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Comments on "The Mechanism of Isobutane Cracking over Amorphous and Crystalline Silicoaluminates" by E. A. Lombardo and W. K. Hall

The authors take issue with our suggestion (*1*, *2*) that isobutane cracking over amorphous and in part over crystalline silicoaluminates is probably initiated by radical cation formation. They have proposed as an alternative that reaction is always initiated by protonation which forms either a *t*-butyl cation and dihydrogen or methane and an isopropyl cation.

There are a number of problems with the latter suggestion. To be concise it is useful to tabulate the information which must be reconciled. Thus,

1. Nonacidic and weakly acidic alumina, halided alumina and *amorphous* silica/alumina catalysts (nonzeolitic solid acids), crack isobutane to form relatively constant ratios of products, (a) hydrogen and butylene and (b) methane and propylene. The constancy is maintained as the cracking activity of the solids is increased by several orders of magnitude (*1*).
2. The proposed cleavage of isobutane to methane and an isopropyl cation, while observed in SbF_5 containing superacids (*3*), is a reaction which has not often been seen and whose detailed mechanism is uncertain. [Whether this involves protonated alkanes as transition states or intermediates or whether redox processes associated with the reduction of Sb^V or Sb^{III} play a role is not very clear.]
3. The more active nonzeolitic solid acids isomerize butylene to an equilibrium distribution of its isomers *without forming n-butane* (*1*).
4. The kinetics of isobutane's cracking change from first to second order [in its pressure] when nonzeolitic solid acids are replaced by more acidic crystalline zeolites (*1*).
5. The nonzeolitic acids exhibit a strong preference to dehydrogenate or crack 3-methylpentane rather than to isomerize it to 2-methylpentane (*2*). The reverse is true of the protic form of numerous zeolites such as faujasite.
6. The latter catalysts rearrange 2-methylpentenes to 3-methylpentenes with activation energies *very* similar to those of the corresponding carbonium ion isomerizations in superacids while the amorphous acids do not (*2*).

Thus with a large number of solid acids including alumina, halided alumina, and amorphous silica/alumina we are dealing with materials which have the ability to support the existence of intermediates which can carry out only a small number of the reactions usually associated with relatively free carbonium ions [we use the old terminology of carbonium ion for the t-$C_4H_9(+)$ cation]. It is noteworthy that these intermediates do not participate in intermolecular hydride transfer reactions, because if they did one would have to expect the formation of *n*-butane whenever the butylenes were rearranging. [See Ref. (*1*) for an in-depth discussion.]

Poor selectivity in isomerizing 3-methylpentane to 2-methylpentane is also indicative of the inability of the acids to support a relatively free carbonium ion. This is a reaction which occurs more easily than many other cationic rearrangements and with selectivity in concentrated sulfuric acid, which may be regarded as at the beginning or low end of any superacidity scale. [See F. C. Condon's chapter in "Catalysis," Vol. 6.]

It is worth noting that the small amount of 2-methylpentane which is formed over

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nonzeolitic solid acids [observable at say 500°C with γ-Al_2O_3] may be due to either a free radical process or a radical cation process. Thus successive hydrogen atom transfers to 2-methylpent-2-ene or transfer of a pair of hydrogen atoms from an alkane to the radical cation of this olefin is a possible conversion mode with precedent in the literature. The latter type reactions have been observed by Ausloos (*4a*) in the gas phase and by Kramer and Pancirov (*5*) in superacids at low temperatures.

The solids are hence behaving like acids much *weaker* than ca. 90% sulfuric acid where alkyl carbocationic intermediates just begin to participate in the hydride transfer reactions. There is simply no precedent for such acids to react with alkanes in the manner proposed by Lombardo and Hall.

Alkanes containing tertiary C–H bonds are activated by concentrated sulfuric acid, but there is substantial evidence that initial carbonium ion formation is due to a redox reaction in the absence of a simple carbonium ion precursor such as an olefin or an alkyl halide. Protonated SO_3, $HSO_3(+)$ can be hypothesized as an initiator as in the example

$$\text{i-}C_4H_{10} + HSO_3(+) \Leftrightarrow \text{t-}C_4H_9(+) + H_2O + SO_2$$

There is an enormous difference in acidity between concentrated sulfuric acid which has a Hammett H_0 acidity function near −10 and superacids composed of SbF_5/HSO_3F which typically have H_0's near −19. Yet even in the latter, protonation of an alkane to break a C–C bond is at best a poorly characterized reaction.

The question of whether a protonated alkane is an *intermediate* as opposed to a transition state in reported reactions is uncertain as is the role of oxidation. The possible importance of redox chemistry in reactions quite similar to those found in superacids is raised in a recent paper by Gretz *et al.* (*6*). These workers report on the conversion of methane and adamantane under mild conditions to esters in trifluoracetic acid containing Pd^{II} salts.

Failure of the nonzeolitic solid acids to catalyze reactions indicative of relatively free carbonium ions is prima facie evidence of their absence during both the initiation step and the subsequent conversions over these acids. The proposal of an unusual acid catalyzed cleavage [to methane and the isopropyl cation] as a major pathway over apparently weakly acidic substances appears to be impossible to reconcile with the known catalytic behavior of these solids.

The *constancy* of the [H_2 + butylene]/[methane + propylene] ratio over nonzeolitic catalysts having a wide range of activity is extremely difficult to rationalize with the hypothetical cleavage of isobutane to *t*-butyl and isopropyl cations.

Crystalline aluminosilicates such as an ultrastable faujasite, however, do provide evidence of the occurrence of both oxidative initiation to radical cations and the presence of carbonium ion chain reactions involving intermolecular hydride transfer. We have suggested that the extent of radical cation formation can be inferred by the amount of methane formed, assuming that the R^+ species fragments just as it does when formed over an amorphous solid acid and that the number of products formed as a result of intermolecular hydride transfer when divided by this estimate provides a measure of the carbonium ion chain length in the system being studied. This still appears to be a reasonable way to assess the situation.

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