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The Reaction of Triphenylmethane and Perylene with Silica-Alumina The Nature of the Acid Sites*

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It is generally accepted that the chemisorption of triphenylmethane on silica-alumina involves hydride ion abstraction and constitutes evidence for a few ($5 \times 10^{12}/cm^2$) strong Lewis acid sites. Observations contrary to this interpretation include (1) about ten molecules of NH_3 or *n*-butylamine per "Lewis site" are required to poison the reaction; (2) protonic acids mounted on silica also catalyze this reaction; (3) 90% or more of the chemisorbed trityl ion is recovered as triphenylcarbinol, not triphenylmethane; (4) the rate of formation of trityl ions is strongly accelerated by light; (5) the generation of trityl ions by $SiO_2 + BF_3$ does not proceed at a significant rate in the dark, and triphenylcarbinol is a product of the light reaction.

The evidence suggests that triphenylmethane is oxidized to triphenylcarbinol, followed by reaction with a Bronsted acid to generate the trityl ion. In support of this interpretation, Ph_3CH and Ph_3COH give substantially the same endpoint when used as indicators in the titration of catalyst acidity with *n*-butylamine.

Evidence is also presented that in the reaction of perylene with silica-alumina to form the perylene cation radical, Bronsted sites catalyze the reaction with some form of chemisorbed oxygen which acts as the electron acceptor. The spin concentration is therefore not a measure of the number of strong Lewis acid sites.

INTRODUCTION

The reaction of triphenylmethane with a silica-alumina catalyst to form a chemisorbed triphenylcarbonium ion has been interpreted by Leftin and Hall (*1*) as a hydride abstraction by Lewis acid sites on the surface. It was proposed that the number of chemisorbed trityl ions, about $5 \times 10^{12}/cm^2$, is a measure of the number of strong Lewis acid sites (*1*). These observations have been rather widely accepted as proof of the presence of strong Lewis acid sites on cracking catalysts.

More recently, it has been shown (*2*, *3*, *4*) that perylene is chemisorbed on silica-alumina as a positive radical ion and it was suggested that this interaction takes place on Lewis acid sites. The spin concentration has been reported to be 1.6 to $2 \times 10^{12}/cm^2$ (*2*b, *4*); it has been proposed that the spin concentration is a measure of the number of Lewis acid centers on the catalyst surface (*3*b, *4*). Brouwer (*2*b) and Rooney and Pink (*3*b) have advanced the hypothesis that the identical Lewis sites are responsible for the conversion of triphenylmethane to the triphenylcarbonium ion and the oxidation of perylene and other polynuclear aromatic hydrocarbons to the corresponding radical ions.

As part of a research program designed to help elucidate the nature, strength, and concentration of the acid sites present on silica-alumina and other acid catalysts, we have studied the reaction of triphenylmethane and perylene with silica-alumina. Several significant observations are detailed below which do not appear to be consistent

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with the view that a small population of strong Lewis sites removes hydride ions from triphenylmethane or acts directly to accept electrons in the formation of perylene radical ions. It is the intent of this paper to present the evidence for an alternative explanation of the nature of these reactions. In the case of triphenylmethane, the evidence favors the reaction:

$$\underset{\text{(I)}}{Ph_3CH} + O \rightarrow \underset{\text{(II)}}{Ph_3COH}$$

The implications of these and other observations on the question of the nature of the surface acid sites will be discussed.

EXPERIMENTAL

Equipment and procedures. Optical spectra of catalysts were determined using an improved technique involving transmission through a thin wafer (~0.6 mm) of catalyst immersed in solvent approximating it in refractive index. This procedure minimizes scattered light, and transmissions of over 50% in the visible can be obtained. This technique has been independently suggested by Hall (*4*).

Powdered catalyst, sieved to minus 325 mesh, was pressed into a 30-mm disc using pressures of 30–80 tons/sq. inch as described by Webb (*5*). These discs were trimmed into approximately square wafers of about 3 cm^2 area and mounted into rectangular quartz cells using a platinum wire screen support with a circle of 1 cm diameter cut out for the light beam. The weight (after activation, usually at 500°) and area of the wafer were determined before mounting. Spectra were obtained with a Cary Model 11 recording spectrophotometer, using a blank catalyst wafer in the reference beam. If necessary, calibrated screens were used to adjust the transmission of the reference beam.

In some cases where rigorous exclusion of air or moisture was not required, the catalyst wafers were mounted in standard 3 × 3 × 1-cm rectangular quartz cells which were placed perpendicular to the long axis of 5 × 25-cm Pyrex test tubes fitted with 50/50 female standard taper joints. A short 5-mm side tube fitted with a serum cap was located near the joint, and indentations were provided so that the quartz cell could be properly positioned to inject liquids into the cell via a hypodermic syringe. The male joint was fitted with a two-way vacuum stopcock and standard taper joint for attachment to a vacuum line equipped with a molecular sieve trap and capable of reaching 10^{-6} mm of mercury or better. The catalyst wafer was activated at 450° *in vacuo,* the quartz cell filled with the desired solution through the serum cap, then the quartz cell was removed from the activation tube, covered, and the spectrum obtained.

For spectral measurements requiring rigorous exclusion of air and moisture a 3 × 4 × 1.6-cm rectangular quartz cell was sealed to one end of a 40-mm quartz tube, and a 65/40 Pyrex O-ring joint to the other. A 5-mm quartz tube fitted with a serum cap was attached at an angle near the top of the quartz tube so that the cell could be filled via a hypodermic syringe. The catalyst wafer was mounted in a 2.5 × 5 × 1.2-cm inner cell equipped with hooks to facilitate lowering into the rectangular cell attached to the activation tube. The other half of the O-ring joint was provided with a two-way vacuum stopcock and a gas-inlet tube ring-sealed to the stopcock and extending to just above the quartz inner cell when the assembly was closed. A special cell holder and cover were constructed for use with the Cary Model 11. Buna N O-rings were employed.

For certain experiments where it was necessary to exclude oxygen from the solution added to the activated catalyst wafer, a glass tube closed with a Teflon-bore stopcock was attached to the serum-cap fitting by a short piece of Tygon tubing. The desired solution was placed in this tube, degassed by evacuation with alternate freezing and thawing, and pressured with purified nitrogen to superatmospheric pressure. The stopcock was closed, and after activation of the catalyst, the solution was admitted to the evacuated spectrometer cell by opening the stopcock with the tube inverted. Using this technique with a disc of M-46 hydrogenated at 450°C, the oxidation of perylene to the cation radical was inhibited to about the same degree as reported by Fogo (*6*) employing rigorous high-vacuum technique and break seals; the procedure was therefore considered adequate for studies of the oxidation of triphenylmethane.

In solution spectroscopy, extinction coefficient and absorptivity values are usually based on a 1-cm light path and concentrations expressed in g/liter. Concentrations of species adsorbed on catalyst wafers were expressed in units of mg/cm^2 in order that calculated absorptivity and ϵ values would be numerically equal to those in solution. (In 1-cm cells, a solution of 1 g/liter concentration contains 1 mg of solute per cm^2 of area exposed to the light beam.)

In some cases, e.g., NH_3, gases were admitted to the activated catalyst by means of a gas syringe and the serum-cap fitting. In some cases it was possible to replace the rubber serum cap after puncture; in others, it was sealed with glyptal to prevent leaking.

Treatment of silica with HF or BF_3 was carried out by placing the powdered catalyst in the bottom of one of the Pyrex activation tubes (omitting the quartz Cary cell) and activating by heating under vacuum. The HF or BF_3 was weighed into a small stainless steel bomb equipped with a needle valve, and rapidly admitted to the evacuated tube through the stopcock. Even so, HF reacted sufficiently with the Pyrex to cause the stopcock tube to become warm. The powdered catalyst was shaken during admission to promote uniform reaction. The tube was reevacuated after allowing 30 min for reaction.

Sulfuric and perchloric acids were mounted on silica by adding sufficient water to form a thick slurry with the silica, mixing thoroughly, and drying at 120°C.

Catalysts. The M-46 and S-34 are commercial silica-alumina catalysts containing about 11% alumina, and obtained from the Houdry Process Corp. The surface area of M-46 was 280 m^2/g, measured by nitrogen adsorption. Davison Chemical Co. No. 55-280 fluid silica-alumina, grade C-1-25, contains about 25% alumina.

The silica used for mounted acids and for HF and BF_3 treatment was Mallinckrodt silicic acid designated "for chromatographic purposes according to the procedure of Ramsey and Patterson."

Reagents. The triphenylmethane and perylene used were commercial products purified by recrystallization. The source of the arylmethanol indicators and the *n*-butylamine titration procedure have been described elsewhere (*7*). The trifluoroacetic acid was Eastman White Label purified by an efficient fractionation. Reagent grade benzene was dried by percolation through freshly activated molecular sieves.

Analysis for triphenylmethanol in the presence of triphenylmethane. Triphenylmethanol is immediately and quantitatively converted to the trityl ions by 80–85% H_2SO_4, whereas triphenylmethane does not react (except for a slow photocatalyzed oxidation which requires several hours for development of a visible color). Concentrated H_2SO_4 converts both species to the carbonium ion. Two aliquots are evaporated to dryness in volumetric flasks, the residue dissolved in a few drops of glacial acetic acid, and 80–85% H_2SO_4 added to one flask while concentrated H_2SO_4 is added to the other. Trityl ion concentrations are measured spectrophotometrically, the 85% acid being run within a few minutes after mixing. The difference in absorbance between the two solutions is a measure of the triphenylmethane in the sample. This procedure may not differentiate between Ph_3COH and Ph_3COOH.

RESULTS AND DISCUSSION

Molar extinction coefficient of trityl ion chemisorbed on silica alumina. Before an accurate measurement of the concentration of a carbonium ion chemisorbed on a catalyst surface can be made by spectrophotometric measurements, it is necessary to know the molar extinction coefficient ϵ of the chemisorbed ion. To our knowledge, no such data have been reported; hence measurements of the extinction coefficient of the adsorbed ion were carried out.

One procedure used was to equilibrate a

pressed disc of M-46 silica-alumina activated at 450° with a known amount of triphenylmethanol dissolved in benzene or cyclohexane and measure the absorbance. Correcting for the small amount of triphenylmethanol not adsorbed by the disc and assuming the adsorbed Ph_3COH is quantitatively converted to adsorbed trityl ions, an ϵ of 28 000 was calculated.

The second method used was to mount the disc in a standard rectangular quartz cell, treat with a solution of Ph_3COH as before, then transfer the cell and its contained disc to a Soxhlet extractor and extract overnight in a closed system with benzene refluxing over CaH_2 to remove all physically adsorbed Ph_3COH from the catalyst. A blanket of dry purified nitrogen was maintained. The spectrum of the disc, immersed in benzene, was then measured. The disc was completely covered by benzene during transfer to exclude moisture. The disc was again extracted overnight using a 50:50 v/v mixture of methanol and benzene. The amount of Ph_3COH recovered was determined by measurement of the absorption spectrum of a conc. H_2SO_4 solution of the extract. The average of three ϵ determinations by this method was 31 000 (30 100, 29 200, 33 400).

Blank experiments indicated that under the conditions used recovery of adsorbed Ph_3COH from the catalyst disc by benzene-methanol extraction was about 95%; hence ϵ values obtained by the second method might tend to be somewhat high. An average of the values obtained by the two procedures, 29 500, is probably the best value for ϵ of the chemisorbed trityl ion.

Determination of the ϵ value at 432 mμ for the trityl ion in conc. H_2SO_4 resulted in a value of 38 700. This is in good agreement with the 38 400 reported by Harmon (*8*). The ϵ value for the trityl ion adsorbed on silica-alumina catalyst is about 77% of the value in conc. H_2SO_4.

Similar measurements on the trianisylcarbonium ion and the diphenylcarbonium ion adsorbed on silica-alumina led to ϵ values of 75–80% of those measured in conc. H_2SO_4.

Capacity of silica-alumina for chemisorption of trityl ions. In another paper (*7*) we have described the use of a series of arylmethanol indicators in the determination of the acid strength distribution of solids by nonaqueous titration with *n*-butylamine. One of the indicators used is Ph_3COH, which requires 50 wt % H_2SO_4 for half conversion to the carbonium ion. Using this indicator, and titrating to the disappearance of the chemisorbed trityl ion from the catalyst, M-46 was found to have a titer of about 0.21 meq/g (4.6×10^{13} sites/cm^2). This figure is almost ten times the number of chemisorbed trityl ions reported by Leftin and Hall (*1*).

Several methods were used to recheck the capacity of M-46 for chemisorption of trityl ions, using the same lot of catalyst as employed in the acidity titrations. Considerable dilution with an inert material is required in the spectrophotometric measurements of the concentration of chemisorbed trityl ions because of the very high optical density of a thin wafer of pure M-46 saturated with trityl ions. In all cases the catalyst, after activation at 500°, was saturated with trityl ion by equilibrating with a solution containing a large excess

TABLE 1

CHEMISORPTION OF TRITYL ION BY M-46 SILICA-ALUMINA

Method	Meq Ph_3C^+/g $\times 10^3$
Pressed disc, 27% M-46 in Cabosil[a]	15
Pressed disc, 5.1% M-46 in silicic acid[a]	13.7, 12.6
1% M-46 in KBr disc[b]	13.1, 14.0
Slurry of 5.1% M-46 in silicic acid[c]	13.3
Extraction[d]	12.2, 12.1

[a] Absorbance measured with disc immersed in cyclohexane.

[b] M-46 powder saturated with trityl ion, then dried *in vacuo* before mixing with powdered KBr and pressing.

[c] Slurry suspended in decalin.

[d] Several discs saturated with trityl ion, excess physically adsorbed triphenylmethanol removed by 24-hr extraction with benzene refluxing over CaH_2. Chemisorbed material recovered by 24-hr extraction with CH_3OH-benzene, residue dissolved in conc. H_2SO_4, and trityl ion determined spectrophotometrically.

of triphenylmethanol. The results obtained by the several procedures are summarized in Table 1, and range from 1.2 to 1.5 × 10^{-2} meq of trityl ion per gram of catalyst. A value of 1.5 × 10^{-2} meq/g corresponds to 3.2 × 10^{12} ions/cm^2, somewhat less than the figure of 5 × 10^{12} reported by Leftin and Hall (*1*). These data confirm the existence of a fourteenfold discrepancy between the capacity of the catalyst to chemisorb trityl ions and the number of acid sites sufficiently acidic to stabilize trityl ions as measured by butylamine titration employing the trityl ion as indicator.

Effect of NH$_3$ on trityl ion concentration. In an attempt to shed some light on the discrepancy in the number of sites able to stabilize trityl ions, the effect of NH$_3$ on the concentration of chemisorbed trityl was determined. The catalyst wafer was activated, then NH$_3$ added to the evacuated cell and equilibrated overnight before covering the disc with a solution containing excess Ph$_3$COH. The results are plotted in Fig. 1 and show that the trityl ion concentration is a linear function of the amount of NH$_3$ added. Extrapolation of this plot to zero trityl ion concentration gives a value of 0.21 mmoles/g of NH$_3$, which is identical with the visual endpoint obtained by butylamine titration. The slope of this curve corresponds to the loss of one trityl ion for each 13 NH$_3$ molecules added.

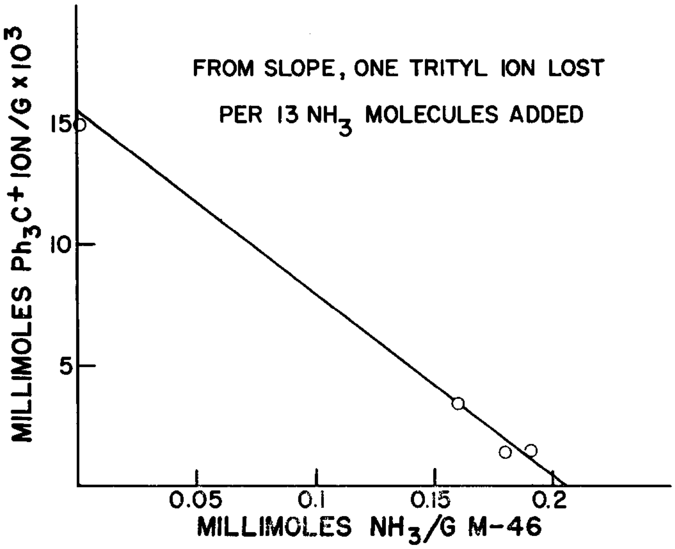

FIG. 1. Effect of ammonia on trityl ion concentration. M-46 silica-alumina.

The data suggest that the number of acid sites is measured by the butylamine or NH$_3$ titer and not by the number of chemisorbed trityl ions. Steric considerations (*5*b) plus electrostatic repulsion between adjacent charged ions would be expected to limit the number of chemisorbed trityl ions. The diameter of the trityl ion is about 14 Å. If 0.21 meq/g of sites were uniformly distributed on the surface of M-46 in a square checkerboard array, the distance between sites would be 14.8 Å; the actual distance is undoubtedly less than this and might be about 5 Å if the picture proposed by Danforth (*9*) is correct. Further, the data do not support the view (*1*) that silica-alumina contains 5 × 10^{12}/cm^2 (0.02 meq/g) strong Lewis sites able to abstract hydride ions from triphenylmethane or react with triphenylmethanol to form chemisorbed trityl ions. The strongest Lewis sites should be the first to chemisorb NH$_3$ and thereby become poisoned after the addition of about 0.02 meq/g of NH$_3$.

Trityl ions adsorbed on the surface of M-46 have a greater affinity for NH$_3$ than the catalyst acid sites. A disc of M-46 containing 1 μmole/g of trityl ion (and about 205 μmole/g of acid sites) was treated with 5.9 μmole/g of NH_3, reducing the trityl ion concentration by 30% to 0.7 μmole/g. On the basis of the number of sites involved, the trityl ion has about an 11 times greater selectivity for reaction with NH_3. The significance of this observation is that basic substances present in too small a concentration to neutralize more than a small fraction of the acid sites present can considerably lower surface carbonium ion concentrations and thereby have a disproportionate effect on the rates of catalytic reactions which involve carbonium ion intermediates.

The above observations are not in agreement with the findings of others (*1*) that approximately one ammonia molecule was required to destroy one carbonium ion. A possible reason for this difference is a discrepancy between the number of trityl ions reported to be present, and the measured absorbance at 405 mμ (*1*). (If one assumes 1 cm^2 as the cross section of the platelet, an absorbance of 1.6 corresponds to only 2.3×10^{11} ions/cm^2 rather than 8×10^{12}.)

Triphenylmethane and perylene as indicators for butylamine titrations. Triphenylmethane and perylene have been employed as indicators in the butylamine titration of acid sites in a manner similar to that described using arylmethanol indicators (*7*). In the case of triphenylmethane, the catalyst was allowed to react several hours after addition of the indicator, if necessary, to permit development of the yellow color characteristic of the adsorbed trityl ion. The butylamine titers of a number of catalysts are given in Table 2 along with data for Ph_3COH as indicator. The following conclusions emerge from these data:

1. The protonic acids H_2SO_4 and $HClO_4$ mounted on silica react with both Ph_3CH and perylene to form the chemisorbed trityl ion and perylene radical ion.

2. M-46 poisoned by quinoline at 300° or by adding NH_3 and evacuation at 200° have no cracking activity, but both poisoned catalysts not only form chemisorbed ions from both Ph_3CH and perylene, but considerable additional base must be added to suppress these reactions.

TABLE 2
ACIDITY TITRATIONS USING TRIPHENYLMETHANE AND PERYLENE AS INDICATORS

Catalyst	*n*-Butylamine titers (meq/g) Ph_3COH	Ph_3CH	Perylene
$SiO_2 + H_2SO_4$	1.35	1.05	—
$SiO_2 + HClO_4$	0.93	0.72	0.72
M-46	0.22	0.21	0.21
M-46 + quinoline, 300°[a]	0.08	0.04	0.08
M-46 + NH_3, evac. 200°[b]	0.16	0.11	0.14
M-46 + 0.1 meq/g NH_3[c]	0.21	0.19	0.14
M-46 + NaAc (0.25 *N*)	0.17	0.14	0.17
S-34	0.14	0.14	0.14
Davison Fluid (25% Al_2O_3)	0.30	0.30	—

[a] Catalyst equilibrated at 300° with excess quinoline, then swept with a stream of purified nitrogen at 300° for 3 hr.

[b] Excess NH_3 added at room temperature, evacuated for 18 hr at 200°.

[c] NH_3 added at room temperature to catalyst in closed evacuated tube, equilibrated for 1 hr at 65°.

3. Addition of 0.1 meq/g of NH_3 to M-46 or base exchange with 0.25 *N* sodium acetate only moderately reduces the butylamine titer.

4. Both the perylene and Ph_3CH endpoints are about the same as, or more often slightly lower than, the Ph_3COH endpoint. Comparison of the perylene titer with a plot of the titers obtained with a series of arylmethanol indicators shows that on a variety of catalysts perylene is oxidized to the radical ion whenever H_R acidity stronger than about 55–60% H_2SO_4 is present.

5. In order to poison the reaction of Ph_3CH with M-46, at least ten molecules of base must be added for each "Lewis site" as measured by the chemisorption of trityl ions.

6. In order to poison the oxidation of perylene by M-46 about 40 molecules of base must be added for each "Lewis site" as measured by the spin concentration of 1.6×10^{12}/cm^2 (*2*b). Therefore, it is un-

likely that a few strong Lewis sites are directly involved as electron acceptors in the formation of perylene radical ions, or that the spin concentration is a measure of the number of such Lewis sites present.

Effect of light on reaction of triphenylmethane with silica-alumina. The rate of trityl ion generation in the reaction of triphenylmethane with silica-alumina has been found to be strongly photocatalyzed both when the reaction takes place *in vacuo* on the dry catalyst and when the catalyst is immersed in a solution of triphenylmethane. The rate of the reaction was followed spectrophotometrically on a disc of M-46 immersed in cyclohexane with the results shown in Fig. 2. Exposure of the disc to room light between absorbance measurements caused a sevenfold increase in the rate of the reaction. In another experiment the disc was exposed for 1 min on each side to the light of a Hanovia mercury arc; this illumination increased the rate by a factor of more than 500 times. While it is conceivable that a hydride abstraction could be photocatalyzed, this light sensitivity strongly suggests the possibility of a free-radical oxidation to triphenylmethanol (or perhaps to triphenylhydroperoxide).

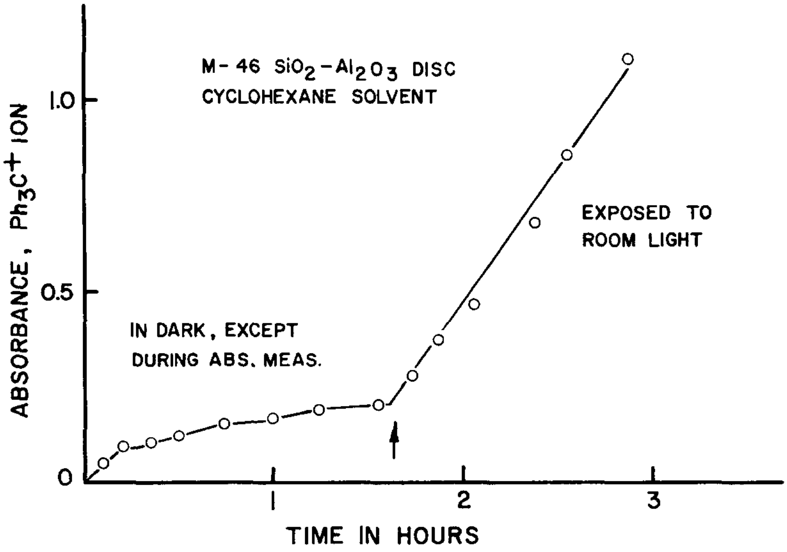

FIG. 2. Effect of light on Ph_3CH reaction.

Reaction of triphenylmethane with SiO_2-HF. A key argument in the case for a hydride abstraction mechanism for the chemisorption of triphenylmethane was the observation (*1*) that silica treated with HF failed to generate any trityl ions while silica treated with BF_3 did chemisorb triphenylmethane. We have found, however, that silica treated with HF does chemisorb triphenylmethane in low concentration provided the water formed in the reaction is pumped off so that it does not poison the remaining acid sites.

In one experiment, 7.5 wt % HF (3.5 mmole/g) was added at room temperature to silica activated by evacuation at 300°, allowed to react for 30 min, then re-evacuated to remove water. A benzene solution of triphenylmethane, degassed by alternate freezing and melting under vacuum, was introduced into the evacuated chamber containing the catalyst. A faint yellow color was observable in about 1 min. The reaction was allowed to proceed overnight, NH_3 added to kill the carbonium ions, and the catalyst extracted with ethanol-benzene. The product was found to contain 4.6×10^{-5} mmole/g of triphenylmethanol.

In a second experiment, silica was evacuated to 10^{-5} mm at 400°C with a boat containing powdered triphenylmethane placed in the cold end of the tube. The Ph_3CH was mixed with the cooled silica, heated to 100° for 30 min, cooled, and anhydrous HF admitted. It was allowed to react, then water removed by reevacuation to 10^{-5} mm. A yellow color was visible after about 3 hr. The reaction was allowed to proceed for 3 days. At that time, benzene was admitted to the evacuated cell and the cell opened. By extraction with EtOH-benzene, 6.8×10^{-5} mmole of Ph_3COH/g of catalyst was recovered.

Silica treated with HF was found to give a strong yellow color when treated with tritolylmethanol but only a weak yellow color with Ph_3COH indicator. This is very significant, for it means that SiO_2-HF has many acid sites which are stronger than 36% H_2SO_4, but very few ($\ll 0.01$ meq/g) as strong as 50% H_2SO_4 and thus able to stabilize a chemisorbed trityl ion on the surface (*7*).

Reaction of triphenylmethane with SiO_2-BF_3. Silica treated with 4 mmole/g of BF_3 was found to have much stronger acidity than SiO_2-HF. Titration with *n*-butylamine using H_R indicators revealed the presence of 0.47 meq/g of acidity stronger than 77% H_2SO_4 and 1.41 meq/g of acidity using Ph_3COH as indicator (*7*).

In daylight, contacting SiO_2-BF_3 with a benzene solution of triphenylmethane results in a strong yellow color in 5–10 min, and Ph_3COH was recovered from a benzene extract of the catalyst. On the other hand, when the reaction is allowed to proceed in the dark, only a trace of color was observed after 3 days, and this was undoubtedly due to brief light exposure during mixing. Thus, if SiO_2-BF_3 is a Lewis acid, it is incapable of removing a hydride ion without the intervention of light.

It is at least open to question whether the reaction products of BF_3 with a hydroxylated silica surface would retain strong Lewis acidity. Coordination of the boron atom with an oxygen atom in a hydroxyl group would eliminate the Lewis acid center and make the hydrogen atom *strongly acidic*. The above results suggest that it is at least unlikely that the trityl ion is formed by a hydride abstraction mechanism.

Oxidation of triphenylmethane to trityl ion in Bronsted acids. Solutions of Bronsted acids which have an H_R acid strength greater than 50% H_2SO_4 catalyze the oxidation of triphenylmethane to the trityl ion in the presence of light. The rate of oxidation in 60–80% H_2SO_4 is relatively slow due to limited solubility. However, when a few crystals of triphenylmethane are added to either 57:32:11 or 44.5:44.5:11 v/v CF_3COOH–AcOH–C_6H_6 and shaken, a perceptible yellow color appears almost immediately, and the solution is a deep yellow within 15 min. No color is observed in a similar experiment kept 4 days in the dark. A 2 *M* solution of trichloroacetic acid in benzene also oxidizes triphenylmethane. Since these latter acids are not oxidizing agents, and there is no possibility of hydride abstraction, it appears that triphenylmethane is oxidized by dissolved molecular oxygen to the carbinol or hydroperoxide which is then protonated to generate the trityl ion. The isolation of a product converted by 80% H_2SO_4 to trityl ion indicates that a similar oxidation reaction takes place on the surface of acid catalysts.

The rate and extent of oxidation in CF_3COOH–AcOH–C_6H_6 mixtures was shown to increase with the acid strength; however, a small amount of triphenylmethane was oxidized to triphenylmethanol even in a 11:78:11 v/v solution whose acid strength ($\sim$36–39% H_2SO_4) is too low to convert any of the Ph_3COH formed to the trityl ion.

Recovery of chemisorbed triphenylmethane as triphenylmethanol. It has been reported (*1*) that upon addition of NH_3, the chemisorbed trityl ions were reconverted to Ph_3CH, although no quantitative data were cited to eliminate the possibility of excess unreacted Ph_3CH. The following experiment was performed to provide such quantitative data.

A disc of M-46 mounted in the spectrophotometer cell was treated for 18–20 hr at 450° in a flowing stream of hydrogen to remove chemisorbed oxygen, evacuated to 10^{-5} mm, and allowed to react with a degassed solution of triphenylmethane in benzene under air-free conditions to a suitable trityl ion concentration. The disc was extracted in an atmosphere of purified nitrogen with benzene refluxing over calcium hydride to remove physically adsorbed and unreacted Ph_3CH. The trityl ion concentration on the disc was measured spectroscopically (under benzene). The benzene was removed by evacuation, anhydrous ammonia in excess added to eliminate the trityl ions, and the disc extracted as before with benzene to remove the organic material. The results of two such experiments were as follows:

Recovery of trityl ion (%)	% Ph_3COH	% Ph_3CH
68	93	7
73	99	1

While complete recovery of the chemisorbed trityl ion was not accomplished, presumably because the extraction was not carried out long enough to remove all of the strongly adsorbed triphenylmethanol from the interior of the disc, the material recovered contained very little triphenylmethane. The small quantity found could result from incomplete extraction of unreacted triphenylmethane from the disc. Since triphenylmethane is much less strongly adsorbed than triphenylmethanol, it is not likely that the unrecovered material contains much of the former.

To eliminate any possibility that the source of the recovered triphenylmethanol could be the reaction of the chemisorbed trityl ions (generated by hydride abstraction) with water in the benzene or with traces of oxygen during the extraction process, powdered M-46 was hydrogenated 18 hr at 450°, evacuated to 10^{-5} mm, cooled, and mixed with 0.05 meq/g of triphenylmethane contained in a boat kept at the cold end of the tube. The catalyst was heated to 60° for 2 hr to promote reaction, then cooled in ice, and excess NH_3 added to eliminate the chemisorbed trityl ions. Ethanol was admitted to desorb the organic material, and the tube then opened and the catalyst filtered out. Measurement of the absorbance in 85% and 96% H_2SO_4 showed that 30–40% of the material recovered was Ph_3COH. In this case, oxygen and water were excluded until after all trityl ions were destroyed by NH_3, yet a rather high yield of Ph_3COH was still obtained. The most probable source is the oxidation of triphenylmethane with either strongly chemisorbed oxygen which is not removed by hydrogen treatment, or with oxygen ions in the silica-alumina lattice which are activated by irradiation. There are more than enough surface oxygen ions available to account for the amount of triphenylmethanol observed.

Reaction of perylene with acid catalysts. Brouwer (*2*) has reported that fluorided γ-alumina, silica-BF_3, and silica-alumina treated with sodium acetate all oxidize perylene to the cation radical, while γ-alumina, silica, and fluorided silica all fail to do so. While sodium acetate drastically reduces the cumene-cracking (*2*) and propylene-polymerization (*10*) activity of silica-alumina it had only a small effect on the oxidation of perylene (*2*, *3*b, *10*). The conclusion has been drawn from these observations that Bronsted sites are responsible for cumene-cracking (*2*b) and polymerization (*10*) activity, while the oxidation of perylene to the cation radical takes place on independent Lewis sites, which are not readily interconvertible with the Bronsted sites (*2*b, *3*b, *10*). We have found that all the catalysts reported by Brouwer (*2*) to oxidize perylene have H_R acidity stronger than 60% H_2SO_4 as measured by arylmethanol indicators; on the other hand, none of the group of catalysts which fail to oxidize perylene has acidity as strong as 55% H_2SO_4. It was also noted above for the group of catalysts in Table 2 that the butylamine titer with perylene as an indicator corresponds to the titer with H_R indicators at an acid strength of 55–60% H_2SO_4.

Fogo (*6*) has observed that when silica-alumina is hydrogenated at 500° to remove adsorbed oxygen and treated with perylene in a high-vacuum system with rigorous exclusion of air, the oxidation of perylene to the cation radical is largely, though not entirely, suppressed. It was concluded that oxygen, not a catalyst Lewis site, is the electron acceptor. We have also confirmed this result using the same apparatus employed in the reaction of SiO_2–HF and hydrogenated M-46 with triphenylmethane, which indicates air was rigorously excluded by our procedure even though sealed tubes equipped with breakseals were not used.

Aalbersberg and co-workers (*11*) find that in the presence of Bronsted acids perylene is oxidized to the cation radical by oxygen and that the equilibrium constant of the reaction

$$M + O_2 \rightleftharpoons M^+ \cdot O_2^-$$

is strongly dependent upon the acid strength of the medium, and decreases from 1000 in CF_3COOH-benzene (89:11 v/v) to 5 in 57:32:11 CF_3COOH–AcOH –C_6H_6, and 0.02 in a 44.5:44.5:11 v/v mixture.

Using arylmethanol indicators, we have estimated the H_R acidity of these latter two acid solutions to be equivalent to approximately 62 and 55–57 wt % H_2SO_4, respectively. Although it was reported (*11*) that the mixture containing 57% trifluoroacetic required a high pressure of oxygen to oxidize the perylene to the cation radical, we observed a slow development of purple color at atmospheric pressure when a few crystals of perylene were shaken with this solution. After standing about 2 hr the absorbance of the solution at 545 mμ (characteristic of the cation radical) was about one and continued to increase slowly. The 44.5:44.5:11 v/v acid mixture did not develop an observable color with perylene in 5 hr.

The above facts point to the important conclusion that in the presence of Bronsted acidity stronger than about 60% H_2SO_4, perylene is converted to the cation radical in low but readily observable concentrations by oxygen acting as an electron acceptor. Further, those solid acid catalysts which exhibit an H_R acidity stronger than 60% H_2SO_4 all develop a purple color on contacting with perylene; those whose H_R acidity is significantly weaker than this do not. Removal of chemisorbed oxygen from silica-alumina by hydrogenation greatly reduces the concentration of the perylene cation radical (*4*, *6*), and within experimental error, the decrease in the number of radical ions formed when the catalyst is reduced corresponds to the number of oxygen molecules removed (*4*). The following conclusions are indicated:

1. Lewis acid sites, such as electron-deficient aluminum atoms, need not be postulated to explain oxidation of perylene by acidic solids.
2. Acidic solids may oxidize perylene by a mechanism similar to that observed by Aalbersberg *et al.* (*11*) in CF_3COOH–AcOH–C_6H_6 solutions, i.e., a combination of strong Bronsted acidity and oxygen as electron acceptor (*6*).
3. The spin concentration observed when perylene is added to an acidic solid will depend both upon the H_R (presumably Bronsted) acid strength and the concentration of electron acceptors such as oxygen.
4. Adding BF_3 to silica is much more effective than adding HF in catalyzing the oxidation of perylene, not because of the fact that it is a Lewis acid but because the H_R acid strength of the treated silica is much greater.

Discussion

The Nature of the Acid Centers

The nature of the active acid centers on a cracking catalyst has been a matter of dispute for some years. The pertinent literature has been reviewed elsewhere (*12*). The results cited above can be construed as additional strong evidence for protonic acidity for reasons discussed below.

The evidence against the hydride abstraction mechanism for the chemisorption of triphenylmethane on silica-alumina may be summarized as follows:

1. Up to 14 moles of base per hypothetical Lewis site are required to poison the chemisorption.
2. Strong protonic acids mounted on silica also chemisorb triphenylmethane.
3. In the presence of oxygen and light,

solutions of strong Bronsted acids oxidize triphenylmethane to the trityl ion.

4. The chemisorbed trityl ions are desorbed by NH_3 almost quantitatively as triphenylmethanol (or possibly the hydroperoxide).

5. Light greatly accelerates the rate of chemisorption.

6. Silica treated with BF_3 does not chemisorb triphenylmethane in the dark, and Ph_3COH is a product of the light reaction.

7. Leftin and Hall (*1*) observed that after desorption of the chemisorbed triphenylmethane by adding water, 5 min pumping at room temperature completely restored the original concentration of trityl ions, whereas the original chemisorption required many days at 100°. Such behavior would be expected only if the triphenylmethane had been converted to triphenylmethanol in a very slow reaction.

The first three of the above arguments, substituting perylene for triphenylmethane, also apply against the hypothesis that perylene is oxidized to the cation radical by these same strong Lewis sites. The oxidation of perylene in a solution of BF_3 also required photocatalysis (*13*). An atom or molecule of oxygen is required for each molecule of perylene oxidized by silica-alumina (*4, 6*). The reactions of triphenylmethane and perylene with silica-alumina are not therefore good evidence for a few strong Lewis sites on this catalyst and can take place on sites inactive for catalytic cracking or polymerization.

The observation that perylene is no longer oxidized to the cation radical when the H_R acidity falls below about 60% H_2SO_4, both in solutions of Bronsted acids and on the catalyst surface, strongly suggests the solid acids are also of the Bronsted type, i.e., arylmethanols are converted to the carbonium ions on acid catalysts by the reaction

$$ROH + H^+ \rightleftharpoons R^+ + H_2O \qquad (1)$$

rather than by

$$ROH + L \rightarrow R^+ + LOH^- \qquad (2)$$

where L is a Lewis acid. Even if Lewis acids on a solid surface gave rise to indicator color changes, the results could not be expressed in terms of a single acidity function such as the H_0 or H_R function, for the relative strengths of Lewis acids depend both on the solvent medium and the base used for reference (*14*). Were the solid acids of Lewis type, it is highly improbable that the perylene endpoint would occur at the same H_R acidity as in the case of liquid Bronsted acids.

Additional reasons for preferring reaction (1) are:

1. In the absence of sites with a demonstrated capability of removing hydride ions, removal of hydroxide ions from arylmethanols by Lewis acids is a less likely mechanism for generation of carbonium ions than reaction with a protonic acid according to Eq. (1).

2. Titrations of acid catalysts with 1,1-diphenylethylene as an indicator suggest that this olefin and arylmethanols are measuring the same type of acidity (*7*). Generation of a carbonium ion from this olefin is more readily explained on the basis of proton addition than Lewis acidity (*3*a).

3. Treatment of alumina with HF greatly increases the acid strength toward H_R indicators, but not toward Hammett indicators (*7*); the fluorided alumina is also able to convert 1,1-diphenylethylene to the carbonium ion.

4. Ion exchange of Linde 13X zeolite with ammonium ions followed by heating to 400° to drive off ammonia would be expected to generate protonic rather than Lewis sites. The resulting catalyst has been found to convert arylmethanols including diphenylmethanol (77% H_2SO_4) to the respective carbonium ions and to have a cumene cracking activity of the same order of magnitude as M-46 (*15*).

The effect on H_R acidity of ion exchange of silica-alumina with alkali and alkaline earth ions is a selective reduction of H_R acid strength without much change in the number of acid sites (*7*). If arylmethanols are converted to their respective carbonium ions by protonic acids, there follows the important and surprising conclusion that ion exchange of silica-alumina with alkali and alkaline earth ions does not eliminate the protonic acidity but reduces the acid strength to a degree depending on the amount and identity of the exchanging ion. Bases such as quinoline and ammonia have an analogous effect. The poisoning of activity for hydrocarbon conversion reactions means that only very strong protonic acids have high activity for these carbonium ion reactions.

The assumption of independent Lewis and protonic active sites on silica-alumina (*2*b, *3*b, *10*) need not be invoked to explain the different effect of the Na^+ ion on perylene oxidation as compared to cumene cracking or propylene polymerization. Both types of reaction can be catalyzed by protonic sites, but perylene oxidation is initiated at an acidity of 60% H_2SO_4 while cumene cracking requires much stronger acidity, in the range of 77–88% H_2SO_4 (*7*, *15*). The sodium-treated M-46 in Table 2 has lost all acidity stronger than 88% H_2SO_4 but still retains considerable acidity stronger than 77% H_2SO_4. It has been found (*7*) that all cracking catalysts have H_R acidity stronger than 77% H_2SO_4, but aluminas and chlorided aluminas do not. Fluorided alumina does have acidity of this strength and is known to possess considerable cracking and isomerization activity.

The protonic or Bronsted-like sites must be more sophisticated than a simple proton which can be replaced by ion exchange with complete elimination of acidity, and additional work is needed to elucidate their nature. The fact that these sites do not behave as simple free protons may perhaps in part explain why infrared frequencies characteristic of the NH_4^+ ion are not prominent when NH_3 is chemisorbed on silica-alumina (*16*) or fluorided alumina (*17*).

Hydrogenation of silica-alumina at 450–500°C appears to remove most, but not all, of the chemisorbed oxygen capable of oxidizing perylene, but does not greatly affect the oxidation of triphenylmethane. One possibility is that there is an equilibrium between the surface oxygen concentration and the perylene cation radicals similar to that reported in solution (*11*), and that if triphenylmethane is the more easily oxidized, a lower concentration of oxygen on the surface would be effective in oxidizing triphenylmethane than in the case of perylene. That triphenylmethane is indeed more readily oxidized is suggested by the observation that a 57:32:11 v/v mixture of CF_3COOH–$AcOH$–C_6H_6 is required for significant oxidation of perylene at atmospheric pressure while some oxidation of triphenylmethane took place with a 11:78:11 v/v mixture. Alternatively, if triphenylmethane is more easily oxidized, there might be more than one type of available surface oxygen capable of oxidizing Ph_3CH, only one of which is capable of oxidizing perylene. This latter type of site might be more susceptible to hydrogen treatment than the other kind or kinds of surface oxygen. The role of oxygen in these reactions needs further study; it should be determined whether hydrogenation affects the ability of HF- or BF_3-treated silica to oxidize triphenylmethane.

Very recently, Terenin *et al.* (*18*) studied the reaction of perylene and other polynuclear aromatics with silica-alumina and its component oxides. Their experimental observations are consistent with our interpretation of the mode of formation of the perylene radical ion on silica-alumina although they claim to have "disproved the participation of oxygen traces in this phenomenon." These authors appear to have considered only physically adsorbed oxygen or oxygen dissolved in organic solvents, and not oxygen so strongly bound that it can only be removed by hydrogenation at >450°C. The failure of SiO_2 and Al_2O_3 gels to generate perylene radical ions can be simply explained by the absence of Bronsted acidity of the requisite strength.

Finally, we wish to briefly suggest some implications of these studies in regard to reactions during catalytic cracking. Catalytic cracking is generally considered to proceed via a carbonium ion mechanism. The chief routes which have been proposed for formation of the initial carbonium ions are removal of a hydride ion from a saturated hydrocarbon, or the addition of a proton to an olefin or aromatic hydrocarbon. In order to avoid postulating hydride ion removal by the catalyst, it has been suggested that saturates first undergo some thermal cracking to give olefins, which then become carbonium ions by simple proton addition (*19*). Our results on the oxidation of Ph_3CH suggest an alternate mode of initiation of paraffin cracking, namely, oxidation to an alcohol or hydroperoxide followed by protonation to produce the carbonium ion and water or hydrogen peroxide. Oxygen on the surface of a cracking catalyst may also contribute significantly to coke formation by generating radical ions from polynuclear aromatic hydrocarbons, which ions condense further in a series of reactions leading to coke.

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