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LETTER TO THE EDITORS

On the Generation of Carbonium Ions by Electrophilic Sites as Proposed by Porter and Hall

Earlier interpretations of Leftin and Hall (*1*) that electrophilic (Lewis) sites on silica-alumina (a) abstract hydride ions from triphenylmethane and (b) chemisorb triphenylcarbinol and trityl chloride as the carbonium ions have been reaffirmed in modified form by Porter and Hall (*2*). This paper fails to take notice of most of the evidence assembled by Hirschler and Hudson (*3*) favoring generation of carbonium ions, not by electrophilic, but by Bronsted sites. For the following reasons, it does not present an objective view of the state of this controversial issue.

1. Leftin and Hall (*1*) proposed that silica-alumina has $5 \times 10^{12}/\text{cm}^2$ conventional Lewis sites able to abstract hydride ions from Ph_3CH. Porter and Hall find that there are only $6 \times 10^{11}/\text{cm}^2$ sites able to abstract hydride ions in the dark; they suggest these are most likely cation–anion vacancy pairs since they regard these as more electrophilic than Lewis sites. They still contend there are $5 \times 10^{12}/\text{cm}^2$ electrophilic sites which convert Ph_3COH or Ph_3CCl to the carbonium ion; it follows (by difference) then that there are $4.4 \times 10^{12}/\text{cm}^2$ electrophilic (most likely Lewis) sites which do not abstract H^- ions in the dark. Many of these latter sites are able to chemisorb Ph_3CH in a photolytic reaction which they admit (*2*) is "probably an oxidation" as we suggested (*3*) rather than hydride abstraction. Porter and Hall imply (*2*) that these two pictures (*1, 2*) are substantially equivalent. In our view they are substantially different, not only because the capacity to abstract hydride ions is smaller in one than in the other by an order of magnitude, but because Porter and Hall now postulate that the hydride ion is attached to a silicon, rather than to an aluminum, atom.

Recent work (*4*) suggests that at least for aliphatic carbonium ions there is a small tendency for hydride to transfer from silicon to carbon, rather than the reverse, since transfer of a hydride ion from isobutane to $(CH_3)_3Si^+$ is endothermic by 8 ± 7 k cal/mole.

2. Objections have been raised (*3*) to nearly all of the arguments for hydride abstraction relied on by Leftin and Hall, yet most of these objections have not been taken into account. The only direct evidence for hydride abstraction, conversion of Ph_3C^+ to Ph_3CH by NH_3 (*1*), is now admittedly (*2*) unproved.

3. Porter and Hall in reiterating the earlier suggestion (*1*) that Ph_3COH and Ph_3CCl are converted to carbonium ions by electrophilic Lewis sites rather than by Bronsted sites have chosen to overlook the existence of several lines of evidence pointing to a contrary conclusion (*3*). Two of these which are supported by additional information will be cited. M-46 silica-alumina treated with excess NH_3 (saturated at atmospheric pressure, poisoning all acid sites), and pumped at 200° has recovered many sites able to form carbonium ions from Ph_3COH and Ph_3CH (*3*). At 200°, most of the NH_3 chemisorbed by silica-alumina is retained (*5*) and polymerization

activity is completely poisoned (*6*). It seems almost axiomatic that a highly electrophilic aprotic site able to chemisorb Ph_3CH or Ph_3COH as Ph_3C^+ would retain the more basic and much smaller NH_3 molecule; the many sites that retain NH_3 at 200° must be considered the more electrophilic. Actually, when M-46 is saturated with NH_3 at atmospheric pressure, NH_3 can be freed from sites able to chemisorb Ph_3COH by pumping at temperatures as low as 50°, and from sites able to chemisorb Ph_3CH in the dark at room temperature by pumping at 125° (*7*). These results are difficult to reconcile with the electrophilic view (*2*) because one must assume chemisorption of Ph_3COH and Ph_3CH takes place on the most electrophilic sites; generation of the Ph_3C^+ ion by protonic sites is less difficult to accept because relatively weak acidity—50% H_2SO_4—suffices, and a considerable amount of base must be added to lower the acidity of M-46 to that level (*3, 7, 8*).

It was also shown (*3*) that 1,1-diphenylethylene and H_R indicators (aryl methanols) fell on the same curve when the butylamine titers of M-46 were plotted vs. the acid strength required for the *protonation* of these indicators, suggesting that protonic rather than aprotic electrophilic sites were responsible for the generation of carbonium ions. Adding considerable weight to this argument is the recent finding by Taft (*9*) that BCl_3, a strong Lewis acid, has no tendency to generate a carbonium ion from 1-phenyl-1-(4-fluorophenyl)ethylene in methylene chloride solution (no fluorine NMR shift is observed). By contrast, the carbonium ion is readily generated by H_2SO_4 resulting in a marked shift (34.9 ppm) in the fluorine resonance. By analogy, the ability of aprotic electrophilic sites on silica-alumina to generate carbonium ions from olefins is therefore in doubt.

The conclusion (*2*) that Ph_3COH cannot be an intermediate in the chemisorption of Ph_3CH in view of the differences in stability of trityl ions derived from Ph_3CH and Ph_3COH shown in Figs. 4 and 6 of ref. 2 may be questioned. One would expect the stability, especially at higher temperatures, to be adversely affected by chemisorbed oxygen on the surface. For the experiment in Fig. 4, the amount of chemisorbed oxygen was reduced by hydrogenation while in Fig. 6 it was not. However, even had both catalysts been pretreated similarly in hydrogen, significant difference in stability would be expected. It is admitted by Porter and Hall that "the photolytic reaction is probably an oxidation as claimed (*3*)"; certainly the effect of oxygen on the photolytic reaction (*2*) supports this view. If so, in Fig. 4, chemisorbed oxygen on the surface not removable by hydrogenation is cleaned off by the photolytic reaction with Ph_3CH at room temperature prior to heating the catalyst. Adding Ph_3COH to the catalyst cannot clean the surface of oxygen in this manner, and in fact adds an additional atom of oxygen per molecule. Even in Fig. 4, 75% of the Ph_3C^+ was derived from the photolytic reaction where Ph_3COH is the most probable product.

Hirschler and Hudson (*3*) studied the photolytic reaction of Ph_3CH because they supposed the data of Leftin and Hall (*1*) were obtained largely under photolytic conditions since no attempt to control light exposure was reported. Though the contribution of the photolytic reaction was undoubtedly less than we thought, we would question the conclusion (*2*) that it was insignificant, since the photolytic reaction is much faster than the dark reaction and multiple exposures to light were involved.

In summary, while there is no conclusive proof that silica-alumina does not abstract hydride ions from Ph_3CH to a level of $6 \times 10^{11}/cm^2$, the evidence advanced for this proposal (*1, 2*) is subject to criticism and many of these criticisms (*3*) are yet unanswered. Evidence adverse to the electrophilic picture of the silica-alumina surface and favoring protonic sites for generation of carbonium ions is much more substantial than indicated by Porter and Hall. The *number* of protonic sites is more uncertain. Hall and co-workers (ref. *10* and prior papers cited therein) have placed upper limits on the number of these sites on the basis of tracer experiments. These numbers are arrived at on the basis of *assumed* mechanisms which may or may not prove to be the correct ones; they are also much smaller than the postulated number (*2*) of strong electrophilic sites. Space does not permit a detailed discussion; additional details will appear in a forthcoming publication (*7*).

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