Ring-opening of Alkyl-substituted Cyclopropanes in the Presence of Hydrogen on Copper

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In the presence of hydrogen on copper, the cyclopropanes (**1**), (**2**), and (**3**) are transformed into saturated hydrocarbons containing the same number of carbon atoms (alkenes are also formed, through isomerization of the cyclopropanes); these studies reveal the importance of a previously unknown property of copper in heterogeneous metal catalysis.

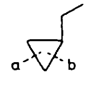
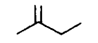
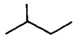
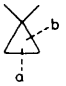
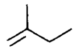
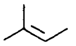
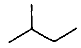
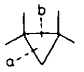
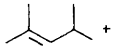
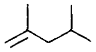
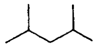
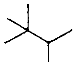
The ring-opening of cyclopropanes is one of the most frequently studied reactions in metal catalysis (*e.g.* references 1—3) and experiments on this topic have mainly involved the transition metals. In spite of the fact that there are reports of cyclopropane transformations on copper[2,4a] and on bimetallic catalysts containing copper,[2a,4] no special attention has been devoted to these experimental data when this subject has been reviewed.[5]

These reports and our own experience of the catalytic role of copper[6] led us to study the reactions of certain alkyl-substituted cyclopropanes on a 6.8% Cu/Cab-O-Sil catalyst[6b] (Cab-O-Sil is a fused silica from BDH) in the presence of hydrogen, in a circulation system.[7] The compounds investigated were ethylcyclopropane (**1**), 1,1-dimethylcyclopropane (**2**), and 1,1,2,2-tetramethylcyclopropane (**3**), which were prepared by literature methods.[8] We are not aware of any previous reports on the transformations of these alkyl-substituted cyclopropanes on copper. However, investigations on (**1**),[9] (**2**),[3,10] and (**3**)[11] have revealed that on various transition metals ring-opening takes place at the bond opposite to the substituted carbon atom.

Our experimental results, given in Table 1, lead to the following conclusions. (i) Copper has proved to be an active catalyst in the cleavage of the C–C σ bond in substituted cyclopropanes. [The most characteristic feature in this respect is the transformation of (**3**) at relatively low temperature.] (ii) In the course of the transformation, the ring-opening in a and b directions takes place in parallel. In one reaction the corresponding saturated hydrocarbon is formed *via* an alkene intermediate, while the other reaction involves hydrogen uptake and results in the saturated hydrocarbon directly. The ratio of cleavage a : b depends strongly on the experimental conditions. (iii) The main process for (**1**) is cleavage a, which leads *via* alkene (**4**) to isopentane. Higher temperatures favour cleavage b. (iv) For (**2**) at low hydrogen pressure, the favoured reaction is cleavage b, catalysed by the electrophilic active sites of the catalyst (Cu^+ and Cu^{2+}); at high hydrogen pressure, the favoured reaction is cleavage a, with the formation of neopentane. (v) For (**3**), ring-opening involving direct hydrogen uptake proceeds with high selectivity, even under very mild conditions (cleavage a). (vi) In contrast with the other transition metals, copper exhibits opposite regioselectivity in the ring-opening, insofar as the ring breaks at the most substituted C–C bonds. We consider that Cu^+ and Cu^{2+} ions play a part in this latter process, similar to that already observed in other catalytic transformations.[12] (vii) Our experimental results are in accordance with the conclusion[13] that polycrystalline copper is capable of the chemisorption of hydrogen at lower temperatures too.

Our investigations to date lead to the conclusion that copper

Table 1. Product compositions in transformations of (**1**), (**2**), and (**3**) on Cu/Cab-O-Sil.

Compound	$p(H_2)$/ kPa	Temp./K	Reaction time/min	% Conversion	Selectivity/mol %				a/b
				→	 + (**4**)	 +	 +	$<C_5$	
(**1**)	13.3	473	5	1.86	37.1	49.5	7.0	6.4	12.4
(**1**)	13.3	523	5	3.67	24.0	52.3	11.2	12.5	6.8
(**1**)	13.3	573	5	10.48	13.6	54.4	25.3	6.7	2.7
				→	 +	 +	 +		
(**2**)	6.7	423	5	3.14	7.3	92.7	—	—	0
(**2**)	6.7	423	50	8.13	18.8	78.6	2.6	—	0
(**2**)	6.7	423	110	11.22	14.2	74.9	10.9	—	0
(**2**)	53.0	423	5	2.09	—	31.6	5.7	62.7	1.7
(**2**)	53.0	423	95	21.35	—	—	12.6	87.4	6.9
				→	 +	 +	 +		
(**3**)	6.7	318	10	11.40	—	—	—	100	∞
(**3**)	6.7	423	5	30.59	13.2	63.4	—	23.4	0.3
(**3**)	25.7	423	5	16.04	6.3	46.6	—	47.1	0.9
(**3**)	54.4	423	5	37.28	—	—	4.1	95.9	23.4

displays outstanding activity in the ring-opening of cyclopropanes containing a quaternary carbon atom in the ring. We suggest that the surface Cu^0, Cu^+, and Cu^{2+} species all play a part in the observed chemical events: Cu^+ and Cu^{2+} participate in ring-opening involving an ionic mechanism, while Cu^0 takes part in the chemisorption of hydrogen and in the hydrogenolysis of the Cu–C bonds formed in the ring-opening.

In order to interpret these unexpected experimental observations, we are currently carrying out H–D exchange and kinetic investigations on copper catalysts with different dispersions, together with the application of various methods to study the active sites of the catalysts.

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