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Oxidation of Aromatic Hydrocarbons by Silica-Alumina

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Perylene is oxidized to its monopositive ion when chemisorbed on silica-alumina or fluorided γ-alumina in the absence of air. The radical ion has been detected and identified by both its electron spin resonance spectrum and its electronic spectrum. The oxidizing properties of these catalysts prove to be connected with their highly acidic nature. Evidence is presented that Lewis sites are the oxidizing centers. In particular, selective poisoning with sodium ions of the Brönsted sites of silica-alumina, which drastically reduces the activity for cumene cracking, has but little effect on the perylene-oxidizing properties. The oxidation of perylene apparently occurs on the same centers as the oxidation of triphenylmethane to triphenylcarbonium ion. Some reactions which possibly involve aromatic radical ions are briefly discussed.

INTRODUCTION

The catalytic properties of silica-alumina have for a long time been considered in terms of acidic properties that induce carbonium ion reactions (*1*). It has been shown recently that silica-alumina may catalyze oxidation reactions and that it possesses certain oxidizing properties by itself. The silica-alumina catalyzed oxidation of anthracene by molecular oxygen has been described by Roberts, Barter, and Stone (*2*). The oxidation of perylene to its monopositive ion by silica-alumina, in the absence of oxygen, has been reported by the author (*3*) and by Rooney and Pink (*4*).

The oxidation of perylene and other polynuclear aromatic hydrocarbons in solution has been investigated by Aalbersberg, Hoijtink, Mackor, and Weyland (*5*). Their results showed that oxidation can be effected by typical Lewis acids, such as BF_3, in e.g., 1,2-dichloroethane solution. The Brönsted acid HF does not oxidize perylene, provided that no molecular oxygen is present (*6*).

The present study was made in order to verify that the oxidizing properties of silica-alumina are connected with its acidic character and to determine the nature of the oxidizing centers. To this end we have investigated the oxidation of perylene in the strict absence of oxygen and water on a number of acidic solids: silica-alumina, silica-alumina in which H^+ had been replaced by Na^+ (by ion exchange), γ-alumina, fluorided γ-alumina, silica, silica-HF and silica-BF_3. The oxidizing properties of the silica-alumina and the ion-exchanged silica-aluminas were compared with their cumene cracking activities, which have been stated to be due to the Brönsted acidity (*7, 8*).

Although other polynuclear aromatic hydrocarbons are oxidized by silica-alumina as well [see e.g. ref. (*4*)] we have confined our study to perylene for two reasons. First, it is readily oxidized and the monopositive ion is stable; secondly, the positive ion of perylene is readily detected and identified by its characteristic electron spin resonance spectrum and its electronic absorption spectrum in the visible region.

The results point to Lewis sites being responsible for the oxidizing properties.

They further indicate a close relation between the perylene oxidation and the hydride ion abstraction by silica-alumina from triphenylmethane reported by Leftin and Hall (*9*).

EXPERIMENTAL METHOD

Oxidation of Perylene

The catalysts were heated at 500°C and at a pressure of 10^{-4} mm Hg or less for 16 hr prior to perylene adsorption. Perylene was adsorbed from a solution in *n*-heptane which had been purified by the procedure given by Roberts, Barter, and Stone (*2*). Both perylene and the solvent were thoroughly degassed. The perylene was dissolved in *n*-heptane, adsorbed on the catalyst, and freed from the solvent in a completely sealed all-glass apparatus to prevent any contact with air or greases, break-seals being used where necessary. Provisions were made for further addition of gases after taking of the electron spin resonance spectra by a similar procedure.

Electron Spin Resonance Spectra

Electron spin resonance measurements were made with a Varian Model V-4500 EPR spectrometer operated at 9500 Mc/s and magnetic field modulation 100 kc/s. For quantitative estimation of the perylenium ions the derivative spectrum was integrated and the area under the integrated curve was determined. This area was compared with that obtained with solid vanadyl disalicylalethylenediamine.

Optical Spectra

The sample was prepared as above and shaken into a quartz cell, which had been sealed to the apparatus. This cell, which had a diameter of 4 cm and could contain a 3 mm thick layer of sample, was placed against the sample opening of the reflection atttachment (RA 3) of a Zeiss spectrophotometer (PMQ 11) provided with a double monochromator (MM 12).

Catalysts

Silica-alumina. Commercial low-alumina fluid catalyst (Ketjen MS3-A) was steam-treated to remove adsorbed ammonia; it had a surface area of 550 m^2/g.

Na^+-containing silica-alumina. About 25 g of silica-alumina was shaken for 16 hr with 100 ml 0.2 *M* Na-acetate solution and filtered off. This procedure was repeated three times and the catalyst was then washed on a glass filter with ten 100 ml portions of distilled carbonate-free water, dried, and calcined at 500°C. Its sodium content was 1.1 wt %. Another portion of silica-alumina was shaken seven times with 1 *M* Na-acetate solution and further treated as before; it contained 1.6 wt % of sodium.

γ-Alumina. Aluminium isopropylate was subjected to neutral hydrolysis and the hydroxide obtained was dried and calcined at 500°C.

Fluorided γ-alumina. Calcined γ-alumina was treated with an aqueous HF solution, dried, and calcined at 500°C. Its fluorine content was 3.5 wt %.

Silica, a.r., was obtained from Mallinckrodt.

Cumene Cracking Activity

The cracking activity was determined by measuring the conversion of cumene to benzene in a stainless steel flow reactor containing about 0.1 g of catalyst. The cumene was purified by percolation over silica-alumina to remove possible peroxides and the catalyst was heated at 500°C *in situ* in a flow of purified hydrogen for 16 hr prior to the cracking run. A cumene-hydrogen mixture (mole ratio 1:9) was passed over the catalyst at 427°C and atmospheric pressure. At regular intervals samples of the effluent were analyzed for benzene and cumene by gas-liquid chromatography. The reaction rate being of first order under the conditions used (*10*), the rate constant could be computed from the measured conversion and the cumene feed rate.

RESULTS

When perylene is adsorbed on silica-alumina under high-vacuum conditions the solid turns brown to violet. The formation of the monopositive ion of perylene is apparent from both the electron spin resonance spectrum and the optical spectrum. The former is shown in Fig. 1. The g-value (2.00), line distances (3.5 gauss), and relative intensities agree with those found for the perylene monopositive ion in homogeneous acidic systems (*6, 11*). The resolution of the hyperfine structure is much less than can be obtained with solutions of the perylene positive ion (*6*). This is due to some contribution of the anisotropic part of the paramagnetic absorption in the case of adsorbed perylene ions. This contribution, which is absent with dissolved radicals, leads to line broadening in those cases where the absorbing radicals are neither completely free to perform tumbling motions nor too rigidly fixed (*12*). Quantitative evaluation of the spectrum indicated the presence of 1.6×10^{12} unpaired electrons per cm^2 of catalyst surface.

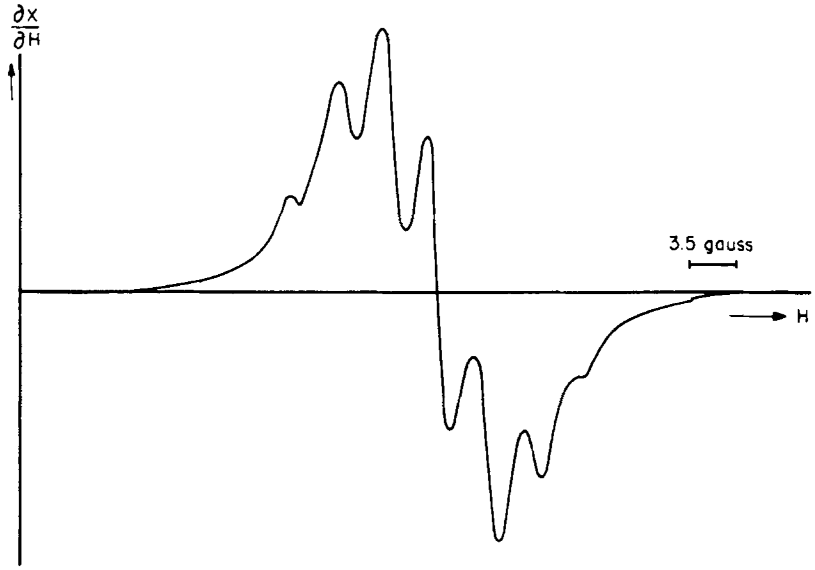

FIG. 1. Electron spin resonance spectrum of perylene monopositive ion on silica-alumina.

The reflection spectrum in the visible region of perylene adsorbed on silica-alumina is shown in Fig. 2, curve *a*. The high adsorption peak at 18500 cm^{-1} and the small one at 13600 cm^{-1} clearly originate from the monopositive ion. The absorption maximum at 23200 cm^{-1} is due to unchanged perylene molecules which are either physically adsorbed or left behind after evaporation of the solvent. The unchanged perylene is also responsible for the shoulder at 26000 cm^{-1} and, in part, for the maximum at 24500 cm^{-1}. The presence of the proton complex (carbonium ion) of perylene, presumably formed on Brönsted centers, is indicated by the shoulder at 15000–16000 cm^{-1}; part of the adsorption at 24500 cm^{-1} is also due to this proton complex. Finally, the rise in absorption between 11000 and 13000 cm^{-1} may be attributed to the presence of a charge-transfer band in the region above 12000 cm^{-1}. Charge-transfer complexes are likely to be present on electron-accepting sites that are too weak to effect the complete electron transfer necessary for the formation of the perylene positive ion. The absorption due to charge transfer complexes would be expected in the region mentioned.

Upon contact with air or water vapor both the color of the system and the shape of the electron spin resonance spectrum changed rapidly. When kept in a sealed-off tube the perylene positive ion proved to be stable for a year at least.

In order to ascertain that the oxidizing

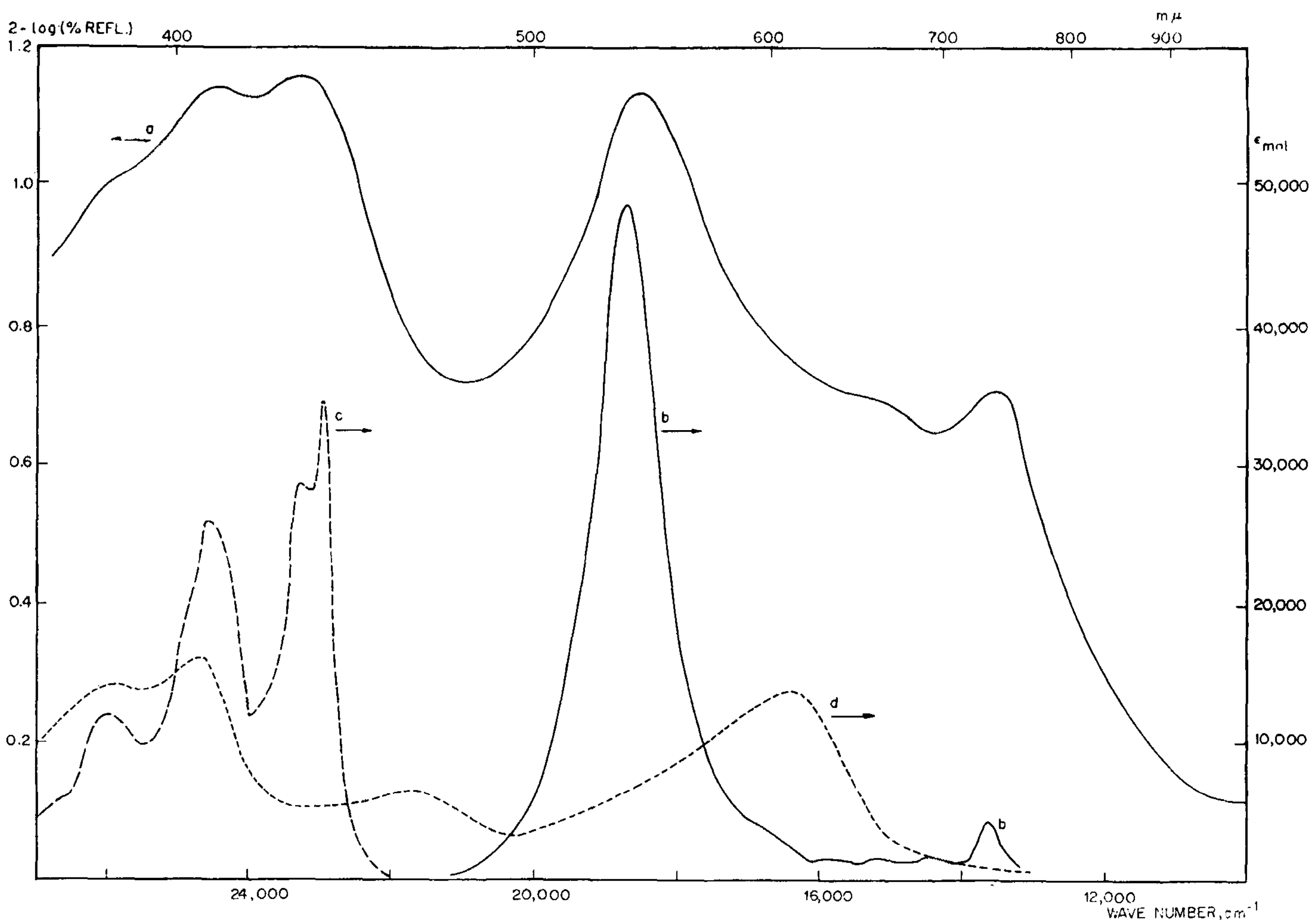

FIG. 2. Visible spectrum of perylene on silica-alumina. Curve *a*: reflection spectrum of perylene on silica-alumina; curve *b*: absorption spectrum of perylene monopositive ion in $CF_3COOH—BF_3—H_2O$ [after ref. (*5*)]; curve *c*: absorption spectrum of perylene in *n*-heptane; curve *d*: absorption spectrum of the proton complex of perylene in HF [after ref. (*5*)]. The scale on the left-hand ordinate refers to curve *a*, that on the right to curves *b* through *d*. On the upper side of the figure the wavelength is given in mμ; the lower scale gives the wave number in cm^{-1}.

properties are indeed connected with the acidic nature of the catalyst and do not result from transition metal impurities, perylene was adsorbed on γ-alumina, on fluorided γ-alumina, and on a γ-alumina that had been impregnated with ferric nitrate and recalcined (iron content 0.02 wt %). Whereas the fluorided γ-alumina showed fairly strong oxidizing properties, no perylenium ion could be detected on γ-alumina itself nor on the Fe (III)-containing alumina.

Adsorption of perylene on silica gives rise neither to color changes nor to an electron spin resonance signal; the adsorption is purely physical. When BF_3 is admitted to the perylene-on-silica system an intense violet color develops and a strong resonance signal characteristic for the perylene cation is found. Upon contact with gaseous HF, however, the perylene-on-silica system turns intensively yellow, which indicates the formation of the proton complex of perylene, and but a very weak electron spin resonance absorption is detected.

Replacement in silica-alumina, to various degrees, of H^+ by Na^+ had only a slight influence on the oxidizing properties. Yet the cumene-cracking activity of the two samples of Na-silica-alumina catalysts thus prepared had dropped to 14% and 2%, respectively, of that of the untreated silica-alumina catalyst.

DISCUSSION

The results provide strong evidence that the oxidizing properties of silica-alumina and fluorided γ-alumina are indeed connected with their acidic nature and are not due to contaminating transition metal ions. This is in agreement with the observation by Rooney and Pink (*13*) that highly purified $AlCl_3$ is capable of oxidizing perylene to the monopositive ion.

That oxidation can be effected by $AlCl_3$ and other Lewis acids (*5*), but not by HF (*6*), suggests that the oxidizing centers on silica-alumina and on fluorided γ-alumina are of the Lewis type. Indeed, all evidence thus far obtained sustains this hypothesis. It has been stated (*7*) 'that incorporation of Na^+ ions in silica-alumina by the ion exchange procedure blocks the Brönsted sites allegedly responsible for cumene cracking activity but hardly affects the Lewis sites. Our findings with the Na^+-treated silica-alumina catalysts, then, point to Lewis sites as the oxidizing centers.

Oxidation of perylene is effected by recalcined, fluorided γ-alumina but not by γ-alumina. This can be interpreted in terms of an increase of the intrinsic acidity of the Lewis sites at the alumina surface brought about by replacement of hydroxyl groups by the more electronegative fluoride ions.

Recently, Leftin and Hall (*9*) reported that triphenylmethane upon adsorption on dehydrated silica-alumina is converted into the triphenylcarbonium ion by hydride ion abstraction. They suggested that this reaction is effected by Lewis centers, one of the arguments being that triphenylmethane adsorbed on silica is converted into the carbonium ion upon addition of BF_3 but not when anhydrous HF is admitted. Similarly, perylene adsorbed on silica gives rise to a strong electron spin resonance absorption upon contact with BF_3 but not with HF. Thus, it is reasonable to assume that the hydride ion abstraction from triphenylmethane, which can be considered as an oxidation of this hydrocarbon, and the oxidation of perylene to its positive ion are closely related reactions occurring at the same centers on the catalyst. Quantitative comparison of the two reactions lends strong support to this hypothesis. The value found by Leftin and Hall for the number of triphenylcarbonium ions was 4.3×10^{12} ions per cm^2 of catalyst surface for a low-alumina Houdry M-46 catalyst. This is in close agreement with the number of perylene cations found in the present work, namely 1.6×10^{12} ions per cm^2 for the low-alumina Ketjen catalyst.

It is not surprising that sites capable of abstracting hydride ions also possess oxidizing, i.e., electron-accepting properties. For in both reactions the formal charge of the metal ion forming the Lewis center is decreased. The parallelism of the two reactions from an energetic point of view is apparent from the following comparison.

	Oxidation	Hydride ion abstraction
(a)		$\Phi_3C{-}H \rightarrow \Phi_3C\cdot + H\cdot$
(b)	$P \rightarrow P^+ + \ominus$	$\Phi_3C\cdot \rightarrow \Phi_3C^+ + \ominus$
(c)	$\ominus + L \rightarrow L^-$	$L + \ominus \rightarrow L^-$
(d)		$L^- + H\cdot \rightarrow L^-{-}H$

where P stands for perylene and L represents a Lewis center. Presumably, the high value of the third ionization potential of aluminum is the main driving force, reaction (c) essentially being

$$Al^{3+} + \ominus \rightarrow Al^{2+}$$

The situation here is quite analogous to that which arises when aromatic hydrocarbons are adsorbed on metal surfaces at low temperature at which no further reaction occurs. There the adsorbed aromatic molecule becomes positively charged (*14, 15*) to form a positive ion or a charge transfer complex (*16*) ("positive adsorption"). In the case of metal surfaces the electron affinity is expressed by the work function; upon adsorption of an aromatic hydrocarbon the work function is found to decrease (*14, 15*).

No definite conclusions can be drawn from the electron spin resonance spectra as to the fate of the electron abstracted by silica-alumina from the aromatic molecule. The resonance spectrum is fairly symmetric and the second moment of the integrated spectrum is about 30–40 gauss^2, which is in agreement with that found for the perylene monopositive ion in solution (*6*). The absence of an apparent signal due to the abstracted electron, which we believe to have remained unpaired, can be explained in two ways. First, the possibility cannot be excluded that the abstracted electron has given rise to paramagnetic resonance absorption at the same *g*-value and with about the same line width as the unpaired electron in the aromatic ion; the absorption lines would then merge and that of the abstracted electron would escape detection. This would be quite fortuitous. We consider it more likely, therefore, that the absorption caused by the abstracted electron has been smeared out over a wide field range, thus leaving a signal too weak for detection.

Monopositive ions of aromatic hydrocarbons have an unpaired electron and may, therefore, lead to the occurrence of free radical reactions on acidic catalysts. The reaction with molecular oxygen of anthracene adsorbed on silica-alumina (*2*) is an example of this.

The formation of aromatic radical ions seems important in connection with coke formation. Polynuclear aromatic hydrocarbons are known to be precursors of coke, the coke-forming reaction being condensation of aromatics to larger aggregates. If such reactions occur via a radical mechanism, as has been suggested by Rooney and Pink (*13*), coke formation would largely occur on Lewis centers. This view would explain why the activity for cumene cracking, which is due to Brönsted centers, is little or not affected by coke deposition (*17*).

Possibly the formation of molecular hydrogen during catalytic cracking (*1*) also proceeds via a free radical mechanism in which aromatic radical ions are involved. Leftin and Hall (*9*) have shown that the hydride ion abstracted from triphenylmethane does not combine with a proton of the catalyst to form H_2; apparently the *ionic* reaction $H^- + H^+ \rightarrow H_2$ does not occur. On the other hand, formation of H_2 during coke-forming radical reactions seems quite feasible. The reverse of the hydrogen formation reaction might well cause the influence of high pressure hydrogen on acid-catalyzed reactions (*18, 19*). Dissociation of H_2 into a hydride ion and a proton is highly unfavorable energetically as compared to dissociation into two hydrogen atoms.

Recently, Fogo [*J. Phys. Chem.* **65,** 1919 (1961)] reported that treatment of silica-alumina with hydrogen gas at 500°C decreases the oxidizing activity. We have confirmed these results, finding a decrease of the number of oxidizing centers by about 90%, as is also reported by Hall [*J. Catalysis* **1,** 53 (1962)]. It is not known whether the "reduced" catalyst contains too little or the "oxidized" form too much oxygen with respect to stoichiometry. If the latter is the case it is possible that oxygen atoms are adsorbed on Lewis sites where they are transformed into mononegative ions by charge redistribution. These O^- ions then would be the actual oxidizing agents.

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