JOURNAL OF CATALYSIS **115**, 611–615 (1989)

In Reply to Kramer and McVicker

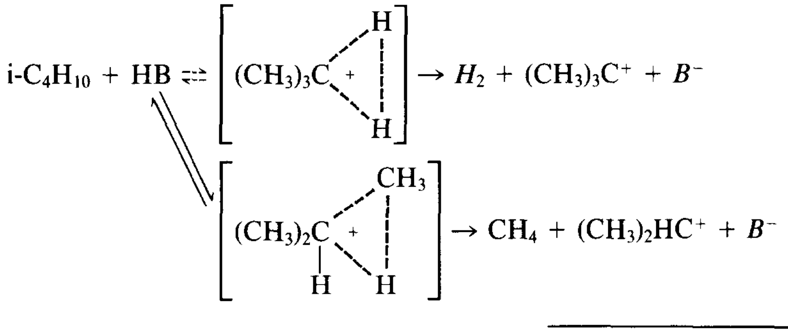
In the preceding letter (*1*), these authors have listed six objections to our reinterpretation (*2*) of their data (*3, 4*) on the cracking of isobutane. Here we counter these objections and update the perspective to show how some of the differences in viewpoint are converging into a common picture.

First, we have no disagreement concerning the experimental facts; our data (*2*) confirm theirs (*3*). The principal difference in viewpoint arises in how the *primary products,* H_2 and isobutene, and CH_4 and propene are formed. A second difference is the feature controlling the extent of secondary reactions (which they call "carbonium ion" processes). They have written

$$i\text{-}C_4H_{10} + EA \xrightarrow{k_i} [i\text{-}C_4H_{10}^{+\cdot}][EA^{\cdot -}] \quad (1)$$

where EA is an electron-accepting site on the surface of all catalysts, from silica–aluminas and halided aluminas to ultrastable Y-zeolite. The cation–anion radical pair was then supposed to decompose, reforming the EA site and the aforementioned primary products. These were implicitly assumed to be the same as those formed in the gas-phase free radical decomposition at much higher temperatures. The olefins produced could then be protonated to form alternatively "free carbenium ion intermediates" on Linde LZ-Y-82 (u.s.-HY) or "polarized surface (alkoxy) intermediates" over the weaker acids, the diagnostic difference being the ease of H^- transfer to the former and its absence with the latter. We agree with the experimental facts; hydride transfer, when it occurs, makes possible carbenium ion chain reactions and is responsible for formation of paraffinic products. Note, however, that a "free carbenium ion" is equivalent to a "long-lived" and an "alkoxide intermediate" may be a "short-lived" carbenium ion. Note also that the steady-state concentration of "live carbenium ions" controls the extent of the *secondary* reaction processes identified by McVicker *et al.* (*3*) as "carbenium ion reactions."

Our alternative suggestion stems directly from known chemistry in strong acids (*5*) as invoked by Haag and Dessau (*6*) to explain the formation of H_2, CH_4, and C_2H_6 in the cracking of 3-Me-pentane, i.e., as rewritten for isobutane,



$$i\text{-}C_4H_{10} + HB \rightleftarrows \left[(CH_3)_3C^{+}\begin{matrix}H\\ \vdots\\ H\end{matrix}\right] \rightarrow H_2 + (CH_3)_3C^+ + B^- \quad (2a)$$

$$i\text{-}C_4H_{10} + HB \rightleftarrows \left[(CH_3)_2\underset{H}{C}^{+}\begin{matrix}CH_3\\ \vdots\\ H\end{matrix}\right] \rightarrow CH_4 + (CH_3)_2HC^+ + B^- \quad (2b)$$

where HB is a Brønsted acid site, B^- is the conjugate base, and the structures in brackets are the pentacoordinated carbonium ion intermediates described repeatedly by Olah and co-workers (*5, 7–9*)); these contain three center two-electron bonds (proton-

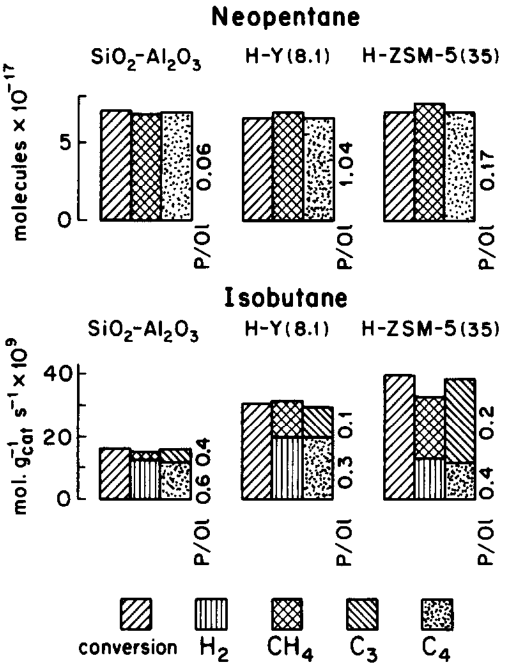
0021-9517/89 $3.00

ated σ-bonds). According to this chemistry the carbenium ions are formed directly as a result of the primary reaction; their ultimate fate depends upon their stability or lifetime as described by the pseudoequilibrium

$$(CH_3)_3C^+ \text{ [or } (CH_3)_2HC^+] + B^- \overset{K}{\rightleftharpoons} HB + (CH_3)_2C{=}CH_2 \text{ [or } CH_3CH{=}CH_2] \quad (3)$$

The position of this "equilibrium" is a measure of the intensive factor of the acidity.

Our choice of first neopentane (*10*) and then isobutane (*2, 11*) made possible very simple product distributions and thus analyses of the results. With the former all the C–C bonds are identical and only primary C–H bonds are present. Experimentally, virtually no H_2 was produced (*10*); i.e., only reaction (2b) was important. With the weaker acids approximately equal quantities of CH_4, isobutene, and the neopentane reacted were predicted and observed; i.e., only primary products were formed. With isobutane, on the other hand, the formation of H_2 was usually greater than (or at least equal to) the CH_4, but both were always evident. Thus, additional pathways for secondary reactions were made available. As with neopentane, with the weaker acids only the primary products were formed, a result identical with that of McVicker *et al.* (*3*). This feature is depicted by the comparisons shown in Fig. 1. Note, however, with isobutane it is the sum of the H_2 + CH_4 which must be compared with the isobutane reacted and the isobutene and propene produced.



With the longer-lived carbenium ions which are stabilized on the surfaces of much stronger acids, secondary carbenium ion processes were observed as described accurately by McVicker *et al.* (*3*). Diagnostic are the isomerization of isobutene to the *n*-butenes, oligomerization (with subsequent rearrangement and cracking) by reaction of the carbenium ions with the olefins released, and, most important, formation of paraffins (especially propane and *n*-butane) by hydride transfer (mainly from the reactant isobutane). Now more isobutane was reacted than that corresponding to the primary reactions.

McVicker *et al.* (*3*) visualized two distinct intermediates to explain the distinctly different catalytic chemistry over weak and strong solid acids, viz., surface alkoxides and free carbenium ions, respectively. Recent work (*12–14*) has suggested that the former may be the ground state from which the latter may be formed by thermal activation. Our ^{13}C MAS NMR experiments (*12*) have demonstrated conclusively that simple aliphatic "free carbenium ions" are not formed in detectable amounts by reaction of either alcohols or olefins with any of the H-zeolite systems tested; conversely the stable $(C_6H_5)_3C^+$ ion was readily produced even on silica–alumina at room temperature from triphenylcarbinol. Moreover, the transient formation of carbenium ion intermediates was evident from the polymeric products produced (*12, 13*). Most recently

Gorte and co-workers (*14*) have reported that *t*-butanol selectively reacted at the Brønsted centers at and below room temperature forming H_2O and the "silyl ether" (alkoxide). Finally, Kazansky (*15*) has reported quantum calculations showing that these species are generally more stable than the "free carbenium ions." Hence, we concur with Gorte's analysis that even on strong acids, alkoxides are the ground state from which carbenium ions may be produced, given the appropriate activation energy. These ions may then be pictured as metastable intermediates existing in a potential well of variable depth near the top of the reaction coordinate (see Ref. (*10*, Fig. 3)); with weak acids the depth is shallow and, hence, it may be postulated that the lifetime in this state is too short for bimolecular processes to occur. With strong acids the lifetime is longer so that both olefins and carbenium ions are present in the system simultaneously. Now the secondary chemistry becomes apparent. This general picture was established many years ago in studies of the isomerization of the *n*-butenes (*16*) and cyclopropanes (*17*) over silica–alumina catalysts; missing was the role of the alkoxides as a ground state for carbocation formation.

Kramer and McVicker (*1*) cited six objections to our proposals, none of which is convincing. The first, the fairly constant ratio of reaction (2a) to (2b) regardless of the reaction rate, may result from the relative ease of protonating the C–H vs the C–C bond in the primary step; this is no more surprising than that the postulated cation–anion radical pair of Eq. (1) should decompose in the same constant ratio. The second point is not really an objection; it presents an alternative interpretation for which there is no precedent. The proposed cleavage of isobutane into CH_4 and propene has been repeatedly reported (*7–9*); in superacids reaction (2a) is favored over (2b) by a factor of 50 at −78°C, but this falls to about 9 at 25°C. On this basis both pathways should become equally probable at our reaction temperatures. Moreover, reaction (2b) becomes favored with the more sterically hindered homologs of isobutane (*8*). With neopentane, C–C rupture is preferred over cleavage of a primary C–H bond. The third point is not really germane to the present arguments. Butene isomerization is facile over silica–alumina and involves a short-lived carbenium ion intermediate (*16*); hydride transfer cannot be expected in the absence of a paraffin holding a tertiary hydrogen and then only if the intermediate carbenium ion has a sufficiently long lifetime. With regard to the fourth point, kinetics can never prove a mechanism. More important, it has not been shown that the observed pressure dependencies are inconsistent with our picture. Indeed the change from first to second order in isobutane pressure with the onset of hydride transfer may be deduced from Eqs. (2) by making assumptions equivalent to those of McVicker *et al.* (*3*). The first order is expected for the primary reaction, where the rate depends on the activation of the paraffin to the pentacoordinated intermediate; the second order results from reaction of the parent isobutane with any carbenium ion other than the *t*-butyl cation. The fifth item refers to the reactions observed with 3-methylpentane. The dehydrogenation and cracking over weak acids are exactly as predicted by Eqs. (2) in the absence of much secondary reaction. When longer-lived carbocations are formed, these occur, including hydride transfer to the 2-methylpentyl cation formed by a conventional carbenium ion rearrangement from the 3-methylpentyl ion, which in turn was formed in the primary reaction (Eq. (2a)). Similarly, the sixth and last item is not inconsistent with our picture. In superacids, the carbonium ions are stable, but may undergo transformations to equilibrium into other carbenium ions. Some zeolitic catalysts may approach solid superacids in strength; they do form carbenium ions with lifetimes long compared with those formed on weaker acids.

In drawing analogies between reactions in acid solutions weaker than 90% H_2SO_4 with those catalyzed by the weaker solid acids it is stated that (*1*) "there is simply no precedent for such acids to react with alkanes in the manner proposed by Lombardo and Hall." Overlooked is the fact that reactions in acid solutions are carried out at or near room temperature whereas our observations were in the range $473 \text{ K} < T < 673$ K. Interestingly, the weaker acids simply require higher temperatures to effect the chemical transformation described by Eqs. (2). The data indicate that the stronger the acid the lower the temperature required (*2, 10, 11*).

We have several reasons for preferring our interpretation over that of McVicker *et al.* (*3*). No new chemistry is invented; all we have done is recognize the changes that may be expected as one moves away from solutions of superacids at room temperature to somewhat weaker, and then to much weaker, solid acids at higher temperatures. The mechanism advanced by McVicker *et al.* (*3*) requires that redox centers be present on a wide variety of surfaces capable of oxidizing paraffin molecules to their cation radicals. Further, these sites must reversibly release the borrowed electron on demand. We know of no such centers. Polynuclear aromatic hydrocarbons, multiply methylated benzenes, and some related nitrogen compounds are known to form cation radicals on aluminum silicates. It has been shown (*18*), however, that these involve irreversible surface chemistry, viz., oxidation by some form of bound surface oxygen which can be removed as H_2O by reduction in H_2 at temperatures above 773 K. We have shown (*2*) that such treatments do not affect noticeably the activity or selectivity in the cracking of isobutane or neopentane. Moreover, so far as we are aware there is no reliable evidence of radical cation formation with these simple hydrocarbon molecules.

Richardson (*29*) showed many years ago that the extent of formation of cation radicals on a given surface was an inverse exponential function of the ionization potential of the substrate. The ionization potentials (*20*) of i-C_4H_{10}, *n*-C_4H_{10}, neo-C_5H_{12}, i-C_5H_{12}, and *n*-C_5H_{12} are 10.57, 10.63, 10.35, 10.32, and 10.35 eV, respectively; their heats of formation are 212, 215, 199, 201, and 204 kcal/mol. Accordingly one would not expect much difference in reaction rates with structure of the hydrocarbon. This is certainly not true. Branched chain hydrocarbons react much more readily than do the straight chain molecules, presumably because of their tertiary hydrogen.

Brenner and Emmett (*21*) studied the isomerization of isopentane near room temperature over a silica–alumina catalyst. They noted the formation of H_2 and at first thought that the catalyst must have a dehydrogenation function provided by an impurity center. After doping the catalyst with possible redox centers such as Fe^{3+} and making comparisons with ethylene hydrogenation, however, they concluded that this process must be "intrinsic" to the silica–alumina. Their results can now be readily understood in terms of Eq. (2a). Moreover, their results counter the picture described by Eq. (1).

In conclusion, we have proposed and defended chemistry alternative to that suggested by McVicker *et al.* (*3*) for the reactions of isobutane and related compounds over acid catalysts. Their picture has not been disproved, but like ours, it contains some concepts which remain to be demonstrated. Finally, these simple reactions provide valuable tools for the assay of acid catalysts.

ACKNOWLEDGMENTS

This work was initiated by a grant from Air Products and Chemicals Co. and has since been carried out under a grant by the Department of Energy, Division of Chemical Sciences, under Contract DE-FG02-87ER13774.

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Received October 10, 1988