4*). The total volume of this apparatus was 800 cm^3 and the speed of the gas pump was 1000 $cm^3 \cdot min^{-1}$. The microreactor contained 2000 mg of catalyst. The apparatus was filled with 32 cm^3 oxygen, 291 cm^3 butene, and 477 cm^3 helium. For investigating the diene inhibition, instead of 291 cm^3 butene, we used 253 cm^3 butene together with 38 cm^3 butadiene and 32 cm^3 oxygen. For study of the influence of ammonia, we used 291 cm^3 1-butene and 32 cm^3 oxygen together with 25 cm^3 ammonia and 453 cm^3 He. After each run, the catalyst was treated with oxygen at 420°C for ½ hr. All components, except steam, were analyzed with use of a gas chromatograph. In the calculations of the gas composition, oxygen and steam were neglected which means that the total of carbon-containing compounds was taken as 100%.

The pulse isomerizations were carried out in an apparatus similar to the Keizer apparatus (*4*). Conditions were as follows: column pressure, 0.8 atm; He carrier gas, 40 $cm^3 \cdot min^{-1}$; catalyst weight, 1.76 g, pulses of 0.23 cm^3 butene and 0.18 cm^3 oxygen. The catalyst used was Koechlinite with a surface area of 2.8 $m^2 \cdot g^{-1}$. After each pulse, the catalyst was cleaned by pulses of pure oxygen at 360°C.

Before use of the catalyst in recirculation and in pulse reactions, it was tested on its activity in a continuous flow experiment (*5*): Below 400°C an activation energy for oxidation of 30 $kcal \cdot mole^{-1}$ was obtained and above 400°C an activation energy of 13 $kcal \cdot mole^{-1}$.

Experimental Results

Figure 1 shows the isomerization and oxidation of 1-butene at two different temperatures as a function of recirculation time. It is obvious that at these relatively low temperatures, the production of isomers dominates that of oxidation products. Furthermore, it is shown that the lines obtained represent simple parabolas. Figure 2A shows the isomerization and oxidation of *cis*-2-butene and Fig. 2B shows that of *trans*-2-butene as a function of time, both carried out at 205°C. Again the isomerizations are higher than the oxidations and simple parabolas are obtained. Figure 3 shows the isomerizations at 170–172°C of, respectively, 1-butene, *cis*-2-butene, and *trans*-2-butene in the presence of a relatively low amount of butadiene in comparison with the amounts of butenes.

The inhibition was too strong to be ac-

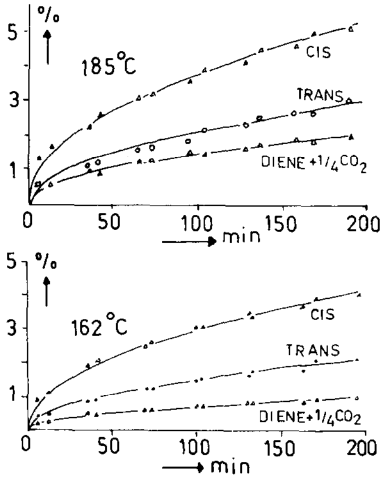


FIG. 1. Recirculation reaction of 1-butene over the Bi/Mo = 2/1-catalyst in presence of gaseous oxygen at two different temperatures.

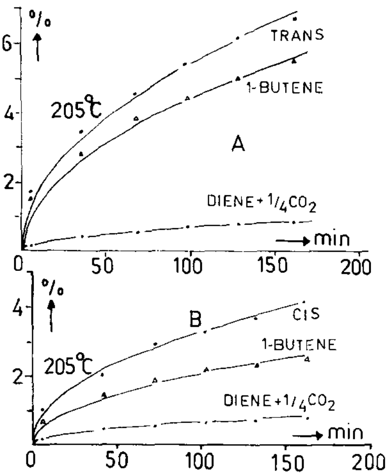


FIG. 2. Recirculation reactions of *cis*- and of *trans*-2-butenes over bismuth molybdate in presence of oxygen at 205°C.

counted for by a weak competitive adsorption of butenes and butadiene on the same site. (See the weak adsorptions of butene and butadiene on the B center reported by Matsuura *et al.* (*3*)). To solve the kinetics of isomerization, we have to reconsider the experiments of Prette *et al.* (*4*) who also found simple parabolas for the strongly inhibited reaction of butene to butadiene under circulation conditions; kinetics were expressed by them with the formula,

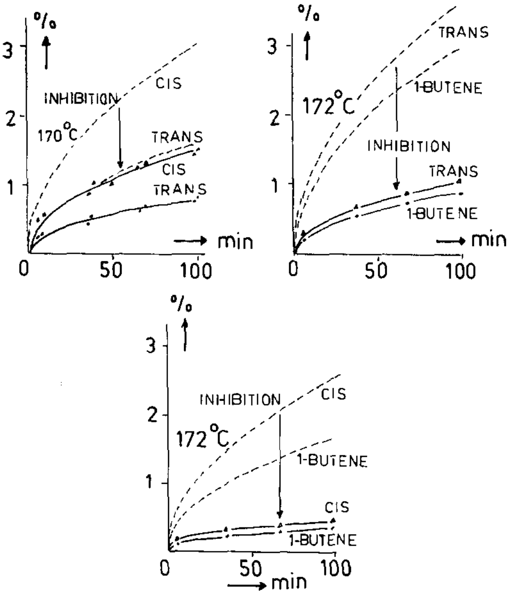


FIG. 3. Inhibition by butadiene of the isomerizations of butenes. (- - - - without addition, —— with addition of butadiene.)

$$-\frac{dc}{dt} = +\frac{dD}{dt} = +\frac{k'}{D}, \qquad (1)$$

where c represents the butene and D the diene concentration.

After integration,

$$D = (2k't)^{1/2}. \qquad (2)$$

In the case of a weak butene adsorption and of a strong inhibition of the isomerization by the diene produced, we may write for the isomerization

$$-\frac{dc}{dt} = +\frac{d(\text{iso})}{dt} = +\frac{k''c}{D}. \qquad (3)$$

Because of the large excess of butene and the small conversions Eq. (3) degenerates into

$$+\frac{d(\text{iso})}{dt} = +\frac{k^*}{D}. \qquad (4)$$

The rate constant k^* of isomerization can be obtained if one combines Eqs. (2) and (4):

$$+\frac{d(\text{iso})}{dt} = k^*(2k')^{-1/2}(t)^{-1/2} = k(t)^{-1/2}. \qquad (5)$$

After integration,

$$(\text{iso}) = 2kt^{1/2}. \qquad (6)$$

Eq. (6)[2] represents the simple parabolas which were found in our isomerization experiments, represented in Figs. 1, 2A, and 2B. In Eq. (1), k' is the rate constant for the oxidation, and k^* in Eq. (4) is the rate constant for the isomerization, both under strongly inhibited conditions. In Eq. (5), k represents the parameter of the experimental parabola. K^* can be obtained from the experimental k' and k values according to the relation

$$k^* = k(2k')^{1/2}. \qquad (7)$$

From the parabolic diene lines in Figs. 1, 2A, and 2B, we calculated the k' values. They are summarized in Table 1.

The corresponding activation energies are represented in Fig. 4. They are high in comparison with the 12 kcal·mole^{-1} reported by

TABLE 1

RATE CONSTANTS FOR THE INHIBITED OXIDATIONS

Temp (°C)	k' (%)$^2 \cdot$ min^{-1} 1-butene oxidation	Temp (°C)	k' (%)$^2 \cdot$ min^{-1} *trans*-2-butene oxidation
185	99. 10^{-4}	205	21.5 10^{-4}
170[a]	39.6 10^{-4}	172[a]	19.8 10^{-5}
162	21.4 10^{-4}	°C	*cis*-2-butene oxidation
145[a]	7.05 10^{-4}	205	207.5 10^{-5}
		172[a]	23.6 10^{-5}

[a] Not represented in figures.

Keizer *et al.* for the noninhibited oxidation in pulse experiments. The high values obtained confirm the oxidation to be inhibited by its own product.

From the isomerizations represented in Figs. 1, 2A, and 2B, we calculated with Eq. (6) the parameter values k. They are summarized in Table 2, together with the k^* values calculated according to Eq. (7).

From the log k^* vs $1000/T$ values, we calculated the activation energies for the inhibited isomerization. They are in the order of 17.5 kcal·mole^{-1} (see Fig. 5).

The effect of ammonia on oxidation and isomerization during recirculation is represented in Fig. 6. When 25 cm^3 of NH_3 is added to 291 cm^3 of 1-butene and 32 cm^3 of O_2, both reactions are strongly suppressed at 260°C. It should be noticed that at this temperature ammonia hardly reacts with the catalyst.

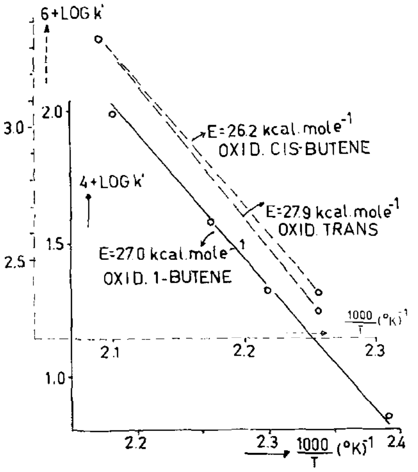


FIG. 4. The Arrhenius plots for the oxidation of the different butenes.

The results of pulse isomerization and oxidation of 1-butene are represented in Fig. 7. Here it is shown that between 205 and 240°C, isomerization is the dominant reaction. The low activation energy for oxidation (14 kcal·mole^{-1}) obtained here agrees with the value of 12 kcal·mole^{-1} given in Keizer's pulse oxidations (*4*) where it was shown that butadiene inhibition was non operative, and where the rate of oxidation was found to be zero order in the oxygen pressure and first order in the butene pressure. For the pulse kinetics of isomerization we used a similar expression as given by Keizer for the pulse oxidation:

$$-\frac{dc}{dt} = +\frac{d(\text{iso})}{dt} = k''(c) = k, \qquad (8)$$

in which c = 1-butene concentration and iso = isomer concentration.

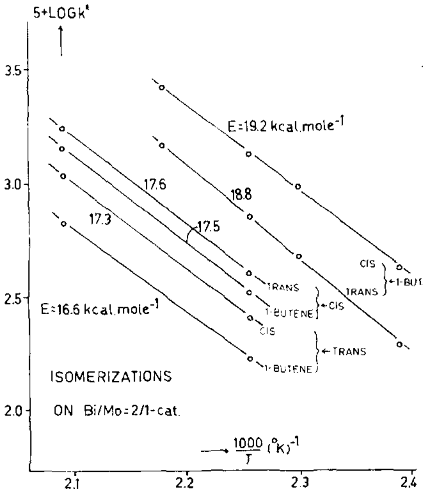


FIG. 5. The Arrhenius plots for the isomerization of the different butenes.

TABLE 2
THE PARABOLIC PARAMETERS k AND THE RATE CONSTANTS k^* FOR THE INHIBITED ISOMERIZATION

Temp (°C)	k (%) · (min)$^{-1/2}$		k^* (%)^2 · (min)$^{-1}$	
	1-butene—*cis*	1-butene—*trans*	1-butene—*cis*	1-butene—*trans*
185	0.1855	0.1025	0.0262	0.0145
170[a]	0.1505	0.0775	0.0133	0.0069
162	0.146	0.0725	0.0095	0.0047
145[b]	0.111	0.0515	0.0042	0.0019
	trans—1-butene	*trans*—*cis*	*trans*—1-butene	*trans*—*cis*
205	0.1015	0.1635	0.00669	0.01076
172[a]	0.084	0.1265	0.00167	0.00253
	cis—1-butene	*cis*—*trans*	*cis*—1-butene	*cis*—*trans*
205	0.2179	0.2695	0.01403	0.01736
172[a]	0.148	0.1815	0.00322	0.00395

[a] See Fig. 3.

[b] Not represented in figure.

In view of the low conversion of butene, we used the zero-order expression from which we calculated the activation energy for isomerization of 1-butene. It was found to be low (See Fig. 7). The results of pulse isomerizations and oxidations of *cis*- and *trans*-2-butenes are represented in Figs. 8 and 9, respectively. Again the isomerization was found to be the dominant reaction. In both experiments we obtained 15 kcal·mole^{-1} as the activation energy for oxidation and low activation energies for isomerization (2.5–4.5 kcal·mole^{-1}).

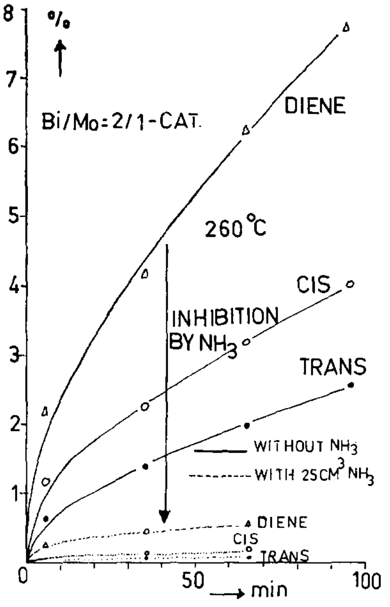


FIG. 6. Inhibition effect of ammonia at 260°C during recirculation of 291 cm^3 1-butene and 32 cm^3 O_2 over the Bi/Mo = 2/1-catalyst.

DISCUSSION

The results presented in this paper should be discussed primarily in connection with the surface model proposed by Matsuura and Schuit (*3*), in which the surface contains two types of oxygen anions. One type (O_B) represents the larger population and on pairs of O_B we find a dissociative adsorption of the olefin, presumably in the form of a H atom and an allylic intermediate. The other class (O_A) is less frequent by a factor g 10: It furnishes the oxygens necessary for the formation of water or the introduction of oxygen into the hydrocarbon. In the Bi–molybdate catalyst with Bi/Mo = 2/1 it has the additional property of strongly adsorbing butadiene. Matsuura has produced evidence that the cluster of sites responsible for the oxidation of butenes to butadiene contains both O_B and O_A sites probably one O_A and four O_B. Isomerization of the double bond might be visualized by the formation of the allylic intermediate followed by a reattachment of the H atom on a carbon atom different from

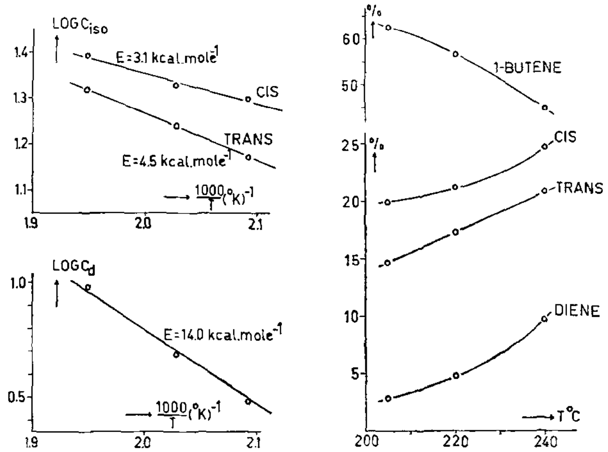


FIG. 7. Pulse isomerization and oxidation of 1-butene and the Arrhenius plots for isomerization and oxidation.

that from which it became separated. For example,

$$CH_2{=}CH{-}CH_2{-}CH_3 \rightarrow$$
$$CH_2{=}CH{=}CH{-}CH_3 + H \rightarrow$$
$$CH_3{-}CH{=}CH{-}CH_3.$$

Evidently, although double-bond isomerization can occur in this way, direct *cis-trans* isomerization is impossible and the formation of *cis*-2 from *trans*-2 or its reverse can only take place via 1-butene. Therefore,

cis-2 ⇄ 1-butene ⇄ *trans*-2.

From Matsuura's model one might expect the double-bond isomerization to occur on site combinations that contain only O_B, although it does not need to be restricted hereto. Whether or not this is the case could be found by investigating whether double-bond isomerization is inhibited or not by butadiene. As we have shown here, it is indeed strongly inhibited and double-bond isomerization, therefore, occurs in a reaction or series of reactions involving also O_A.

Now, since it was found that adsorption of olefins could occur without isomerization, formation of a system of an adsorbed H atom and allylic structure is not sufficient *per se* to produce double-bond isomerization. Either, therefore, the H atom has to migrate to another position before uniting

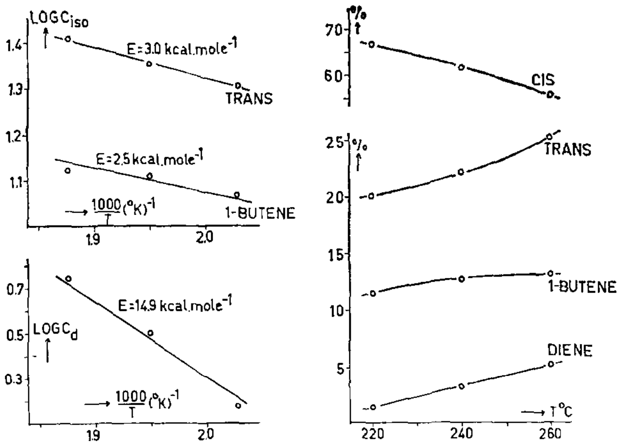


FIG. 8. Pulse isomerization and oxidation of *cis*-2-butene and the Arrhenius plots for isomerization and oxidation.

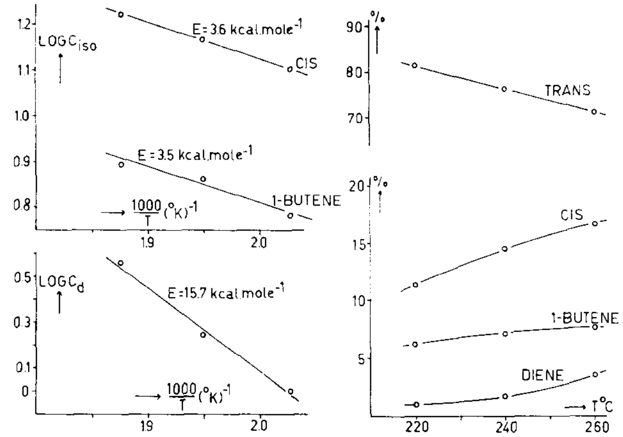
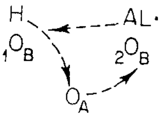


FIG. 9. Pulse isomerization and oxidation of *trans*-2-butene and the Arrhenius plots for isomerization and oxidation.

again with the allyl, or the σ-bonded allyl structure has to "move over" to another O_B thereby changing its point of attachment, or both events has to occur simultaneously. Since in Matsuura's model it was assumed that for the actual oxidation to butadiene migration of H from O_B to O_A is a necessary prerequisite one might propose the following reaction model:



Adsorption of the olefin occurs by the attachment of H on one O_B (e.g., No. 1) and an allyl group on the other O_B (No. 2). The H atom then moves to O_A leaving ${}_1O_B$ free for a jump of the allyl to ${}_1O_B$, the allyl radical becoming bonded to a surface oxygen by a different C atom. Migration of H from O_A to ${}_2O_B$ leads to a situation whereby desorption furnishes an olefin with its double bond shifted from the original position. The simultaneous inhibition of both the isomerization and the oxidation by NH_3 can be envisaged by an interaction of NH_3 with the H atom on O_B to form a NH_4 group. Consequently the migration of H from O_B to O_A, necessary for both isomerization and oxidation, is slowed down. The model readily explains the observation that both isomerization and oxidation are inhibited by butadiene since in both cases butadiene adsorption on O_A stands in the way of the reactions. However, the model does not allow the direct *cis-trans* isomerization and, therefore, is not completely satisfactory. The observation that direct *cis-trans* isomerization occurs indeed appears to indicate a reaction in which hydrogen atoms are accepted by instead of donated from olefins hence the formation of alkyl radicals or carbonium ions. This requires the presence of H atoms or protons on the surface. The problem is how they arrive there. The simplest way to account for their presence appears to assume the oxidation of butene to butadiene to leave H atoms on the surface. Consider in this connection Matsuura's observation that one A site and two B sites are necessary to form a reaction site or, in other words, one O_A and four O_B.

$$\begin{array}{ccc} {}_1O_B & & {}_2O_B \\ & O_A & \\ {}_3O_B & & {}_4O_B \end{array}$$

Formation of the allyl + H combination would for instance occupy ${}_1O_B$ and ${}_2O_B$. The subsequent dissociation of a second H atom might be envisaged by placing the second H atom on either ${}_3O_B$ or ${}_4O_B$ leaving the other O_B for the adsorption of butadiene in the weak form. This is then desorbed and the surface is left with two H atoms on two O_B. The reaction is complete if the two H atoms move to O_A and H_2O is desorbed from the A site. Now, at lower temperatures

H migration may be assumed as relatively slow so that the H atoms stay long enough on O_B to let them interact with other olefinic molecules that then are converted to alkyl groups and desorbed subsequently in the isomerized form. The reason why the H on O_B is connected with the *cis-trans* isomerization and not that on O_A is because O_B was found to be bonded to Mo^{6+} and O_A to Bi^{3+}. Since it must be more acid on O_B, its tendency to give rise to isomerization is better understood. The inhibition by butadiene of the isomerization reaction was then to be explained by the inhibition of the oxidation reaction. As a consequence less H atoms are formed on the surface. On the other hand, the inhibition by NH_3 of the isomerization reaction is readily explained by the formation of NH_4 groups with H atoms on O_B. Because the H atoms are then hindered in their migration to O_A also the oxidation reaction is inhibited.

The two mechanisms presented here are not mutually exclusive. One could assume that the first mentioned is responsible for the double-bond isomerization while the second one is an additional feature that takes care of the *cis-trans* isomerization. Further experiments will be necessary to study the isomerization in more detail and to estimate the actual importance of the various reactions suggested.

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