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The Formation of Cation Radicals on the Surface of Silica-Alumina Catalysts

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Optical and electron paramagnetic resonance (EPR) spectra have been obtained for a number of polynuclear aromatic hydrocarbons and phenylated amines adsorbed on a silica-alumina catalyst. Both compound types react to form cation radicals on the surface. The results for the amines suggest that the electrophilic centers involved are identical with those required for carbonium ion type reactions. The maximum number of paramagnetic species formed per unit area of surface was found to be in fair agreement with an earlier estimate of Leftin and Hall (1), obtained for triphenylmethane and related compounds. However, it was also found that the spin density was dependent upon the oxidation state of the catalyst surface. A possible relationship of the present results with those for phenylated olefins is pointed out.

INTRODUCTION

In recent years, there has been much discussion about the nature of the acid present on the silica-alumina surface. A recent spectroscopic study (1a) established the existence of strong electrophilic centers. In this work, it was demonstrated that when molecules such as triphenylmethane, 1,1-diphenylethane, and cumene were adsorbed, carbonium ions were formed as a result of the abstraction of tertiary hydrogen in the form of hydride ions which were retained by the catalyst surface. It was further shown that these reactions were typical of strong Lewis, but not of strong Bronsted, acids. Spectra obtained for olefins adsorbed on silica-alumina (2, 3) invariably contained a band which could be unambiguously attributed to the corresponding classical carbonium ions in addition to one or more bands of uncertain origin at longer wavelength. The electronic spectra alone are insufficient to distinguish between the classical carbonium ion formed by proton addition to the olefin and the corresponding Lewis acid adduct (2, 3); however, in view of the results obtained with the saturated hydrocarbons, it was presumed to be the latter.

Similar situations are known to exist in acidic solutions. For example, Evans *et al.* (4) showed that two bands appeared in the electronic spectrum of 1,1-diphenylethylene, when dissolved in a mixture of acetic acid and sulfuric acid. One, at 423 mμ, corresponded to the classical methyldiphenylcarbonium ion; the other, at 607 mμ, was attributed to a π-complex of Dewar type, formed by interaction of a proton of the weak acid with the olefinic double bond. (This assignment was arrived at by a process of elimination.) These same two bands have been observed (2, 3) for the same substrate, when adsorbed on the surface of silica-alumina. Webb (2), following Evans, assigned the 607-mμ band to a charge-transfer complex, formed by interaction on the catalyst surface of a hydrogen atom (or proton) with the olefinic double bond. Hall and Leftin (1b) raised objections to this assignment and pointed out that their data (5) indicate that the band is due to an intermediate in the oxidation of the olefin. This situation will be discussed more fully in a forthcoming paper (3); it will suffice to say here that all of their data, with one notable exception, are consistent with the view that the 607-mμ band corresponds to a cation radical. This exception is that the expected paramagnetism could not be detected by the usual EPR technique. Although this is a serious shortcoming, it does not necessarily mean that a paramagnetic species is absent, since special circumstances may exist to prevent its detection. Attention was therefore turned to the study of substrates, known to form cation radicals in acidic media, which can be identified by both optical and EPR spectra. It is the purpose of the present communication to present what is believed to be convincing evidence for the formation of cation radicals on the surface of silica-alumina catalysts when the substrate is an alternant polynuclear aromatic hydrocarbon, such as anthracene or perylene, or a phenylated amine.

EXPERIMENTAL METHOD

All work was carried out using conventional high-vacuum techniques. Optical spectra were obtained by measuring the transmissions through thin platelets of catalyst, immersed in isooctane solutions of the substrates contained in sealed, quartz, optical cells. The closely similar refractive indices of the solutions and catalyst prevented more than minimal refractive loss in light intensity. The catalyst platelets were prepared according to the method of Webb (2). For EPR work, the catalyst was used in the powdered form, and the apparatus was modified so that the finely ground material could be slurried with the solution and allowed to settle into the quartz probe tube. The concentrations of the isooctane solutions varied, as required, from about 10^{-3} to 10^{-6} mole/liter. For optical spectra, the catalyst platelets weighed about 100 mg; in the EPR work, 2.5 g were used. In both cases, they were contacted with 10 cc of solution.

In every case the catalyst was treated in flowing oxygen for 16 hr at 530°C for the removal of residual adsorbed organic matter, and evacuated for 24 hr at the same temperature. In one EPR experiment, prior to the final evacuation, the catalyst was treated with flowing H_2, which had been dried over charcoal at the temperature of liquid nitrogen, for 24 hr at 530°C. The solutions were degassed by repeated freezing and pumping and were brought into contact with the catalyst just prior to placing the absorption cell in the spectrometer. Adsorption was effected by rupturing a break-off seal which separated the solution chamber from the evacuated catalyst compartment and by pouring the solution onto the catalyst. Details of the procedure have been described elsewhere (3, 6).

Reducible oxygen was determined by circulating hydrogen over the catalyst at 530°C in an all-glass system. The water evolved was collected in a liquid nitrogen trap and was measured volumetrically in a Brunauer-Emmett-Teller system. The latter was connected to the circulation loop through stopcocks.

American Cyanamid Company *Aerocat* cracking catalyst was used in most of the work; this catalyst is reported (7) to contain 22.1% Al_2O_3 and following pretreatment was found to have a surface area of 480 m^2/g and a total micropore volume of 0.76 cc/g. In a few instances optical spectra were obtained with thin, transparent platelets of catalyst DSA-1, used in earlier work; the preparation of this catalyst and its properties are described elsewhere (1, 6). Since results with this latter catalyst were generally consistent with those obtained with the Cyanamid product, they are not reported here.

Isooctane (Philips spectrograde) was used as solvent, after being allowed to stand for some time over a large sample of cracking catalyst. A check on its absorbance showed it to be completely transparent over the spectral region of interest.

The absorbates were commercial products of the highest purities available (>99 mole %). Since their absorption spectra in isooctane or in sulfuric acid revealed no unexpected bands, they were used without further purification.

The EPR measurements were carried out with a Varian Associates X-band spectrometer Model B-4500, employing audiomagnetic field modulation and phase sensitivity detection. The magnet system consisted of the standard 6-in. diameter pole face unit (V-4007) with 2-in. air gap and matching power supply (V-2200 A). The derivative of the absorption line was traced automatically with a conventional pen recorder. A Cary Model 14 spectrophotometer was used for determination of the optical spectra.

RESULTS

The spectra of anthracene in the adsorbed state and in isooctane solution are compared in Fig. 1. Bands appearing below 400 mμ are common to both and, in the case of the catalyst, correspond to physically adsorbed reagent. As shown by Aalbersberg and co-workers (8) and by Verrijn-Stuart and Mackor (9), the band at about 400 mμ can be attributed to the classical carbonium ion, formed at the 10-position by reaction with either a proton or a Lewis acid at the 9-position. Similarly, the band at about 720 mμ can be identified with the cation radical (8). The small band appearing at about 665 mμ cannot be identified so unambiguously, but a tentative assignment to a dipositive anthracenium ion may be made on the basis of Aalbersberg's work with tetracene in the presence of strong Lewis acids (8) and from the calculations of Balk *et al.* (10) of the energy levels of the alternant hydrocarbon dinegative ions.

The spectrum obtained for adsorbed perylene is compared with that from an isooctane solution in Fig. 2. Again, the bands below 450 mμ correspond to physi-

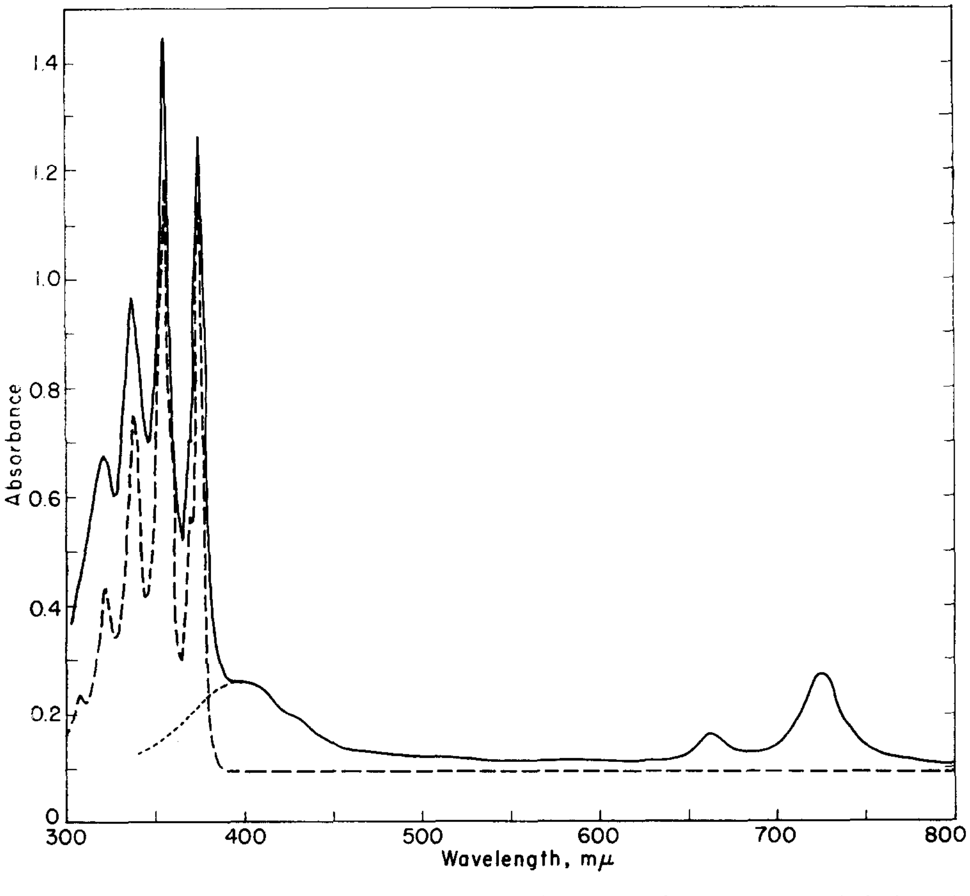

FIG. 1. Anthracene adsorbed on silica-alumina (solid line) and in isooctane (dashed line).

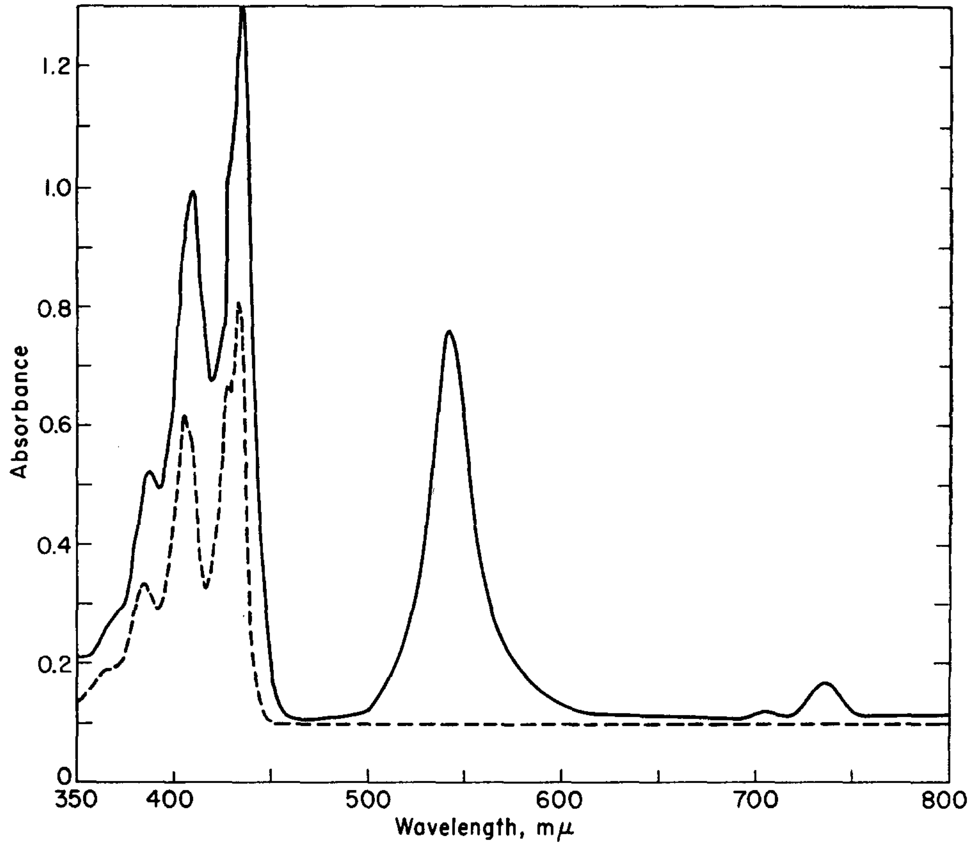

FIG. 2. Perylene adsorbed on silica-alumina (solid line) and in isooctane (dashed line).

cally adsorbed substrate, whereas the strong band at about 545 mμ establishes the presence of the perylene cation radical. The two weak bands in the 720–750 mμ region have not been assigned with certainty, but they also appear in the published spectra attributed to the cation radical (8, 11) and may result from a second weak intramolecular transition of this species. Perylene was the only hydrocarbon studied for which no evidence was obtained for the formation of a covalent complex of the nature of a classical carbonium ion.

Spectra were also obtained for adsorbed pyrene (bands at 462 and 447 mμ) and 3,4-benzopyrene (520 and 782 mμ). Although spectra were not determined for tetracene and 1,2-benzanthracene, a dark brown and a pea-green color, respectively, formed when the catalyst was treated with these reagents in the EPR experiments. The results are consistent with Aalbersberg's assignment (8) of bands for cation radicals and covalent Lewis acid complexes, formed from these substrates.

When triphenylamine was adsorbed, a band at about 660 mμ developed rapidly. After standing for several hours, an additional band at about 485 mμ became noticeable. Both bands continued to grow until, after about 6 hr, they had roughly the same intensity. The band at 660 mμ can be readily identified with the cation radical of this amine (12), but the band at shorter wavelengths has thus far not been assigned. With diphenylamine and aniline, colors also developed, although their spectral characteristics have not been determined so far.

All of these amines and polynuclear aromatic hydrocarbons were shown by EPR methods to be strongly paramagnetic when adsorbed on silica-alumina. Spectra were obtained with a view to (a) using hyperfine splittings for the purpose of identifying the adsorbed species, and (b) evaluating the unpaired spin concentration on the catalyst surface. With respect to the former, it was not found possible to resolve completely the hyperfine spectrum of any catalytic system tested. The most favorable result obtained is shown in Fig. 3 where the EPR spectrum for adsorbed perylene is compared with that for a sulfuric acid solution of this hydrocarbon. In both cases, the strongest seven of the nine, equally spaced hyperfine, lines of the perylene positive-ion spectrum are clearly resolved. The data obtained for the acid solution are generally in good agreement with earlier work (13, 14), even for the fine structure, which is superimposed on the major lines. This detail was not developed in the spectrum obtained with the catalyst, where the spacing between the major lines was slightly broadened. Of the other substances tested, only naphthalene gave a reasonably well-developed hyperfine pattern, although with triphenylamine three broad lines appeared, indicating a splitting of around 15 gauss because of the nitrogen nucleus. These data are in excellent agreement with the preliminary results of Rooney and Pink (15) and of Brouwer (16).

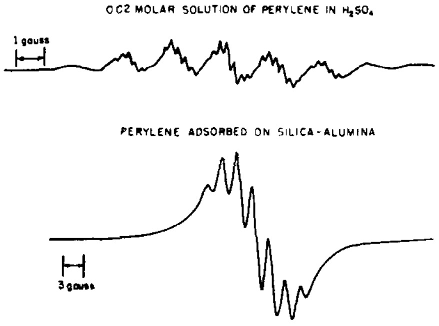

FIG. 3. EPR spectra of perylene dissolved in sulfuric acid and adsorbed on silica-alumina.

When silica-alumina was allowed to adsorb tetracene, 1,2-benzanthracene, pyrene or 3,4-benzopyrene, the resonance adsorptions were found to be quite broad, with only vague evidence of hyperfine splittings, superimposed on the principal absorption derivatives. Results obtained for adsorbed diphenylamine and aniline were similar to those for triphenylamine. No paramagnetism was observed for quinoline in the absence of air. When air was admitted, however, a signal developed immediately.

Only approximate values of spin concentrations could be obtained for several reasons. In the first place, at ordinary power levels ($\sim$ 50 mw) the signals were found to be partially saturated in all cases. By lowering the power level to the lower limit of the instrument ($\sim$ 1 mw), relatively, although not completely, unsaturated signals could be obtained. Saturation could be avoided by admitting air into the system but, in this case, evidence of decomposition and side reaction was frequently obtained. In the second place, the measurements were made on catalyst slurries from which the catalyst had been allowed to settle. Thus, the amount of catalyst surface area contained in 1 cc of volume had to be estimated. The highest value obtained was for adsorbed perylene. This was found to be 6×10^{18} spins/cc which leads to a value of 2×10^{12} paramagnetic entities per cm^2 of surface; the figure is believed to be accurate within a factor of three, and is probably too low. The signals obtained from some of the other substrates tested were much weaker. When the catalyst which had been treated with hydrogen was mixed with a perylene solution, the slurry developed a brownish-yellow color instead of royal purple, as in other experiments. Nevertheless, the characteristic EPR spectrum shown in Fig. 3 was still obtained, although the signal intensity was lower by nearly an order of magnitude. When the tube was opened to air, the normal color was generated (as a result of the appearance of a strong absorption band at 545 $m\mu$) and the EPR signal intensity increased to about the usual level. When another sample of the same catalyst was reduced in hydrogen in the all-glass circulating system at 530°C for 24 hr, water amounting to 0.53 cc (NTP)/g was collected in the liquid nitrogen trap; this corresponds to some 3.3 $\times 10^{12}$ atoms of oxygen per cm^2 of surface. This subject is being investigated further and a more detailed report of the results will be reported later.

Comparative experiments were made using solutions of 1,1-diphenylethylene. Under conditions that yielded strong signals for the polynuclear aromatic hydrocarbons, no paramagnetism was detected. Even with pure liquid 1,1-diphenylethylene in the presence of air, no paramagnetism was found, although the catalyst-hydrocarbon system became deep blue-black in color.

Discussion and Conclusions

That cation radicals are formed from both polynuclear aromatic hydrocarbons and phenylated amines is amply demonstrated by the results from the combination of spectroscopic techniques used in this work. Since the silica-alumina surface has the ability to abstract hydrogen as hydride ions from saturated molecules and to hold up to 5×10^{12} of these ions per cm^2 of surface (1a), there is no apparent reason why these same, strongly electrophilic centers should not remove electrons from unsaturated molecules of low ionization potential, if this is energetically more favorable. The demonstration of the presence of adsorbed cation radicals from optical and EPR spectra (15, 16) supports this view. However, the possibility exists that the catalyst effects an auto-oxidation-reduction reaction of the substrate. The fact that the results obtained with phenylated amines, where the active nucleophilic center is localized on the nitrogen atom, are similar to those for the polynuclear aromatic hydrocarbons renders this possibility unlikely. Moreover, the data for the amines establish a connection between the catalytically active centers involved in hydrocarbon reactions and the electrophilic centers required for the formation of the ion radicals. As shown by Oblad *et al.* (17) some years ago, there is a direct relationship between the decrease in catalyst activity and the number of centers poisoned by the strong chemisorption of a nitrogen base such as quinoline. Also, numerous examples of the use of nitrogen bases in the evaluation of catalyst acidity have appeared in the literature during the last few years.

At present, it is only possible to speculate on the chemical nature of the electrophilic sites involved in these interactions. In our earlier work (1a) it was supposed that they were Lewis acid sites, but the exact nature of these was defined only in terms of their ability to abstract hydride ions from triphenylmethane. Fogo's recent observation (18) that the spin intensity obtained from catalyst samples in contact with polynuclear aromatic hydrocarbons is lowered by reduction of the catalysts with hydrogen, led him to suggest that oxygen acts as the electron acceptor. The present work confirms the fact that oxygen is in some way involved. Further, the observed spectral changes (judged by difference in color) show that the actual radical concentration is diminished by removing oxygen from the catalyst, i.e., that the decrease in intensity is not brought about by saturation of the signal. However, these observations do not prove conclusively that oxygen is directly involved as the electron acceptor. It may be possible to introduce a small degree of nonstoichiometry into the catalyst by the reduction process; this sort of behavior is well known, e.g., with zinc oxide, and evidence that something of this sort actually occurs with alumina has already been presented by Teichner and co-workers (19). In this case, the catalyst surface would be expected to become less electrophilic (a weaker Lewis acid) as oxygen is removed. Arguments can be advanced in support of either point of view. Some pertinent observations are listed below to put the problem into perspective.

1. The amount of O_2, equivalent to the H_2O removed by reduction, was 0.27 cc (NTP)/g. In the pore volume of the catalyst (0.76 cc/g) this much oxygen gas would exert a pressure of 1.045 atm., at the temperature of the evacuation; it is evident, therefore, that the oxygen (atoms or

molecules) must be strongly bound to the catalyst surface or perhaps is part of its structure.

2. The ability of the catalyst to form radical ions is reduced by treatment with hydrogen, but it is not eliminated. Even after treatment for 24 hr, followed by evacuation for an additional 16–18 hr, the surface concentration was no more than an order of magnitude lower than usual and the hyperfine pattern was well resolved.

3. The amount of oxygen removed corresponds, within experimental error, to either one oxygen atom or molecule per radical ion formed (with the unreduced catalyst). Hence it follows that, within the experimental error, the decrease in the number of radical ions formed when the catalyst is reduced corresponds to the amount of oxygen removed.

4. Aalbersberg and co-workers showed gaseous oxygen was effective in converting protonated polynuclear aromatic hydrocarbons to their radical ions (20a). With Lewis acids, these same workers showed that some of the same substrates could be converted to the radical ion in the absence of both air and water (20b). A photochemical effect was also noted, e.g., with anthracene it was reported (20b) that, in 1,2-dichloroethane in contact with 1 atm of BF_3, 20% of the substrate was present as the radical ion, 25% as the covalent carbonium ion complex, and the remainder was unreacted. With perylene, the corresponding figures were in both cases less than 1%. After ultraviolet irradiation, the corresponding figures for anthracene were 30% and 35% and for perylene greater than 98% and less than 1%, respectively. With the system CF_3COOH–AcOH–C_6H_6 (57:32:11, v/v), it was shown (21) that the formation of the perylene monopositive ion depended upon the pressure of molecular oxygen and was reversible; the ratio of the radical ion to substrate concentration was linear in oxygen pressure, suggesting that a complex of the type $M^+O_2^-$ was being formed.

5. Leftin and Hall (1a) reported that treatment of their catalyst with hydrogen did not affect its ability to abstract a hydride ion from the tertiary carbon atom of triphenylmethane. Because of the relevence of this observation, some additional information will be given here. A transparent platelet of catalyst DSA-1 having a total surface area of 8.8 m^2 was used (1a). Triphenylmethane (0.18 mg) was vacuum transferred to the catalyst by placing the entire, sealed, greaseless assembly in a drying oven (6) controlled at 100°C. As carbonium ions were formed, the absorbance at 405 $m\mu$ increased from 0.08 to 1.02 in 107 hr. Pretreatment for this experiment involved burning in oxygen at 500°C for 16 hr, followed by evacuation for an additional 24 hr prior to sealing off the tube. After completion of the experiment, the platelet was regenerated in a stream of oxygen, evacuated for 4 hr, treated with static H_2 gas for 24 hr, and finally evacuated for 20 hr, all at 500°C. On exposing the platelet to triphenylmethane (0.16 mg) at 100°C, an absorbance of 1.64 was obtained after 100.5 hr. In both cases, complete conversion of the available reagent would have resulted in a coverage of about 5×10^{12} carbonium ions per cm^2. This level is consistent with the optical densities obtained, as judged by related experiments (1a). Since the results were apparently not influenced by treatment with hydrogen, the subject was not pursued.

6. No paramagnetism could be observed from adsorbed quinoline until air was admitted to the system.

It can be seen from the foregoing that the available data do not accurately define the role of oxygen in the formation of radical ions. With protonated hydrocarbons, molecular oxygen apparently can remove a hydrogen atom (reversibly) from the substrate. With Lewis acids, as in the present experiments, oxygen is apparently not required and data defining its influence are unfortunately not available (20b). The silica-alumina surface, in acting as an oxidizing agent, may either accept electrons or provide oxygen atoms; it seems doubtful that it supplies oxygen gas.

Roberts *et al.* (7) found that silica-alumina catalyzed the reaction of anthracene with oxygen. One EPR experiment was designed to duplicate theirs. Under high vacuum conditions, the silica-alumina turned green when brought into contact with a solution of anthracene and, from the integrated intensity, it was determined that ~ 10^{18} unpaired spins/g were associated with the catalyst-substrate complex. In agreement with their work, the catalyst quickly turned brown when air was admitted and the paramagnetism appeared to increase by a factor of about 5. This increase was, in part at least, fictitious, as the signal was now completely unsaturated. These data suggest that intermediates of the ion radical type may be involved in the oxidation process rather than carbonium ions as suggested by these authors. Furthermore, there is reason to believe that these species may be important in a number of other catalytic processes, e.g., coke formation (2).

Anthracene and 1,1-diphenylethylene are both alternant polynuclear aromatic hydrocarbons. From the quantum mechanical viewpoint, they are quite similar. Therefore, their spectra would be expected to be much the same, and this should apply not only to the neutral molecules but to their carbonium ions (proton adducts) and their cation radicals as well. That this is true at wavelengths below 500 mμ was demonstrated by Gold *et al.* (22); it is also demonstrated by the data shown in Fig. 4 for the sulfuric acid solutions of these substrates taken over a more extended range of the spectrum. Here, the strong bands at about 425–430 mμ correspond to the classical carbonium ions. The band at about 720 mμ for the anthracene is identified with its cation radical; the band at 607 mμ for diphenylethylene is open to question.

The same difficulty exists in solution studies as for the catalyst surface. Although the entity corresponding to the 607-mμ band has many of the characteristics of the cation radical, paramagnetism cannot be detected by the EPR technique (5,23). Although the data presented here do not solve the problem, they demonstrate that the silica-alumina surface is capable of forming cation radicals where such a reaction is energetically favorable. Further, they suggest that cation radicals may, indeed, form from diphenylethylene, but that the expected paramagnetism is not observed for some special reason, e.g., unfavorable relaxation properties. This idea has received support by a recent report from another laboratory (24), to the effect that a weak EPR signal was obtained when a silica-alumina catalyst is treated with

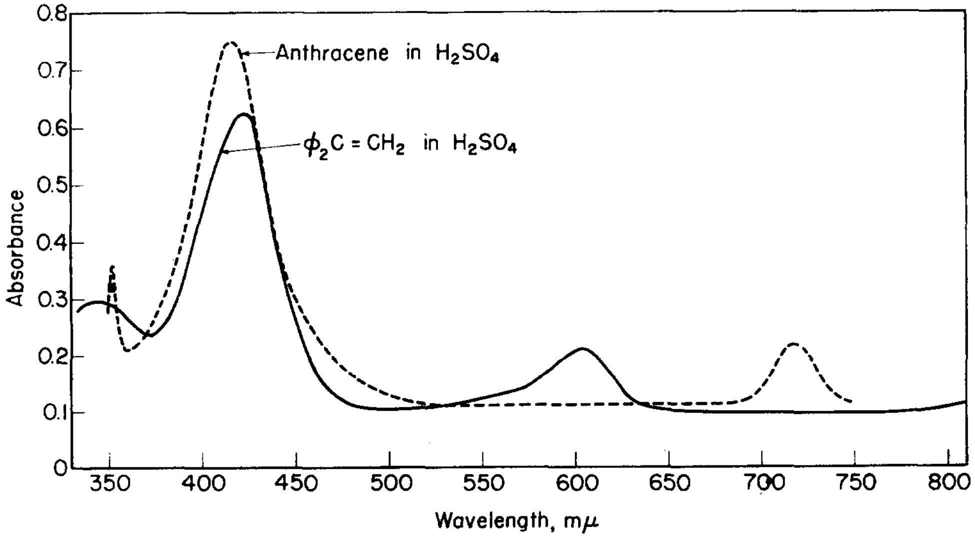

FIG. 4. Comparison of spectra of anthracene and 1,1-diphenylethylene in sulfuric acid.

this reagent. Further work will be required to resolve this question satisfactorily.

The fact that hyperfine splittings can be resolved at all with the catalyst-hydrocarbon systems indicates that the radical maintains some degree of mobility on the catalyst surface. Otherwise, the anisotropy of the system would be expected to broaden the signal. Actually, the work of Aalbersberg *et al.* (21) in acid solutions of perylene indicates that saturation broadening of the hyperfine structure may be expected as well.

In conclusion, it should be noted that the highest value for the number of paramagnetic species obtained in this work ($2 \times 10^{12}/\text{cm}^2$) is in good agreement with our earlier estimate of the number of Lewis acid sites ($5 \times 10^{12}/\text{cm}^2$) as judged by the adsorption of triphenylmethane, triphenylcarbonyl, and the trityl halides (1a). It should also be noted that this value falls about an order of magnitude lower than the amount of chemisorbed ammonia which cannot be pumped off the silica-alumina surface at 500°C. However, as pointed out by Webb (1c), this lower value may result because it is not geometrically possible to populate the surface to higher levels with these large molecules without overlapping.

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