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LETTER TO THE EDITORS

In Answer to Hirschler*

Our position is this: Recent studies of the decationated zeolites (*1*) have confirmed the older concept that Bronsted acids are converted into Lewis acids via dehydroxylation. However, in addition to the conventional Lewis acid sites, corresponding to incompletely coordinated aluminum ions, another possibility has emerged, viz., the anion–cation vacancy pair sites, which we presume (but cannot be sure) are the more electrophilic. Moreover, under our pretreatment conditions, the majority of the Bronsted sites became dehydroxylated, yet these dehydroxylated materials showed the same principal features (*2*) in their interaction with triphenylmethane and perylene as those reported by Porter and Hall (*3*) for silica-alumina.

There is a considerable body of independent evidence indicating that the surface of dry silica-alumina is mainly electrophilic, as opposed to protonic, in nature. This does not mean that the terminal hydroxyl groups cannot act as acid to sufficiently strong bases or as co-catalyst to substrates held on electrophilic sites (*4*). It does mean that the amount of residual Bronsted acid is much less than the number of electrophilic centers. For example, when care was taken to leave the decationated Y-type zeolites in the Bronsted form, one acidic OH was present for nearly every decationated site; these reacted quantitatively with NH_3 to yield NH_4^+ (*1*). By contrast, the *initial* adsorption of NH_3 on silica-alumina took place without even hydrogen-bonding the hydroxyls (*4*b). At higher coverage, only 15% to 20% of the adsorbed NH_3 appeared as NH_4^+ and it was suggested (*4*b) that the latter was due to proton transfer from terminal hydroxyl groups induced by the NH_3 held on adjacent Lewis sites. Significantly, the Bronsted OH frequency of the decationated zeolite (reacts with NH_3) appears at about 3650 cm^{-1}, i.e., at 100 cm^{-1} lower frequency than the OH vibration of silica-alumina, which is indistinguishable from that of silica gel. This shift is thought to be caused by interaction of the electrons of the oxygen with an adjacent aluminum ion (*1*). Hirschler has agreed (*5*) that the strong Bronsted sites of silica-alumina may be Si–OH adjacent to Al, as with the zeolites. Evidently, most of the hydrogen of silica-alumina does not constitute part of this acid.

Tracer experiments (*6–8*) have provided another means of estimating the Bronsted acidity and has led to the same conclusion, i.e., that the surface density of Bronsted sites must be smaller than that of Lewis sites. Hirschler (*9*) has commented that: "These numbers are arrived at on the basis of *assumed* mechanisms which may or may not prove to be the correct ones." This is true; we have assumed that cyclopropane and butene-1 isomerize by classical carbonium ion mechanisms involving catalyst protons. This is tantamount to the assumption made by Hirschler (*10*) that *n*-butylamine is adsorbed as $n\text{-}C_4H_9NH_3^+$. It should be emphasized that the Bronsted acidity arrived at in these titrations (*10*)

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* This letter was intended to appear simultaneously with the letter of A. E. Hirschler in this journal 5, 390–392 (1966), but through no fault of either author, publication of this letter was delayed.

($\sim 5 \times 10^{13}/\text{cm}^2$) is about 33% of the total OH present (*6*); this much acid should be easy to characterize by the techniques used. We think the n-$C_4H_9NH_2$ titration technique (*10, 12*) is a useful way to characterize catalysts, but we seriously doubt that it measures a strength distribution of Bronsted acid.

In our paper (*3*), we have not wished to imply that triphenylcarbinol will not react with a Bronsted acid when present; our earlier work (*11*) demonstrated the contrary. Rather, we have suggested that it can react with the dominant electrophilic sites as well.

With regard to the formation of carbonium ions from triphenylmethane, the question under debate is whether H^- is removed from the substrate by the catalyst or whether it is necessary to oxidize triphenylmethane to triphenylcarbinol so that OH^- can be reacted with catalyst protons to form water. In the former view, whatever sites are effective would be termed electrophilic, while in the latter (espoused by Hirschler) they would be protonic. Leftin and Hall (*11*) showed that the H^- remained with the catalyst; it was not transferred to a carbonium ion formed by reaction of catalyst protons with impurity olefins, nor was H_2 generated by reaction with these protons. An attempt was made to eliminate the possibility that it was in some way oxidized to OH^-; the catalyst was treated with H_2 at 500° to remove possible chemisorbed oxygen, but carbonium ion formation was not repressed. It has since been demonstrated (*2, 3*) that this same treatment is effective in removing oxygen which is necessary for the formation of radical ions. These facts have been confirmed by Hirschler and Hudson (*12*) as well as by ourselves. Since we have found that the chemisorption of triphenylmethane on silica-alumina is significantly enhanced by O_2 gas *only* when the system is irradiated, we have supposed that this substrate cannot be converted to triphenylcarbinol (or hydroperoxide) in the dark by oxygen associated with the catalyst. Even in the event that catalyst oxygen is in some way involved, we doubt that a major portion of the carbonium ions result from reaction of triphenylcarbinol intermediate with catalyst protons, because of their relative scarcity. Nevertheless, it was admitted (*5*) that until the fate of the H^- is known exactly the role of catalyst oxygen cannot be accurately assessed. We do not argue that triphenylcarbinol may have been a product in Hirschler's experiments (*12*), but we were able to obtain comparable carbonium ion concentrations in the dark on reduced catalysts sealed *in vacuo* while at 550°.

Distinction must be made between what we have said and how it has been interpreted by Hirschler (*9*). Leftin and Hall (*11*) found that about 5×10^{12} carbonium ions/cm² were formed from triphenylcarbinol and the trityl halides. They also noted that, because of steric considerations, it might not be possible to populate all of the sites, if these occurred in clusters. As described elsewhere (*3*), due to an unfortunate choice of an analytical procedure, nearly the same value was also obtained for triphenylmethane. The work of Porter and Hall (*3*) confirmed that the density of sites capable of reacting with trityl chloride was *at least* $5 \times 10^{12}/\text{cm}^2$. They did not say, however, that only $6 \times 10^{11}/\text{cm}^2$ of these were capable of reacting with triphenylmethane in the dark nor did they make a quantitative division of these sites into several kinds. They noted that since the reaction of triphenylmethane with silica-alumina is kinetically controlled, this reagent should not be used to measure site densities. The presently available data do not define the exact nature of the sites; they only indicate that they are acceptors for H^-. Since the efficiency of the photocatalytic step [see Fig. 5 of ref. (*3*)] appeared to correlate with the availability of oxygen left after pretreatment, it was deduced that this step was "probably an oxidation as claimed" (*12*). This does not mean, however, that catalyst protons were involved. There is no reason to suppose that the substrate cannot be oxidized directly to the carbonium ion rather than to intermediate triphenylcarbinol, or that the latter cannot be dissociated by the catalyst surface in the event that it is.

Hirschler (*9*) cited the recent work of Hess, Lampe, and Sommer (*13*) as evidence that H^- should transfer from silicon to carbon. The authors of this paper concluded that: "In equilibrium between analogous silicon and carbon cations and their molecular precursors, there is an approximately equal tendency for the silicon or carbon cation to be formed." These same data strongly suggest that the triphenylcarbonium ion should form spontaneously on the vacancy pair sites and that these should be effective catalytically.

In a similar vein, Hirschler (*9*) cited some unpublished work of Taft showing that BCl_3 does not effect carbonium ion formation from *p*-fluorodiphenylethylene in methylene chloride. This was given as evidence that the sites on silica-alumina must be Bronsted. This same work showed that *p*-fluorobenzophenone was completely complexed with BCl_3. More to the point, however, is the recent report (*14*) that tris-4-phenylphenylmethane and triphenylmethane form carbonium ions by hydride transfer to boron halides; with the former, the reaction is nearly complete, while with the latter the reaction was incomplete.

Hirschler has complained (*9*) that we have not chosen to offer a point-by-point rebuttal of his criticisms of our work. We considered doing this and decided against it for several reasons. In the first place, neither Hirschler's data nor ours are really conclusive. Thus, although we can offer alternatives to each of the issues raised, the only possible result is a polemic argument. Secondly, some of his points appeared to us to be either irrelevant or else dependent on the acceptance of his framework of reference. Finally, we have further unpublished experimental results, which would make such a discussion more meaningful at a later time. We therefore would have preferred to state our position and to have awaited the results of more critical experiments. The ensuing discussion will illustrate these points.

Of the seven reasons listed (*12*) as evidence against hydride removal by the catalyst, the first was that up to 14 moles of base per mole of carbonium ion were required to bleach silica-alumina on which carbonium ions were already formed (or to prevent formation of carbonium ions). In addition, new data (*9*) have now demonstrated that after a catalyst was saturated with NH_3, its ability to form carbonium ions could be restored by evacuation under relatively mild conditions. While these data suggest that NH_3 chemisorbs on sites which do not react with triphenylmethane or that the two processes of chemisorption are different, they do not define the differences. In particular, they do not demonstrate that catalyst protons are involved in either reaction. Hirschler has reasoned that since there are only $5 \times 10^{12}/\text{cm}^2$ electrophilic sites (there may be more) and since there are $5 \times 10^{13}/\text{cm}^2$ catalyst protons (we suspect there are less), the poisoning by adsorption of $\sim 10^{13}/\text{cm}^2$ NH_3 molecules should be serious if the sites are electrophilic, but modest if the sites are protonic. If there really are not $5 \times 10^{13}/\text{cm}^2$ strong protonic acid sites present, as we believe, the problem of why $\sim 10^{13}/\text{cm}^2$ NH_3 molecules does not completely poison carbonium ion formation still exists. Hirschler argues that it should be possible to put fixed values on the numbers of sites of given strength and that, therefore, the first NH_3 molecules adsorbed should poison the strongest sites. This viewpoint overlooks, among other things, the possibility that the site density may not be as he supposes, or that sites are formed by a coordination shift on the approach of a base. The latter suggestion, advanced many years ago by Milliken, Mills, and Oblad (*15*), found support in recent studies of decationated zeolites (*1*).

The second reason given (*12*) was that strong protonic acids mounted on silica gel effect carbonium ion formation. This does not happen (*11*) in the absence of an oxidizing agent. Hirschler and Hudson (*12*) used $HClO_4$ and H_2SO_4. They also reported that $1.5 \times 10^{10}/\text{cm}^2$ trityl ions were formed when they used HF. The impurity in their silica could have been responsible for this small amount of oxidizing agent.

That triphenylmethane may be photochemically oxidized to the trityl ion in solutions of strong acids in the presence of

O_2 (third reason) is irrelevant to the question of whether the same result can be effected by reduced and evacuated silica-alumina in the dark and in the absence of a strong Bronsted acid. The same can be said concerning the effect of light on the rates of chemisorption on silica-alumina (fifth reason) and on silica treated with BF_3 (sixth reason).

The strongest evidence advanced was that trityl ions were almost quantitatively recovered as triphenylcarbinol when desorbed with NH_3 (fourth reason). As mentioned in our paper (*3*), we have been unable to confirm this finding and think that triphenylcarbinol must result from the chemistry of the recovery process rather than the chemistry of carbonium ion formation. Although our published experimental data (*11*) failed to prove that triphenylmethane can be recovered from the chemisorbed trityl ion, we now have information indicating that a major fraction can be. We hope to publish these data in the near future.

The final reason given was that initial carbonium ion formation was very slow (*11*), whereas after bleaching by adding H_2O, the original spectrum could be regenerated by 5 min evacuation at room temperature. We now think that the ion is not desorbed, but is complexed, with H_2O. At least this is a reasonable alternative. The statement (*12*): "Such behavior would be expected *only* if triphenylmethane had been converted to triphenylcarbinol in a very slow reaction," is simply untrue.

In summary, while some trityl ion formation may result from reaction of the residual Bronsted acid of silica-alumina with an oxidation product of triphenylmethane under photolytic conditions, we do not feel that the available data support the view that this pathway is the major one under other circumstances. Moreover, while the chemistry of formation of the trityl ion from triphenylmethane must remain unsettled until the fate of the H^- can be ascertained, the possibility that the reaction may occur by direct hydride abstraction into electrophilic sites (*3, 11*) cannot be discounted. Finally, we regard the question of the relative importance of Lewis and vacancy pair sites vs. Bronsted sites for other purposes as largely unsettled and perhaps dependent upon the function in question.

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W. KEITH HALL
R. P. PORTER

Mellon Institute
Pittsburgh, Pennsylvania