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The Formation of Carbonium Ions from Arylmethanes on Silica–Alumina

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The chemisorption of triphenylmethane, diphenylmethane, and 4,4′-dimethoxydiphenylmethane on silica–alumina cracking catalysts was studied *in vacuo* and in the dark. The substrate reacted on the surface forming stable carbonium ions, e.g., the triphenylcarbonium ion from triphenylmethane. The fate of the H^- ion which is stoichiometrically lost concomitant with ion formation was ascertained by extracting and analyzing the products of the surface reaction. With triphenylmethane the results were found to conform to the following Friedel-Craft's chemistry:

$$Ph_3CH + H^{\oplus} \rightarrow C_6H_6 + Ph_2\overset{\oplus}{C}H,$$

$$Ph_2\overset{\oplus}{C}H + Ph_3CH \rightarrow Ph_3C^{\oplus} + Ph_2CH_2.$$

Surface densities of triphenylcarbonium ions, determined by recovery as triphenylcarbinol, agreed with those determined spectrophotometrically ($\sim 5 \times 10^{11}/cm^2$). With diphenylmethane the primary reaction involved alkylation, i.e.,

$$Ph_2CH_2 + H^{\oplus} \rightarrow C_6H_6 + Ph\overset{\oplus}{C}H_2,$$

$$Ph\overset{\oplus}{C}H_2 + Ph_2CH_2 \begin{array}{l} \nearrow PhCH_2C_6H_4CH_2Ph + H^{\oplus} \text{ (major)} \\ \searrow Ph_2\overset{\oplus}{C}H + PhCH_3 \text{ (minor)} \end{array}$$

The reaction of 4,4′-dimethoxydiphenylmethane followed both reaction paths, but the alkylation products were too complicated to characterize. It was concluded that the formation of the triphenylcarbonium ion on these catalysts does not demonstrate that hydride ions are abstracted from paraffinic carbon atoms by the silica–alumina surface as previously supposed.

INTRODUCTION

The nature of the acidity of silica–alumina cracking catalysts is still a matter of considerable controversy. The experimental evidence (*1*) suggests that both Lewis- and Bronsted-type centers are present and may be interconvertible with the addition or removal of H_2O (*1–3*). Contributions from this laboratory have reported experiments designed to detect electrophyllic centers (*4–6*), intrinsic Bronsted acid as part of the hydrogen held by the solid (*7, 8*), and to discriminate between Bronsted- and Lewis-catalyzed mechanisms of reaction of hydrocarbons on these surfaces (*9–11*). The salient findings were: (a) that regardless of the nature of the sites, the reactions can best be described by simple protonic mechanisms; (b) that the protons appear to be furnished by "residues" formed by reaction of the substrate with the catalyst surface; (c) that only a *small* fraction of the hydrogen held by the catalyst (if any) is directly or indirectly involved; and (d) that a very strongly held form of chemisorbed oxygen acts as the electron acceptor in radical ion formation (*12*), but is not involved in the formation of carbonium ions from triphenylmethane.

Leftin and Hall (*4*) demonstrated that the H^- ion, which stoichiometrically disappears when the triphenylcarbonium ion is formed from triphenylmethane, remains associated with the catalyst; H_2 was not evolved, nor was H^- transferred to a carbonium ion formed by reaction of olefinic impurities with catalyst protons. Since treatment of the catalyst with H_2 did not repress carbonium ion formation (as it does radical ion formation), it was supposed that catalyst-held oxygen was not a factor in the reaction. In view of these results it was suggested that the H^- ion was abstracted and held by the Lewis acid centers on the silica–alumina surface. Hirschler and Hudson (*13*) questioned this interpretation and presented evidence in support of their view that triphenylcarbinol (or triphenylhydroperoxide) was formed by oxidation of triphenylmethane on the catalyst surface, and that this reacted with catalvst protons to form the carbonium ion. The question was restudied by Porter and Hall (*6*), who concluded that this was not the mechanism, but that the true mechanism could not be unambiguously determined until the fate of the H^- ion was determined.

In view of the importance of deciding whether or not the formation of the triphenylcarbonium ion from triphenylmethane is a demonstration of the ability of the catalyst to abstract hydride ions, we have investigated the course of the reaction on the catalyst surface by extracting and characterizing the reaction products. The results of these experiments demonstrated that the oxidation of triphenylmethane to triphenylcarbonol was not a significant path in the formation of the carbonium ion. Moreover, the chemistry of the chemisorption was found to be kinetically limited by reactions of the type outlined in the abstract, which for brevity we will call Friedel-Craft's chemistry. The fate of the H^- ion has been ascertained and the surface density of Bronsted sites sufficiently strong to effect dearylation at 100°C has been determined. A preliminary account of this work has been given (*14*).

Experimental Methods

American Cyanamic Company Aerocat cracking catalyst was used in most experiments. It contained 22.1% Al_2O_3 and was found to have a surface area of 433 m^2/g when pretreated. A few experiments were made with Houdry M-46 cracking catalyst. It contained 11% alumina and had a surface area of 250 m^2/g.

The same high purity triphenylmethane and triphenylcarbonol was used in this work as was used previously (*6*).

Pyridine, Baker Analyzed Reagent, and quinoline, Fisher Scientific Company, were distilled before use and stored over molecular sieves.

The benzene, cyclohexane, and ethylacetate were Fisher certified reagents. They were dried over molecular sieves. Absolute ethanol was obtained from Commercial Solvents Corporation and was used without further purification. Baker Analyzed acetone was used without further purification.

Oxygen and hydrogen were purified as previously described (*6*).

About 20 g of catalyst in a sample tube were given one of several pretreatments. In these, all steps were carried out at 540 ± 10°C. When the catalyst was treated 1 day in flowing oxygen and then evacuated for 1 day using a mercury diffusion pump, the catalyst was said to have had the *standard pretreatment*. When the standard pretreatment was followed by a 1 day reduction in flowing H_2 and another 1 day evacuation, the catalyst was reduced. If, following the 1 day treatment in O_2, the catalyst was allowed to cool slowly to room temperature under 1 atm of O_2 before being evacuated for 24 hr, the catalyst was O_2 cooled. Following catalyst pretreatment, the catalyst sample tube was sealed off with a torch.

A weighed amount of triphenylmethane in 100 ml of solvent was thoroughly degassed by the freeze–pump–thaw–freeze technique (8–10 times) in a 200-ml flask attached to the catalyst sample tube through a break-off seal and a fritted glass disk. The latter was used to prevent transfer of catalyst from one section of the sample tube to the other. Following degassing of the solution, the flask was sealed from the atmosphere with a torch. The break-off seal was broken when the reagent was transferred to the catalyst. Solvent was subsequently removed by vacuum transfer to the flask and the solvent was maintained at liquid nitrogen temperature throughout the course of the reaction.

Products of reaction of either triphenylmethane or triphenylcarbinol following adsorption on AAA cracking catalyst were examined following vacuum extraction to remove physically adsorbed reagent and treatment with base to desorb triphenylcarbonium ions and any other reactive intermediates. Several solvents were employed successively in these extractions. Products collected from the various fractions were analyzed using gas–liquid chromatography and by reaction with sulfuric acid to stable carbonium ions.

In the experiments with diphenylmethane, 4,4′-dimethoxydiphenylmethane, and in some experiments with triphenylmethane, samples were transferred without solvent by heating the entire evacuated vessel in a large oven at 100°C. In these cases, weighed amounts of purified substrate were melted and degassed in a smaller flask (ca. 15 ml), attached to the catalyst sample tube through a break-off seal. The catalyst was shielded from light during the reaction by wrapping the entire vessel with aluminum foil.

Two working-up procedures were employed. In Type A experiments, emphasis was placed on the study of desorption of carbonium ions from solid surface while in Type B experiments, emphasis was placed on complete analysis of the reaction products.

In Type A experiments, following reaction the solvent in the attached flask was warmed to room temperature and poured onto the catalyst. The solvent was then poured off into the flask until the catalyst appeared dry. The solvent was evaporated from the flask onto the catalyst and poured off a second time. This vacuum extraction was repeated 10 times. The solvent was finally frozen into the flask at liquid nitrogen temperature and sealed off from the sample tube with a torch. The solvent from the flask was evaporated to dryness following filtration to remove catalyst particles that passed through the fritted glass disk and the solids were collected for analysis.

Ten ml of pyridine or 5 ml of quinoline in 100 ml of benzene were thoroughly degassed in the manner described above in a second 200 ml flask attached to the same sample tube. The solution was introduced into the sample tube through a second break-off seal. The yellow color of the catalyst was immediately discharged and the catalyst turned white. The catalyst was vacuum extracted as above and the solution was evaporated to dryness following filtration. The solids from this solution were also collected for analysis. For some experiments, 8 g of sodium hydroxide in 75 ml of H_2O were degassed and poured onto the catalyst. Vacuum extraction was then not possible.

Following the vacuum extractions, the vessel was opened and the catalyst was removed to a separatory funnel containing 8 g of sodium hydroxide, water, and benzene. The catalyst was extracted several times with benzene and the benzene several times with water to remove traces of base. The benzene solution was filtered and evaporated to dryness; the solids obtained were retained for analysis.

The catalyst was finally extracted in a Soxhlet for 1 day with a solution of 20 ml of water in 200 ml of acetone. The solids were again collected for analysis following filtration and evaporation of this solution.

When quinoline was used as base, the procedure had to be modified because quinoline would not evaporate at room temperature. The solutions from each fraction were extracted several times in a separatory funnel with dilute hydrochloric acid and benzene to remove quinoline. The benzene solution was then extracted several times with water to remove traces of acid.

Solids were collected following filtration and evaporation as above.

Each fraction was weighed and aliquots were taken for the various analyses. An aliquot of each fraction was treated with 75% sulfuric acid and about 2 ml of benzene to dissolve the organic material, and the absorption spectrum was determined. Under these conditions, triphenylcarbinol is ionized to the triphenylcarbonium ion and triphenylmethane is not. The triphenylcarbonium ion gives a characteristic absorption maximum at 405 and 430 mμ suitable for determining the maximum amount of triphenylcarbinol in the sample (E 430 m$\mu = 3.95 \times 10^4$ liter mole^{-1} cm^{-1}). These results are not unique for triphenylcarbinol but also include any trityl compound ionizable in 75% H_2SO_4 to the carbonium ion. The extracted catalyst was analyzed for triphenylmethane remaining by treatment of an aliquot with 96% H_2SO_4.

Experiments were also undertaken in which the triphenylcarbonium ion was generated from triphenylmethane under high vacuum conditions on optical platelets of AAA catalyst. The method used has already been described (*6*). Pretreatment of the catalysts was similar to that used for bulk catalysts except for evacuation times which were shortened to 7 hr. When reaction was to be carried out at 100°, the substrate was degassed and transferred by heat alone, no solvent being used.

The platelets were extracted in a manner analogous to that employed with bulk catalyst except that smaller quantities of reagents were used, about 7 ml of solvent for each extraction. All extracts were analyzed with 75% H_2SO_4 as before using 2 ml of acid. The extracted platelets were also analyzed with 2 ml of 96% sulfuric acid to see if the extraction was complete.

Essentially the same procedures were followed in Type B experiments for catalyst pretreatment and for introduction of the substrates. After chemisorption at 100° in the dark, the volatile fractions (benzene and toluene) were vacuum transferred into an attached trap at —195°. The collected fraction was analyzed with a mass spectrometer. In other experiments, small amounts (2 ml) of degassed solvents were distilled directly into the trap to make either a CCl_4 solution for PMR analysis or an ether solution for GLC analysis. The PMR analysis was made with a Varian A-60 spectrometer using TMS as an internal reference. The GLC analysis of the volatile fractions was made with a 6-ft column of 20% SE 30 on 80–100 mesh chromport XXX at room temperature.

The catalyst sample was then extracted with cyclohexane or benzene *in vacuo* to remove most of the unreacted reagent and was finally transferred to a Soxhlet and extracted for several days with wet cyclohexane or wet benzene. The two extracts were condensed to a final volume of a few milliliters by careful distillation of solvent after it had been dried with Drierite. The GLC analyses of the two extracts were made with a 6-ft column of 20% SE 30 on 80–100 mesh chromport XXX. To identify the retention times and to calibrate the quantities of products with authentic samples by means of peak heights, the GLC column was temperature programmed from 25 to 300°C. The preparative GLC were performed using a 5-ft 10 × ¼-in. stainless steel column packed with Anakrom ABS coated with 10% Apizon L and temperature programmed from 70 to 250°C at 21°/min. The high resolution mass spectrograms were obtained with an A.E.I. Model MS-9 mass spectrometer.

Results

Results from several Type A experiments are summarized in Table 1. These experiments were designed to determine how quantitatively the reaction products could be recovered. The available triphenylmethane was about 3×10^{13} molecules/cm^2 of catalyst surface and the total weight of material recovered was usually 20 to 25 mg greater than the material balance. This probably stemmed from very fine particles of catalyst which passed through the filters, but stopcock lubricant from the separatory funnel and impurities from solvents may also have contributed. About 3 liters of solvent were used in each experiment for extracting, washing, etc.

TABLE 1

Removal of Chemisorbed Triphenylmethane by Extraction (Type A experiments)[a]

No. of expts.:	3	1	1	2	1	1	1	1
Catalyst wt (g):	20	20	20	20	20	20	20	20
Pretreatment:	Standard	Reduced	Reduced	Standard	Reduced	Standard	(8.25 ml O_2 preadsorbed)	(101 ml O_2 preadsorbed)
Initial wt ϕ_3CH (mg):	1000	1000	1000	1000	3.14	30.7	1000	1000
Reaction conditions:	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C	24 hr, 100°C
Vacuum extraction with benzene								
ϕ_3CH (mg)	963	953	969	1014.3	25.3	20.0	954	Not extracted
ϕ_3COH (mg) (75% H_2SO_4)	0.25	0.40	0.05	0.30	0	0	0.28	
Vacuum extraction with base and benzene								
Base used	Pyridine	Pyridine	Quinoline	—	Pyridine	Pyridine	Pyridine	Pyridine
ϕ_3CH (mg)	3.45	0.33	2.27	—	0.03	0.03	0.72	913
ϕ_3COH (mg)	0.07	0.21	1.74	—	0.00	0.00	0.02	0.18
Extraction in the air with aqueous base and solvent followed by Soxhlet extraction with aqueous acetone								
ϕ_3CH (mg)	5.28	2.46	0.28	7.23	0.12	0.66	21.73	6.3
ϕ_3COH (mg	11.53	7.64	3.61	9.96	0.11	1.07	15.03	25.39
Weight of material collected from all fractions								
Recovered material (mg)	1050	1008	1036	1055	54.8	51.4	1027[b]	1032[c]
ϕ_3CH (mg)	972	956	972	983	25.4	20.7	976	919
ϕ_3COH (mg)	11.87	8.25	5.4	10.3	0.11	1.02	15.3	25.6
ϕ_3C (ions/cm^2)	3.4×10^{11}	2.4×10^{11}	1.6×10^{11}	3.0×10^{11}	3×10^{9}	3×10^{10}	4.4×10^{11}	7.4×10^{11}
Loss from mass balance (%)	2.7	4.3	3.8	2.9	18.8	29.3	3.3	10.7

[a] Emphasis was placed on quantitative recovery; catalyst surface area was 433 m^2/g before pretreatment.

[b] Also recovered were 0.16 mg of benzophenone and 0.05 mg of benzhydrol.

[c] 36.7 mg of benzophenone were also formed. This is not included in the mass balance.

Extraction with benzene under vacuum served to remove most of the triphenylmethane. The catalyst remained yellow following this treatment, but the intensity of coloration invariably decreased somewhat. It is not known with certainty whether a portion of the carbonium ions were desorbed (or destroyed) or the extinction coefficient of the ion lowered by solvation. However, experiments with platelets revealed that the process was semiquantitatively reversible and that very little triphenylcarbinol could be recovered from the (vacuum) benzene extract. The decrease in carbonium ion concentration was quite large in some cases ($\sim$50%).

The catalysts turned white on treatment with base, but very little triphenylmethane or triphenylcarbinol was recovered on vacuum extraction with base and benzene. Most of the triphenylcarbinol appeared when samples were subsequently extracted with aqueous solutions. The amounts of triphenylmethane recovered in these fractions was not large but frequently comparable with those of triphenylcarbinol. These data alone do not permit decision of whether or not any of the triphenylcarbonium ion remaining after the first extraction with benzene was discharged as triphenylmethane. Similar results were obtained in experiments where the available substrate was severely limited (to $\sim 5 \times 10^{11}/\text{cm}^2$), except that significantly lower carbonium ion concentrations were found.

The final extraction in a Soxhlet was conducted in many different ways to verify that the solvent used in extracting did not influence the results. Benzene + aqueous acetone, benzene + ethyl acetate + aqueous acetone, and cyclohexane + benzene + ethanol + aqueous acetone were tested. When ethanol or ethyl acetate was used, high molecular weight gums were recovered in the extract. The results of these experiments showed that the recovery of triphenylmethane and triphenylcarbinol was insensitive to the solvents, bases, and method used to "kill" the carbonium ions. Also, the amount of triphenylcarbinol formed was rather insensitive to catalyst pretreatments. The results suggest that triphenylcarbinol is produced during extraction through reaction with atmospheric moisture or with water in the extracting solvent.

The influence of oxygen on the reaction is demonstrated in the last two columns of Table 1. When 8.25 ml (NTP) of oxygen, corresponding to a coverage of 2.3×10^{12} molecules/cm^2 were admitted to the pretreated sample at room temperature, over 90% was immediately absorbed by the catalyst. The total triphenylcarbinol recovered was not (by itself) significantly higher than the corresponding results of experiments conducted in the absence of oxygen, the salient difference being the appearance of small amounts of benzophenone and benzhydrol. In the experiment, sufficient oxygen was used to oxidize 84 mg of triphenylmethane if one molecule of oxygen were used to oxidize one molecule of triphenylmethane. Evidently, the adsorbed oxygen is rather unreactive in the absence of light. When sufficient oxygen was present in the gas phase, however, its influence was unmistakeable. Not only was the yield of triphenylcarbinol about twice as large as usual, a by-product of 36.7 mg of benzophenone was also assayed. The side reaction in the presence of gaseous oxygen may be primarily thermal and not catalytic. Stephens and Roduta (*15*) have shown that triphenylmethane is readily oxidized at temperatures above its melting point to give primarily benzophenone and phenol. The latter would be lost in the present work, in the benzene extractions.

Results from several Type B experiments are summarized in Tables 2 and 3. These experiments were designed to obtain complete analysis of reaction products when arylmethanes were chemisorbed on cracking catalysts. In the experiments with triphenylmethane (Table 2), the available reagent ranged from about 3×10^{12} to 3×10^{13} molecules/cm^2 of catalyst surface and the total recovery by calibrated GLC was usually between 85 and 96%. The yield of unidentified compounds, mostly low-boiling materials, was less than 2% and the agreement between the total weight of recovered materials and the amount of

TABLE 2

Summary of Extraction Data for Triphenylmethane Reaction (Type B experiments)[a]

Pretreatment temp (°C)	No. of expts.	Substrate	Available reagent (No./cm^2 × 10^{-11})	Reaction time	Product (No./cm^2 × 10^{-11}) Benzene	Product (No./cm^2 × 10^{-11}) Ph_2CH_2	Product (No./cm^2 × 10^{-11}) Ph_3COH	Recovery (%)
550	2	Ph_3CH	29	2 days	4.8	2.7	2.4	85
550	1	Ph_3CH	58	3 hr	—	2.1	1.9	95
550	2	Ph_3CH	58	2 days	5.9	3.7	2.6	91
550	1	Ph_3CH	290	2 days	—	8.8	8.0	96
550	1	Ph_3CH	290	5 days	—	8.8	6.5	63[c]
550	1	Ph_3CH	290	5 days[b]	—	14.5	9.8	35[c]

[a] Emphasis was placed on characterization of reaction products; catalyst surface area was 433 m^2/g before pretreatment; except as noted, the reaction temperature was 100°C.

[b] Reaction temperature was 130°C.

[c] This value does not include the formation of some high molecular weight materials.

major products by calibrated by GLC was within 5% when the reaction system was not heated above 100°. No attempt was made to identify these fractions, but the GLC indicated that they were mainly C_7 to C_{22} compounds. When solvent was used to introduce the reagent, the amount of benzene produced could not be determined because the few milligrams of benzene were dissolved in more than 1 liter of cyclohexane. The identification of benzene was made by observing the single PMR peak at 435 cps from TMS and by mass spectrography; it was assayed by GLC calibrated with a 2% solution of benzene in diethyl ether. An alternative determination was made by PMR calibrated with a 2% solution of benzene in carbon tetrachloride. The two determinations agreed within 5%. Both the diphenylmethane and triphenylcarbinol were identified by exact retention time of GLC calibrated with 0.5% cyclohexane solutions of authentic samples.

The retention times for diphenylmethane, triphenylmethane, and triphenylcarbinol were 9, 12, and 13 min, respectively. In several cases, the diphenylmethane fraction was purified by preparative GLC, and its identity was further established by mass spectrography. Both the parent peak and the fragmentation pattern agreed with literature values (*16*).

When the chemisorption was carried out at 100° for 2 days (Table 2), almost equimolar quantities of diphenylmethane and triphenylcarbinol were formed. However, the mole ratio of benzene to diphenylmethane was 1.7 ± 0.1. The yield of the three major products depended more on the amount of available reagent than on reaction time. When the amount of available reagent was increased from 3×10^{12} molecules/cm^2 of catalyst to 3×10^{13}, the yield of diphenylmethane increased from 2.7×10^{11} molecules/cm^2 to 8.8×10^{11}. With a surface coverage of 5.8×10^{12} molecules/cm^2, the yield of diphenylmethane was 2.1×10^{11} after heating for 3 hr at 100° while the corresponding value was 3.7×10^{11} after heating for 2 days. With a surface coverage of 2.9×10^{13}, when the reaction time was increased from 2 to 5 days the yield of diphenylmethane remained unchanged but the yield of triphenylcarbinol decreased slightly from 8.0×10^{11} to 6.5×10^{11}. That the yield depended on reaction temperature was demonstrated in the last experiment of Table 2. When triphenylmethane was heated for 5 days at 130°, instead of 100°, the yield of diphenylmethane and triphenylcarbinol increased 65 and 50%, respectively. In the last two experiments, the reaction time was 5 days, and GLC analysis indicated the presence of appreciable amounts of high-molecular weight compounds (Fig. 1). The twin peaks at retention time 16 and 17 min are thought to correspond to two isomeric $\alpha,\alpha,\alpha',\alpha'$-

TABLE 3

SUMMARY OF EXTRACTION DATA FOR REACTION OF DIPHENYLMETHANE AND 4,4′-DIMETHOXYDIPHENYLMETHANE (Type B experiments)[a]

Pretreatment temp (°C)	No. of expts.	Substrate	Available reagent (No./cm × 10^{-11})	Reaction time	Product No./cm² × 10^{11})				Total recovery (%)
					C_6H_6	$PhCH_3$	$PhCH_2C_6H_4CH_2Ph$	Recovered PH_2CH_2	
550	3	Ph_2CH_2	87	3 days	38	1.8	7.5	29	81
550	2	Ph_2CH_2	130	6 days	53	1.5	6.8	48	67
550	1	Ph_2CH_2	130	11 days[b]	100	7.2	0.5	13	71
					Product (No./cm² × 10^{11})				Recovered An_2CH_2
					$PhOCH_3$ + $PhOH$		$CH_3OC_6H_4CH_3$	An_2CHOH	
550	1	An_2CH_2	17	6 hr	5.3		0.3	0.1	4.8
550	1	An_2CH_2	120	5 days	52.5		6.5	0.8	—

[a] Emphasis was placed on characterization of reaction products; catalyst surface area was 433 m²/g before pretreatment; except as noted, the reaction temperature was 100°C.

[b] Reaction temperature was 120°C for this experiment.

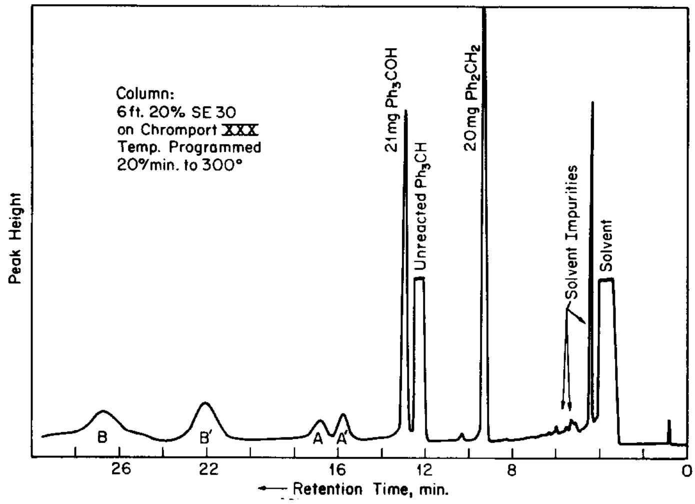


FIG. 1. Chromatogram of products of reaction of triphenylmethane on a silica-alumina catalyst for 5 days at 130°C.

tetraphenylxylenes because the retention time was about that expected for a compound having this molecular weight (410) on this column. The other twin peaks in Fig. 1 with the retention times of 22 and 27 min were not identified, but may stem from the isomers of pentaphenylxylene since these peaks were not found in experiments where only a small amount of triphenylcarbonium ion was formed. The tetraphenyl- and pentaphenylxylenes could result from alkylation of the parent triphenylmethane by the diphenylmethyl and triphenylmethyl carbonium ions, respectively, vide infra.

Quite different products were obtained from the reaction with diphenylmethane. The available reagent was $\sim 10^{13}$ molecules/cm^2 of catalyst surface. After the chemisorption at 100° for several days, the catalyst did not acquire the characteristic yellow color of the diarylcarbonium ions. A comparatively large volatile fraction was obtained and GLC analysis revealed that it consisted of two components, benzene and toluene. From three experiments carried out at 100° for 3 days (Table 3), average values of 3.8×10^{12} molecules/cm^2 of benzene, 1.8×10^{11} molecules/cm^2 of toluene, and 7.5×10^{11} molecules/cm^2 of the isomeric α,α'-diphenylxylenes (most likely the *ortho* and *para* derivatives) were obtained. There was no detectable benzhydrol (less than 3×10^{10} molecules/cm^2) and the recovered diphenylmethane was 2.9×10^{12} molecules/cm^2. Figure 2 shows a typical GLC of the cyclohexane extract. There was little change in the product yields in an experiment where the reaction time was doubled, except that more benzene was produced.

In another experiment where the reaction was carried out at 120° for 11 days, a still different product distribution was found. Here the yield of benzene almost doubled, while toluene increased five times and α,α'-diphenylxylene decreased by over an order of magnitude. Only 10% of diphenylmethane was recovered unreacted and there was indication of formation of "coke." In this case, it is probable that the primary product diphenylxylenes underwent secondary reactions.

The calibration of α,α'-diphenylxylenes was accomplished by comparing its peak height with that of a 1% solution of triphenylethylene since they had almost identical retention times in the GLC. The two C_{20}-fractions were purified by preparative GLC and were identified as α,α'-diphenylxylene by mass spectrography. The two mass spectrograms were identical

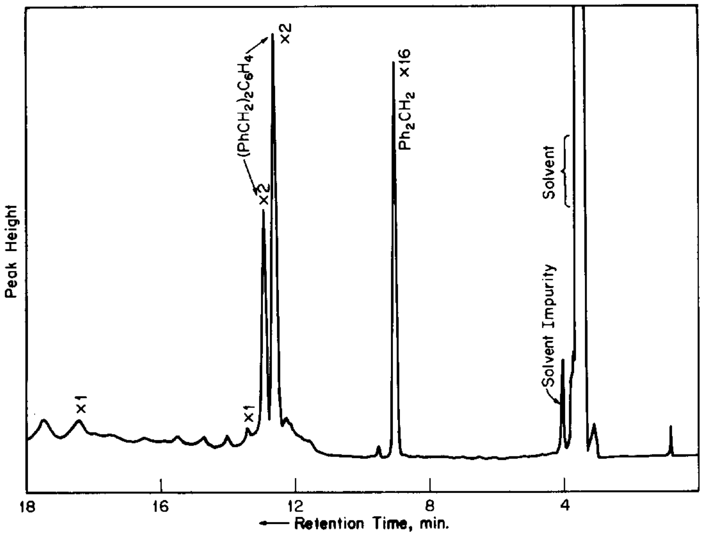


FIG. 2. Chromatogram of reaction products contained in cyclohexane extract from reaction of diphenylmethane on silica–alumina for 3 days at 100°C.

and contained not only the parent peak of $M/e = 258$, but also fragmentation peaks corresponding to ionic species of

$C_6H_5CH_2C_6H_4$, $C_6H_5CH_2C_6H_4CH_2$ and $C_6H_5C_6H_5$,

as expected from the work of Eland and Danby (*16*). The heavier fractions (greater than C_{20}-compounds) were not identified. This could be the reason for the lower percentage of recovery in these experiments.

The results from chemisorption of 4,4′-dimethoxydiphenylmethane on silica–alumina at 100° are also given in Table 3. After the chemisorption, no condensable material could be recovered from the catalyst by heating to 100° in vacuum. The reaction products were recovered from the catalyst by a Soxhlet extraction, first with cyclohexane and then 1:1 mixture of benzene and wet ether to remove any possible hydroxy-compounds. The yields of anisole, phenol, methylanisoles, 4,4′-dimethoxydiphenylcarbinol, and unreacted 4,4′-dimethoxydiphenylmethane were all

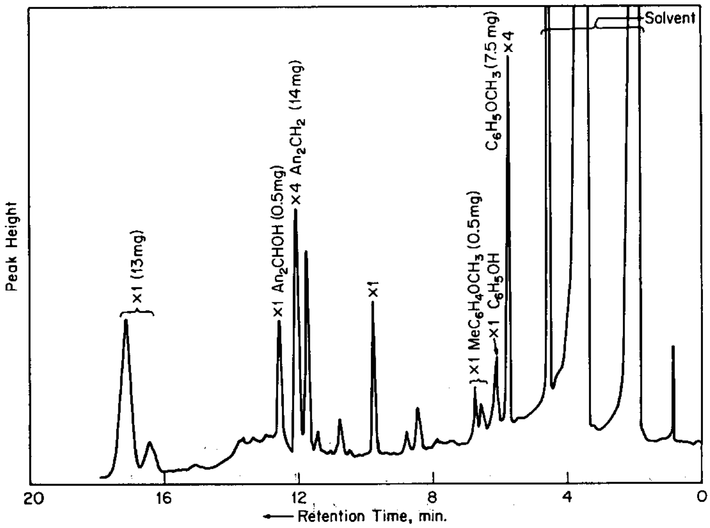


FIG. 3. Chromatogram of products of reaction of p,p'-dianisylmethane with silica–alumina at 100°C.

determined by GLC, calibrated with authentic samples.

A typical GLC analysis of the products is given in Fig. 3. The total amount contained in the long-retention time fraction was obtained by subtracting from the weight of extraction residue the total weight of major products. In the first experiment, 50 mg of 4,4′-dimethoxydiphenylmethane were chemisorbed on 20 g of catalyst at 100° for 6 hr. The major products were: anisole, 7.5 mg; phenol, 0.5 mg; methylanisoles, 0.5 mg; 4,4′-dimethoxydiphenylcarbinol, 0.5 mg; and unidentified long-retention products, 13 mg. The recovered 4,4′-dimethoxydiphenylmethane was 14 mg. In the second experiment, 400 mg of 4,4′-dimethoxydiphenylmethane were chemisorbed on 20 g of catalyst at 100° for 5 days. The major products were: anisole, 31 mg; phenol, 40 mg; methylanisole, 11 mg; 4,4′-dimethoxydiphenylcarbinol, 2.5 mg; and 29 mg of unidentified low molecular weight compounds (probably C_9-compounds). The recovered 4,4′-dimethoxydiphenylmethane was only 31 mg. This means that more than 90% of the original reagent reacted during the chemisorption.

DISCUSSION

In the early work of Leftin and Hall (*4*), several unavoidable mistakes were made. In the absence of data to the contrary, these workers thought that the extinction coefficients of electronic spectra of adsorbed molecules might be very different from those for the same species in solution. Therefore, they determined the triphenylcarbonium ion concentration by a procedure which involved extraction of adsorbed reagent with solvent. Recently, Porter and Hall (*6*) showed that while this technique was satisfactory for the chemisorption of triphenylcarbinol and triphenylmethyl halides, it was not for triphenylmethane and that the carbonium ion concentrations quoted by Leftin and Hall for adsorbed triphenylmethane were probably from 5 to 10 times too high. In this discussion, the value of 6.0×10^{11} ions/cm², reported by Porter and Hall, will be used.

Leftin and Hall (*4*) considered possible ways by which carbonium ions may form from triphenylmethane. One of these involved hydride transfer to existing carbonium ions formed from olefinic impurities. Since solvents were not used and since triphenylmethane itself is not an olefin precursor, the only source of such olefins was thought to be impurities in the triphenylmethane. At their estimated carbonium ion concentrations of $5 \times 10^{12}/\text{cm}^2$, it was found that unreasonably high olefinic impurity levels were required to explain the data, i.e., from 15 to 50 mole %. The actual carbonium ion concentrations ($9 \times 10^{10}/\text{cm}^2$) now calculated from their spectroscopic data could be explained by an impurity level of 1%. Nevertheless, Porter and Hall (*6*) confirmed this point with additional spectroscopic experiments made using triphenylmethane whose purity was believed to exceed 99.95%.

A second error in the earlier work was the assumption that carbonium ions were desorbed by water, ammonia, and nitrogen bases through competition for sites, a view adopted by Hirschler and Hudson (*13*). In the intervening years, new information has appeared which makes this idea dubious. Smith and Rao (*17*) showed that diethyl ether forms a 1:1 complex with the triphenylcarbonium ion in acid solution. This complex does not contribute to the carbonium ion adsorption band, and this fact was used to determine equilibrium constants. Ruttiger (*18*) showed that trityl-halides react with pyridine in a similar way. Thus, the readily reversible bleaching of the triphenylcarbonium ion with water, reported by Leftin and Hall, can best be explained by the analogous reaction

$$Ph_3C^+ + H_2O \rightleftharpoons Ph_3C{:}OH_2^+. \qquad (1)$$

Similarly, nitrogen bases (as exemplified by NH_3) react

$$Ph_3C^+ + NH_3 \rightleftharpoons Ph_3C{:}NH_3^+. \qquad (2)$$

The data of Table 1 show that these complexed ions can be destroyed by water but not by nitrogen bases, i.e., the carbonium ion may be desorbed as triphenylcarbinol but not as triphenylamide because of the more favorable position of the equilibrium

$$2H_2O \rightleftharpoons H_3O^+ + OH^-. \qquad (3)$$

The reactions are

$$Ph_3C{:}OH_2^+ \text{ (or } Ph_3C{:}NH_3^+\text{)} + OH^- \rightleftharpoons Ph_3COH + H_2O \text{ (or } NH_3\text{)} \qquad (4)$$

Nitrogen bases such as pyridine instantly "kill" the color of the carbonium ion complex but do not effect desorption. Instead, triphenylcarbinol is recovered on extraction with aqueous solutions. With aqueous NaOH, which is particularly effective, it is inconceivable that anything else could occur considering the high concentration of hydroxyl ions present. This same chemistry clarifies two issues. It shows that the triphenylcarbonium ion will be desorbed as triphenylcarbinol, regardless of how the carbonium ion was formed, and it explains why it takes about 175 molecules of H_2O (or 13 molecules of NH_3) to remove one carbonium ion from the surface.

Leftin and Hobson (*19*) reported that $(C_6H_5)_3COD$ was not formed when a catalyst containing the triphenylcarbonium ion was contacted with D_2O. However, these workers were unaware that the carbonium ion concentration was an order of magnitude lower than they supposed.

The results shown in Table 1 suggest that the carbonium ion concentration was weakly dependent upon the amount of available oxygen, i.e., compare triphenylcarbinol recoveries for reduced with standard pretreated catalysts and the latter with those having preadsorbed or gaseous oxygen present. That the effects of pretreatment were minimal, however, was shown by our earlier spectroscopic results [see Figs. 2 and 5 of Ref. (*6*)], which showed even smaller effects. Benzophenone was found in relatively large amounts when gaseous oxygen was present. This must be attributed to the well understood (*20*) radical chain oxidation leading to this product, phenol (lost in benzene extraction) and triphenylhydroperoxide. Thus, most, if not all, of the increase in carbonium ion concentration could be due to the acid catalyzed decomposition of the hydroperoxide. Conversely, the absence of benzophenone in detectable amounts in most of the experiments demonstrated that triphenylmethane was *not* oxidized to triphenylcarbinol (or hydroperoxide), preliminary to carbonium ion formation, as suggested by Hirschler and Hudson (*13*). The effects of light were not examined in the present work, but it seems evident that the large photochemical, oxygen dependent increase in ion concentration (*6*, *13*) stems from this free radical process.

It has long been known that silica–alumina catalyze reactions of the Friedel-Craft's type (*21*, *22*). Leftin and Hall (*4*) reported that benzene was the principal volatile product formed when triphenylmethane, adsorbed on silica–alumina, was heated to 100°, but attached no significance to this because they thought the carbonium ion concentration was tenfold higher than it is now known to be. In the present work we have shown that the amount of benzene produced is of the same order of magnitude as the stable carbonium ions. Considering the analogous chemistry usually written for cumene dealkylation, it is not surprising that all of the present work can be incorporated into the following simple Friedel-Craft's chemistry:

$$Ph_3CH + Cat-H^{\oplus} \longrightarrow C_6H_6 + Ph_2\overset{\oplus}{C}H \qquad (5)$$

$$Ph_2\overset{\oplus}{C}H + Ph_3CH \rightleftharpoons Ph_2CH_2 + Ph_3C^{\oplus} \qquad (6)$$

$$Ph_2\overset{\oplus}{C}H + Ph_3CH \rightleftharpoons Ph_2CHC_6H_4CHPh_2 + H^{\oplus}Cat \qquad (7)$$

Equation (5) involves the formation of a benzenonium ion via protonation, which cleaves to the diphenylcarbonium ion and benzene. Equation (6) predicts formation of equimolar amounts of diphenylmethane and triphenylcarbinol. The data in Table 2 not only support this but also agree well with the value of 6×10^{11} triphenylcarbonium ions/cm² catalyst which was spectroscopically determined by Porter and Hall. Competition between the process of Eqs. (6) and (7) determines the relative amounts of diphenylmethane (or triphenylcarbinol) and $\alpha,\alpha,\alpha',\alpha'$-tetraphenylxylenes in the product and, incidentally, the excess amount of benzene over the former. Unfortunately the direct determination of the production of $\alpha,\alpha,\alpha',\alpha'$-tetraphenylxylenes could not be made, but the ratio of the amounts of benzene to diphenylmethane was constant at 1.7 ± 0.1 giving a measure of the relative importance of the two reaction paths.

Leftin and Hall (*4*) determined the upper limit for the amount of H_2 formed when silica–alumina was contacted with triphenylmethane at 110° for 4 days. The value was 3×10^{16} molecules/g catalyst or about 10^{10} molecules/cm^2, i.e., less than 10% of the amount of triphenylcarbonium ion formed. Hence, H^- abstraction by catalyst protons cannot have been an important factor. The good agreement between the amounts of diphenylmethane and triphenylcarbonium ion formed indicates that virtually all of the latter were formed by reaction (6).

Since the reactions represented by Eq. (7) regenerate the protons used in Eq. (5), the surface density of triphenylcarbonium ion formed by Eq. (6) may be a more realistic estimate of the *strong* Bronsted acidity of silica–alumina than the much higher values given by amine titration methods (*13*). The surface density of triphenylcarbonium ions counts the protons which are strong enough to effect dearylation [Eq. (5)] at the test temperature. The effects of temperature and time were not carefully studied, so that the extent to which higher values can be achieved is not known with certainty. However, the following facts are in hand: (a) the ion concentration increased by about 67% when the temperature was raised by 30° (Table 2); (b) ion concentrations about 10 times higher were obtained when triphenylcarbinol was substituted for trophenylmethane (*4*, *6*); and (c) the dimethylphenylcarbonium ion could not be formed from cumene by analogous chemistry below 300° (*4*). These facts can be interpreted by assuming there is an activation energy associated with the protonation of the benzene ring [Eq. (5)] which depends on the strength of the interaction between the surface site (OH group) and the base employed. If it is further assumed that the sites are not all identical, that they differ in the intensive factor of their acidity because of their local environment, then only the strongest will effect the formation of the triphenylcarbonium ions from triphenylmethane, many more from triphenylcarbinol and it is conceivable that all will be leveled by nitrogen bases. The carbonium ion concentration is also strongly dependent upon the amount of available triphenylmethane. This is in accord with the bimolecular reaction scheme of the above Friedel-Craft's chemistry, but it may also indicate some adsorption of substrate at lower concentrations on sites too weak to effect the reaction at 100°C.

Friedel-Craft's chemistry can also explain results from chemisorption of diphenylmethane and of 4,4′-dimethoxydiphenylmethane on silica–alumina, i.e.,

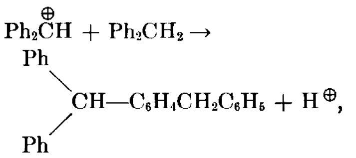
$$\mathrm{Ph_2CH_2 + Cat\,H^{\oplus} \rightarrow Ph\overset{\oplus}{C}H_2 + C_6H_6}, \qquad (8)$$

$$\mathrm{Ph\overset{\oplus}{C}H_2 + Ph_2CH_2 \rightarrow}$$
$$\mathrm{Ph_2\overset{\oplus}{C}H + PhCH_3}\ \text{(minor)}, \qquad (9)$$

$$\mathrm{Ph\overset{\oplus}{C}H_2 + Ph_2CH_2 \rightarrow}$$
$$o\text{- and } p\text{-}\mathrm{PhCH_2C_6H_4CH_2Ph + H^{\oplus}}\ \text{(major)}. \qquad (10)$$

Since the catalyst was almost colorless after it had been heated with 1×10^{13} moles/cm^2 of diphenylmethane at 100° for several days and since no benzhydrol could be detected in the products (probably less than 3×10^{10}/cm^2), it was concluded that diphenylcarbonium ion is not very stable on the catalyst surface. As a matter of fact, the stability of the triphenylcarbonium ion must be a driving force when triphenylmethane is chemisorbed. Hirschler and Hudson (*13*) used diphenylcarbinol as an H_R indicator and reported that silica–alumina contains 0.27 meq/g of acid sites strong enough to form the diphenylcarbonium ion; in contrast, we found a diphenylcarbonium ion concentration of 3.4×10^{10} ions/cm^2 (1.6×10^{-4} meq/g) from diphenylcarbinol in an experiment involving direct spectroscopic measurement. These results suggest that Eq. (9) is a minor one when compared with Eq. (10) or else that Ph_2C^+ is consumed as fast as it is formed.

The formation of a large amount of benzene (38 to 53 × $10^{11}/cm^2$), and the actual recovery of the α,α'-diphenylxylenes further supports these conclusions. It also explains why almost 10 times as many benzene molecules were recovered from the chemisorption of the diphenylmethane as compared with chemisorption of triphenylmethane. Formation of 1.5 to 1.75 × $10^{11}/cm^2$ of toluene and the fact that the mole ratio of benzene to α,α'-diphenylxylenes is greater than five could be explained by Eq. (9) and



$$Ph_2\overset{\oplus}{C}H + Ph_2CH_2 \rightarrow Ph_2CH{-}C_6H_4CH_2C_6H_5 + H^{\oplus}, \quad (11)$$

$$PhCH_2C_6H_4CH_2Ph + H^{\oplus} \rightarrow C_6H_6 + PhCH_2C_6H_4CH^{\oplus}_2,$$

$$PhCH_2C_6H_4CH_2^{\oplus} + Ph_2CH_2 \rightarrow Ph(CH_2C_6H_4)_2CH_2Ph + H^{\oplus}. \quad (12)$$

Indeed, the high-boiling fractions in the GLC, shown in Fig. 2, could be the results of these secondary alkylations. The reactivity of α,α'-diphenylxylenes is well demonstrated in the experiment where the chemisorption of diphenylmethane was carried out at 120° for 11 days. More than 90% of α,α'-diphenylxylenes was decomposed.

In the chemisorption of 4,4′-dimethoxydiphenylmethane, the first dearylation reaction should form a relatively stable 4-methoxybenzylcation, and hydride transfer from another molecule of 4,4′-dimethoxydiphenylmethane would result in the formation of the more stable 4,4′-dimethoxydiphenyl carbonium ion, i.e.,

$$(CH_3OC_6H_4)_2CH_2 + \text{Cat } H^{\oplus} \rightarrow CH_3OC_6H_5 + CH_3OC_6H_4CH_2^{\oplus}, \quad (13)$$

$$CH_3OC_6H_4CH_2^{\oplus} + (CH_3OC_6H_4)_2CH_2 \rightarrow CH_3OC_6H_4CH_3 + (CH_3OC_6H_4)_2CH^{\oplus}, \quad (14)$$

$$CH_3OC_6H_4CH_2^{\oplus} + (CH_3OC_6H_4)_2CH_2 \rightarrow CH_3OC_6H_4CH_2C_6H_3(OCH_3)CH_2C_6H_4OCH_3 + H^{\oplus}. \quad (15)$$

From spectroscopic measurements we obtained a 4,4′-dimethoxydiphenylcarbonium ion concentration of 0.75 × 10^{11} ions/cm^2. An almost identical value was obtained by the extraction technique. On the other hand, the presence of the methoxy group should also enhance the reactivity of the benzene ring toward Friedel-Craft's alkylation. Thus, the reaction rates of both Eqs. (14) and (15) should be greatly increased. This was borne out by the fact that only 30% of the reagent remained unreacted when 4,4′-dimethoxydiphenylmethane was chemisorbed on silica–alumina at 100° for only 6 hr.

A relationship between the stability of a carbonium ion in acid solution and on the silica–alumina surface would be anticipated on the basis of the data for H_R indicators (*13*, *23*). The present data show that more is involved. Although the stability of 4,4′-dimethoxydiphenylcarbonium ion is almost 10 times that of triphenylcarbonium ion in acid solution (*24*), the final ion concentration of the former is only one fifth that of the latter on the catalyst surface. In other words, carbonium ion formation from arylmethanes on the surface of cracking catalyst does not depend solely on the stability of carbonium ion being formed.

There are at least three factors which contribute to the final carbonium ion concentration: (a) the ability of the catalyst surface to stabilize (solvate) the carbonium ions formed; (b) the ease of the dearylation step; and (c) the ability of the ions formed to alkylate the substrate. Kinetic studies of McDonough (*25*) and of Deno *et al.* (*26*) have established that the rate of the hydride transfer is directly proportional to $\Delta_P K_R^+$ of the two carbonium ions involved. Using Deno's equation:

$$\log k = 0.76\,(\Delta_P K_{R^+}) - 2.86,$$

a value of $\log k = 2.24$ (k in $mole^{-1}\ sec^{-1}$) is obtained. Therefore, the formation of carbonium ions from arylmethanes on cracking catalyst should not be limited by rate of hydride transfer, but will be affected by the competition between transfer and alkylation. Thus, different results were obtained for the chemisorption of triphenylmethane and 4,4′-dimethoxydiphenylmethane despite the fact that there is little difference between the values of $\Delta_P K_R{}^+$ corresponding to Eqs. (6) and (14).

While the present work has shown that carbonium ion formation from arylmethanes can be accounted for by Friedel-Craft's chemistry, it does not prove that hydride ions cannot be abstracted from paraffin molecules such as isobutane by a few centers on the silica-alumina surface. The Friedel-Craft's chemistry depends upon the unsaturation contained in the benzene ring; where this is absent an alternative pathway must be found. However, convincing evidence of the presence of strong Lewis acid sites, capable of the reversible abstraction of H^- ions, is lacking.

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