Selectivities in Brönsted Acid-catalysed Reactions of Alkenes on Ga_2O_3

By FRANCIS B. CARLETON, T. ALAN GILMORE, D. THEODORE LAVERTY, and JOHN J. ROONEY*
(*The Queens' University of Belfast, Belfast* BT9 5AG, *N. Ireland*)

Summary Evidence is presented that Brönsted acid sites on the surfaces of Ga_2O_3 and Al_2O_3 catalyse exchange with $^2H_2$ and double bond shift in branched alkenes, but not linear alkenes, where such reactions occur *via* different mechanisms on separate sites.

Ga_2O_3[1] has catalytic properties very similar to those of Al_2O_3,[2] but, unlike the latter, when activated at as low a temperature as 573 K possesses very few sites capable of double bond shift in linear alkenes (π-allyl mechanism[2]). It therefore has the advantage that the mechanisms and sites for σ-vinylic exchange with $^2H_2$,[1,2] σ-allyl exchange,[1–3] and selective *cis–trans* isomerism in alk-2-enes,[1] reactions common to both oxides, may more readily be investigated without the complication of simultaneous double bond migration.

We now report results of exchange with $^2H_2$ and isomerism of branched alkenes on Ga_2O_3 which clearly show that surface hydroxyl groups[1] possess sufficient Brönsted acidity to generate carbonium ions at quite moderate temperatures, but not with linear alkenes or less strained cycloalkenes. By analogy with extensive data[2] concerning Al_2O_3 catalysis of similar exchange and isomerization reactions these results help also to resolve an important problem concerning the role of Brönsted sites on Al_2O_3.[2] Results for exchange of some representative olefins on Ga_2O_3 activated at 573 K (Table), even under diffusion control conditions, at 503 K reveal striking selectivities (at lower temperatures only stepwise exchange is observed[1]). Full experimental details have already been reported.[1]

Further experiments reveal that in the presence or absence of $^2H_2$, even at 403 K, 2-methylbut-1-ene isomerizes readily to 2-methylbut-2-ene but not to 3-methylbut-1-ene, and methylenecyclopentane to 1-methylcyclopentene, but not to the other methylcyclopentene isomers. At this temperature there is no double bond shift in but-1-ene but totally selective *c*-B-2⇌*c*-B-2† interconversion.[1] The results for cyclopentene in the Table are therefore consistent with a combination of σ-vinylic and σ-allylic exchange, but with little simultaneous double bond shift. However the results for the branched olefins and norbornene cannot be explained in this fashion.

H_2S has been reported[4] as selectively poisoning double bond shift and *cis–trans* interconversions in n-butenes but not exchange with $^2H_2$ on Al_2O_3 at 298 K. We have now found that amounts of H_2S vastly in excess of a monolayer poison *c*-B-2 ⇌ *t*-B-2 interconversion at 453 K on Ga_2O_3, but have very little effect on 2-methylbut-1-ene isomerism at 403 K. Because we had good evidence[1] that the σ-allylic exchange sites also catalyse selective *c*-B-2 → *t*-B-2 isomerism our present results seemed to conflict with the selective poisoning of Al_2O_3.[2–4] We therefore examined the influence of excess of H_2S on these reactions at 323 K on boehmite activated by outgassing overnight at 823 K. Again H_2S does not influence isomerism of 2-methylbut-1-ene but now totally suppresses *c*-B-2 → B-1 conversion, the major initial reaction (π-allyl mechanism[2]), leaving *c*-B-2 → *t*-B-2 isomerism (σ-allylic exchange sites[3]) totally selective, but somewhat diminished in rate. Apparently the degree of selective poisoning by H_2S of catalysis by these oxides is a function of reaction temperature.

TABLE. Isotopic distributions for exchange with $^2H_2$

Compound	[$^2H_0$]	[$^2H_1$]	[$^2H_2$]	[$^2H_3$]	[$^2H_4$]	[$^2H_5$]	[$^2H_6$]	[$^2H_7$]	[$^2H_8$]	[$^2H_9$]	[$^2H_{10}$]
Cyclopentene	13·0	2·8	3·0	4·0	6·4	14·7	33·2	9·6	13·2		
Cyclopentene[a]	0·3	0·7	1·4	1·5	8·1	25·7	52·4	5·3	4·5		
Isobutene	20·0	3·2	1·3	1·0	1·2	3·3	10·1	21·6	39·0		
2-Methylbut-1-ene	20·0	2·7	1·9	2·0	3·0	7·7	20·6	37·3	5·6	0·7	
2-Methylbut-2-ene	20·0	1·8	1·8	2·0	3·4	7·7	19·5	33·0	8·4	1·2	
Methylenecyclopentane	20·0	2·2	0·5	0·6	2·5	10·3	37·4	12·6	4·4	3·3	3·7
Norbornene[b]	20·0	5·8	24·6	11·4	10·1	13·4	6·8	4·4	2·2	1·3	

[a] reaction at 469 K. [b] 10% hydrogenation.

† *c*-B-2 = *cis*-but-2-ene; *t*-B-2 = *trans*-but-2-ene; B-1 = but-1-ene.

The main conclusion from this work is that the branched alkenes are sufficiently basic to form tertiary-carbonium ions as intermediates in rapid exchange and isomerism about the tertiary-centre (the rate of isobutene exchange is 3-fold that of propene at 453 K). However, these OH groups are not sufficiently acidic to catalyse reactions *via* secondary-carbonium ions. The results for norbornene bear this out, since the maxima at the [$^2H_3$]- and [$^2H_5$]-isomers in the deuterio-isomers (Table) are explained by formation and Wagner–Meerwein rearrangements of the norbornyl carbonium ions (possibly accompanied by some σ-vinylic exchange) and addition of $^2H_1^-$ to give a little norbornane. The results therefore show that there is no need to postulate 'concave' and 'convex' π-allylic species as suggested by Hightower and Hall[5] to explain exactly analogous results for reactions of methylenecyclopentane on Al_2O_3. Indeed their idea cannot apply to the present results for the methylbutenes.

Finally, our results indicate that *cis–trans* interconversion of stilbenes[1] is not a good test for the σ-vinylic mechanism proposed for selective *c*-B-2 $\rightleftharpoons$ *t*-B-2 isomerism,[1] since *cis*-stilbene may readily form carbonium ions. In fact toluene exchanges the 5 ring hydrogens much more rapidly than the methyl hydrogens on Ga_2O_3 at 453 K in agreement with participation of the protonated aromatic ring, but apparently contradicting a simple σ-allylic exchange mechanism (the methyl groups should by σ-benzylic formation, analogous to direct σ-allylic formation, have exchanged rapidly). We therefore now favour the more subtle formulation suggested by Guisnet *et al.*[6] that while the allylic C–H bond at C-1 in *c*-B-2 is broken the σ-allylic bond to the surface forms at C-3. The reverse reaction yields selective σ-allylic exchange, and rotation in the σ-allylic intermediate affords *c*-B-2 $\rightleftharpoons$ *t*-B-2 interconversions without double bond shift.[6]

(*Received, 3rd October* 1977; *Com.* 1031.)

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