Evidence for the Formation of Tertiary Carbonium Ions from Alkenes on Alumina at *ca.* 300 K

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Summary Evidence is presented that alkenes able to produce tertiary carbonium ions by proton addition will indeed react by such a Brönsted acid mechanism on alumina at temperatures below 300 K.

Double bond migration (DBM) in alkenes over alumina catalysts has received considerable attention but there remains some controversy concerning the mechanisms of these reactions.[1] Recent work[2] has shown that propene undergoes DBM at 300 K by a dissociative mechanism involving π-allylic intermediates, but at *ca.* 470 K it reacts by an associative mechanism involving carbonium ions. Thus, reaction temperature has been found to influence the mechanism of DBM. It seems reasonable that alkene structure should have a similar influence on mechanism; carbonium ion reactivity follows the order tertiary >secondary >primary and, as propene reacts through secondary carbonium ions at *ca.* 470 K,[2] tertiary ion activity, where permitted by molecular structure, might be observed over alumina at significantly lower temperatures.

Rosynek and associates[3,4] have shown that H_2S is a selective poison for DBM of but-1-ene which they believe to proceed through π-allylic intermediates on alumina at *ca.* 300 K, in agreement with the above findings for propene reaction mechanism. The experiments reported here utilise H_2S poisoning of isomerization reactions and are interpreted to show that alkenes able to produce tertiary carbonium ions indeed do so on alumina at *ca.* 300 K.

The same batch of Kaiser SAS γ-alumina (SAS) as described previously[2,5] was used and some experiments were made with Universal Matthey chlorided alumina (UM; code 1395-L; Cl 0·3%; area 210 $m^2 g^{-1}$). Catalysts were used in 150—500 mg lots and activated at 723 K or higher temperatures as described before.[5] Analyses of reaction mixtures were made using mass spectrometry or g.l.c. and, where appropriate, microwave spectroscopy. The dose of H_2S used ($7{\cdot}9 \times 10^{17}$ H_2S m^{-2}) was somewhat more than that suggested by Rosynek *et al.*[4] and, in some cases, following its adsorption at reaction temperature a pressure of *ca.* 100 Pa remained above the catalyst.

Table 1. Kinetic data for reactions over alumina

Reactant	Catalyst[a]	Reaction temperature/K	Reaction rate/ 10^{14} molecule s^{-1} m^{-2}
$CH_2{=}CH{-}CH_2{-}Me$	SAS(723)	316	1·27
$CH_2{=}CH{-}CH_2{-}Me + H_2S$	SAS(723)	316	0·06
$CD_2{=}CH{-}Me$	SAS(1023)	283	5·2
$CD_2{=}CH{-}Me + H_2S$	SAS(1023)	283	0·0
$CH_2{=}CH{-}CMe_3$	SAS(723)	352	0·84
$CH_2{=}CH{-}CMe_3 + H_2S$	SAS(723)	352	0·84
MCP[b]	SAS(723)	293	85·6
MCP + H_2S	SAS(723)	293	85·6
$Me_2C{=}CMe_2$	SAS(723)	293	25·0
$Me_2C{=}CMe_2 + H_2S$	SAS(723)	293	4·2
$Me_2C{=}CMe_2$	SAS(948)	273	46·9
$Me_2C{=}CMe_2 + H_2S$	SAS(948)	273	46·9
$Me_2C{=}CMe_2$	UM(723)	273	45·7
$Me_2C{=}CMe_2 + H_2S$	UM(723)	273	25·6

[a] Figure in parentheses is activation temperature/K. [b] MCP = Methylenecyclopentane.

Results of experiments are shown in Table 1. DBM of but-1-ene at 316 K over SAS was more than 95% poisoned by H_2S, confirming previous results.[4] Similarly, reactions of propene through π-allylic intermediates[5] at 283 K over SAS activated at 1023 K were 100% poisoned by H_2S, a temperature of *ca.* 470 K being necessary before reaction restarted. The poisoning effect of H_2S for π-allylic intermediates is therefore confirmed.

The skeletal isomerization of 3,3-dimethylbut-1-ene, to 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene, a reaction believed to require carbonium ion intermediates,[6] was unaffected by H_2S at *ca.* 350 K; H_2S seems therefore to have no effect on reactions involving (secondary) carbonium ions.

DBM of methylenecyclopentane (MCP; a molecule that could form a tertiary carbonium ion), to 1-methylcyclopentene, was unpoisoned by H_2S over SAS at 273 K. This implies the involvement of tertiary carbonium ions for this reaction over alumina at < 300 K.

Similarly, DBM of 2,3-dimethylbut-2-ene, to 2,3-dimethylbut-1-ene, was completely unaffected by H_2S at 273 K over SAS activated at 950 K; again tertiary carbonium ions seem to be involved at < 300 K.

Interestingly, DBM of 2,3-dimethylbut-2-ene over SAS activated at 723 K was partially poisoned (*ca.* 80% activity loss), suggesting the involvement of both π-allylic and carbonium ion intermediates for reaction of this alkene over this particular catalyst. Over UM activated at 723 K poisoning by H_2S at 273 K was less pronounced (*ca.* 40% activity loss), as might be expected from a greater involvement of carbonium ions with this more acidic catalyst.

Lastly, isobutene exchange with D_2 at 296—313 K was investigated over SAS using microwave spectroscopy. Contrary to Hightower and Hall,[7] preferential vinyl exchange was not observed; exchange followed the binomial distribution over all 8 hydrogen atoms and microwave spectroscopy revealed random exchange of [$^2H_1$] species (Table 2). This observation could be produced either from tertiary carbonium ion intermediates or from exchange by any mechanism together with rapid DBM by any mechanism. H_2S reduced the exchange rate but, notably, had no effect on product distribution, for SAS activated at either 723 or 823 K. This again is good evidence for the involvement of tertiary carbonium ion intermediates on alumina at *ca.* 300 K.

Table 2. Distribution of [$^2H_1$]isobutenes produced over alumina

Catalyst[a]	Reaction temperature/K	Ratio[b] $(CH_2D)MeC{=}CH_2$: $Me_2C{=}CHD$
SAS(723)	313	*ca.* 3 : 1
SAS(723) + H_2S	313	*ca.* 3 : 1
SAS(823) + H_2S	296	*ca.* 3 : 1
Equilibrium value		3·0 : 1

[a] Figure in parentheses is activation temperature in K. [b] Deduced from both 3_{03}–2_{12} and 3_{13}–2_{02} transitions at *ca.* 32 GHz; full details of analysis C. S. John, C. Kemball, R. A. Rajadhyaksha, L. V. F. Kennedy, and J. K. Tyler, unpublished results.

We conclude, therefore, that where possible alkenes will produce tertiary carbonium ions on alumina at *ca.* 300 K, and that reaction will be significantly controlled by these species. This provides a serious alternative to the explanation of deuterium exchange data over alumina reported by Hightower and Hall.[7] They interpreted these data in terms of preferential vinyl exchange together with DBM through π-allylic intermediates when alkene geometry permitted; for DBM at < 370 K, the molecule needed to possess a chain of 3 carbons, including the double bond, that could appear concave when viewed from outside the molecule. All those molecules which satisfied this criterion, however, could also form tertiary carbonium ions, except for the linear alkenes, in which case it has since been shown[8] for propene that the methyl hydrogens can be directly exchanged through σ-allyl intermediates. It is suggested then that ready isomerization of these molecules at < 370 K is due to tertiary carbonium ion formation rather than to their ability to drape over surface ions and undergo DBM through a dissociative mechanism.

It is at present uncertain whether D incorporation in isobutene occurs through vinyl exchange followed by DBM involving carbonium ions or whether the Brönsted centres can be directly deuteriated by D_2. The former is favoured but further work with $CD_2{=}CMe_2$ is underway both to clarify this point and to confirm, without recourse to H_2S, the involvement of carbonium ions.

Three variables may now be recognised as having significant influence on the mechanism for reaction of alkenes on alumina: (i) alumina activation temperature;[5] (ii) reaction temperature;[2] (iii) molecular structure. Cognizance of these factors should help rationalise some apparent discrepancies, concerning alkene reactivity on alumina, that have been reported in the literature.

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