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A Comparative Spectrophotometric Study of the Adsorption of Triphenylmethane and Perylene on Silica-Alumina*

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Studies were made of the effects of pretreatment and of base exchange of silica-alumina on carbonium ion and cation ion radical formation. Pretreatment of silica-alumina with H_2 at 550° nearly eliminated radical ion formation; carbonium ion formation was unaffected. The surface density of carbonium ions was not a function of surface area; radical ion formation increased with area, but the dependence was not simple. Base exchange decidedly lowered the ability of the catalyst to form carbonium ions and, at high sodium concentrations (2.9%), radical ions; at lower concentrations (1.0% Na^+), the effect on the latter was not appreciable. Triphenylcarbonium ions formed in the dark, but the reaction was photocatalyzed. Extinction coefficients were determined for the carbonium ion and the radical ion. Additional bands appeared in the optical spectrum when either catalyst–substrate system was heated above 100°, indicating secondary reaction. It was shown that equilibrium generally was not obtained, i.e., that the reactions were kinetically controlled. Hence, these reagents should not be used to measure site densities. The results suggest that different kinds of sites or different processes may be involved with the two substrates; they are consistent with the idea that chemisorbed oxygen is involved in the formation of radical ions but is not essential for carbonium ions.

INTRODUCTION

During the past decade, spectroscopy has provided powerful new tools for studies of chemisorption and catalysis. The infrared region was first to be successfully exploited and is now being intensively investigated (*1*, *2*). Applications of optical and EPR spectroscopy are more difficult and so far have not been widely used although their great potential is already apparent (*2*). Electronic spectra have revealed that radical ions are formed from polynuclear aromatic hydrocarbons and arylamines on silica-alumina cracking catalysts (*3*, *4*) and acid clays (*5*), and that triphenylmethane, 1,1-diphenylethane, and cumene are converted to the corresponding carbonium ions with the loss of the tertiary hydride ion to the catalyst (*6*). Several unstable intermediates, including carbonium ions, have been characterized in studies of chemisorbed phenylated olefins (*7–9*). EPR spectroscopy has been applied even more recently (*3*, *4*, *9–15*), but its usefulness in studies of paramagnetic species, in conjunction with optical spectroscopy, has already been demonstrated; this work has dealt with polynuclear aromatic hydrocarbons, phenylated amines, and olefins.

In view of the limited amount of data available, it is not surprising that certain inconsistencies have appeared and that sometimes the data have been unduly extrapolated to reach questionable conclusions. While it is generally supposed (*3*, *4*, *10*, *16*) that radical ions are generated from perylene on the same sites that oxidize triphenylmethane, treatment of the catalyst with hydrogen strongly suppressed radical ion formation (*3*, *4*, *12*, *17*) but left the carbonium ion concentration unaltered (*3*, *6*,

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* For a discussion of this paper see Letters to the Editors, p. 390.

17). It has been claimed (*4*, *10*, *16*) that base exchange of silica-alumina with sodium acetate does not materially lower cation radical or, by implication, carbonium ion concentration, yet no data are available defining the effects of base exchange on the chemisorption of triphenylmethane. More recently, Flockhart and Pink (*14*a) have shown that under some conditions base exchange does indeed lower radical ion concentration. Rooney and Pink reported that the spin density of perylene radical ions was decreased by O_2 (*10*), in contradiction to our own results (*3*), while Flockhart and Pink (*14*b) claimed it was not. Sheppard, Rooney, and Kemball (*16*) found that the activity of silica-alumina for the polymerization of propylene was completely eliminated by base exchange, but noted (*10*) that the ability to form perylene radical ions was not repressed; moreover, the chemisorption of perylene had little effect on the polymerization rate. They interpreted these results by assuming that radical ions form on Lewis acid sites while polymerization is effected by Bronsted sites (the latter were supposed to be eliminated by base exchange while the former remained unaffected). Brouwer (*4*) reached similar conclusions concerning cumene dealkylation. Hodgson and Raley (*15*), however, found that propylene alkylates the chemisorbed ion radicals rather than polymerizing. The present work shows that base exchange adversely affects the catalyst's ability to generate both radical ions and carbonium ions, particularly above 100° where the polymerization (*16*) and dealkylation (*4*) experiments were carried out.

The effects of base exchange and pretreatment of the catalyst on its ability to form perylene radical ions and triphenylcarbonium ions have been systematically investigated as a function of time, temperature, and substrate concentration. Extinction coefficients for these species were determined and some of the uncertainties mentioned above have been resolved. The behavior of these catalyst–substrate systems has been better defined. A more comprehensive understanding of these interactions is essential to any detailed molecular description of hydrocarbon catalysis over acidic surfaces.

EXPERIMENTAL

Catalysts. American Cyanamid Co. Aerocat silica-alumina and catalysts prepared from it by base exchange with solutions of NaAc were used. The latter were found by flame photometry (*18*) to contain 0.8%, 1.0%, 1.5% and 2.9% Na^+. The parent catalyst was 22% Al_2O_3 and had a BET surface area of 433 m^2/g when pretreated but unpressed, as in our EPR work.

Reagents. The cyclohexane (Fisher spectrograde) solvent was vacuum-transferred from sodium mirrors. Blank experiments with catalyst plates showed no absorption over the accessible region of the spectrum.

The perylene (Aldrich Chemical Co.) had only the expected optical bands (*19–21*) when dissolved in cyclohexane and in 96% H_2SO_4; it was used without further purification. Triphenylmethane yielded similar results (*22*, *23*) after repeated recrystallization from ethanol; this material had a melting point of 92.5° to 93°, lit. 91–93° (*24*). It was free of triphenylcarbinol as it did not immediately discolor 75% H_2SO_4 (*17*); no impurities appeared in the GLC chromatogram.

Triphenylcarbinol (Fisher Scientific Co.) was recrystallized several times from ethanol. Vapor-phase chromatography revealed no impurities nor did spectra taken in cyclohexane and sulfuric acid (*23*, *25*). An extinction coefficient of 3.95×10^4, lit. 3.84×10^4 (*26*), for the triphenylcarbonium ion was determined in the latter. A melting point of 164–164.5° was found, lit. 162–162.5° (*27*).

Eastman pyrene was used as received; it had no impurities which were detectable by GLC; its melting point was 150°, lit. 149–150° (*28*). Eastman thianthrene melted at 158–159° after three recrystallizations from ethanol, lit. 159° (*28*).

Oxygen for pretreatment was passed through anhydrous $Mg(ClO_4)_2$; that used to contact catalyst–substrate systems was also distilled from liquid oxygen to ensure removal of the last traces of water. Hydrogen was passed through a train consisting of a deoxo purifier, $Mg(ClO_4)_2$, Pd on asbestos at 360°, more $Mg(ClO_4)_2$ and a charcoal-filled trap thermostated at $-195°$.

Equipment and Procedures. These were the same as used previously (*3*, *6*); conventional high-vacuum techniques were employed. Solutions containing the required amounts of substrate were degassed by repeated freeze–pump–thaw–freeze (8 to 10 times) techniques and sealed in vials fitted with break-off seals. These vessels were attached to the quartz optical cells through graded seals (*3*). Catalyst platelets were mounted on quartz racks which positioned them in the optical cells. After pretreatment, the cells were sealed *in vacuo* by "pulling-off" the connections with a torch.

The catalyst plates were prepared by pressing powder (*7*) at 50 tons/sq inch. This pressure was chosen as optimum after a brief preliminary study revealed that the specific surface area decreased and the transparency increased with pressure. Due to the high extinction coefficients of the ions formed, lower area, more transparent plates were advantageous. Most plates had specific surface areas within 25% of 216 m^2/g, although the values ranged from 170 to 300 m^2/g. Steam sintering yielded plates of still lower surface area. Surface areas were determined using krypton adsorption.

In some experiments, the catalysts were kept in the dark by wrapping the entire tubes in aluminum foil. The wrapping could be removed to test for photochemical effects. Effects of temperature were investigated by heating the sealed tubes in ovens. The sample tubes were fitted with auxiliary break-off seals so that they could be resealed to the vacuum system when required.

Absorption spectra were determined using a Cary Model 14 spectrophotometer, about 15 min being required to scan the region of interest. Degassed solutions (~5 cc) of the substrates were brought into contact with the evacuated catalysts (~40 mg) by rupture of the break-off seal. Solvent was distilled away by immersing the solvent vial in ice (30 min to remove bulk liquid) and in liquid nitrogen (90 min to ensure complete removal from catalyst pores). The vial was then removed with a torch. Solution concentrations were adjusted so that 5 cc contained sufficient substrate (2×10^{-3} or 2 mmole/g cat.) to provide surface coverages of $\sim 10^{11}$ or $\sim 10^{14}/cm^2$ if adsorption were quantitative, which it was not. The two sets of data were intended to approximate (a) coverage of a fraction of the Lewis acidity (*6*), and (b) conditions of surface saturation. In some experiments, triphenylmethane was transferred, without solvent, by heating the entire evacuated vessel. In these cases, weighed amounts of purified substrate were melted and degassed in the solvent vial.

Absorbance values were converted to surface coverages of the absorbing species by means of the equation

$$\sigma = ANL \times 10^{-3}/EWS \qquad (1)$$

where σ is the surface concentration (ions cm^{-2}); A, the absorbance; N, Avogadro's number; L, the geometric area of the catalyst pellet (cm^2); E, the extinction coefficient of the absorbing ion (liter $mole^{-1}$ cm^{-1}); W, the weight of the pellet (g); and S, the internal surface area of the pellet (cm^2 g^{-1}).

Similar techniques were used in EPR experiments with perylene, pyrene, and thianthrene, where the catalyst was in the unpressed, finely ground form. Packing of the powder in the EPR probe tube limited the accuracy to ±20%. Hence, averaged values are quoted.

Three conditions of pretreatment were examined. In these, all steps were carried out at 540° ± 10°. When the catalyst was treated overnight in flowing oxygen and then evacuated for 7 hr, the catalyst was said to have had the *standard pretreatment.* When the standard pretreatment was followed by an overnight reduction in flowing H_2 and another 7-hr evacuation, the catalyst was *reduced.* If, following the overnight treatment in O_2, the catalyst was allowed to cool slowly to room temperature in an atmosphere of O_2 before evacuation (overnight), the catalyst was *O_2-cooled.* Base-exchanged catalysts were given only the standard pretreatment.

RESULTS

Carbonium Ion Formation

Triphenylcarbonium ion formation on silica-alumina, as characterized by a double-peaked absorption band in the 410–435 mμ region of the spectrum (*6*), was examined under conditions (1.8 mmole/g cat.) where

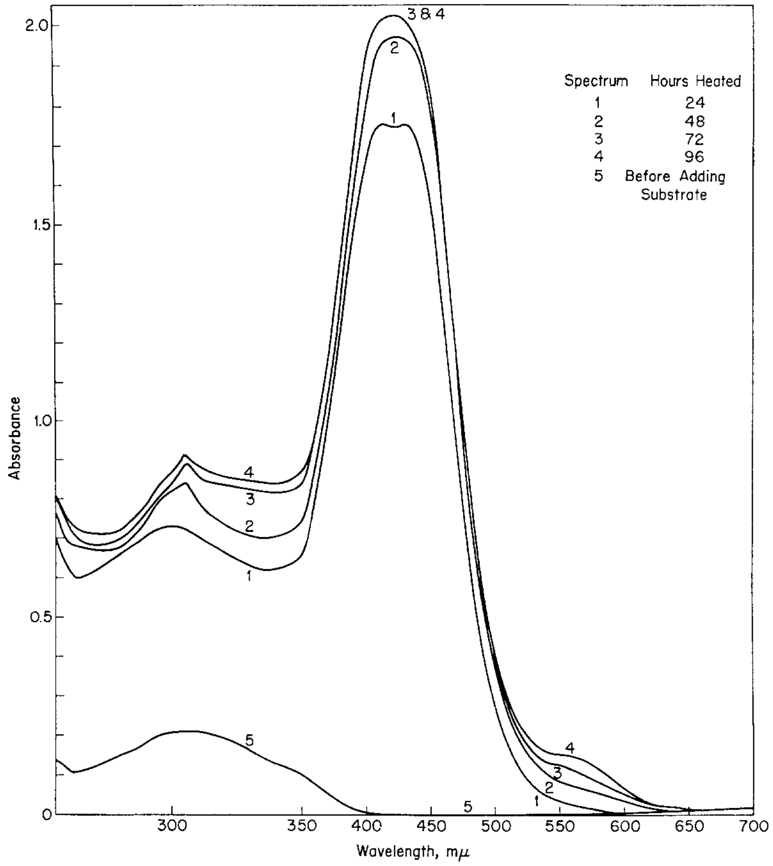


FIG. 1. Spectra from triphenylmethane on silica-alumina (AAA) at 100°C; standard heat treatment; 1.8 mmole ϕ_3CH/g.

excess reagent remained on the walls of the sample tube. Figure 1 presents results of an experiment in which triphenylmethane was vacuum-transferred to the catalyst in the dark at 100°. Maximum concentrations of carbonium ions could be generated at this temperature without the complications which arise from secondary reactions. Moreover, the vapor pressure of triphenylmethane was sufficient at 100° so that the reaction was not seriously limited by diffusion. Absorbance in the region of 420 mμ increased between the 24th and 48th hr but changed slightly thereafter. This is shown in Fig. 1 for a typical sample and in Fig. 2 for a number of samples. Readings were not taken during the first few hours because the initial adsorption was not uniform. As reagent diffused through the sample cell, the pellets first turned yellow at their tops; the coloration gradually moved downward and finally became uniform. A time-invariant state was reached much more quickly in these experiments than in those of Leftin and Hall (*6*) in which a different catalyst was studied.

Absorbance values after 96 hr, taken from Fig. 2, are plotted in Fig. 3 as a function of the specific surface areas of the various catalyst plates. These data indicate that carbonium ion formation is independent of catalyst pretreatment, but is lowered by base exchange at both the 1.0% and 2.9% Na^+ levels.

The slope of Fig. 3 [A/S of Eq. (1)] is proportional to the surface concentration of carbonium ions. To evaluate this quantity, however, the extinction coefficient, E, had to be determined. If a spectrum is taken and the assumption made that *all* the adsorbed substrate is in the form of the carbonium

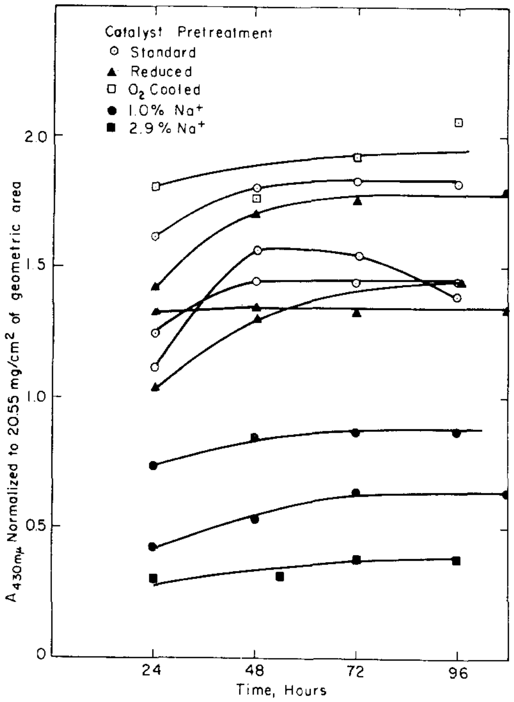


FIG. 2. Carbonium ion formation from triphenylmethane on silica-alumina at 100°C; available reagent, 1.8 mmole/g cat.

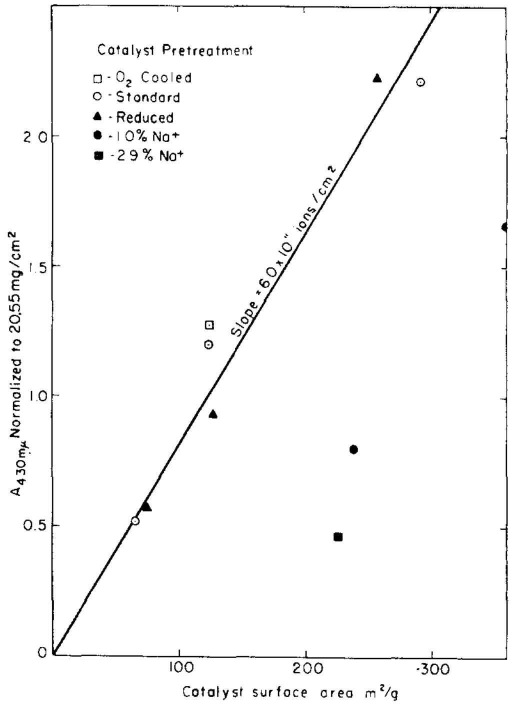


FIG. 3. Carbonium ion concentration as a function of surface area; available reagent, 1.8 mmole/g cat.

ion, the extinction coefficient calculated from Eq. (1) is equal to or less than its true value. Thus, the highest value derived from a series of measurements is most nearly correct.

The following experiment yielded a lower limit of the extinction coefficient of chemisorbed triphenylcarbonium ion. Two aliquots containing 1.53×10^{-5} g of trityl chloride in 5 cc of cyclohexane were degassed in compartments attached to an optical cell containing a catalyst platelet. The catalyst weighed 83.8 mg and was 2.3 cm² in cross section; it had a surface area of 158 m²/g. When contacted with the first aliquot, the absorbance at 430 mμ was 0.57 after 24 hr. The apparent extinction coefficient calculated from this result was 2.5×10^4 liter mole^{-1} cm^{-1}. When solvent was removed by freezing it back into the reagent compartment, the absorbance immediately increased to a final value of 0.97, corresponding to an extinction coefficient of 4.25×10^4. This is, within experimental error, the sulfuric acid value (3.95×10^4). When the solvent was poured back onto the platelet, the absorbance fell to 0.43, demonstrating that either the carbonium ion concentration or the extinction coefficient was lower in the presence of solvent. When the contents of the second compartment were poured onto the catalyst, the absorbance slowly increased to 0.97; this yielded an extinction coefficient of 2.2×10^4 in fair agreement with the data from the first compartment. When the solvent was removed, the absorbance increased to 1.78, corresponding to $E = 4.08 \times 10^4$. Again, pouring back the solvent reduced the absorbance. The solution was then *poured* into its compartment where it was frozen and removed with a torch. The contents of this solution, on analysis with H_2SO_4, were sufficient to provide an absorbance of only 0.08 were it adsorbed on the pellet. Thus, the decrease in absorbance in the presence of solvent was not due to desorption of substrate from the platelet. Since the values of the extinction coefficient found for the dry platelet were in excellent

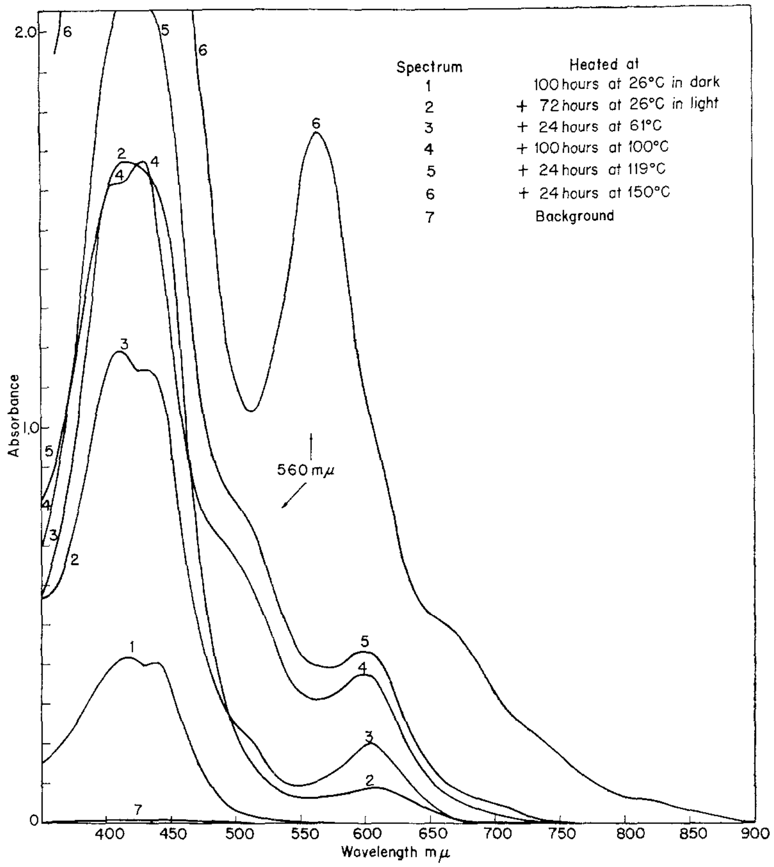


FIG. 4. Spectra from triphenylmethane on reduced silica-alumina (AAA) catalyst; available reagent 1.8 mmole/g; surface area, 214 m^2/g.

agreement with those for sulfuric acid solutions, a value of 4.0 × 10^4 liter mole^{-1} cm^{-1} was used in the calculations made herein.

Similar experiments with triphenylcarbinol, in agreement with Hirschler (*17*), yielded values about 25% to 35% lower. It will be shown later that the catalyst–triphenylcarbinol system is less stable than the catalyst–trityl chloride system. Hence, the lower values reflect substrate decomposition.

The slope of the line in Fig. 3 corresponds to a triphenylcarbonium ion concentration of 6.0 × 10^{11} ions/cm^2. This value is considerably less than that (5 × 10^{12}/cm^2) reported by Leftin and Hall (*6*). In their work, the chemisorption of trityl halides and triphenylcarbinol was studied by a procedure which involved extraction of adsorbed reagent (*6*). It is now evident that this technique was satisfactory for these substrates, but not for triphenylmethane. That this is the case is indicated as follows: When triphenylcarbinol was adsorbed at room temperature, the plates became so deeply colored that spectra could not be taken unless the available reagent was severely limited. When a sufficiently low concentration was used so that a good spectrum could be obtained, over 65% of the available reagent formed carbonium ions at room temperature. The indications are, therefore, that the higher values found (*6*) for the trityl derivatives are correct, but that carbonium ion formation from triphenylmethane is very much less.

The influence of light, heat, and catalyst pretreatment were assessed in a second series of experiments. A high concentration of reagent (1.8 mmole/g cat.) was transferred in solvent, which was subsequently removed.

Figure 4 characterizes the triphenylmethane–catalyst system. Although a reduced catalyst is shown, the spectra of standard or O_2-treated catalysts were qualitatively similar. This is reflected in the data of Fig. 5.

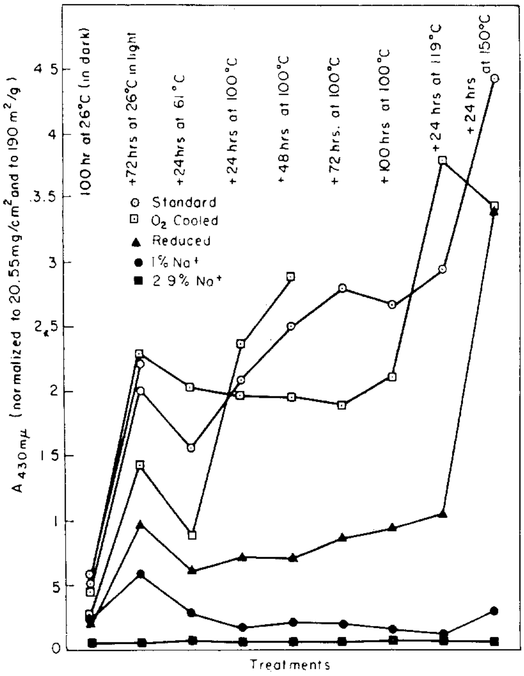


FIG. 5. Effect of light and heat on carbonium ion formation; available reagent, 1.8 mmole/g.

The catalyst plate to which reagent was to be added was balanced against a similar plate in the reference compartment of the spectrometer (Fig. 4, Curve 7). Curve 1 was recorded after reagent had been in contact with the catalyst for 100 hr in the dark. The absorption at about 420 mμ increased considerably on exposure to light (fluorescent lamp—Curve 2). A band, which grew on heating, also formed at 600 mμ. This band was observed only on samples which had been exposed to light. On heating to 61° (Curve 3), the carbonium ion concentration decreased as the 600-mμ band increased. If triphenylcarbinol (or peroxide) is produced by photolysis (*17*), this may reflect the greater instability of carbonium ions formed from this reagent (compare with Fig. 1). Above 100°, both bands increased and a shoulder developed above 500 mμ which became a band at 560 mμ. The latter band, of unknown origin, was weakly in evidence in the earlier work of Leftin and Hall (*6*).

Effects of temperature and of light from a fluorescent desk lamp on triphenylcarbonium ion formation are described in Fig. 5. Absorbance values greater than about 2.5 were derived by extrapolation. Values for samples heated in the dark at 100° were similar in magnitude to those for samples exposed to light at room temperature (compare Figs. 3 and 5), but the 500 to 700-mμ region of the spectra was markedly different (Figs. 1 and 4). Base exchange strongly suppressed triphenylcarbonium ion formation, especially at higher temperatures. Absorption at 600 mμ was also suppressed on the sample containing 1.0% Na and was eliminated on that containing 2.9%. No absorption at 560 mμ was found for either sample.

The lower triphenylcarbonium ion concentration for the reduced catalyst of Fig. 5 may be related to the fact that these samples had been exposed to light before heating. Reduction had no apparent effect in experiments run in the dark at 100° (Fig. 3). Exposing standard-treated and oxygen-cooled catalysts to light enhanced carbonium ion formation to a greater extent than with the reduced catalyst. Heating to 61° following photolysis generally lowered the carbonium ion concentration (Figs. 4 and 5). Following heating at 150°, a concentration of 1.7×10^{12} ions/cm² was calculated for the sample given the standard pretreatment, approaching the higher triphenylcarbinol value (*6*).

Small additions of H_2O (1.5×10^{13}/cm²) to catalyst–substrate systems containing triphenylmethane in large or small amounts did not alter the spectra, while, in agreement with earlier work (*6*), larger amounts bleached the color. Triphenylmethane was readily oxidized to the triphenylcarbonium ion when O_2 was added to the catalyst–substrate system in the light at room temperature, but the absorbance at 560 and 600 mμ was unaffected. Evidently, these latter species stem from decomposition as distinguished from oxidation. When oxygen at 26 Torr was added to a sample containing excess triphenylmethane, the absorbance at 420 mμ immediately increased and continued to do so more slowly. At the end of 100 hr, the absorbance was nearly as great as that observed when an equivalent amount of triphenylcarbinol contacted the catalyst, i.e., a carbonium ion concentration of the order of $10^{12}/cm^2$ was formed. The mechanism of this oxidation is a matter of speculation, but may be analogous to that occurring in the Etard reaction (*29*) which involves free radicals. In the dark at 100°, 300 Torr of O_2 had no effect.

Adsorption of triphenylcarbinol on catalyst plates that had been given the standard heat treatment was examined at low reagent concentrations (3.6×10^{-3} mmole/g). Solvent was used to transfer substrate to the catalyst, but was then removed. In contrast to the triphenylmethane results, a major portion of the maximum carbonium ion formation was effected at room temperature in the dark (Fig. 6). Only a small increase in carbonium ion concentration was noted on exposing the sample to the fluorescent light; this increase may have been due to warming the sample and not to a photochemical effect. When a sample which had been kept in the dark for 120 hr was exposed to a fluorescent lamp for only 2 hr and finally to a powerful mercury lamp for an additional 1.5 hr, no increase in carbonium ion concentration was noted.

On heating to 61° (Fig. 6), further dissociation took place and the results now indicated that 33% of the reagent in the sample tube had been converted to the carbonium ion. Heating to higher temperatures resulted in a decrease in triphenylcarbonium ion concentration. Unlike the behavior of triphenylmethane, triphenylcarbinol gave high absorption in the ultraviolet region of the spectrum which tailed-off into the visible. This assumed greater importance with increasing temperature and at the higher temperatures severely overlapped the bands due to the triphenylcarbonium ion (Fig. 6). Absorption throughout the ultraviolet may be associated with decomposition products. Evidently, decomposition did not proceed via the 600-mμ species, as with triphenylmethane. Comparison of Curves 4 and 5 of Fig. 6 with the corresponding data in Figs. 1 and 4 illustrates the greater instability of the triphenylcarbinol–catalyst system. Substantial further evidence of this behavior will be detailed in a later paper.

Results of a similar triphenylcarbinol experiment using one-third as much substrate yielded analogous results except that the triphenylcarbonium ion concentration decreased to nearly zero on heating to 119°. Similar effects were also noted in the triphenylmethane system in that proportionately greater decomposition of triphenylmethane took place at extremely low coverages.

Radical Ion Formation

The perylene–catalyst system was examined as a function of the variables studied in the triphenylmethane system to ascertain their influence on radical ion formation, and to compare these effects with those found for carbonium ion formation. The perylene radical ion has a strong optical band at 535 mμ (*19–21*); absorbance at this wavelength provides a convenient measure of its concentration (*3*). Behavior of the perylene system is considerably more complicated than that of the triphenylmethane system because of its greater instability. Triphenylmethane was more extensively adsorbed by the catalyst than was perylene, e.g., about 33% of the reagent was removed from a cyclohexane solution (1.5 mg in 10 cc) by 40 mg of catalyst in 22 hr. Only negligible quantities of perylene were adsorbed under these conditions.

The spectra of Fig. 7 exemplify the changes which occur on heating the perylene-silica-alumina system. Curve 1 was recorded after 48 hr at room temperature when a catalyst, pretreated in the standard way, was contacted with a nominal perylene concentration of 2.5×10^{-3} mmole/g cat. Curves 2–4 resulted when the catalyst was heated at successively higher temperatures. Curve 5 corresponds to matched plates before substrate was added. The bands of nearly equal intensity at 408 and 430 mμ and the shoulder at 380 mμ are associated with physically adsorbed perylene. It is evident that con-

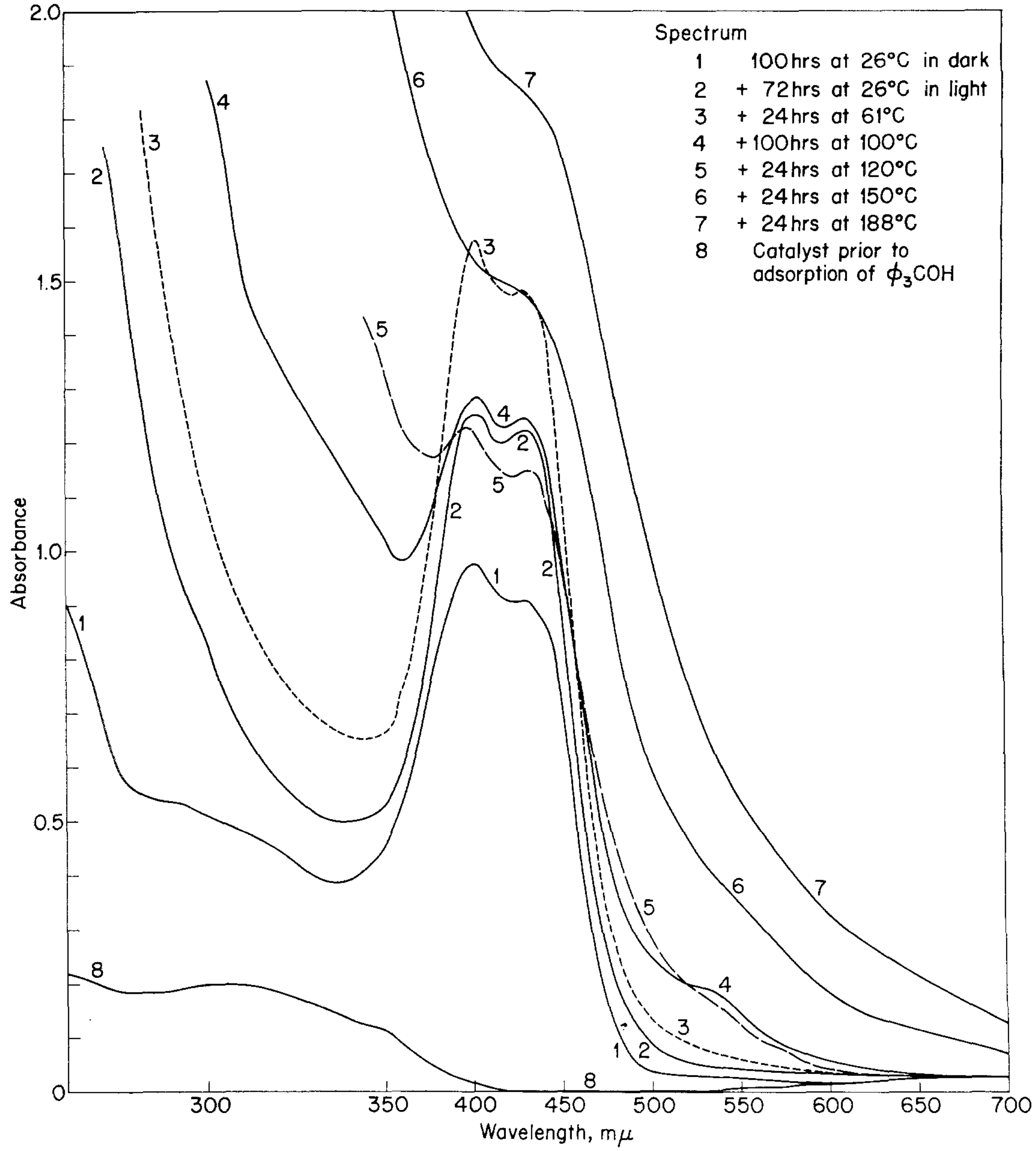


FIG. 6. Spectra from triphenylcarbinol on silica-alumina catalyst (AAA); standard pretreatment; 3.6 × 10^{-3} mmole ϕ_3COH/g, 230 m²/g.

siderable substrate was transported from the glass walls to the catalyst surface on heating to 61°. The weak band at 735 mμ probably stems from the radical ion since, in solutions, it has been shown to appear in a constant absorbance ratio with the 535-mμ band (*19–21*). In the present work with catalysts, the ratio of intensities of these bands was also constant, but higher (0.2) than for solutions (0.1). After heating to 119° (Curve 3), a band appeared at 605 mμ while that at 535 mμ increased in intensity. The band at 605 mμ increased further when the system was heated to 150° (Curve 4), while that at 535 mμ decreased sharply. Brouwer (*4*) noted these same bands in

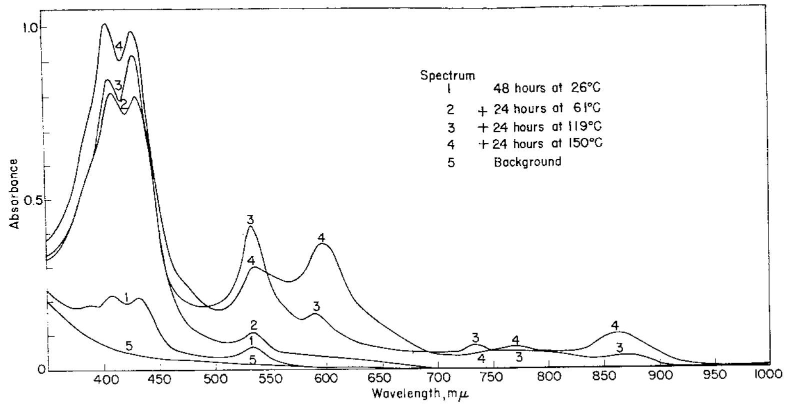


FIG. 7. Spectra from perylene adsorbed on silica-alumina; standard heat treatment; 2.5×10^{-3} mmole of perylene/g; 189 m^2/g.

spectra of perylene on silica-alumina and assigned the 605-mμ band to a proton complex (carbonium ion) because of its coincidence with the spectrum of perylene dissolved in air-free HF (*19*, *30*). There are, however, reasons to doubt this assignment. Exposure of the catalyst to air (or O_2), or irradiation or both, failed to convert the 605-mμ species into the radical ion. In the solution work of Aalbersberg *et al.* (*19*), the proton complex (or Lewis acid complex) of perylene was found to be quite unstable and readily converted into the radical ion under these conditions. The 605-mμ band in liquid HF was accompanied by bands at 480 mμ and at 410 mμ. The latter bands were formed in the present work, but only when the solvent was dried over molecular sieves rather than metallic sodium. Moreover, the 605-mμ band appeared on base-exchanged catalysts under conditions where formation of a proton complex would be unlikely (see Fig. 12). It would appear, therefore, that Brouwer's assignment of the 605-mμ band (and its relationship to those at 480 mμ and 410 mμ) is questionable. If it were valid, our data would indicate that the perylenium ion was formed from the radical ion on heating to 120°. This process requires the addition of a *hydrogen atom* to the radical ion.

Absorption at 605 mμ was concentration-dependent, suggesting that a dimerization may have been taking place. No effect of pretreatment was noted except that the formation of this species was strongly suppressed by 2.9% Na^+. The available data are consistent with the possibility that it is a radical ion of a self-condensation product of perylene.

Spectra recorded following heating of a standard pretreated sample on which excess perylene (1.8 mmole/g) was adsorbed are shown in Fig. 8. Absorption at 535 mμ decreased with increasing temperature above room temperature. On heating to 119°, bands at 605, 770, and 880 mμ appeared. The latter band increased greatly with increasing temperature. These bands are also in evidence in the spectra of Fig. 7. Brouwer (*4*) attributed the 770-mμ band to a charge-transfer complex which he stated was expected in this region. The 880-mμ band was very concentration-dependent, suggesting that it is due to a species composed of several perylene molecules.

The effects of reducing the catalyst with H_2 can be appreciated from Fig. 9. The principal differences between these spectra and those of catalysts treated in the standard way lie in the negligible absorption at 535 mμ and in the formation of a broad band which extends from about 700 mμ to the region of 400 mμ. Negligible amounts of radical ion were formed on reduced catalysts, even with a large excess of perylene, when high-vacuum conditions were maintained. However, the ion formed spontaneously when O_2 (or air) was admitted, as shown in Fig. 10. This process was nearly instantaneous and not reversible.

Addition of oxygen to the perylene–

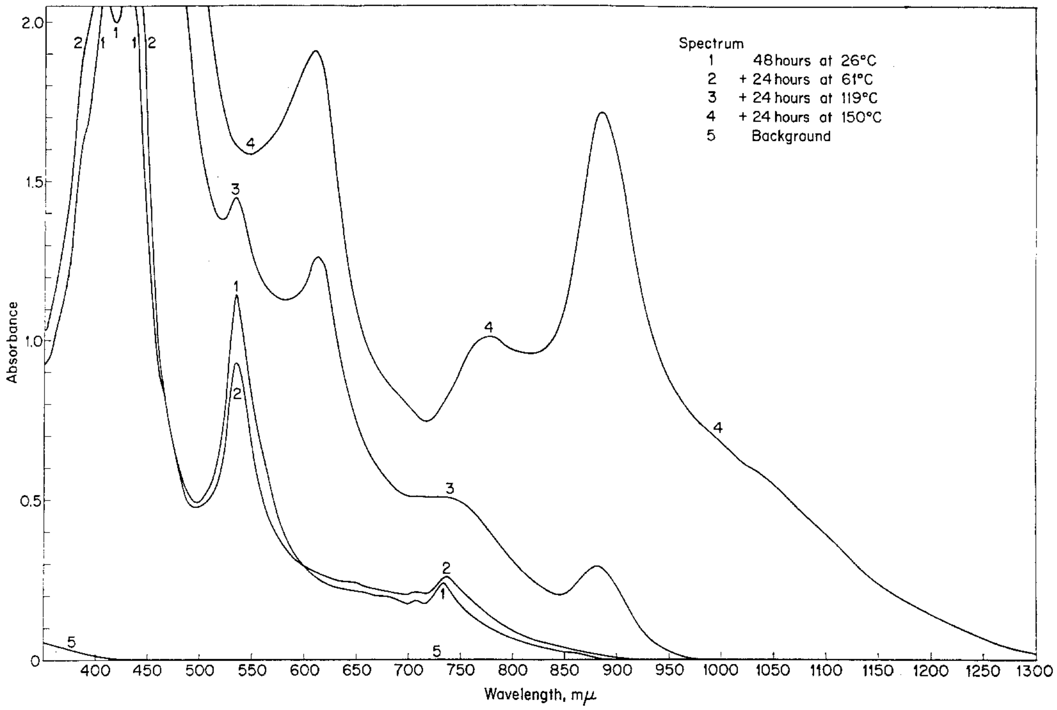


FIG. 8. Spectra from perylene adsorbed on silica-alumina; standard heat treatment; 1.8 mmole of perylene/g; 270 m²/g.

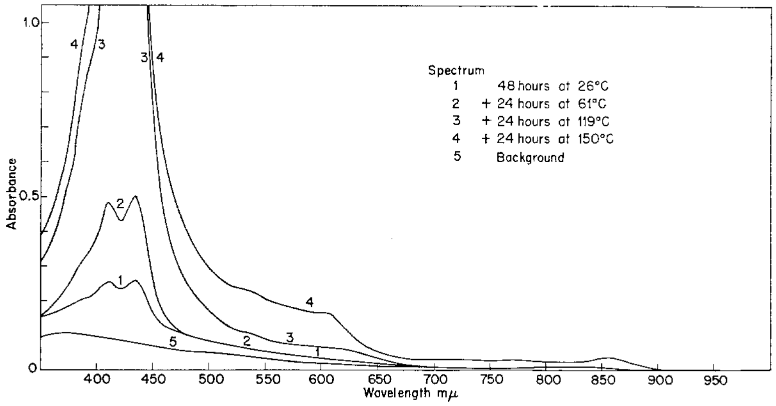


FIG. 9. Spectra from perylene adsorbed on a reduced silca-alumina catalyst; available reagent, 2.5 × 10^{-3} mmole/g.

catalyst system in the presence of solvent effected a large increase in radical ion concentration, just as it did with dry catalysts. Over half of the adsorbed perylene was converted. This was found for all catalyst pretreatments as well as for base-exchanged catalysts. Oxygen equivalent to coverages of 7 × 10^{13} molecules/cm² of catalyst surface was nearly as effective as oxygen at 1/2 atm pressure. However, oxygen did not affect the absorption band at 605 mμ, when present. Since pumping out the oxygen for prolonged periods did not alter absorption at 535 mμ, the apparent decrease in radical ion concentration on addition of oxygen noted in similar EPR experiments (*10*) is a physical rather

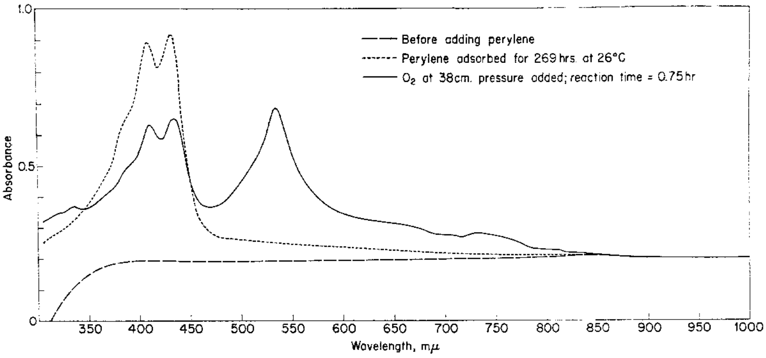


FIG. 10. Effect of O_2 on spectra of perylene on reduced silica-alumina (2.5×10^{-3} mmole/g).

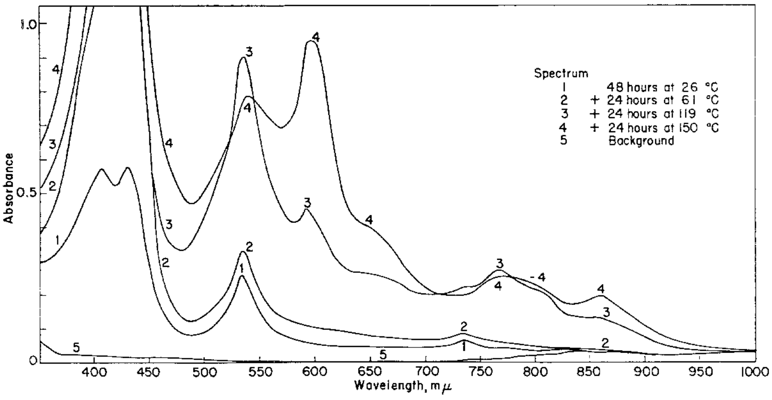


FIG. 11. Spectra from perylene adsorbed on an oxygen-cooled silica-alumina catalyst; available reagent, 2.5×10^{-3} mmole/g; surface area, 172 m^2/g.

than a chemical phenomenon. Moreover, the EPR intensity increased on adding oxygen when solvent was present (*3*). Evidently, the physical effect of O_2 on the EPR spectrum is eliminated when the catalyst is immersed in benzene or cyclohexane (*37*).

The decrease in absorbance at 430 mμ and concomitant increase at 535 mμ on adding oxygen provided a convenient means of determining the extinction coefficient ratio for these species. Within experimental error (±10%), it was the same as in solution. The absolute value of the extinction coefficient for physisorbed perylene (430 mμ) was also the same as in solution. This was determined by recording spectra of the solution before and after immersion of a plate as well as through the solution plus plate. It follows, therefore, that the extinction coefficient of the radical ion is that reported (*19*) for solutions.

With oxygen-cooled catalysts, the results were similar to those from catalysts treated in the standard way (Fig. 11). Cation radical concentrations were several times higher on these surfaces, but their greater tendency to hold physically adsorbed substrate was at least partly responsible. The general spectral characteristics of adsorbed perylene (2.5×10^{-3} mmole/g) on a base-exchanged catalyst (1.0% Na) were quite similar to those of the control (compare Figs. 12 and 7). In fact, absorption in the 535-mμ region persisted to higher temperatures, with the base-exchanged catalyst, suggesting that secondary reactions were less important. Spectra from catalysts containing 2.9% Na^+ were also qualitatively similar, but radical ion formation was unmistakably repressed. In contrast to triphenylmethane, perylene displayed no photochemical effects.

The amount of perylene initially deposited

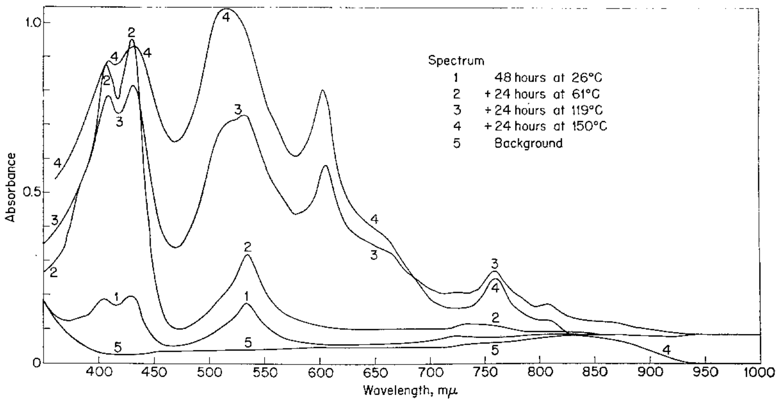


FIG. 12. Spectra from perylene adsorbed on base-exchanged silica-alumina (1.0% Na^+); standard pretreatment; available reagent, 2.5×10^{-3} mmole/g; surface area, 230 m^2/g.

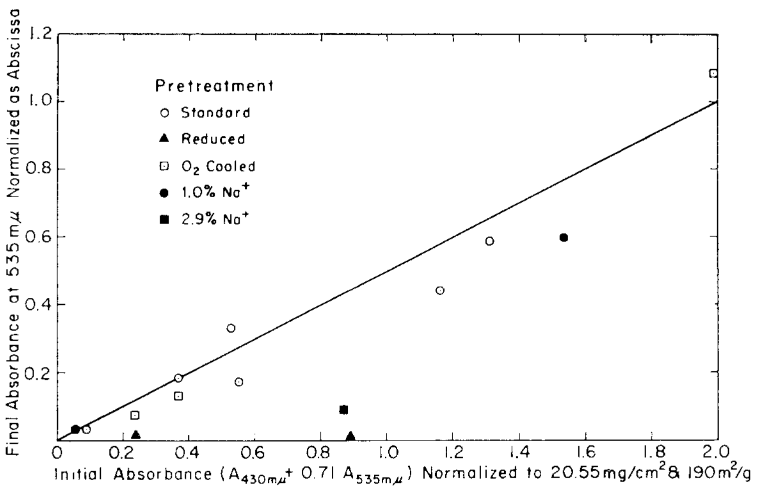


FIG. 13. Dependence of radical ion formation on initial deposition of substrate.

on the catalyst responded to pretreatment and varied considerably from plate to plate; the surface concentrations of radical ion and other unstable intermediates varied accordingly. Perylene sublimed slowly from the cell wall to the catalyst surface, even at room temperature. This increased the absorbance at 408 and 430 mμ by as much as 0.3 units per 100 hr (and was independent of the amount of available perylene), but usually did not effect an increase in radical ion concentration. On heating to 61°, the amount of physically adsorbed perylene increased by about 0.5 absorbance units when small amounts were present. When larger amounts were available, the results were erratic, but the increase was usually less than this. Heating to 119° and higher effected further increases in the amount of physisorbed perylene. In these cases, a hundredfold increase in available reagent increased the adsorption by only twofold. Even so, the average surface concentration of adsorbed perylene remained quite low, viz., $\sim 1 \times 10^{12}/cm^2$.

Radical ion formation at 26°C was dependent upon the amount of perylene *initially* deposited *by the solvent*. This is shown in Fig. 13, where absorbance at 535 mμ after 48-hr reaction time is plotted against the amount of perylene initially deposited on the catalyst, as expressed by absorbance at 430 mμ plus the ratio of the extinction coefficient (*19*) at 430 mμ (3.45

TABLE 1

RADICAL ION FORMATION FROM PERYLENE ON STEAM-SINTERED SILICA-ALUMINA[a]

Surface area (m^2/g)	Absorbance at 26°C[b] A 535 mμ	 A 430 mμ + 0.71 A 535 mμ
311	1.68	6.2
151	1.67	5.4
70	1.30	2.8
After heating to 120° overnight		
270	0.66	6.9
238	0.67	2.14
190	0.68	2.45
72	0.66	1.56

[a] Parent catalyst was American Cyanamid AAA (25% Al_2O_3). Surface areas were varied by pressing and steam-sintering.

[b] Normalized to 20.55 mg/cm^2.

$\times 10^4$) to that at 535 mμ (4.82×10^4) multiplied by the absorbance at 535 mμ. Its slope indicates that, except for catalysts which have been reduced or base-exchanged, about one-third of the adsorbed perylene was converted to the radical ion; this may be contrasted to the catalyst of Flockhart and Pink (*14*), where the conversion to radical ion was quantitative. Since substrate which sublimed onto the plates was ineffectual in increasing the radical ion concentration, it is likely that this reagent never reached active surface. Radical ions were not detected on several samples of reduced catalyst and only very slight absorption at 535 mμ was noted on others. This would suggest that a reduced catalyst does not characteristically form radical ions and that the slight absorbance noted in some cases arose from traces of oxygen inadvertently introduced into the system through incomplete degassing of the solvent, etc. The

TABLE 2

COMPARISON OF RESULTS FROM OPTICAL SPECTRA AND EPR METHODS[a,b]

Surface area (m^2/g)	Visible spectra Radical ions per g $\times 10^{-17}$	 per $cm^2 \times 10^{-11}$	SPR Radical ions per g $\times 10^{-17}$	 per $cm^2 \times 10^{-11}$
311	10	3	—	—
151	10	7	11	8
70	8	11	—	—
446	—	—	18	4
446	—	—	14	3
261	—	—	12	4
58	—	—	7	12

[a] Standard pretreatment used in all cases. Pressed plates used for optical spectra; powdered catalyst for EPR. Excess reagent added in benzene and solvent removed.

[b] Parent catalyst was American Cyanamid AAA (25% Al_2O_3). Surface areas were varied by steam sintering and by pressing.

TABLE 3

EFFECT OF SURFACE AREA ON ABILITY OF SILICA-ALUMINA TO GENERATE RADICAL IONS[a,b]

A. Perylene				
Available reagent (No./$cm^2 \times 10^{-14}$)	1.0	1.8	3.2	8.2
Surface area (m^2/g)	450	261	151	58
Room temp.[c]	18	12	11	7
+22 hr at 62°	20	11	12	—
+22 hr at 119°[d]	25	14	8	—
B. Perylene (Lot No. 2 of AAA)				
Available reagent (No./$cm^2 \times 10^{-14}$)	1.0	1.5	3.7	6.4
Surface area (m^2/g)	467	328	128	75
Room temp. [c]	8.7	7.7	6.1	3.3
Room temp. in benzene	8.8			
C. Thianthrene				
Available reagent (No./$cm^2 \times 10^{-14}$)	1.0	1.8	3.2	
Surface area (m^2/g)	450	261	151	
Room temp.[c]	11	7.6	3.6	
+22 hr at 62°	10	6.9	2.4	
+22 hr at 119°[d]	22	1.0	1.2	
D. Pyrene (Lot No. 2 of AAA)				
Available reagent (No./$cm^2 \times 10^{-14}$	1.0	1.5	3.7	6.4
Surface area (m^2/g)	467	328	128	75
Room temp.[c]	13	6.4	5.8	3.0

[a] EPR spin densities in spins/g $\times 10^{-17}$. Catalysts were prepared from parent batches of American Cyanamid AAA by steam sintering.

[b] Accuracy is within ±20% of the value given; major source of error is in packing. EPR method yields spins/cc; these must be divided by bulk density to get spins/g.

[c] These data are an average of measurements made during the period 48 hr to 170 hr, where the intensity was nearly constant.

[d] Decomposition was important at this temperature. Much of the paramagnetism probably did not stem from the radical ion.

TABLE 4

EFFECT OF PRETREATMENT ON ABILITY OF SILICA-ALUMINA TO GENERATE RADICAL IONS[a,b]

Available reagent:	$\sim 10^{12}/cm^2$			$\sim 10^{14}/cm^2$		
Pretreatment	Stand.	Reduced	O_2-cooled	Stand.	Reduced	O_2-cooled
		A. Perylene				
Room temp.[c]	14	1.6	18	18	1.8	15
+22 hr at 62°	17	2.2	18	20	4.2	14
+22 hr at 119°[d]	13	3.8	11	25	20	37
		B. Anthracene				
Room temp.[c]	5.8	0.8	7.0			
+22 hr at 62°	2.6	0.1	2.2			
+22 hr at 119°[d]	0.2	1.1	0.03			
		C. Thianthrene				
Room temp.[c]	4.0	0.14	6.6	11	0.8	19
+22 hr at 62°	3.3	0.16	3.8	10	3.5	21
+22 hr at 119°[d]	0.9	0.05	0.13	22	6.3	24

[a] EPR spin densities in spins/g $\times 10^{-17}$. All experiments made using a single batch of American Cyanamid AAA (25% Al_2O_3) having a surface area, following pretreatment, of 450 m^2/g.

[b] Accuracy is within ± 20% of the value given; see footnote *b*, Table 3. For this catalyst, 10×10^{17} spins/g $= 2.2 \times 10^{11}$ spins/cm^2.

[c] These data are an average of measurements made during the period 48 hr to 170 hr, where the intensity was nearly constant.

[d] Decomposition was important at this temperature. Much of the paramagnetism probably did not stem from the radical ion.

adverse effect of base-exchange is also evident.

Some interesting effects were discovered when the surface area of the parent catalyst was varied by steam sintering, a process which leaves the specific catalytic activity unaltered (*31*, *32*). On contact with excess perylene, similar absorbance values were obtained, when catalysts of widely different surface areas were employed. This is shown in Table 1, where radical ion formation and perylene coverage are given for catalysts having surface areas between 70 and 311 m^2/g. The results suggest that radical ion formation may be limited by bulk properties of the catalyst in some cases.

The EPR technique yielded generally consistent results. A cross comparison of the radical ion concentrations found by the two methods is given in Table 2; the quantitative agreement is as good as can be expected. The number of radical ions *per gram* appears to be more nearly constant than the number *per* cm^2. Further information on this point is contained in Table 3. These results suggest that the ability to generate radical ions is a function of both mass and surface area. However, thianthrene appeared to be less mass-dependent than either perylene or pyrene. In Series B, a control was run in which the solvent was not removed; this made no noticeable difference in the spin intensity–time behavior. Although the reagent available per unit area increased as the surface area was decreased, a large excess of reagent was present in all cases.

The effects of pretreatment and heating are shown in Table 4. Radical ion formation was not completely eliminated by reduction of the catalyst with hydrogen when the EPR technique was used, but it was very strongly repressed. The difference was less marked when compared after heating, but the perylene radical ion hyperfine lines were broadened (following heating to 119°), indicating that other paramagnetic species were formed. The effects of base exchange are shown in Table 5. Base exchange tended to decrease the spin density, but not in proportion to its effects on catalyst activity or on carbonium ion formation. With perylene, base exchange rendered the ion less stable to heating; with the other substrates, this was not evident.

Water (~10^{13} molecules/cm^2) was added to a number of systems to test its effect before and after heating. (Some of these systems had been heated previously; others not had.) No alterations in spectra were observed.

TABLE 5

EFFECT OF BASE EXCHANGE ON ABILITY OF SILICA-ALUMINA TO GENERATE RADICAL IONS[a,b]

A. Perylene (Available reagent ~10^{12}/cm^2)

Sodium content (%)	0	0.8	1.0	1.5	2.9
Room temp.[c]	14	14	12	11	8.0
+22 hr at 62°	17	8.0	13	8.6	4.3
+22 hr at 119°[d]	13	2.0	3.7	1.6	1.7

B. Anthracene (Available reagent ~10^{12}/cm^2)

Sodium content (%)	0	0.8	1.0	1.5
Room temp.[c]	5.8	3.1	2.5	2.2
+22 hr at 62°	2.6	1.4	0.6	0.9
+22 hr at 119°[d]	0.2	0.5	0.2	0.2

C. Thianthrene (Available reagent ~10^{12}/cm^2)

Sodium content (%)	0	1.0	2.9
Room temp.[c]	4.0	2.6	0.34
+22 hr at 62°	3.3	2.1	0.25
+2 hr at 119°[d]	2.3	1.4	0.11

[a] EPR spin densities in spins/g × 10^{-17}. All experiments made using a single batch of American Cyanamid AAA (25% Al_2O_3) having a surface area, following pretreatment, of 450 m^2/g.

[b] Accuracy is within ± 20% of the value given; see footnote *b*, Table 3. For this catalyst, 10 × 10^{17} spins/g = 2.2 × 10^{11} spins/cm^2.

[c] These data are an average of measurements made during the period 48 hr to 170 hr, where the intensity was nearly constant.

[d] Decomposition was important at this temperature. Much of the paramagnetism probably did not stem from the radical ion.

DISCUSSION

In attempting to assess the present results, certain limitations imposed by the systems being investigated must be borne in mind. Because of the low volatility of perylene, equilibrium could not be achieved at room temperature in the absence of solvent. At sufficiently high temperatures where equilibrium could be attained, the system was unstable and the situation was further complicated by the presence of species of uncertain identity. Similarly, with the triphenylmethane–catalyst system, additional amounts of triphenylcarbonium ions were frequently formed when the temperature was raised and lowered again to room temperature; here too, additional species appeared on heating to 120° or higher. Solvent could not be employed because of secondary reaction, as evidenced by fading of the carbonium ion band. It follows, therefore, that in the temperature range over which these systems can be investigated, the results were at least partially kinetically controlled. Hence, considerable caution must be used in drawing conclusions concerning the surface density of active sites, especially from the triphenylmethane data where strong photochemical effects were observed. Leftin and Hall's results (*6*) with the more ionic trityl compounds may be free from these limitations. Trityl chloride, trityl bromide, and triphenylcarbinol all formed about 5 × 10^{12} carbonium ions/cm^2. With these bases, however, the size of the molecule may limit the number of triphenylcarbonium ions which can be formed per unit area. Leftin and Hall also reported 5 × 10^{12}/cm^2 for triphenylmethane. This is about an order of magnitude higher than the value derived from Fig. 3, but it was in fair agreement with the present findings for triphenylcarbinol. This discrepancy, which was pointed out by Hirschler (*17*), stemmed from the method used to determine the number of carbonium ions formed from triphenylmethane. Rather than assume that the extinction coefficient for triphenylcarbonium ions was the same when adsorbed, as in solution, Leftin and Hall extracted the catalyst with dry benzene to remove physically adsorbed substrate, and then with aqueous acetone to desorb the carbonium ion. Values determined from the acetone extract were nearly 10-fold higher than the carbonium ion concentration calculated from the absorbance data. Work still in progress indicates that the method of analysis was unsatisfactory for those experiments where triphenylmethane was substrate, and in general yielded results which were much too high. When trityl chloride or triphenylcarbinol was used, however, correct results were obtained, and as demonstrated herein, these are in agreement with those calculated from spectra fusing the solution extinction coefficient. These questions will be dealt with more fully in a later paper.

Hirschler and Hudson (*17*) noted the similarities of the reactions of triphenylmethane or perylene with the silica-alumina surface and suggested that both involved chemisorbed oxygen. These workers recognized that treatment of the catalyst with H_2 at 500° strongly repressed radical ion, but not carbonium ion formation, but argued that triphenylmethane is more easily oxidized than perylene, or else that the two substrates are not oxidized by the same form of surface oxygen. Since reaction with triphenylmethane is slow and photolytic, while reaction with perylene is unaffected by light, it seems unlikely to us that triphenylmethane is more easily oxidized; rather, the data suggest that the processes are not the same. These characteristics, together with others discovered in the present work, suggest that the differences in the behavior of the two substrates are more striking than the similarities. Thus, in the presence of excess reagent, carbonium ion concentration increased on heating to the point where secondary reactions set in; radical ion concentration was maximum at room temperature except when the available substrate was limited. The carbonium ion concentration (per gram) increased linearly with surface area (Fig. 3); radical ion concentration increased with surface area, but depended on mass as well. The affinity of the catalyst for triphenylmethane was high; only a small portion of the available perylene adsorbed. Radical ion concentration was unaffected by the presence of solvent, whereas carbonium ion concentration was lowered both by partition between the two phases and by secondary decomposition processes. Base exchange strongly affected carbonium ion formation, while with the acenes the effect was less pronounced.

In the earlier work of Leftin and Hall (*6*), the effect of light was not recognized; hence, precautions were not taken to avoid it. Nevertheless, most of these results were obtained under the conditions of the dark reaction, as evidenced by the fact that the published spectra (*6*) are comparable with those of Fig. 1 and not with those of Fig. 4. In the earlier work (*6*), sealed, greaseless systems were used and no solvent was employed. The sealed tubes were placed in an oven (in the dark) where contact between catalyst and substrate was effected by vacuum transfer on elevating the temperature. Hence, catalysts were only exposed to light for brief periods when the tubes were moved between the oven and the spectrometer. One of Hirschler and Hudson's arguments was that since the formation of carbonium ions is accelerated by light, and since these may be recovered from the catalyst as triphenylcarbinol, the contribution due to hydride abstraction under photolytic conditions is either insignificant or nonexistent. The present data show that different processes may be taking place in the light and in the dark. In the dark there was no effect of pretreatment, particularly of reduction of the catalyst; the band at 600 mμ did not form, even at 150°. Even so, the concentration of carbonium ions which could be formed was nearly as large as could be effected by light (compare Figs. 3 and 5). The magnitude of the photochemical effect with triphenylmethane did depend on pretreatment of the catalyst, however, decreasing with reduction or base exchange. Since the surface density of carbonium ions could be increased by contact with O_2 only in the presence of light, the photolytic reaction is probably an oxidation as claimed (*17*). The available data suggest, however, that this is an *additional* process which is superimposed on the result of the dark reaction, and is therefore not pertinent to the question of whether or not the catalyst has the capability of removing hydride ions. Furthermore, the marked differences in the stability and decomposition pattern of the triphenylcarbonium ion when generated from triphenylcarbinol (Fig. 6) compared with when it is formed from triphenylmethane (Fig. 4) may be taken as evidence that triphenylmethane is not converted to the carbonium ion (in the dark) via a triphenylcarbinol intermediate. Since the fate of the hydride ion which is lost when the triphenylcarbonium ion is formed is not known exactly, i.e., only that it remains associated with the catalyst (*6*), reactions of the type

$$H^- + O_2(s) = O(s) + OH^-(s) \qquad (2)$$

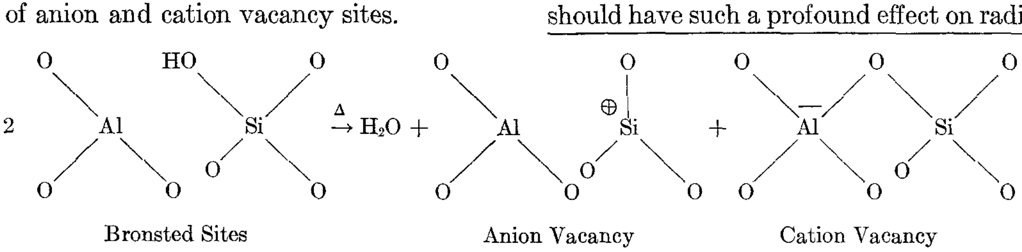
cannot be ruled out, but the lack of an effect of H_2 treatment makes this path unlikely for the dark reaction. The important point is, however, that in this case the hydride ion is removed from triphenylmethane by an *electrophilic* site; catalyst protons need not be involved.

Uytterhoeven, Christner, and Hall (*34*) recently have studied the chemistry of decationation of zeolites. This has resulted in a rather clear definition of the types of sites which may occur in this material and, by analogy, on silica-alumina. In the course of this work, it was found that the principal effects described here for silica-alumina were reflected in the zeolite system, e.g., the effect of the high-temperature treatment with H_2 on perylene chemisorption. Hence, zeolite chemistry provides a framework for consideration of the present results, particularly those dealing with the effects of base exchange.

As prepared, the unit cell composition of a Y-type zeolite is $Na^+{}_{56}(AlO_2^-)_{56}(SiO_2)_{136}$. On base exchange with NH_4^+, part of the sodium is replaced, and on heating, NH_3 is evolved, i.e.,

$$Na^+{}_{56-x}(NH_4^+)_x(AlO_2^-)_{56}(SiO_2)_{136} \xrightarrow{\Delta} xNH_3 + Na^+{}_{56-x}H_x^+(AlO_2^-)_{56}(SiO_2)_{136} \qquad (3)$$

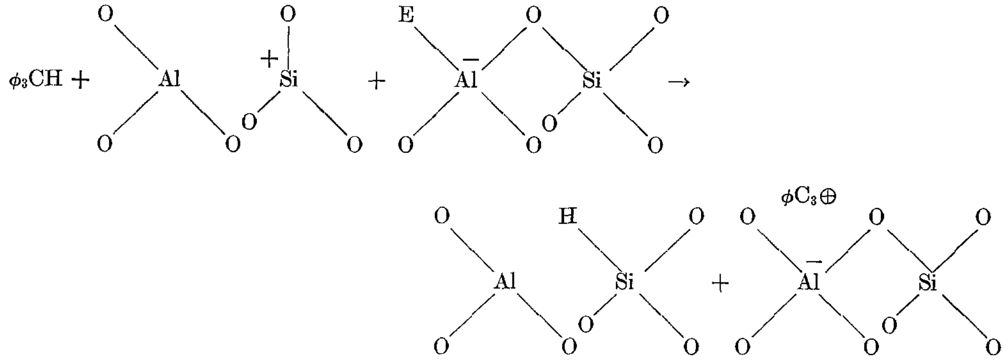
The Bronsted acid of the right-hand member of Eq. (3) exists in the form written for the left-hand member of Eq. (4), which describes the conversion of the Bronsted acid to pairs of anion and cation vacancy sites.



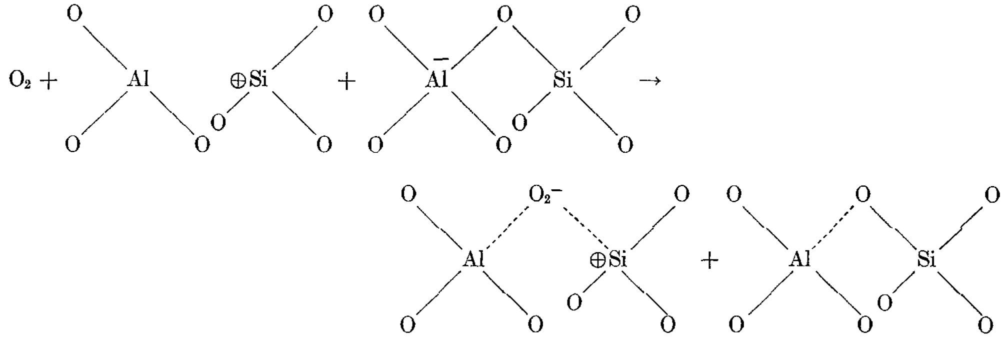
(4)

In addition to these sites, conventional Lewis acid sites may exist on the broken faces where the giant molecule crystals are terminated with Al-OH and SiOH groups. (The OH group is removed from Al as H_2O on decationation.) It was concluded (*34*) that the same kinds of sites probably exist on silica-alumina but in different proportions. Whereas Bronsted and anion–cation vacancy pairs predominate with the zeolites, conventional Lewis acid sites are probably present in greatest abundance on silica-alumina. Moreover, it was found that when the decationated zeolite was given the standard pretreatment used in the present work, Eq. (4) was far to the right, i.e., few Bronsted sites remained. Consideration of this chemistry also revealed that "base exchange" is not a simple metathesis involving replacement of catalyst protons with Na^+ ions, as frequently supposed (*4*, *10*, *16*). Only the Bronsted sites [Eq. (4)] undergo metathesis; a reconstitution of structure, which involves incorporation of NaOH back into the lattice, occurs with the Lewis sites and with the cation–anion vacancy pairs. Thus, while base exchange eliminates Bronsted acidity, it also diminishes Lewis acidity. This would appear to invalidate arguments based on the premise that "base exchange" affects only Bronsted acid (*4*, *16*).

If direct hydride ion abstraction by the catalyst occurs, as previously postulated (*6*), the cation–anion vacancy pairs afford the most likely sites for reaction, i.e., as in Eq. (5). Conventional Lewis acid sites may also remove H^-, but they would not be expected to be as strong and, therefore, not as effective. Stamires and Turkevich (*9*) have made related suggestions concerning radical ion formation, i.e., that the ionized electron goes into the anion vacancy. It is not easy to see, on this basis, why the H_2 treatment should have such a profound effect on radical ion formation but none for the reaction with triphenylmethane. The supposition that chemisorbed oxygen may be responsible for


(5)

the former affords a reasonable interpretation. Presumably, O_2 would chemisorb on the anion vacancy sites according to


(6)

are unavoidably created during dehydration. On this basis, the extent of O_2 chemisorption may be expected to depend on mass as well as surface area as found for radical ion formation.

This O_2 may be chemisorbed during the standard pretreatment. It may react with perylene and possibly (photochemically) with triphenylmethane; it may be removed by hydrogen leading to the observed effect (*3*, *12*, *17*). The work of Charman *et al.* (*35*) is in accord with this picture. These workers studied the chemisorption of O_2 and H_2 on the surfaces of NiO and MgO and found these chemically dissimilar oxides were qualitatively similar in these reactions. Chemisorption of O_2 was supposed to occur at anion vacancies where metal ions were exposed. The driving force was said to be the increase in coordination number of the positive ions near the surface. Where adjacent exposed metal ions existed, chemisorption of O_2 resulted in two O^- ions, but where single ions were exposed, more loosely chemisorbed O_2^- ions were formed. At higher temperatures, these equilibrated with the oxygen lattice in accordance with the model of Kokes (*36*). With silica-alumina, as with the decationated zeolites, sites of this kind

A number of facts support the view that chemisorbed or surface oxygen is directly involved in some of the processes being studied. It was reported (*3*) that water was formed when silica-alumina was reduced, in an amount comparable with the number of radical ions which could be formed without this treatment. Rooney and Pink (*10*) noted that ring closure took place with 1,1′-dinaphthalene to form perylene, which was observed as its radical ion; evidently, H_2O was formed in this process. When triphenylamine was adsorbed on silica-alumina, the corresponding cation radical (band at 660 mμ) formed rapidly (*3*, *37*). On standing, an additional band appeared (485 mμ) which was identified as the semiquinone of tetraphenylbenzidine. The coupling of two amine molecules in the para position involved the loss of hydrogen, presumably as H_2O. Atkinson, Jones, and Baughan (*38*) have demonstrated recently that perylene (Pn) is quantitatively oxidized to the radical ion in $SbCl_3$ in excess O_2 according to

$$O_2 + 4Pn + 6SbCl_3 = 4Pn\cdot^+ + 4SbCl_4^- + 2SbOCl \qquad (7)$$

Cation radical formation was slight or nonexistent in the absence of O_2, even when HCl was added, but was effected by $SbCl_5$ (*19*, *38*). On the other hand, both radical ions and carbonium ions were formed on silica gel (*4*, *6*) and radical ions in solution (*19*), when treated with anhydrous BF_3; radical ions also formed on anhydrous $AlCl_3$ (*10*). It is not easy to define the source of the oxidizing agents in these cases, if it is other than the Lewis acid itself.

Leftin and Hall (*6*) demonstrated that the H^- ion, which stoichiometrically disappears when the triphenylcarbonium ion is formed from triphenylmethane, remained associated with the catalyst; H_2 gas was not generated, nor was H^- transferred to carbonium ions formed by reaction of olefins with catalyst protons. Since reduction of the catalyst with H_2 *did not* repress carbonium ion formation, it was supposed that catalyst-held oxygen was not a factor in the reaction. Hirschler and Hudson (*17*) have questioned this interpretation (under their photolytic conditions) and have suggested that triphenylmethane must be oxidized to triphenylcarbinol (or triphenylhydroperoxide) so that it can react with catalyst protons. In support of this, they reported that on adding NH_3, the carbonium ion was recovered from the catalyst nearly quantitatively as triphenylcarbinol, rather than as triphenylmethane as was reported by Leftin and Hall. In work to be reported later (*39*), we were unable to confirm this observation (under nonphotolytic conditions). In these experiments, the catalyst–substrate system was first vacuum-extracted with anhydrous benzene at room temperature to remove excess triphenylmethane; this was followed by a second vacuum extraction in the presence of a nitrogen base. In this second extraction, neither triphenylmethane nor triphenylcarbinol was extensively desorbed into benzene at room temperature. Nevertheless, the characteristic yellow color was bleached, suggesting that the nitrogen base complexed with the carbonium ion rather than desorbing it. Triphenylcarbinol was extensively desorbed when H_2O was present. In this case, it may reasonably be supposed that the reaction is:

$$\phi_3C^{\oplus} + OH^- = \phi_3COH \qquad (8)$$

To unambiguously settle this question, the fate of the H^- must be accurately defined. Leftin *et al.* (*2*a, *6*), thought they had accomplished this by demonstrating that triphenylcarbonium ions were displaced from the surface as triphenylmethane, but as shown herein and elsewhere (*17*), this conclusion is in doubt because the number of carbonium ions actually present was 10 times smaller than supposed (*2*a, *6*). In our opinion, however, further work will be required to determine the fate of the H^-. As of now, we believe that carbonium ions may be formed in the dark according to Eq. (5) and that once this has occurred, it may be difficult, if not impossible, to displace H^- back onto the carbonium ion. Carbonium ions may also form on conventional Lewis acid sites, particularly from substrates such as trityl chloride and triphenylcarbinol. Photochemical oxidation of triphenylmethane may lead to additional carbonium ion formation in this way, which would be superimposed on the result of the dark reaction. The experimental data can best be satisfied if it is assumed that the chemisorbed oxygen is required to form radical ions.

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