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The Electronic and ESR Spectra of Triphenylmethane Adsorbed on Solid Acid Catalysts

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The electronic spectra of adsorbed triphenylmethane have been observed through a study of disk samples made by the compression method from ordinary powder catalysts. Three kinds of adsorbed species of triphenylmethane were obtained for silica-alumina. The band at 265 mμ was due to a physically adsorbed species (Ph_3CH). A new band at 340 mμ was assigned to the triphenylmethyl radical ($Ph_3C\cdot$), formed in the absence of air, with a sharp spectrum ($g=2.004$) observed in the electron spin resonance. The species of the bands at 408 and 435 mμ was identified as triphenylcarbonium ion (Ph_3C^+), the amount of which increased with the light and temperature exposure period. Types of acid present on silica-alumina, alumina, silica, and other catalysts were discussed.

A number of authors have proposed detailed reaction mechanisms of hydrocarbons catalyzed by silica-alumina on the assumption that it is a strong solid acid. Recently the electronic spectra of molecules adsorbed on silica-alumina under a vacuum system have been investigated as will be described later to find evidence of their acidic nature. Strong signals of electron spin resonance were obtained at room temperature, when polynuclear hydrocarbons,[1,2] *e. g.*, anthracene, perylene and tetracene, or diphenylethylene[3,4] were adsorbed on the surface of silica-alumina. The radical adsorbed on the catalyst surface was identified as a positive radical ion as the result of electron transfer from the aromatic hydrocarbon to the electron-deficient site on the surface of the silica-alumina.

Terenin *et al.*[2] used the differential diffuse reflection technique in order to obtain the electronic spectra of aromatic hydrocarbons, such as naphthalene, anthracene, tetracene, and perylene, adsorbed on silica-alumina. They identified two groups of visible absorption bands, one as the positive molecular ion radical (confirmed by the ESR signal), which was formed by electron transfer from hydrocarbon to some specific sites of the catalyst, and the other as the proton complex, with the addition of a proton from the catalyst surface to hydrocarbon.

Concerning carbonium ion formation from triphenylmethane adsorbed on silica-alumina, Leftin and Hall,[5] Porter and Hall,[6] Brouwer[7] and Hirschler and Hudson[8] have all proposed different reaction mechanisms. The fact that triphenylmethane reacts with silica-alumina to give the chemisorbed triphenylcarbonium ion without evolving hydrogen gas was interpreted by Leftin and Hall[5] as hydride ion abstraction by a Lewis acid site on the surface. Brouwer,[7] however, claimed that the oxidation of perylene to the positive radical ion and the conversion of triphenylmethane into its carbonium ion proceed on the same oxidizing center (Lewis acid) of the silica-alumina surface. Hirschler and Hudson[8] objected to the hydride ion abstraction mechanism and proposed that triphenylmethane would be oxidized to triphenylcarbinol, at first by oxygen which had been held strongly on the surface of silica-alumina, followed by reaction with Brönsted acid to change it into the triphenylcarbonium ion.

On the basis of our observations of the electronic and ESR spectra of adsorbed triphenylmethane on silica gel, alumina gel, silica-alumina and other catalysts, the chemical properties of the surface will be discussed in this paper.

Experimental

Measurements of the Electronic Spectra. The cell used for electronic spectroscopy is shown in Fig. 1. All the spectra were measured with a Hitachi spectrophotometer, EPU-2A, for wavelengths down to 220 mμ. Catalyst samples in the cell could be heated

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[1] J. J. Rooney and P. C. Pink, *Trans. Faraday Soc.*, **58**, 1632 (1962).

[2] A. Terenin, V. Barachevsky, E. Kotov and V. Kolmogorov, *Spectrochim. Acta*, **19**, 1757 (1963); V. A. Barachevsky, E. I. Kotov and A. N. Terenin, *Dokl. Akad. Nauk. (USSR)*, **114**, 378 (1962).

[3] J. K. Fogo, *J. Phys. Chem.*, **65**, 1919 (1961).

[4] H. P. Leftin and W. K. Hall, *ibid.*, **66**, 1457 (1962).

[5] H. P. Leftin, *ibid.*, **64**, 1714 (1960); H. P. Leftin and W. K. Hall, Proc. 2nd Intern. Congr. Catalysis, Paris, 1960, **1**, 1307 (1961).

[6] R. P. Porter and W. K. Hall, *J. Catalysis*, **5**, 366 (1966).

[7] D. M. Brouwer, *ibid.*, **1**, 372 (1962).

[8] A. E. Hirschler and J. O. Hudson, *J. Catalysis*, **3**, 239 (1964).

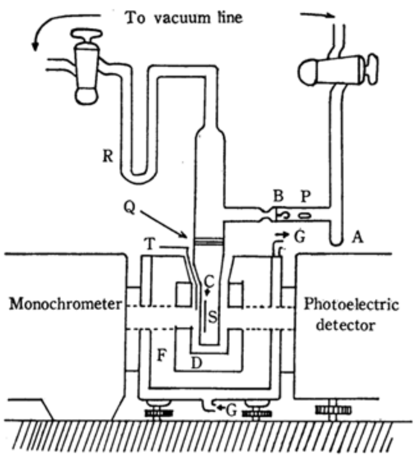

Fig. 1. The cell used for electronic spectroscopy. A: Reactant compartment (triphenylmethane). B: Break-off seals. C: Catalyst sample. D: Copper lining. F: Furnace. G: Cooling water. P: Pyrex bullet. Q: Quartz to pyrex graded seal. R: Cold trap. S: 10 mm square quartz cell. T: Thermocouple.

in situ. Measurements of the electronic spectra were possible at any temperature but only up to 400°C,⁹⁾ because above 400°C radiation from the furnace and the sample cell affected the photoelectric detector. The electronic spectra of a catalyst were determined by using an improved technique which can measure transmission through a thin wafer (0.1 mm) of the catalyst. Powdered catalysts were sieved to less than 300 mesh and then pressed into a 20 mm disk under a pressure of 10—15 ton/cm², as has been described by Webb.¹⁰⁾ This disk was trimmed into a square wafer about 2 cm² in area, then mounted on a rectangular quartz cell, supported with a platinum wire (0.01 mm). Weighed triphenylmethane was introduced into the reactant compartment of the optical cell, which had been evacuated for at least 5 hr and then sealed under a vacuum. After the background spectra of the catalyst disk had been measured, the catalyst was exposed to triphenylmethane vapor by rupturing the break-off seal. Because of the low vapor pressure of triphenylmethane (mp 94°C; bp 359°C), it was often necessary to heat the reactant compartment at about 100°C. In order to avoid the contamination of the catalyst by a stopcock lubricant, a cold trap was inserted between the optical cell and the stopcock.

Measurements of the Electron Spin Resonance Spectra. The measurements of the ESR spectra were carried out by the use of a Varian spectrometer (Model V-4500) at 9181 Mc/sec, with the modulation of 100 kc/sec and with Varian conventional high-temperature equipment. The relative concentrations of the radicals were obtained by measuring the peak heights of the first derivative curves, and all experiments were carried out under the same conditions with regard to the weight of the catalysts and the indicator (Ph_3CH). Hydrocarbon radicals above 10^{11} spin/gauss were easily detected. All catalysts were ground into fine powders (300 mesh or less) and calcined in air at 550°C for 7 hr. The sample was set in one arm of an h-shaped tube, 5 mm in diameter, and made of fused silica, and then a small amount of triphenylmethane was placed in the other arm, made of Pyrex glass. After calcination under a vacuum at 25 or 500°C, triphenylmethane was transferred into the sample arm by heat. ESR spectra were measured at 100, 200 and 300°C after about 10 days in order to ascertain the adsorption equilibrium. No ESR signals were obtained between $g=1.97$ and 2.03 for any catalysts without the addition of triphenylmethane, even though the catalysts were pretreated under a vacuum and measured at each temperature.

Materials. *Silica-alumina Cracking Catalyst (SA-1).* The powdered silica-alumina catalyst (SiO_2 87%, Al_2O_3 13%), supplied by the Shokubai Kasei Co., was calcined in air at 550°C for 7 hr. The BET surface area (N_2 adsorption) was 540 m²/g.

Sodium-exchanged Silica-alumina Cracking Catalysts (SA-1-Na). SA-1 was soaked in sodium hydroxide aqueous solutions to get various final sodium contents as is shown in Table 1. After they had stood for 72 hr with occasional stirring, the catalysts were dried and calcined in air at 550°C for 7 hr. The BET surface areas were 450 m²/g (−1), 480 m²/g(−2), and 480 m²/g(−3).

Alumina Gel. Alumina gel samples were prepared by the neutral hydrolysis of aluminum isopropoxide which had previously been distilled twice. Aluminum

Table 1. Effect of sodium poisoning to silica-alumina catalyst

Catalyst^a)	Na_2O (wt%)	Na meq/g	ESR^b)	Absorbance 340 mμ^c)	Absorbance 408—435 mμ^d)
SA-1	0.008	0.0026	10	1.25	0.36
SA-1-Na-1	0.15	0.049	7	—	—
SA-1-Na-2	0.27	0.087	4	0.60	0.05
SA-1-Na-3	0.52	0.168	3	—	—

a) Each catalyst was evacuated at 500 or 550°C for 5 hr.
b) Numerals represent relative peak height of ESR signals and these spectra were measured at 25°C.
c) Electronic spectra were measured at 25°C.
d) Electronic spectra were measured at 120°C.

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9) B. R. Sundheim and J. Greenberg, *Rev. Sci. Instrument*, **27**, 703 (1956).

10) A. N. Webb, Proc. 2nd Intern. Congr. Catalysis, Paris, 1960, **1**, 1289 (1961).

hydroxide was dried and calcined in air at 550°C for 7 hr and then ground to less than 300 mesh. The BET surface area was 170 m^2/g.

Silica Gel. Silica gel samples were prepared by the hydrolysis of ethylorthosilicate which had previously been distilled twice. The precipitate was calcined in air at 550°C and ground to less than 300 mesh. The BET surface area was 600 m^2/g.

Aluminum Sulfate Mounted on Silica Gel. Aluminum sulfate (G. R. grade) was mounted on the commercial silica gel, used in gas chromatography (Wako gel, Q-12). Anhydrous aluminum sulfate (1.43 g) dissolved in ion-exchanged water was added to 10 g of silica gel to make a viscous slurry. This slurry was evaporated to dryness, then calcined in air at 400°C for 7 hr and ground to a fine powder (less than 250 mesh).

Boron Trifluoride Mounted on Silica Gel. Boron trifluoride (Hashimoto Kasei Co.) vapor was bubbled through sulfuric acid (98.1%) saturated with anhydrous boric acid and then allowed to flow over dried phosphorus pentoxide powder in order to remove any hydrogen fluoride and water.[11] A disk of silica gel which had been evacuated at 550°C for 5 hr was exposed to 150 mmHg of purified boron trifluoride vapor at 25°C for 1 hr and then evacuated at 25°C for 2 hr.

Cyclohexane Solution of Boron Trifluoride. Purified boron trifluoride vapor was bubbled into cyclohexane which had been distilled twice and treated with activated alumina in order to remove any water (less than 15 ppm).

Triphenylmethane. Triphenylmethane (Tokyo Kasei Kogyo Co.) was recrystallized three times from 99% ethanol. The melting point was 94°C. It was ascertained, by means of a study of both ESR and electronic spectra, that purified triphenylmethane contained fewer impurities than the level of the highest detectability.

Results

Silica-alumina (SA-1). *Electronic Spectra.* Triphenylmethane vapor was not detected with the absorption cell 10 mm long. Absorption bands were observed at 265, 340, 408 and 435 mμ, when triphenylmethane was adsorbed on silica-alumina as is shown in Fig. 2. The absorption band at 265 mμ appeared immediately after triphenylmethane vapor was admitted into the cell, (a) in Fig. 2. The adsorbed species of the absorption band at 265 mμ was gradually converted to new species of the absorption band at 340 mμ at 25°C, (b). These phenomena may be interpreted as indicating that the physically-adsorbed triphenylmethane was changed into the triphenylmethane radical on the catalyst surface, as will be discussed in the next section. The absorption band at 340 mμ increased in intensity at higher temperatures (c–e).

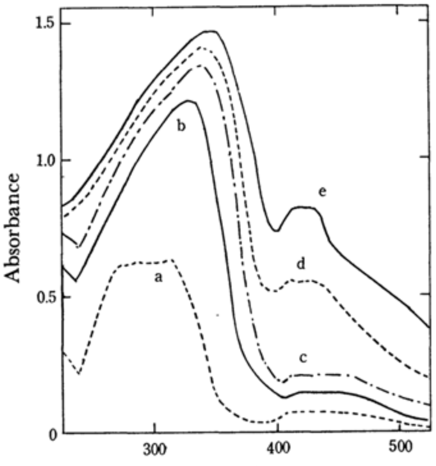

Fig. 2. Electronic spectra of triphenylmethane adsorbed on silica-alumina.
a After 3 hr at 25°C. b After 75 hr at 25°C. c Heated for 2 hr at 90°C. d Heated for 2 hr at 150°C. e Heated for 2 hr at 200°C.

When adsorbed triphenylmethane was either heated above 100°C in the dark or exposed to room light, new absorption bands gradually appeared at 408 and 435 mμ; they increased in intensity at higher temperatures, as Fig. 3 shows. As triphenylmethane is sufficiently stable below 200°C, it is unconceivable to assume that it suffers chemical decomposition. As will be discussed later, this species was assigned to the triphenylcarbonium ion.

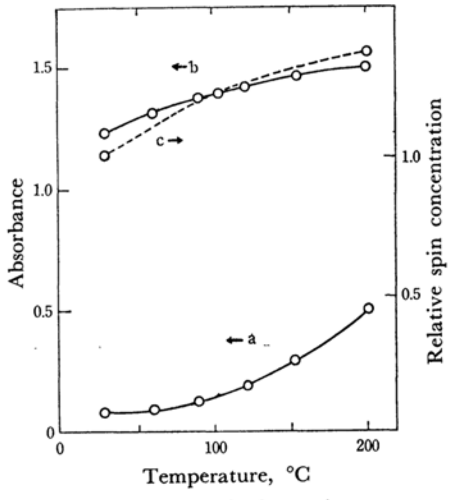

Fig. 3. Peak intensity of electronic spectra and relative spin concentration adsorbed on silica-alumina *versus* temperature.
a Absorbance at 408 and 435 mμ (Ph_3C^+).
b Absorbance at 340 mμ ($Ph_3C\cdot$).
c Relative spin concentration ($Ph_3C\cdot$).

ESR Spectra. Triphenylmethane adsorbed on silica-alumina which had been evacuated at 500°C and at 25°C, both times for 5 hr, gave a single

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[11] L. G. Topchiev. S. V. Zavgorodnii and Ya. M. Panshikin, "Boron Fluoride and Its Compounds as Catalysts in Organic Chemistry," Pergmon Press, London, New York, Paris, Los Angeles (1959), p. 19.

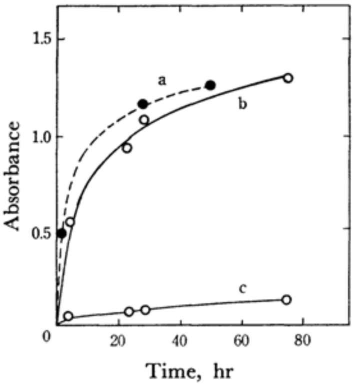

Fig. 4. Peak intensity of electronic spectra of triphenylmethane *versus* time at 25°C.
a Absorbance at 265 mμ on silica gel.
b Absorbance at 340 mμ on silica-alumina.
c Absorbance at 408 and 435 mμ on silica-alumina.

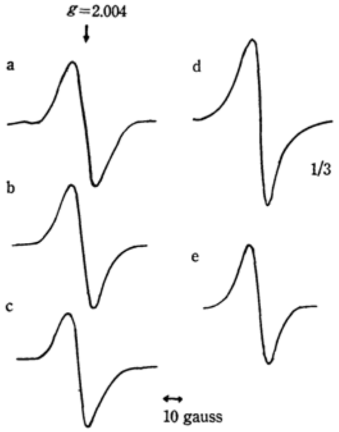

Fig. 5. ESR spectra of triphenylmethane adsorbed on silica-alumina which had been evacuated at 500°C and at 25°C both for 5 hr.
a Evacuation at 500°C and ESR measurement at 25°C.
b Evacuation at 500°C and ESR measurement at 100°C.
c Evacuation at 500°C and ESR measurement at 200°C.
d Evacuation at 500°C and ESR measurement at 300°C.
e Evacuation at 25°C and ESR measurement at 25°C.

broad line of electron spin resonance with a peak-to-peak width of 12.0 gauss and a center of g= 2.004, as is shown in Fig. 5. No difference in the peak height of the first derivative curve or in the shape of the single symmetrical broad line was found for those silica-alumina samples pre-treated by evacuation (*ca.* 10^{-5} mmHg) at 25°C and at 500°C. The intensity and shape of ESR signals remained almost the same when the temperature of the measurements was altered from 25°C to 200°C and back to 25°C again. At 300°C the adsorbed triphenylmethane turned black, probably because of coke formation, and the intensity of the ESR signal became about six times larger than that of 200°C.

Sodium-exchanged Silica-alumina (SA-1-Na). *Electronic Spectra.* Absorption bands at 265, 340, 408 and 435 mμ were obtained for triphenylmethane adsorbed on sodium-exchanged silica-alumina, as Fig. 6 shows. The intensity of the absorption band at 340 mμ for unexchanged silica-alumina was about twice that for the poisoned one at 25°C. A gradual increase in the intensity of this band with time was observed at 25°C. At higher temperature, up to 300°C, the intensity of this band increased. The intensities of the absorption bands at 408 and 435 mμ of unexchanged silica-alumina were changed more effectively by sodium-ion exchange than were those of the absorption band at 340 mμ.

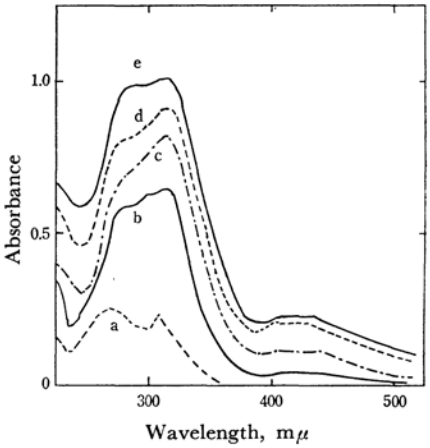

Fig. 6. Electronic spectra of triphenylmethane adsorbed on sodium-exchanged silica-alumina (0.087 Na meq/g).
a After 2 hr at 25°C. b After 22 hr at 25°C.
c Heated for 2 hr at 120°C.
d Heated for 2 hr at 200°C.
e Heated for 2 hr at 250°C.

ESR Spectra. The intensities of the ESR signals of sodium-exchanged silica-alumina with various concentrations decreased with the amount of sodium hydroxide, as is shown in Table 1. The intensity ratio between the absorption band at 340 mμ of silica-alumina and the exchanged one showed a good correspondence with the relative intensities of the ESR signals, as Table 1 also shows. However, there remained weak absorption bands at 408 and 435 mμ. These results suggest that ESR signals resulting from triphenylmethane adsorption have a close correlation with the absorption band at 340 mμ and little correlation with the absorption bands at 408 and 435 mμ.

Alumina Gel. *Electronic Spectra.* Triphenylmethane adsorbed on alumina gel, previously

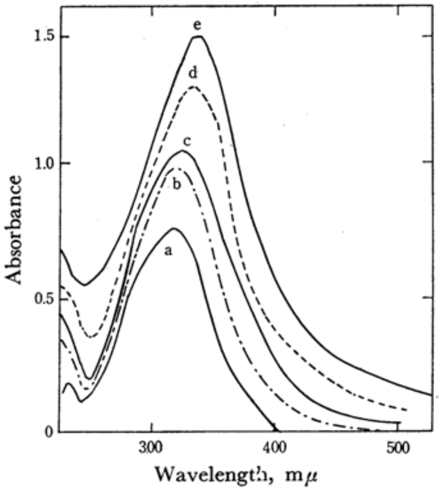

Fig. 7. Electronic spectra of triphenylmethane adsorbed on alumina gel.
a After 22 hr at 25°C.
b Heated for 2 hr at 90°C.
c Heated for 2 hr at 140°C.
d Heated for 2 hr at 200°C.
e Heated for 2 hr at 250°C.

evacuated at 550°C for 5 hr, gave a strong absorption band at 340 mμ at 25°C. The intensity of the band increased at higher temperatures, as is shown in Fig. 7. Alumina gel characteristically gave no absorption bands at 408 and 435 mμ, even at 300°C. No coking phenomena took place below 300°C from triphenylmethane adsorbed on alumina gel, since the adsorbed triphenylmethane did not turn black below 300°C; moreover, the intensity of the ESR signal did not increase at 300°C, contrary to the case of silica-alumina.

ESR Spectra. No ESR signals were obtained at 25°C, nor at 100, 200 or 300°C, for triphenylmethane adsorbed on alumina gel which had been evacuated at 25°C for 5 hr. However, a very strong signal ($g=2.004$) was obtained at 25°C, as well as at 100, 200 and 300°C, as is shown in Fig. 8, when alumina gel had been evacuated at 500°C for 5 hr. The relative spin concentration gradually increased as the temperature rose below 300°C, as Fig. 9 shows. The species responsible for these ESR spectra also has a good correspondence with the electronic spectra at 340 mμ. This species could be kept for one month under a vacuum.

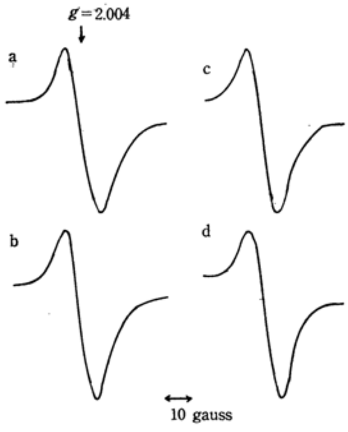

Fig. 8. ESR spectra of triphenylmethane adsorbed on alumina gel which had been evacuated at 500°C for 5 hr.
a Measured at 25°C. b Measured at 100°C.
c Measured at 200°C. d Measured at 300°C.

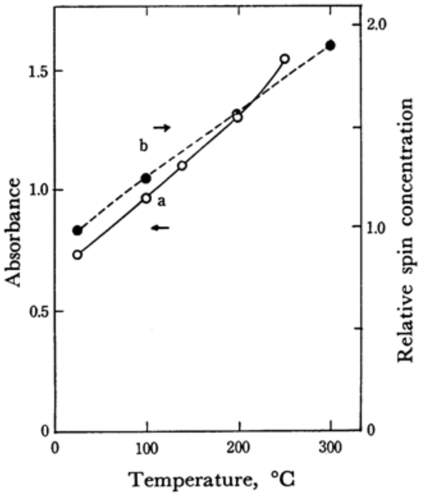

Fig. 9. Peak intensity of electronic spectra and relative spin concentration adsorbed on alumina gel *versus* temperature.
a Absorbance at 340 mμ ($Ph_3C\cdot$).
b Relative spin concentration ($Ph_3C\cdot$).

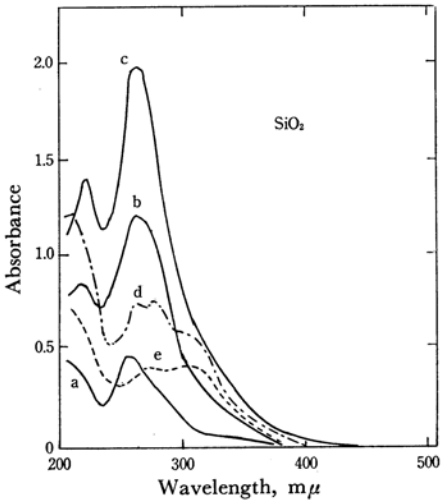

Fig. 10. Electronic spectra of triphenylmethane adsorbed on silica gel.
a After 2 hr at 25°C. b After 50 hr at 25°C.
c Heated for 2 hr at 90°C.
d Heated for 2 hr at 150°C.
e Heated for 2 hr at 300°C.

When air was introduced into this system, however, the intensity of the ESR signal gradually decreased, probably because of water vapor in the air.

Silica Gel. *Electronic Spectra.* The absorption band at 265 mμ for triphenylmethane adsorbed on silica gel was obtained at 25°C, as is shown in Fig. 10. The time dependence of the intensity of this band had a maximum at 90°C in the region between 25°C and 300°C. A small, new absorption band at 330 mμ appeared at higher temperatures.

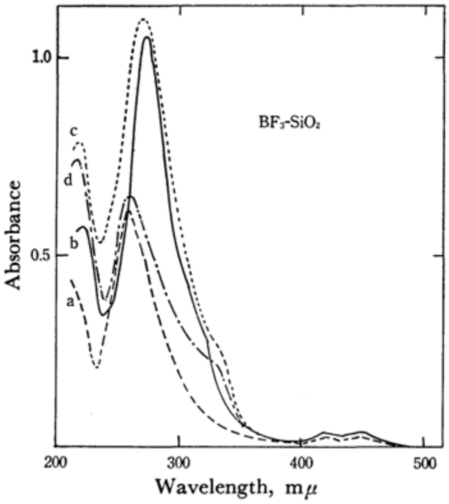

Fig. 11. Electronic spectra of triphenylmethane adsorbed on boron trifluoride mounted on silica gel.
a After 2 hr at 25°C. b After 22 hr at 25°C.
c Heated for 2 hr at 60°C.
d Heated for 2 hr at 90°C.

ESR Spectra. No ESR signals were obtained at 25°C, nor at 100, 200 or 300°C, for triphenylmethane adsorbed on silica gel which had been evacuated at 25°C for 5 hr, while very weak signals of the same intensity appeared at each temperature for silica gel pre-evacuated at 500°C for 5 hr.

Aluminum Sulfate Mounted on Silica Gel. Electronic spectra of triphenylmethane adsorbed on aluminum sulfate mounted on silica gel gave absorption bands at 265, 340, 408 and 435 mμ, as were obtained in the case of silica alumina. A single symmetrical broad line of the ESR spectrum

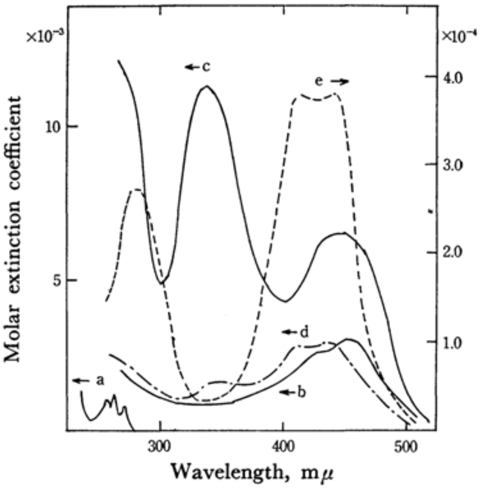

Fig. 12. Electronic spectra of triphenylmethane in various solvents.
a Diethyl ether. b $HClO_4$ (70%).
c H_2SO_4 (98.1%). d H_2SO_4 (88%).
e Triphenylcarbinol in H_2SO_4 (98.1%).

TABLE 2. ABSORPTION MAXIMA OF TRIPHENYLMETHANE IN VARIOUS SOLVENTS

Solvent	H_0[a]	Absorption maxima, mμ[b]
Diethyl ether		245(s), 256(s), 263(s), 271(s)
Cyclohexane		245(s), 256(s), 263(s), 271(s)
H_2SO_4 (98%)	−9.36	340(ss), (11.3×10^3)[c]; 430—450(s), (6.5×10^3)
H_2SO_4 (88%)	−8.02	340(s), (1.5×10^3); 408—440(s), (2.9×10^3)
H_2SO_4 (82%)	−7.24	320(s), (0.62×10^3); 408—440(w), (0.35×10^3)
$HClO_4$ (70%)	−6.38	286(s); 410(s); 445(s), (3.1×10^3)
$HClO_4$ (60%)	−5.21	265(s); 410(s); 445(s), (3.0×10^3)
BF_3-diethyl ether		263(s), 271(s), 300(ss), 340(s), 405—420(s)
BF_3-cyclohexane[d,e]		245(s), 249(s), 256(ss), 262(ss), 265(ss), 271(s)
BF_3-cyclohexane[f]		257(ss), 262(ss), 330(s)
Ph_3COH-H_2SO_4 (98%)[g]		282(s), 408—435(ss).

a) Hammett acidity function.
b) w: weak absorption, s: strong absorption, ss: stronger absorption.
c) Numerals represent molar extinction coefficient.
d) Triphenylmethane was added in BF_3-cyclohexane solution.
e) Fluorescence at 274—330 mμ
f) BF_3 was added in cyclohexane solution of triphenylmethane.
g) Triphenylcarbinol in sulfuric acid.

was obtained at 25°C, as well as at either 100 or 200°C.

Triphenylmethane in Various Solvents. The electronic spectra of triphenylmethane were measured in both non-acidic solvents and strongly acidic solvents. The addition of boron trifluoride vapor to a non-acidic solvent was also attempted in order to verify the Lewis acid interactions. The results are shown in Fig. 12 and Table 2. The electronic absorption of triphenylmethane in cyclohexane and diethyl ether appeared at 245, 256, 263 and 271 mμ. The absorption band at 340 mμ was obtained in both sulfuric acid and cyclohexane with boron trifluoride vapor added, but it was not obtained in perchloric acid, which may be regarded as a strong protonic acid solvent. The characteristic double bands at 408 and 435 mμ were clearly shown in sulfuric acid. The intensity of the absorption bands at 408 and 435 mμ was dependent on the concentration of the acid. These results are very understandable, since sulfuric acids with concentrations higher than 95% have the properties of both protonic acid and an oxidizing agent.

Discussion

Three kinds of absorption bands of electronic spectra for triphenylmethane adsorbed on silica-alumina can be assigned: the physically-adsorbed species, the triphenylmethyl radical, and the triphenylcarbonium ion. The identification of the first band, observed at 265 mμ, as physically-adsorbed triphenylmethane on the surface was made on the grounds that the same band was obtained for non-acidic solvents, such as cyclohexane and diethyl ether, or for silica gel lower than 90°C.

The second band, at 340 mμ, was identified as the triphenylmethyl radical since the same electronic spectra were observed for triphenylmethyl radicals made by various methods; dissociated hexaphenylethane in ether by Anderson(12); decomposed triphenylchloromethane in a mixture of toluene and triethylamine (80 : 20 in volume), with absorption bands at 330 and 340 mμ (relative intensity; 6.5 : 10.0)(13); irradiated triphenylmethane or triphenylchloromethane at a low temperature in a mixture of diethyl ether, isopentane, and ethanol in proportions of 5 : 5 : 2, giving three absorption bands at 342, 336 and 330 mμ (relative intensity; 10 : 8 : 2).(14)

The third band, at 408 and 435 mμ, was identified as the triphenylcarbonium ion because similar spectra were obtained for triphenylcarbonium ions made by various methods. For example, the same absorption bands were observed in the sulfuric acid (stronger than 50%) of triphenylcarbinol, triphenylchloromethane, and triphenylbromomethane.

The various sources are summarized in Table 3.

The formation of paramagnetic species, accompanied by the adsorption of triphenylmethane on silica-alumina, may provide a new approach to the investigation of the surface properties of this important catalyst. Jarrett and Sloan(15) showed that a 0.001 molar benzene solution of the triphenylmethyl radical made by the dissociation of hexaphenylethane gave 21 major peaks, with four closely-spaced hyperfine splittings. However, no hyperfine splittings of the resonance spectra for the adsorbed triphenylmethyl radical on silica-alumina were detected in these experiments for some such reason as the suppression of the motion of the adsorbate. The intensity of the absorption band at 340 mμ and the relative spin concentration of ESR were found to have the same relationship to the temperature, as Fig. 3 and Fig. 9 show.

No ESR signal of the hydrogen atom was obtained for any catalyst.

The intensity of the absorption band at 408 and 435 mμ seemed to be connected with catalytic activities of the dealkylation of cumene around 400°C,(16) the isomerization of xylene between 450°C and 500°C,(17) the isomerization of cyclohexene between 170°C and 400°C,(18) and the coking of triphenylmethane at 300°C, as is shown in Table 4. These results would suggest that the catalytic activities of these reactions or the degree of coking of triphenylmethane are correlated with carbonium ion and, consequently, with Brönsted acid sites. In the case of silica-alumina, the rate of triphenylmethyl radical formation was far larger than that of the carbonium ion at 25°C. The activity of aluminum sulfate mounted on silica gel in the isomerization of xylene and cyclohexene, the dealkylation of cumene, and the coking of triphenylmethane was comparable to that of silica-alumina. Both catalysts gave ESR signals of almost the same intensity and also the same electronic absorpion spectra as the triphenylcarbonium ion.

Light accelerated the formation of the triphenylcarbonium ion, as was observed by Hirschler and Hudson.(8) The absence of any generation of the carbonium ion on alumina gel nor in a boron trifluoride solution would suggest that oxidizing centers are not responsible for the formation of the

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Table 3. Absorption maxima of $\mathrm{Ph_3CH}$, $\mathrm{Ph_3C\cdot}$, $\mathrm{Ph_3C^+}$ and $\mathrm{Ph_3C^-}$

Species	mμ [a)]	log ε [b)]	Method of preparation	Ref.
$\mathrm{Ph_3CH}$	256 263 270	2.86 2.92 2.81	$\mathrm{Ph_3CH}$ in cyclohexane	(19)
$\mathrm{Ph_3C\cdot}$	310 335	3.80 3.95	Hexaphenylethane in ether	(12)
	330 340	3.78 3.96	$\mathrm{Ph_3CCl}$ in a mixture solution of toluene and triethylamine	(13)
	330 336 342	(2)[c)] (8) (10)	Photochemical process of hydrogen atom from $\mathrm{Ph_3CH}$ and chlorine atom from $\mathrm{Ph_3CCl}$ in EPA	(14)
$\mathrm{Ph_3C^+}$	410 435	4.54 4.55	$\mathrm{Ph_3CBr}$ in sulfur dioxide	(12)
	290 400 440	3.1 4.5 4.5	$\mathrm{Ph_3COH}$ in phosphoric acid (90%)	(13)
	420 440	4.2 4.2	$\mathrm{Ph_3CCl}$ in phosphoric oxychloride	(13)
	410 430	4.58 4.58	$\mathrm{Ph_3CCl}$ or $\mathrm{Ph_3CBr}$ in concentrated sulfuric acid	(20)
	405 435	4.5 4.5	$\mathrm{Ph_3COH}$ in formic acid (98—100%)	(21)
	410 435	4.6 4.6	$\mathrm{Ph_3COH}$ in sulfuric acid (98%)	(21)
	250 290 405 435	3.5 3.2 4.6 4.6	$\mathrm{Ph_3COH}$ in concentrated sulfuric acid	(22)
	404 431	4.60 4.60	$\mathrm{Ph_3COH}$ in concentrated sulfuric acid	(23)
	292 408 431	3.1 4.56 4.57	$\mathrm{Ph_3COH}$ in concentrated sulfuric acid	(24)
$\mathrm{Ph_3C^-}$	308 390 485	3.40 3.56 3.75	Sodium triphenylmethyl in ether	(12)
	495	4.4	$\mathrm{Ph_3CH}$ in a solution of potassium amide in liquid ammonia	(25)

a) Wavelength of absorption maxima of each band.
b) ε is molecular absorption coefficient of each band.
c) Relative intensity.

triphenylcarbonium ion. On the contrary, the carbonium ion was formed in perchloric acid (60% and 70%) without oxygen and was accelerated by room light. Upon sodium poisoning of silica-alumina, the formation of the carbonium ion decreased more sharply than that of the radical, as is shown in Table 1. These facts would strongly indicate that the formation of the triphenylcarbonium ion is correlated with the presence of protons for both acid solvents and acidic solids.

Recently several authors have proposed mechanisms concerning triphenylcarbonium ion formation accompanied by the adsorption of triphenyl methane on a silica-alumina catalyst.

Leftin and Hall5) recognized that triphenylmethane on the silica-alumina formed the chemisorbed triphenylcarbonium ion without evolving hydrogen gas; they interpreted these phenomena as direct hydride ion abstraction by a Lewis acid site on the surface. Porter and Hall6)

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TABLE 4. COMPARISON OF ELECTRONIC AND ESR SPECTRA AND CATALYTIC ACTIVITIES OF VARIOUS CATALYSTS

Catalyst[a]	Adsorbed species[b]			Electronic spectra, mμ[b]			ESR[b]	Activity[c]	Coking at 300°C[d]
	Ph_3CH	$Ph_3C\cdot$	Ph_3C^+	265	340	408—435			
SiO_2	s	n	n	s	n	n	n	n	white
Al_2O_3	s	s	n	s	s	n	s	n	white
SA-1	s	s	m	s	s	m	s	s	black
SA-1-Na	s	m	w	s	m	w	m	w	yellow
$Al_2(SO_4)_3$ on SiO_2	s	s	s	s	s	s	s	s	black

a) All catalysts except $Al_2(SO_4)_3$ on silica gel for electronic and ESR spectra were calcined in air at 550°C for 7 hr and evacuated at 550°C or 500°C for 5 hr. $Al_2(SO_4)_3$ on silica gel was calcined in air at 400°C for 7 hr and evacuated at 400°C for 5 hr.

b) n: none, w: weak, m: medium, s: strong.

c) Catalytic activities about cracking of cumene, isomerization of xylene and cyclohexene. n: none, w: weak, s: strong.

d) These color indicated whether triphenylmethane was converted to coke or not.

showed that the sodium exchange of silica-alumina lowered the ability of the catalyst to form the triphenylcarbonium ion, but with little effect on radical ion formation from perylene, while the pretreatment of silica-alumina with hydrogen gas at 550°C nearly eliminated perylene radical ion formation, leaving triphenylcarbonium ion formation unaffected. They claimed that different kinds of sites or different processes might be involved in the two substrates and that chemisorbed oxygen was responsible for only the formation of the perylene radical ion.

Hirschler and Hudson[8] showed much evidence against the hydride ion abstraction mechanism for the chemisorption of triphenylmethane on silica-alumina. They observed that triphenylmethane was oxidized easily into the triphenylcarbonium ion in solutions of strong Brönsted acid in the presence of both oxygen and light, and that light could greatly accelerate the rate of the formation of the triphenylcarbonium ion. They claimed that triphenylmethane was oxidized to triphenylcarbinol, and that the reaction with Brönsted acid then generated the triphenylcarbonium ion, as is shown below:

$$Ph_3CH + O \text{ (adsorbed oxygen)} \rightarrow Ph_3COH$$

$$Ph_3COH + H^+ \rightarrow Ph_3C^+ + H_2O$$

The formation of triphenylcarbinol by the reverse reaction of chemisorbed triphenylcarbonium ion with water has been mentioned as evidence that triphenylcarbinol is the intermediate compound of the carbonium ion formation. They treated silica-alumina with hydrogen gas at 450°C for 18—20 hr in order to remove any chemisorbed oxygen. Therefore, Hirschler and Hudson considered that the most probable source of adsorbed oxygen was either strongly chemisorbed oxygen which had not been removed by hydrogen treatment, or the oxygen ion in the silica-alumina lattice.

The infrared spectra of both silica-alumina and sodium-exchanged silica-alumina were found to be the same in the intensity and wave number of the OH stretching vibration.[26] This suggests that the majority of free hydroxyl groups on the surface observed by infrared spectroscopy do not form an active hydroxyl group exchangeable with sodium ions to form a ONa group. It is difficult to conceive that such stable oxygen, either chemisorbed or of lattice, as was not reduced with hydrogen gas even at 450°C for 18 hr is reduced by less reductive triphenylmethane to give its carbonium ion at 25°C. The recovery of the chemisorbed triphenylcarbonium ion as triphenylcarbinol by the addition of an excess of ammonia, made by Hirschler and Hudson,[8] would be due to the presence of a free hydroxyl group, which still remains on the surface of silica-alumina after pre-evacuation for 5 hr at 550°C, by the following reaction:

$$Ph_3C^+\text{(ad.)} + \text{Surface-OH} + NH_3 \rightarrow$$
$$Ph_3COH + \text{Surface}^+\text{-}NH_3$$

The conclusions from the results of this investigation may be summarized as follows:

The surface of silica-alumina contains at least two kinds of active sites. One kind is sites of the Brönsted acid type. These are very strong acid sites which cannot be found in either alumina gel or silica gel. The number of these active sites was greatly decreased by the exchange of the sodium ion. This fact may be considered as another evidence of protonic acidity. The infrared spectra of silica-alumina and sodium-exchanged silica-alumina were the same in the intensity and wave number of the OH stretching vibration. Therefore, not all of the free hydroxyl groups observed by infrared spectroscopy are necessarily acidic and exchangeable to a ONa group by the sodium ion; only a small part of them have the properties

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[26] H. Arai, Y. Saito and Y. Yoneda, to be published.

of strong Brönsted acid. Nevertheless, this type of acid site plays an important role in many kinds of catalytic reactions. Sodium-exchanged silica-alumina, with weak absorption bands at 408 and 435 mμ, gave an appreciable amount of the radical, as is shown by the electronic absorption bands at 340 mμ and by the ESR signals. This may also indicate that an active site for the formation of the triphenylmethyl radical is not of the Brönsted acid type.

The other kind of site is formed of oxidizing center. This kind of site was found on the surface of alumina gel, too. From the outmost layer of hydroxyl groups over the aluminum ion layer, two hydroxyl groups are removed by calcination under a vacuum, leaving the bare aluminum and oxide ions. Thus the removal of one water molecule from the surface of alumina gel creates one exposed oxide ion and one exposed aluminum ion. The exposed aluminum ion may be considered an electron deficient center which acts as an oxidizing center.

The oxidizing center of silica-alumina may be considered to be the exposed aluminum ion which was diluted by silica gel.

The presence of Brönsted acid sites on the surface of alumina gel is unlikely, since the ESR signal and the electronic absorption bands at 408 and 435 mμ due to the carbonium ion did not appear up to 300°C. Alumina gel was active in the radical formation. Such characteristic phenomena for this catalyst were found that the activity with regard to the radical formation was easily poisoned by water addition in air and that the activity was restored easily by calcination. On the surface of silica gel there are a few oxidizing centers above 100°C, but no Brönsted acid sites up to 300°C. Therefore, triphenylmethane is adsorbed on silica gel only physically below 100°C. Aluminum sulfate mounted on silica gel, as well as silica-alumina, may thus be considered to have both Brönsted acid sites and oxidizing centers.

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