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Activity, Selectivity, and Stereochemical Features in the Copper-Catalyzed Hydrogenative Ring-Opening of Alkyl-Substituted Cyclopropanes—Nature of Active Sites

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The reactions of four alkyl-substituted cyclopropanes in a hydrogen atmosphere in a closed circulation system have been studied over silica-supported and support-free copper catalysts made by different methods. Both isomerization and direct hydrogen addition occur. The ring opens in both the sterically more hindered and less hindered directions. On the basis of the kinetic data, mechanistic considerations are discussed. The catalysts were studied by N_2O titration and TPR (temperature-programmed reduction). The properties of the reactions and the TPR data indicate that the active centers are atomic clusters for the direct hydrogenation and Cu(I) ions for the ring-opening from the sterically hindered direction through the formation of olefinic compounds. © 1990 Academic Press, Inc.

INTRODUCTION

Hydrogenation and hydrogenative ring-opening are important model reactions in studies of the properties of catalysts prepared by different methods. These reactions are relatively simple and much is known about the transformation mechanisms of the model compounds (olefins, acetylenes, cyclopropanes, and other ring systems). The investigations, however, have mainly concentrated on the transition metals. Although studies dealing with the hydrogenation of unsaturated hydrocarbons on copper have been published recently (*1*), papers relating to other hydrocarbon reactions, for example the ring-opening of cyclopropane, appear to be rare (*2, 3*). Due to its low activity, copper has mainly been used as a more or less inactive component of bimetallic catalysts (*4*). Nevertheless, our experience has shown that it is worthwhile to devote more attention to copper as a catalyst, for it can display considerable activity and unusual selectivity in the transformations of various molecules (*5*). We have therefore started a study of the ring-opening reactions of certain substituted cyclopropanes over supported copper catalysts prepared by different methods and over Cu powder (*3*).

In connection with these reactions, the problem of hydrogen chemisorption is an intriguing one. The activity of copper in hydrogenations was not expected because of its completely filled *d* shell. However, even the first observations indicated that copper was active in the hydrogenation of ethylene at 273 K, and it was also found that both ethylene and hydrogen adsorb on copper at this temperature (*6, 7*). The presence of an oxygen or nickel impurity in copper as possible explanations for this adsorption were excluded by careful experiments on specpure copper film (*8*). Further studies (*9–12*) led to the finding that the dissociative chemisorption of hydrogen is an activated process with an activation barrier of 12.5–21 kJ/mol (*13–15*). Speculations about a $d \rightarrow s$ promotion to a $3d^9 4s^2$ configuration at higher temperature could not be proven (2a, *16*), but it was shown that only the $4s$ electron of copper is involved in hydrogen chemisorption, which is in contrast with the situation for transition metals (*17–19*). Theoretical studies also indicated a good corre-

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lation between the experimentally determined activation energy and the value calculated by supposing a $3d^94s^1p^1$ configuration (*20*).

Now that the long-standing debate about the ability of copper to chemisorb hydrogen seems to be resolved (*11, 19*), and methods of making catalysts with a controlled dispersion are available (*21–23*), the above-mentioned reactions can be described on a more quantitative basis.

EXPERIMENTAL

Materials

Four cyclopropanes have been investigated: *cis*-1,2-dimethylcyclopropane (*c*DMCP), *trans*-1,2-dimethylcyclopropane (*t*DMCP), 1,1-dimethylcyclopropane (1,1DMCP), and 1,1,2,2-tetramethylcyclopropane (TMCP). They were prepared and purified through methods given in the literature (*24*).

The other reactant, oxygen-free hydrogen, was prepared in a Matheson 8326 generator, operating with a palladium membrane.

Catalysts and Their Characterization: Preparations and Pretreatment Conditions

Ion-free water and analytical-grade reagents were used throughout the preparations.

Copper-on-silica catalysts (Cu/S-X) were prepared by ion-exchange (*21, 22*): silica gel (Strem, large pore, 120–230 mesh) was immersed in a tetramminecopper(II) solution at pH 11. After 24 h the blue product was washed thoroughly with water, dried at 393 K (24 h) and decomposed at 773 K in air (3 h).

Copper-on-Cab-O-Sil catalysts (Cu/CS) were prepared by precipitation (*23*): following the literature method, basic copper carbonate was precipitated on the support (Cab-O-Sil M5, BDH product). The catalysts were not calcined before reduction.

Cu powder was prepared by the reduction of CuO (Merck) in hydrogen (473, 523, and 563 K with a 1-h hold at each temperature).

Catalysts made by precipitation were reduced in flowing hydrogen (20 cm^3/min), with heating to 473, 523, and 573 K at a heating rate of 8°/min, with a 1-h hold at each temperature, and then cooled in hydrogen. The ion-exchanged catalysts were also reduced in flowing hydrogen (20 cm^3/min), but with heating to 673 K at a heating rate of 8°/min, with a 2-h hold at this temperature, and then cooled in hydrogen. The reduced catalysts were activated in the circulation system under 13.3 kPa hydrogen at 573 K for 30 min.

Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) measurements were carried out in a flow system. Catalyst precursor (10–200 mg) was reduced in a flowing H_2–N_2 mixture (flow rate 20 cm^3/min, 9% H_2 in N_2) from room temperature to 723 K with a temperature ramp of 11°/min. Calibration was made by integrating the TPR curve of CuO treated at 973 K in air for 1 h.

The quantity of unreduced copper species in the Cu/S-X catalysts was calculated by supposing a 1 : 1 stoichiometry based on the $CuO + H_2 = Cu + H_2O$ reaction. The stoichiometry for the Cu/CS catalysts containing basic copper carbonate was determined via the TPR curve and chemical analysis of the unsupported precursor. On the basis of these measurements, a stoichiometry of $H_2/Cu = 1.16$ was established and used in the calculations.

Titration with N_2O

The number of surface Cu atoms was determined through reaction with N_2O at 363 K, using a GC pulse method (*25*) with the modifications suggested in Ref. (*26*). Extreme care was taken to ensure oxygen-free conditions. Helium (99.99%) purified by passage through an Oxy Trap + Indicating Oxy Trap (Alltech) unit was further purified by using a 20-cm guard column containing MnO. It was activated overnight in hydrogen at 723 K before use and operated at 423 K. The column was positioned directly at the inlet of the catalyst holder and was switched off before the N_2O pulses were introduced. The characteristic data on the catalysts can be found in Table 1, together with the Cu(I) contents of the reduced catalysts, calculated from the TPR curves.

Analytical Apparatus and Procedure

The reactions were carried out in a conventional closed circulation apparatus (*27*). The volume of the reactor was 54 cm^3, and the total volume of the system was 175 cm^3. The reactor was heated with an air thermostat. The volume of the sampling capillary was 0.05 cm^3, and the total sampling volume was 0.3 cm^3. A Carlo Erba Fractovap 2150 gas liquid chromatograph with a flame ionization detector was attached to the system. A 4-m-long glass column filled with 5% bis(2-methoxyethyl)-adipate on Chromosorb PAW 80/100 mesh was used for analysis.

The reactants (1.33 kPa of the cyclopropane and different amounts of hydrogen) were premixed in the circulation part of the system before the reaction. Prior to mixing, the cyclopropanes were subjected to several freeze and thaw cycles.

TABLE 1

Characteristic Data on Copper Catalysts

Catalyst	Loading (wt%)	Dispersion[a] (%)	Fraction of Cu(I)[b]
Cu/S-X[c]	6.36	14.3	0.07
	3.45	14.7	0.15
	1.91	16.9	0.29
Cu/CS[d]	46.8	6.7	0[e]
	6.8	9.5	0.11[e]
	3.0	9.0	0.18[e]
	1.1	7.6	0.23[e]

[a] Determined with N_2O titration at 363 K, by pulse method.

[b] Experimental error = ±5 %.

[c] Prepared by ion exchange.

[d] Prepared by precipitation.

[e] Values were calculated by assuming 1.16 : 1 stoichiometry, based on the TPR curve and chemical analysis of the unsupported precursor.

Turnover Frequency (TOF) Data

Under a certain hydrogen pressure, product yield vs time (t) functions were determined. Initial rates were obtained through differentiation of these functions at $t = 0$. These rates were converted to TOF data based upon the number of surface copper atoms (determined by N_2O titration) or on the number of Cu(I) ions (determined by TPR measurements), assuming that every Cu(I) ion is on or near the surface (the validity of this assumption is discussed later).

RESULTS AND DISCUSSION

Activity and Selectivity of Ring-Opening Reactions

All catalysts displayed rather complicated behavior. There were no cracking reactions, but both isomerization and direct ring-opening activity were found. In most cases the ring-opening takes place in both the sterically less hindered (**a:** 1,3 cleavage for *c*DMCP, *t*DMCP, and TMCP and 2,3 cleavage for 1,1DMCP) and more hindered (**b:** 1,2 cleavage for all compounds) directions. Obviously, changes in the reaction conditions (e.g., hydrogen pressure, temperature, etc.) influence the activity and the selectivity of the ring-opening reaction. The effects of the aforementioned parameters are described in detail below.

The hydrogen pressure effect can be seen in the reactions of 1,1DMCP and TMCP (Figs. 1 and 2).

In the low hydrogen pressure region, the main reaction is rupture of the sterically more hindered C–C bond with the formation of olefins. As the hydrogen pressure rises the rate of olefin formation falls dramatically and saturated hydrocarbons (isopentane and 2,4-dimethylpentane) appear as initial products. At the same time, cleavage of the sterically less hindered C–C bond becomes significant. For TMCP above a sufficiently high hydrogen pressure

(p_{H_2} > 30 kPa), this type of bond rupture starts to dominate. Above 50 kPa hydrogen pressure, the product results almost exclusively from 1,3 cleavage. When the reaction temperature is lowered considerably (from 423 to 318 K), the 1,3 C–C bond scission remains the most favored ring-opening direction for TMCP, even at low (6.8 kPa) hydrogen pressure (*3*).

Both the hydrogen pressure and the temperature effects are demonstrated in the transformations of *c*DMCP and *t*DMCP (Figs. 3 and 4).

In the low-pressure region, rupture of the sterically more hindered C–C bond is the main reaction for these two compounds as well. It is also typical that under hydrogen-poor conditions, olefin formation is considerable. As the hydrogen pressure rises, the rate of formation of olefins falls and a saturated hydrocarbon (*n*-pentane) becomes the typical product of this type of C–C bond scission. It is important to note, however, that the rate of olefin formation is much higher from *t*DMCP than from *c*DMCP. The 1,2 cleavage dominates the ring-opening process of *c*DMCP at each temperature, while for *t*DMCP this is true only at low hydrogen pressure. Above 20 kPa hydrogen pressure, the rate of 1,3 bond cleavage approaches that of 1,2 bond scission, and at 573 K it surpasses it. This is true for both cyclopropanes, but, at low temperature (498 K) there is no olefin formation at all. As the temperature is raised, olefins (actually an unresolved mixture of *cis* and *trans*-2-pentene) appear and their formation accelerates as the temperature continues to be increased.

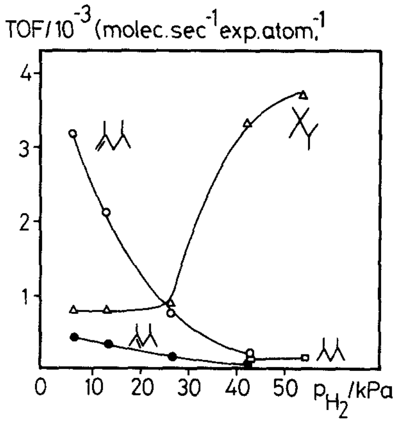


FIG. 2. Formation rate of ring-opening products vs H_2 pressure functions for TMCP over 6.8% Cu/CS catalyst at 423 K.

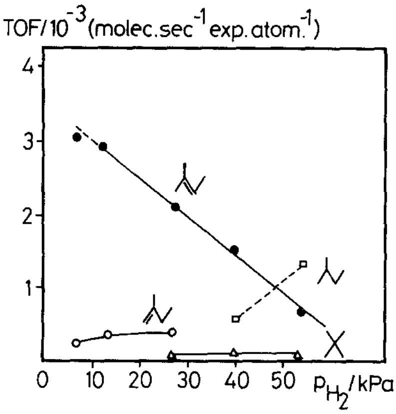


FIG. 1. Formation rate of ring-opening products vs H_2 pressure functions for 1,1DMCP over 6.8% Cu/CS catalyst at 423 K.

Finally, some general points worth mentioning: (i) Cleavage of the sterically more hindered C–C bond occurs via two routes: direct hydrogenation of the ring, and isomerization of the cyclopropanes. The olefins are initial products; nevertheless, they undergo hydrogenation as the reaction proceeds. The ratio of the two routes changes: elevation of the temperature increases the rate of olefin formation, while increasing hydrogen pressure favors direct hydrogenation. (ii) Cleavage of the sterically less hindered bond occurs via the formation of saturated hydrocarbons. There is no olefin formation at any hydrogen pressure and temperature studied.

For characterization of the active sites for the two different types of ring-opening, it is vital to acquire more information about the catalysts.

TPR Measurements

In order to elucidate the possible surface structures over our copper catalysts, we

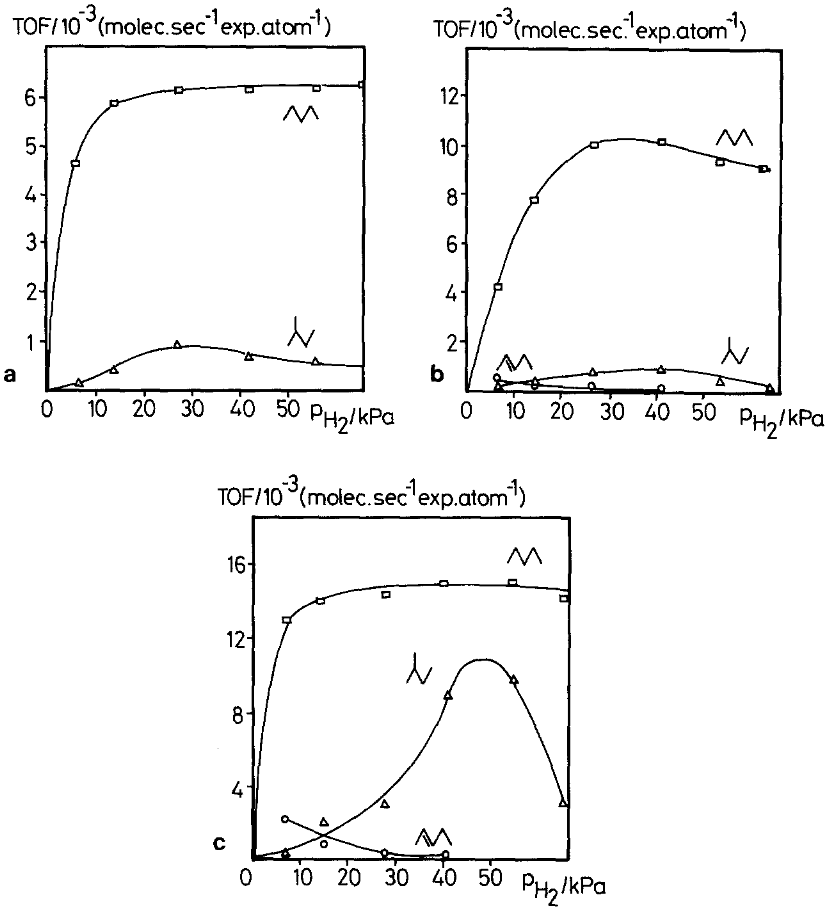


FIG. 3. Formation rate of ring-opening products vs H_2 pressure functions for cDMCP over 6.8% Cu/CS catalyst at (a) 498 K, (b) 523 K, and (c) 573 K.

undertook a TPR investigation and also searched for a suitable probe molecule and test reaction which might be used to indicate differences in surface structure (*28*).

Our observations on ion-exchanged catalysts are similar to those of Kohler *et al.* (*29*): Cu/S-X catalysts contain a certain amount of unreduced copper species, the extent depending on the loading (Table 1). The TPR experiments also revealed that, in contrast with earlier observations (*30*), this unreduced fraction of copper could not be reduced up to a temperature as high as 1073 K.

The other type of catalysts exhibited similar behavior. TPR measurements on the fresh, noncalcined precursors revealed that they also contain increasing quantities of unreduced species with decreasing copper loading (Table 1), with the TPR curves becoming more complex.

Nature of Active Sites

The literature data (for a recent review see Ref. (*31*)) and our own measurements (*32*) reveal that in the presence of even a low amount of hydrogen, these three-membered rings give exclusively saturated hydrocarbons as ring-opening products over transition metal catalysts. Further, the metal-free support and the unreduced catalyst did not show any activity. In our opinion, therefore, isomerization, which occurs via cleavage of the sterically more hindered

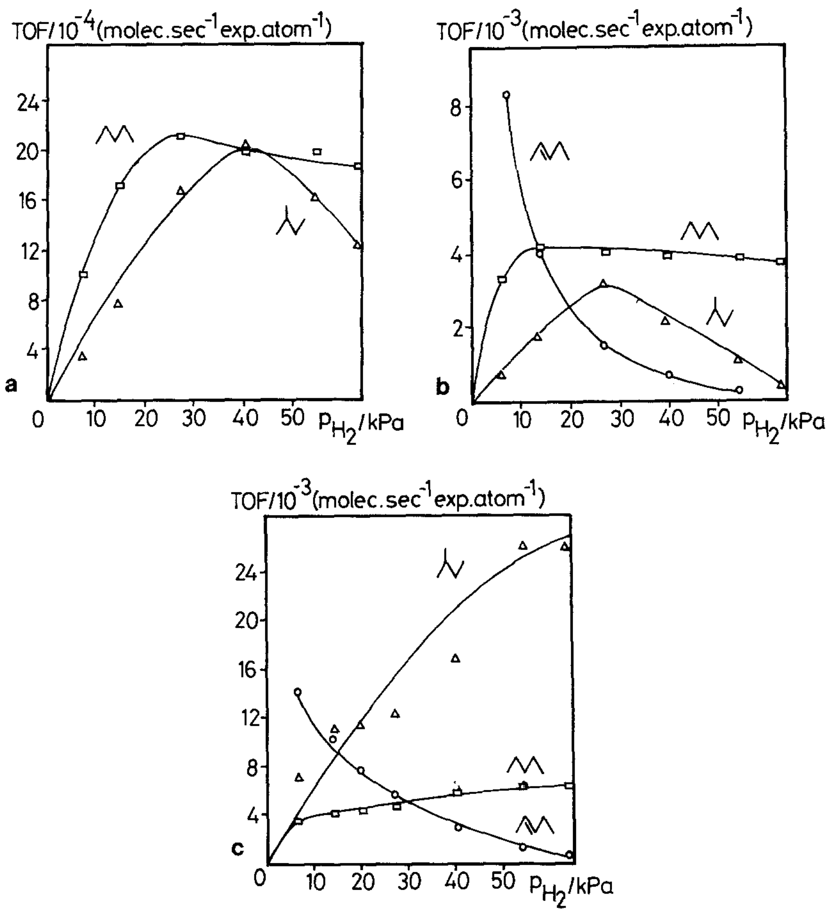


FIG. 4. Formation rate of ring-opening products vs H_2 pressure functions for *t*DMCP over 6.8% Cu/CS catalyst at (a) 498 K, (b) 523 K, and (c) 573 K.

C–C bond, proceeds over ionic copper species which remain on the surface even after the reduction of the catalyst. Nevertheless, copper atoms are also needed, because of the lack of any activity over the unreduced catalyst. Consequently, the active clusters must contain Cu(I) ions and copper atoms as well.

The relative importance of ionic centers can be assessed from the extent of isomerization with some of our probe molecules. The formation rates of 2-pentenes from *c*DMCP (*28*), 2-methylbutenes from 1,1DMCP, and 2,4-dimethylpentenes from TMCP decrease with increased loading for both groups of catalysts, in parallel with the decreasing quantity of Cu(I) ions (Tables 2 and 3).

Since TPR measurements cannot distinguish between bulk and surface Cu(I) ions, it is surprising that the TOF data calculated on the basis of the quantity of Cu(I) ions over ion-exchanged catalysts are fairly constant, showing that most of the unreduced Cu(I) ions are in positions accessible to the reacting molecules (Table 4).

This is not true for the Cu/CS catalysts, however, where the TOF data calculated on the same basis are not constant. Even so, the tendency is valid: the rate of olefin formation decreases with decreasing Cu(I) content of the catalysts.

TABLE 2

Initial TOF Data in the Isomerization Ring-Openings of *c*DMCP, 1,1DMCP, and TMCP over Cu/CS Catalysts Based on Surface Cu Atoms, Determined by N_2O Titration (TOF = molec. s^{-1} exp. $atom^{-1}$)

Catalyst	Turnover frequency/molec. s^{-1} exp. $atom^{-1}$		
	*c*DMCP[a]	1,1DMCP[b]	TMCP[c]
1.1% Cu/CS	5.3×10^{-1}	—	—
3.0% Cu/CS	9.6×10^{-4}	1.3×10^{-2}	—
6.8% Cu/CS	2.4×10^{-4}	3.3×10^{-3}	8.7×10^{-3}
46.8% Cu/CS	6.9×10^{-5}	1.2×10^{-3}	3.5×10^{-4}

[a] Temperature: 523 K; H_2 pressure: 13.3 kPa; products: 2-pentenes.

[b] Temperature: 423 K; H_2 pressure: 6.7 kPa; products: 2-methyl-1-butene + 2-methyl-2-butene.

[c] Temperature: 423 K; H_2 pressure: 27.5 kPa; products: 2,4-dimethyl-1-pentene + 2,4-dimethyl-2-pentene.

The support-free catalyst also exhibits isomerization activity (only 1,1DMCP was investigated). The reaction may be due to the presence of a quaternary carbon atom, which tends to transform to the most stable tertiary carbonium cation, even over a small amount of Cu(I) ions.

As expected, however, ring-opening with direct hydrogen uptake proceeds over surface copper atoms. This is shown by the constancy of the data in Table 5.

TABLE 3

Initial TOF Data in the Isomerization Ring-Openings of 1,1DMCP and TMCP over Cu/S-X Catalysts Based on Surface Cu Atoms, Determined by N_2O Titration (TOF = molec. s^{-1} exp. $atom^{-1}$)

Catalyst	Turnover frequency/molec. s^{-1} exp. $atom^{-1}$		
	1,1DMCP[a] hydrogen pressure/kPa		TMCP[b]
	6.7	53.0	
1.91% Cu/S-X	1.2×10^{-2}	—	2.3×10^{-2}
3.45% Cu/S-X	6.6×10^{-3}	6.0×10^{-3}	1.6×10^{-2}
6.36% Cu/S-X	3.2×10^{-3}	3.3×10^{-3}	8.1×10^{-3}

[a] Temperature: 423 K; products: 2-methyl-1-butene + 2-methyl-2-butene.

[b] Temperature: 318 K; H_2 pressure: 6.7 kPa; products: 2,4-dimethyl-1-pentene + 2,4-dimethyl-2-pentene.

TABLE 4

Initial TOF Data in the Isomerization Ring-Openings of 1,1DMCP and TMCP over Cu/S-X Catalysts Based on the Number of Cu(I) Ions, Determined by TPR (TOF = molec. s^{-1} Cu(I) ion^{-1})

Catalyst	Turnover frequency/molec. s^{-1} Cu(I) ion^{-1}		
	1,1DMCP[a] hydrogen pressure/kPa		TMCP[b]
	6.7	53.0	
1.91% Cu/S-X	7.0×10^{-3}	—	1.3×10^{-2}
3.45% Cu/S-X	6.5×10^{-3}	5.9×10^{-3}	1.6×10^{-2}
6.36% Cu/S-X	6.5×10^{-3}	6.7×10^{-3}	1.7×10^{-2}

[a] Temperature: 423 K; products: 2-methyl-1-butene + 2-methyl-2-butene.

[b] Temperature: 318 K; H_2 pressure: 6.7 kPa; products: 2,4-dimethyl-1-pentene + 2,4-dimethyl-2-pentene.

Mechanisms of Transformations—Possible Surface Structure of Reaction Intermediates

As far as the transformations of the stereoisomeric cyclopropanes (*c*DMCP and *t*DMCP) are concerned, a low-temperature and a high-temperature process can be clearly distinguished. At 498 K, both isomers yield only saturated hydrocarbons as reaction products. Above this temperature olefins (1,2 cleavage) appear as well. Ring-opening via 1,3 C–C bond scission gives only saturated hydrocarbons. The olefin formation decreases with increasing hydrogen pressure. The precursor of the olefin either desorbs or is hydrogenated over the metal atoms, depending on the hydrogen coverage. This process involves either hydrogen migration onto ionic centers where the olefin precursor forms or migration of the olefin precursor to neighboring metal atoms where it is hydrogenated.

The saturated hydrocarbon from the rupture of the sterically more hindered C–C bond may also form through direct hydrogen uptake over surface copper atoms.

Further information can be deduced from the kinetic data. The large difference in the

TABLE 5

Initial TOF Data of Isopentane (1,3 C–C Bond Cleavage) and *n*-Pentane (1,2 C–C Bond Cleavage) Formation in the Ring-Opening Reaction of *c*DMCP Based on Surface Cu Atoms, Determined by N_2O Titration (TOF = molec. s^{-1} exp. $atom^{-1}$)

Catalyst	H_2 pressure/kPa[a]			
	13.3	40.1	53.5	66.7
Isopentane formation				
1.1% Cu/Cs	—	—	—	—
3.0% Cu/CS	7.5×10^{-4}	1.6×10^{-3}	7.8×10^{-4}	1.5×10^{-4}
6.8% Cu/CS	7.6×10^{-4}	1.9×10^{-3}	8.2×10^{-4}	1.4×10^{-4}
46.8% Cu/CS	7.0×10^{-4}	2.1×10^{-3}	8.0×10^{-4}	1.2×10^{-4}
n-Pentane formation				
1.1% Cu/CS	6.5×10^{-3}	9.6×10^{-3}	8.6×10^{-3}	4.2×10^{-3}
3.0% Cu/CS	7.3×10^{-3}	1.2×10^{-2}	9.3×10^{-3}	4.4×10^{-3}
6.8% Cu/CS	7.8×10^{-3}	1.2×10^{-2}	9.4×10^{-3}	4.5×10^{-3}
46.8% Cu/CS	7.9×10^{-3}	1.0×10^{-2}	9.4×10^{-3}	4.3×10^{-3}

[a] Temperature: 523 K.

initial rate of olefin formation (much higher for the *trans* than for the *cis* compound) may be attributed to the difference in adsorption of the two stereoisomers.

Similarly, the form of the TOF vs H_2 pressure functions (Figs. 2 and 3) provides information about the mechanisms of the transformations: a maximum curve suggests dissociative adsorption, while a saturation curve points to associatively adsorbed intermediates. Hence, dissociatively adsorbed species dominate in 1,3 cleavage for both isomers (the only exception is the transformation of the *trans* isomer at 573 K); and associatively adsorbed species are typical for the *cis* and dissociatively adsorbed intermediates for the *trans* compound in 1,2 cleavage.

In order to elucidate the geometry of the adsorbed species, the ratio of the rates of product formation in the two directions was calculated at the maximum rates (Table 6).

TABLE 6

Ratios of Ring-Opening Rate of 1,3 C–C Bond Scission (Cleavage **a**) to 1,2 C–C Bond Scission (Cleavage **b**) for *c*DMCP and *t*DMCP at the Maximum Rate

Temperature/K	$\mathbf{a}_{cis}/\mathbf{a}_{trans}$	$\mathbf{b}_{cis}/\mathbf{b}_{trans}$
498	0.5	2.9
523	0.3	0.9
548	0.3	1.0
573	0.4	0.8

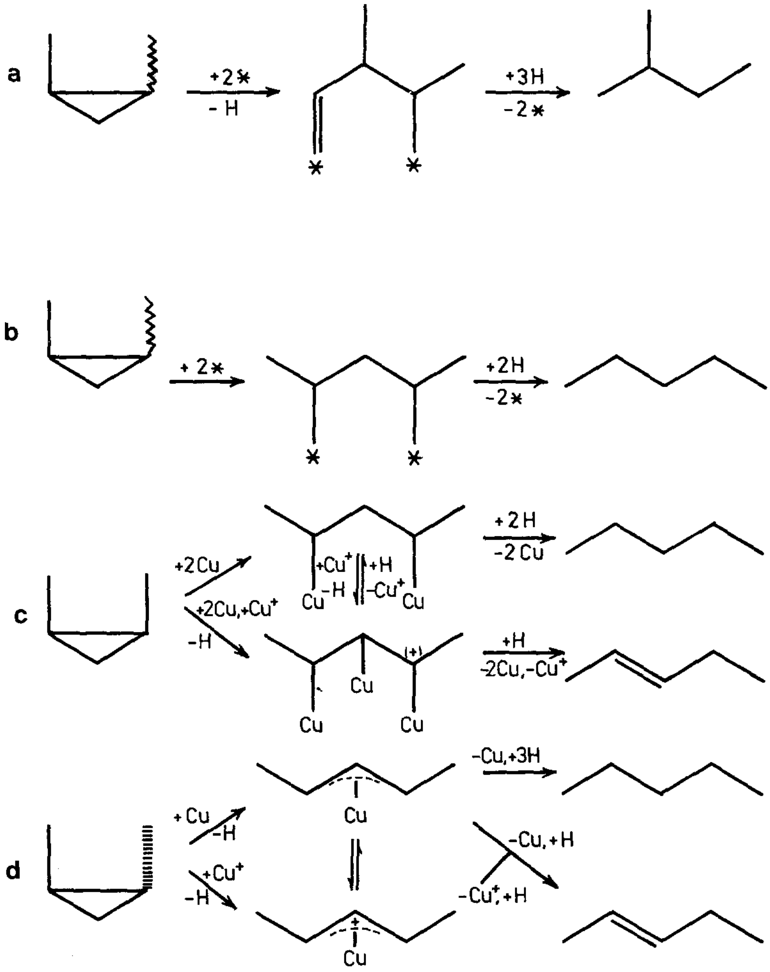
The data in Table 6 and stereochemical considerations (i.e., the planar adsorption of *t*DMCP is hindered) allow the following conclusions:

The distinction between a low- and a high-temperature process is justified.

1,2 C–C Bond Scission

At 498 K this bond scission (cleavage **b**) for *c*DMCP is almost three times as fast as that for *t*DMCP, and consequently the geometries of their adsorption are different: *c*DMCP adsorbs in a planar manner and *t*DMCP in an edgewise manner.

At higher temperature this difference disappears, and therefore the isomers must adsorb similarly; despite the geometric reasoning, this adsorption must be planar, because olefins cannot form in the case of edgewise adsorption.



SCHEME 1. Mechanisms of ring-opening reactions of *c*DMCP and *t*DMCP over copper catalysts: (a) low- and high-temperature processes of 1,3 C–C bond cleavage for both isomers; (b) low-temperature 1,2 cleavage for both isomers; high-temperature 1,2 cleavage for (c) *c*DMCP and (d) *t*DMCP.

Planar adsorption of the *trans* isomer can only occur through an allyl complex (the sp^3 hybrid state becomes sp^2 and the tetrahedral geometry becomes planar).

The rate of olefin formation from *c*DMCP is much lower than that from *t*DMCP (compare Figs. 2 and 3), and consequently the structures of the adsorbed complexes of the two isomers must differ considerably: *c*DMCP does not have an allylic structure.

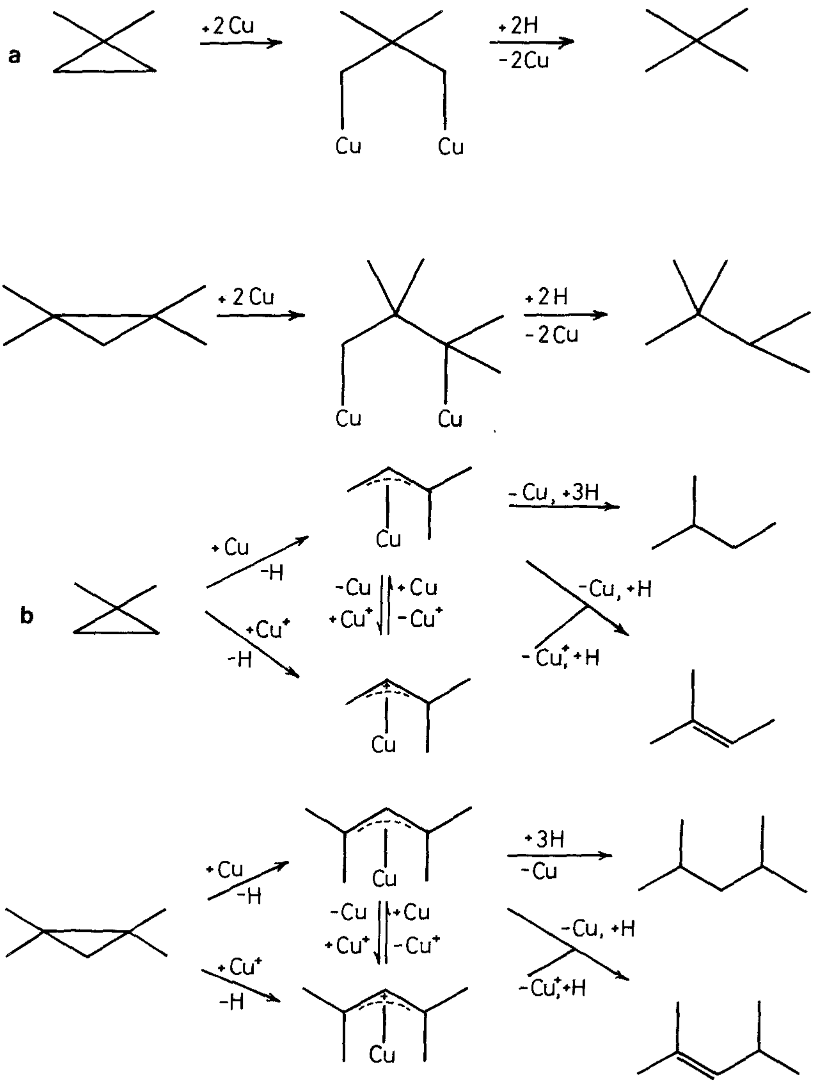
1,3 C–C Bond Scission

At each temperature this bond scission (cleavage **a**) proceeds faster for *t*DMCP than for *c*DMCP, and consequently the geometries of their adsorption are different: *c*DMCP adsorbs in a planar manner and *t*DMCP in an edgewise manner.

All these considerations are summarized in Scheme 1.

The planar adsorption of 1,1DMCP and TMCP is sterically hindered and the shapes of their TOF vs H_2 pressure functions are similar. Therefore, it is quite conceivable that their transformation mechanisms are also similar.

Rupture of the sterically less hindered bond (2,3 cleavage) may proceed through



SCHEME 2. Mechanisms of ring-opening reactions of 1,1DMCP and TMCP over copper catalysts: (a) 2,3 cleavage and (b) 1,2 cleavage.

associatively 1,3-diadsorbed species. The intermediate of 1,2 cleavage (sterically more hindered C–C bonds) is possibly a planar adsorbed allyl complex, which may form over the metal atoms or over ionic centers. This latter may desorb as olefin or migrate to neighboring metal atoms and be hydrogenated or desorb, depending on the hydrogen pressure (Scheme 2). (The migration of hydrogen adsorbed on metal atoms to the olefinic precursor formed on the ionic centers cannot be excluded in this case, either.)

On the bases of the postulated mechanisms and the product distribution, the nonterminal olefins are primary products, while the terminal olefins form from them via double-bond migration.

CONCLUSIONS

Copper has proved to be an active catalyst in cleavage of the C–C bond in substituted cyclopropanes. In contrast with transition metals, copper exhibits mostly opposite regioselectivity in the ring opening, insofar as the ring breaks at the most substituted C–C bond. This regioselectivity can be assigned to the participation of unreduced copper species (Cu(I) ions). These electrophilic centers are responsible for the isomerization, and the hydrogenative ring-opening giving saturated hydrocarbons occurs mostly on the atomic clusters. It follows then that titration with N_2O is not sufficient for the proper characterization of copper catalysts (irrespective of the method of preparation): the investigation should be supplemented at least with TPR measurements. Kinetic data and stereochemical considerations suggest that the transformations occur with the participation of differently adsorbed surface intermediates. Their relative importance depends strongly on reaction conditions, such as temperature and hydrogen pressure (surface coverage).

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