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EPR and Chemical Studies of the Heterogeneous Reaction Between Polycyclic Aromatic Hydrocarbons and Platinum Chlorides

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The reaction between a number of platinum chlorides ($PtCl_4$, $PtCl_2$, $PtCl_4 \cdot 2H_2O$, $PtCl_4 \cdot 4H_2O$) and polycyclic aromatic hydrocarbons, particularly naphthalene and its derivatives, has been studied by EPR, mass spectrometry, and vapor phase chromatography. Only $PtCl_4$ and $PtCl_4 \cdot 2H_2O$ were catalytically active and with naphthalene gave radical cations, chlorinated naphthalenes and coupled derivatives. The chlorination and coupling reactions proceed independently and more readily than radical cation formation. The effects of water, oxygen, hydrogen chloride and substituents in the aromatic ring on radical ion formation are discussed. The results suggest that radical cations are formed by the transfer of an electron from naphthalene or other oxidizable derivative to an electron accepting site on the surface of the platinum compound, probably centered on platinum(IV). Strong chemisorption of the radical cations is responsible for their remarkable stability. The possible role of π-complex intermediates in the current reactions is discussed.

INTRODUCTION

EPR has been used to study the charge-transfer adsorption of polycyclic aromatic hydrocarbons on Group VIII transition metal oxides (*1, 2*), platinum oxide being most active. These EPR results have been related to the catalytic properties of platinum oxide in isotope exchange reactions (*1, 3*). Analogous radical cation formation has also been reported for the interaction of the polycyclics with Group VIII transition metal chlorides and other Lewis acid catalysts (*4*) both in solution and the solid state. In addition, strong Lewis acids such as antimony pentachloride (*5–7*), aluminum chloride (*8*) and boron trifluoride (*9*) can oxidize polycyclics such as perylene and anthracene to radical cations and covalent complexes (*9*). These Lewis acids, in particular aluminum chloride, are also active catalysts for the Friedel–Crafts alkylation and acylation of aromatics (*10*). Further, a number of polyvalent metal halides may chlorinate aromatics by a redox process.

We now wish to report the results of an investigation of the reaction between a number of platinum chlorides ($PtCl_4$, $PtCl_2$, $PtCl_4 \cdot 2H_2O$, $PtCl_4 \cdot 4H_2O$) and polycyclic aromatic hydrocarbons, particularly naphthalene and some of its derivatives. In this system, a series of reactions occurs simultaneously including radical-cation formation, chlorination and coupling. The catalytic activity of platinous and platinic chlorides in the gas phase chlorination of aromatics has been briefly discussed previously (*11*); thus it is of mechanistic importance to examine the interaction between the platinum halides and aromatics in detail, particularly to discover whether radical-cation formation occurs independently of the chemical processes of chlorination and coupling.

Naphthalene was selected as representative aromatic hydrocarbon for detailed studies, because the rate of radical-cation formation could be readily determined by EPR. Other more easily oxidized polycyclics such as anthracene, perylene and pyrene also gave radical cations, but the initial rate of reaction with these compounds was too fast for reliable kinetic data to be obtained (*2*). A further reason for the choice of naphthalene was that this compound is structurally important in the development of the π-complex theory for catalysis, particularly in *homogeneous* and *heterogeneous* metal-catalyzed isotopic hydrogen exchange reactions (*12*, *13*) especially where π-bond localization concepts are involved to give π-olefin type complexes (*14*).

EXPERIMENTAL

Materials. Platinum tetrachloride was prepared by the method of Keller (*15*). Precautions were taken to exclude moisture, and the granular material was ground under vacuum in a heavy-walled Pyrex tube containing a heavy Pyrex ball. The resulting powder was reddish brown and dissolved completely in water, indicating that no platinous chloride had been formed.

The hydrated platinum chloride, containing 85.85% water which approximates the tetrahydrate, was prepared as a bright yellow powder by exposing the anhydrous tetrachloride under vacuum to water vapor at 25°C. The exposure time was 24 hr and the vapor pressure of water was that corresponding to the triple point.

The dihydrate, containing 10.00% water, was prepared as a dull yellow powder by pumping the tetrahydrate for 24 hr to 10^{-3} Torr at ambient temperature.

Platinous chloride was synthesized by heating the tetrachloride in air at 400°C until evolution of chlorine ceased. Residual tetrachloride was leached out with distilled water and the air-dried platinous chloride evacuated to 10^{-3} Torr at 100°C to remove the last traces of water.

Naphthalene was purified by zone refining (sharp mp 80.0°C). 1-Chloronaphthalene was purified by distillation, only a trace of dichloronaphthalene but no naphthalene being present (vpc). Octafluoronaphthalene, 2-nitronaphthalene, 2-fluoronaphthalene and 1,4-dichloronaphthalene were recrystallized from water–alcohol followed by vacuum sublimation. Spectroscopic grade benzene and cyclohexane were used as supplied. The chloroplatinic acid for the preparation of platinum tetrachloride was of commercial grade, the only impurities present being platinum tetrachloride and platinous chloride, but these did not interfere with the preparation.

EPR procedure. Radical concentration measurements were made with a Varian X-band EPR spectrometer (Model V4500) employing a 9 in. magnet with Fieldial field regulation (Model V-FR2501) and 100 kc field modulation. The rate of radical formation was followed by rapidly scanning the spectrum and measuring the peak-to-peak height of the derivative curve. This was sufficiently accurate, as there was no detectable change in line shape during reaction. A ruby standard (*16*) was used to correct for changes in instrument sensitivity.

Absolute concentration measurements were made by the double integration technique using a solution of DPPH in benzene in equilibrium with air as standard. The absolute radical concentration, as well as the rate of reaction depend on the batch of platinum tetrachloride used. The general kinetic equation (see Results) was relevant in all cases; only the magnitude of the rate constant k varied. To minimize these differences, the present experiments were carried out on the same batch of material and the rate constants reported showed a variation of ±5% about the mean values. The variation in absolute radical concentration about the reported mean values was approximately ±25%.

A "g" marker (JEOL) containing a powdered Mn^{2+} sample was used to fix the center of reasonance of the unknown radicals. The scan rate was calibrated by means of an outgassed solution of di-*t*-butyl nitroxide and the "g" value of the unknown radical obtained from Eq. (1).

$$g(\text{unknown}) = 2.0036[1 - (\delta H/H)] \quad (1)$$

where δH is the separation in gauss between the center of resonance of DPPH and the unknown, and H is the field at the center of resonance of DPPH.

Two main techniques were used to obtain the kinetic data. For reactions with air removed, Pyrex H tubes and double H tubes fitted with break seals were used. Where reaction involved naphthalene or its derivatives and the platinum compounds in solution and in the presence of air, a simple silica tube was used. All manipulations of hygroscopic materials were carried out in a dry box and kinetic runs were performed at 25°C. The following typical procedure was used for kinetic runs in air. The platinum compound (25 mg) was weighed into the silica EPR tube in the dry box, the tube stoppered, removed from the dry box, naphthalene solution (2 ml) added, the tube again stoppered then shaken in a water bath. The concentration was determined by removing the tube from the water bath, carefully centrifuging at low speed to pack the platinum compound at the bottom of the tube, then quickly transferring to the microwave cavity, rapidly scanning the spectrum, then returning the tube to the water bath. The whole operation required about 2 min, and, since the ambient temperature was always around 25°C, temperature effects on the kinetics were insignificant.

Analysis. Dichloronaphthalene, chloronaphthalene, and naphthalene were analyzed by vapor phase chromatography on a Perkin-Elmer 800 instrument. A 6 ft column was used, packed with 10% D.C.550 silicone oil on 85–100 mesh "dry-sil" treated celite and operating at a column temperature of 180°C. The remaining products from a particular chlorination reaction were identified by the parent mass numbers and the intensities of the isotope peaks using low voltage mass spectrometry (A.E.I.MS-9 instrument).

RESULTS

Reaction Between Naphthalene and $PtCl_4$—General Phenomenon

At 25°C, only platinum tetrachloride and its dihydrate were active with naphthalene. The reaction between these compounds and naphthalene is complex, both radical cation formation and chlorination with and without coupling occurring simultaneously, the radical cation being stabilized by chemisorption. Although chloronaphthalene and dichloronaphthalene were the major reaction products, examination by low voltage mass spectrometry showed that trichloronaphthalene, perylene (or benzofluoranthene) binaphthyl, chloroperylene (or chlorobenzofluoranthene) chlorobinaphthyl, dichloroperylene (or dichlorobenzofluoranthene), dichlorobinaphthyl, naphthalene trimer, and monochlorinated naphthalene trimer were also formed in small quantities.

Radical cations were readily produced on the surface of the anhydrous platinum tetrachloride by adsorption of naphthalene from solution or the vapor phase. In all cases, a slightly asymmetric EPR signal was obtained which tended towards a Gaussian line shape. The EPR parameters for radical ions derived from naphthalene, 1-chloronaphthalene and other polycyclics are given in Table 1.

In the EPR spectra there was no indication of hfs and all attempts to improve resolution were unsuccessful even with the other polycyclic aromatic hydrocarbons. The absence of hfs, presumably due to dipolar broadening and exchange narrowing effects, makes it impossible to identify the radicals unequivocally. Until recently this same problem existed for the interaction of polycyclic aromatic with platinum oxide; however, if stringent experimental conditions are achieved, the radical ion can be ultimately resolved into hfs only with perylene on PtO_2 (*17*).

In the absence of hfs, other EPR parameters such as "g" values, linewidths, line shapes and saturation behavior of EPR signals need to be used to characterize the radicals. The "g" values obtained for the polycyclic aromatic hydrocarbon–$PtCl_4$ complexes are a suitable indication that the paramagnetism is due to radical cations. From Table 1 it is observed that although there are significant variations from one polycyclic aromatic hydrocarbon to another, the "g" values are close to the free

TABLE 1

EPR PARAMETERS FOR RADICAL CATIONS FROM INTERACTION OF $PtCl_4$ WITH POLYCYCLIC AROMATIC HYDROCARBONS

Compound	Solvent or vapor[a]	*g* Value	Linewidth (gauss)[b]
Naphthalene	Vapor	2.0031	5.84
Naphthalene	Benzene[c]	2.0037	7.05
Naphthalene	Cyclohexane[c]	2.0037	8.05
Naphthalene	Vapor[d]	2.0033	6.24
1-Chloronaphthalene	Cyclohexane[c]	2.0055	9.65
Perylene	Benzene[c]	2.0035	6.24
Pyrene	Benzene[c]	2.0042	4.43
Anthracene	Benzene[c]	2.0048	10.25
N,N'-Diphenylbenzidine	Benzene[c]	2.0036	3.62

[a] All systems evacuated to 10^{-3} Torr to eliminate oxygen broadening effects on the spectra; temperature 25°C; concentrations, where relevant, 10^{-3} *M*.

[b] Measured as distance between points of maximum slope on the derivative trace.

[c] Solution (2 ml) with $PtCl_4$ (25 mg) in H-tube.

[d] $H_2PtCl_4(OH)_2$ used instead of $PtCl_4$.

electron value of 2.002319 which is characteristic of organic radicals. If the EPR signals from the polycyclic–$PtCl_4$ interactions were due to an intermediate Pt(III) oxidation state, the "*g*" values would be significantly different from the free electron value. The fact that the resonance lines are all relatively narrow, ranging from 3.62 to 10.25 gauss (peak-to-peak on the derivative trace) confirms that the paramagnetism is due to organic radicals.

Kinetics of Radical Cation Formation

Although the present interaction is chemically complex, the kinetics of radical cation formation on the surface of anhydrous platinum tetrachloride are simple, curves similar to Figs. 1(b) and 1(c) being obtained. The data followed Eq. (2) where x is

$$g(x) = x/(x'_\infty - x) = k't + c \qquad (2)$$

the radical cation concentration at time t, x'_∞ the final concentration, t the time in minutes and c, k' are constants.

From the kinetic studies, two distinct types of active sites on the $PtCl_4$ surface were observed, each characterized by great differences in activity. On the faster sites, reaction was so rapid that the rate could not be measured. This type of site gave the radical concentration observed immediately upon the addition of reactant to $PtCl_4$. Under these conditions, a value of the rate constant, k, for the less active sites can be obtained. Assuming that the kinetic equation for the less active sites is second order and of the form of Eq. (3), it can be shown that the relationship in Eq. (4) holds.

$$x'/(x_\infty - x') = kt \qquad (3)$$

$$g(x) = x/(x_\infty + x_0 - x) = x_0/x_\infty + [1 + (x_0/x_\infty)]kt \qquad (4)$$

Comparing Eqs. (2) and (4) it can be seen that

$$x'_\infty = x_\infty + x_0 \qquad (5)$$

$$c = x_0/x_\infty \qquad (6)$$

$$k' = [1 + (x_0/x_\infty)]\,k. \qquad (7)$$

Hence, x_∞, x_0 and k can be obtained from the experimental curve and were useful for comparing kinetic data.

Variables Affecting Radical Cation Formation, Chlorination and Coupling

(a) **Solvent effect in radical cation formation.** Solvent significantly affected the rate of radical cation formation. The fastest reaction was between naphthalene vapor and anhydrous platinum tetrachloride. In solution the reaction was considerably slower, and there was a large difference between the rate in cyclohexane and benzene, k values being 1.4×10^{-2} min^{-1} and $4.7 \times$

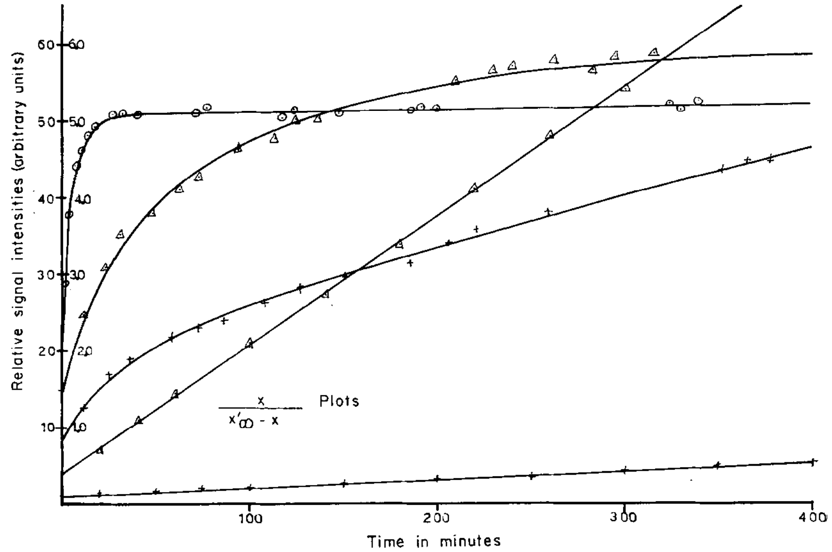


FIG. 1. Reaction between naphthalene and $PtCl_4$ under various solvent conditions: (a) ⊙ Naphthalene vapor; (b) △10^{-3} *M* naphthalene in cyclohexane; (c) + 10^{-3} *M* naphthalene in benzene.

10^{-4} min^{-1}, respectively (Fig. 1). Concentration had a very small effect on the rate. A change in concentration from 10^{-3} to 10^{-2} mole l^{-1} of naphthalene in benzene altered the value of k from 4.7×10^{-4} to 2.1×10^{-3} min^{-1} (Fig. 2).

(b) Water effect on radical ion formation, chlorination and coupling. There was no reaction between naphthalene and $PtCl_4 \cdot 4H_2O$ but the dihydrate reacted readily, yielding both radical cations and chlorinated and coupled products. It is significant that the dihydrate is easily obtained from the tetrahydrate merely by evacuating to 10^{-3} Torr for 24 hr at 25°C. Apparently the active sites on the surface of the dihydrate are poisoned by water, but the adsorption is relatively weak. The re-

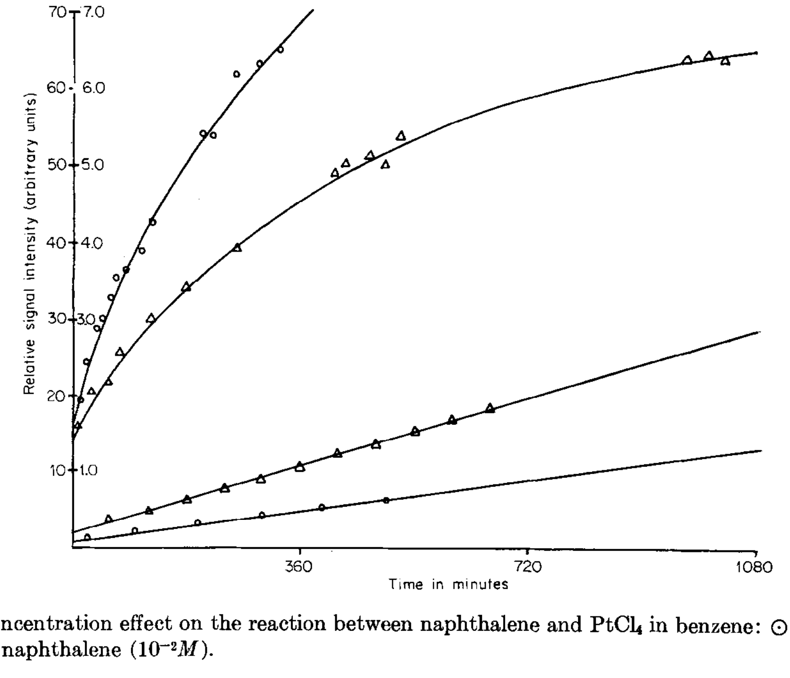


FIG. 2. Concentration effect on the reaction between naphthalene and $PtCl_4$ in benzene: ⊙ naphthalene (10^{-3} *M*); △ naphthalene (10^{-2}*M*).

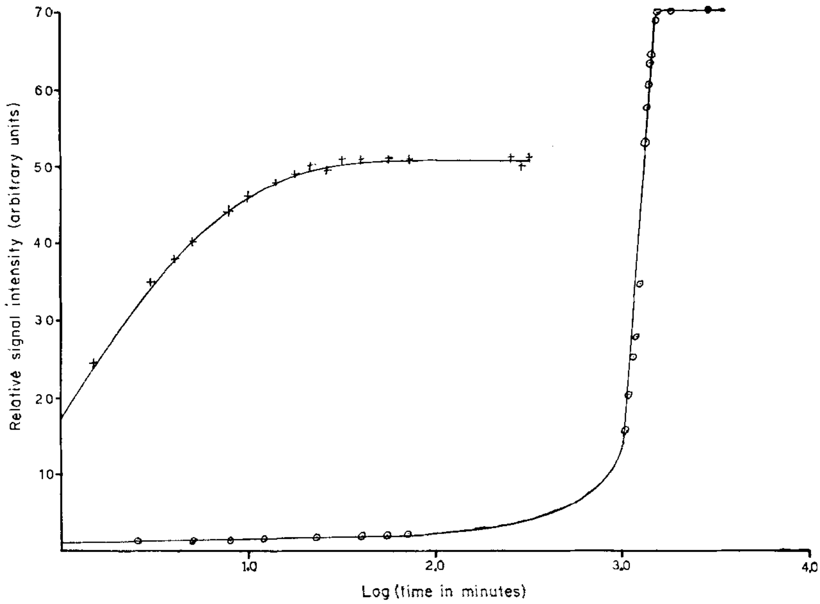


FIG. 3. Reaction between naphthalene vapor and platinum chlorides at 25°C: + $PtCl_4$; ⊙ $H_2PtCl_4(OH)_2$.

actions involving the anhydrous and hydrated material in EPR formation (Fig. 3) with naphthalene vapor at 25°C show that the two catalysts are different, reaction with the dihydrate being characterized by a long induction period.

The presence of water was particularly significant for reaction with anhydrous platinum tetrachloride. Both the yields of radical cations and chlorinated products were increased; however, the magnitude of the effect depended upon the manner in which water was admitted to the sample. Exposure of anhydrous $PtCl_4$ to water vapor *prior to* naphthalene addition decreased the overall reaction rate but increased the final ultimate radical cation concentration. The effect on the radical concentration after 400 min reaction was not large in the 0–10.0% water ranges. Because of the length of time required for reactions to go to completion, no attempt was made to determine the relationship between water content and final radical concentration. With anhydrous $PtCl_4$ a final steady state radical concentration was attained in about 400 min, whereas the hydrated $PtCl_4$ gave steadily increasing values over a period of a week. The final concentration was larger than for an equivalent amount of the anhydrous $PtCl_4$.

The time taken for the reaction to go to completion in the presence of solvent was considerably greater than in the absence of solvent. When $PtCl_4$ with 10% water was used ($H_2PtCl_4[OH]_2$), there was an induction period followed by a considerable increase in reaction rate. Near the completion of the reaction, the rate decreased and a final constant radical concentration was attained. As the reaction proceeded, a rapid color change from dull yellow to green was observed, and analysis of the product showed that extensive reduction of the hydrated $PtCl_4$ had occurred, accompanied by chlorination and coupling of the naphthalene.

When water is added *after* steady state conditions are reached a marked increase in radical concentration is immediately observed (Fig. 4). Water not only increases the radical concentration, but also the yield of chlorinated products. A fivefold increase in the yields of chloronaphthalene and dichloronaphthalene, and also in the radical cation concentration was observed when water (0.05 ml) was added to a solution (2 ml) of naphthalene (10^{-2} M) in cyclohexane containing $PtCl_4$ (25 mg); however, an accurate determination of the increase in radical cation concentration was not possible because the addition of water

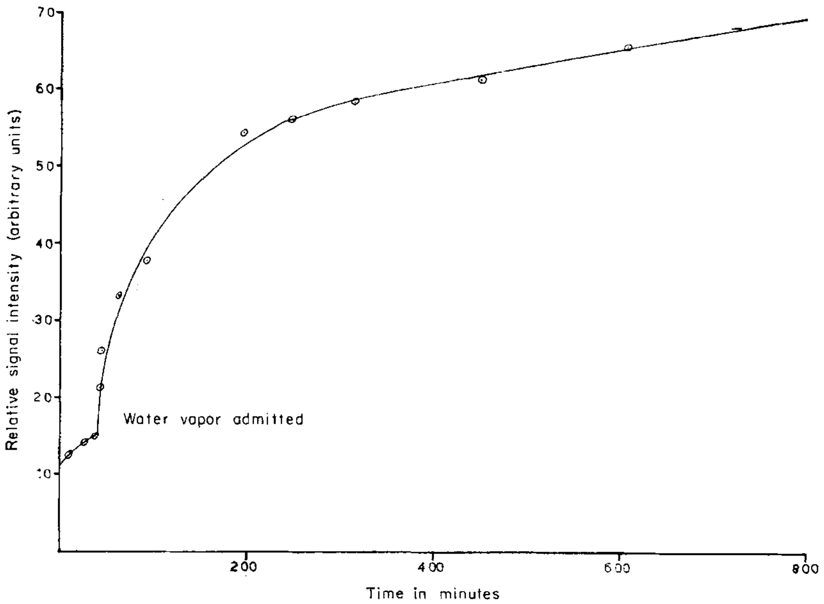


FIG. 4. Effect of water vapor on reaction between naphthalene vapor and $PtCl_4$.

caused platinum tetrachloride to cling to the walls of the EPR tube, thus preventing packing of the material. Hydrogen chloride and oxygen had no effect on the naphthalene–$PtCl_4$ reaction nor was a plausible end product ($PtCl_2$) active in radical ion formation, chlorination and coupling.

(c) **Effect of substituents on radical cation formation.** Since substituent steric effects have already been observed during π-complex adsorption of aromatics in catalytic isotope exchange reactions (*12*), it was of relevance to determine whether analogous effects occurred with radical ion formation in the present system, in particular, the interaction of $PtCl_4$ with the main chlorination products, 1-chloronaphthalene and 1,4-dichloronaphthalene being important. The data (Table 2) fit Eq. (2) and show that chlorination of naphthalene proceeds more readily than radical formation, chlorination products up to trichloronaphthalene being detected by mass spectrometry. No radicals were produced from 1,4-dichloronaphthalene.

DISCUSSION

Nature of the EPR Species

The absence of hyperfine structure, probably due to dipolar broadening effects, makes it impossible to identify the radical cations unequivocally. However, the fact that the linewidths are relatively small, and the g-values are close to the free electron value indicates that they are derived from the aromatic, and are not due to any paramagnetic state of platinum formed in the reaction. This conclusion is confirmed by the significant differences in g-value between the radical cations formed from naphthalene and 1-chloronaphthalene. In general, the g-values of aromatic radicals are considerably lower than those of the chlorinated derivatives because of an increase in spin-orbit coupling due to the presence of chlorine. Although the exact nature of the radicals is uncertain, from the previous oxide work (*1, 8, 17, 18*) they are undoubtedly radical cations formed by the transfer of an electron from the aromatic donor to an electron accepting site on the surface. This explains the remarkable stability of the radicals because they are bound by strong electrostatic forces to the electron accepting site.

Nature of the Active Sites—Factors Affecting Kinetics of Radical Formation

Experimental evidence suggests that the active sites are located on Pt(IV) and not

TABLE 2
FINAL CONCENTRATIONS AND k VALUES FOR REACTION BETWEEN NAPHTHALENE DERIVATIVES IN CYCLOHEXANE WITH $PtCl_4$[a]

Compound	Concentration of radicals in mole/25 mg $PtCl_4$	Rate constant k(min^{-1})
Naphthalene	1.5×10^{-8}	1.4×10^{-2}
1-Chloronaphthalene	5.9×10^{-9}	5.6×10^{-3}
1,4-Dichloronaphthalene	0	—
2-Fluoronaphthalene	8.0×10^{-9}	3.6×10^{-3}
Octafluoronaphthalene	0	—
2-Nitronaphthalene	0	—

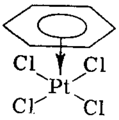
[a] Reaction carried out in the presence of air. Solution (2 ml) containing naphthalene derivative (10^{-3} M) added to $PtCl_4$ (25 mg). Temperature 25°C.

Pt(II) since radical cations are not observed with platinous chloride which is formed in the redox process [Eq. (I)].

$$ArH + PtCl_4 \rightarrow ArCl + HCl + PtCl_2. \quad (I)$$

The suggestion that platinum tetrachloride is responsible for the oxidation is consistent with interpretations in other similar systems such as antimony pentachloride and ferric chloride, since $SbCl_5$ oxidizes perylene to the radical cation whereas $SbCl_3$ is inactive (*19*).

From the kinetics, the platinum tetrachloride surface appears to possess two distinct types of active sites characterized by large differences in activity. Rate of radical cation formation on the very active sites was too fast to be measured. These sites gave the radical concentration observed immediately after the addition of the oxidizable aromatic. The solvent effect was quite marked, and could be interpreted as arising from a competition between the reactant and the solvent for the active sites. The rate in cyclohexane was faster than in benzene (1.4×10^{-2} min^{-1} and 4.7×10^{-4} min^{-1}, respectively) for naphthalene (10^{-2} M) with platinum tetrachloride at 25°C. These results suggest that the role of π-complexes in the adsorption process is significant (*12*). In particular, the π-electrons of benzene are capable of a strong interaction with the electrophilic surface site [species (I)] whereas a saturated hydrocarbon such as cyclohexane is less effective and cannot function as a nucleophile.



(I)

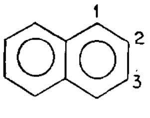
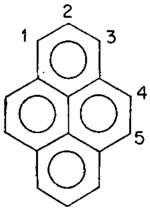
For radical ion formation from solution, diffusion did not appear to be rate determining, because rate of reaction between naphthalene (10^{-3} M) in benzene and $PtCl_4$ was much slower than the rate of reaction with pyrene (Table 3). These results also suggest that π-bond order is important in these reactions (*14*), condensed polycyclic aromatic hydrocarbons exhibiting π-bond localization and forming π-olefin type complexes with $PtCl_4$ on the surface. Pyrene, possessing the highest bond-order system (4,5 bond) will be more strongly complexed than naphthalene (through the 1,2 bond), and thus should react more rapidly (*14*).

Effect of Water

The results (Figs. 3, 4) show that small quantities of water have no deleterious effect upon radical cation formation or chlorination and coupling in the naphthalene–$PtCl_4$ reaction. This is unusual because water normally poisons Lewis acid sites on catalyst surfaces and reacts with Lewis acids in solution to give Brønsted acids. It has been shown (*20*) that water vapor rapidly displaces polycyclic radical cations from the surface of silica–alumina. Similarly, water markedly reduces the activity of

TABLE 3

Comparison of Bond Localization Energies, Bond Orders and Rate Constants for Radical Ion Formation from Solution for Naphthalene and Pyrene with $PtCl_4$

Compound	Positions	$L_B{}^a$	Bond order	Rate constants (min^{-1})
	1,2 2,3	3.259 3.729	1.725 1.603	4.7×10^{-4}
	4,5 1,2	3.057	1.777 1.670	1.4×10^{-2}

[a] L_B = bond localization, see Ref. (*14*).

platinum dioxide in polycyclic oxidation (*1*). Thus it was expected that platinum tetrachloride would behave in a similar fashion since it is a strong Lewis acid; however, only at a water content of 18.9% corresponding approximately to the tetrahydrate, was the normal poisoning effect observed. This effect was reversible and the inactive tetrahydrate could be converted to the active dihydrate by evacuation at 25°C. In this respect the dihydrate was similar to silica-alumina (*20*). Furthermore, the

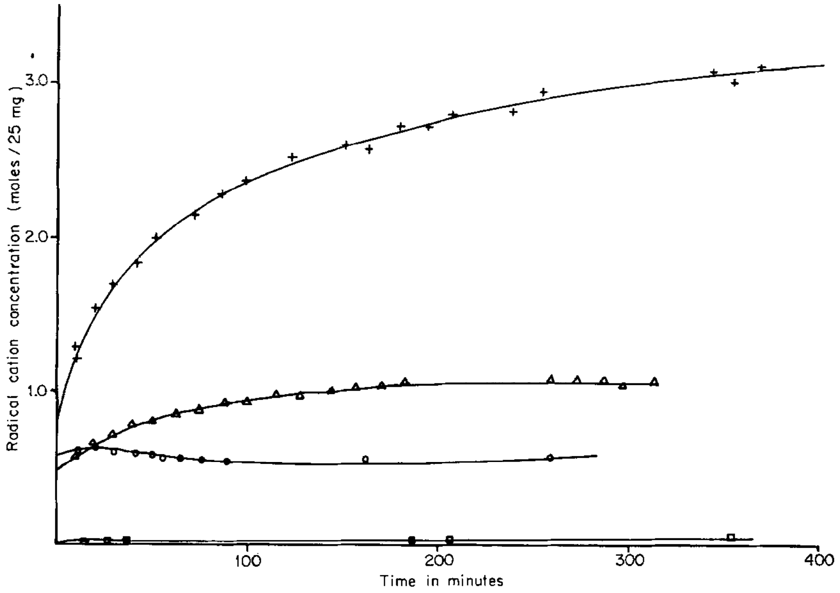


Fig. 5. Reaction between polycyclics (10^{-3} *M*) and $PtCl_4$ in benzene (25°C): + anthracene; △ pyrene; ○ perylene; ☐ naphthalene.

absence of an oxygen effect indicated that radical-cation formation did not involve the oxidation of a polycyclic proton complex as was observed in other systems (*21*).

However, this does not mean that Brønsted acid sites do not participate in the overall reaction between the hydrated platinum tetrachloride and the naphthalene. In the polymerization of naphthalene by ferric chloride, the maximum yield of product was obtained for a water–ferric chloride molar ratio of one (*22*). This indicated Brønsted acid participation in the reaction and it was postulated that the active species was $H^+[FeCl_3(OH)]^-$ formed according to the scheme in Eq. (II). A similar mechanism may be operative in

$$FeCl_3 + H_2O \rightarrow FeCl_3 \;.\;.\;.\;.\; H_2O \rightarrow H^+[(FeCl_3(OH)]^- \quad \text{(II)}$$

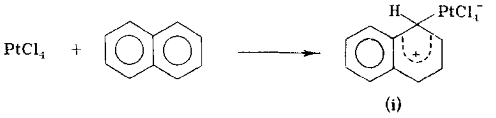
the chlorination and coupling reaction between the hydrated platinum tetrachloride and naphthalene.

Effect of Ionization Potential and Substituent on Radical Formation

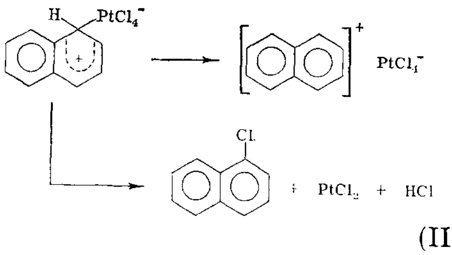
The data (Fig. 5) show the expected (*17*) approximate correlation between ionization potential (*I*) and final radical concentration for the charge-transfer interaction, especially when the compounds are grouped with the following sequence of reactivities, benzene ⩽ naphthalene < pyrene, anthracene and perylene. Where the differences in *I* are relatively large, the relationship involving radical concentration and *I* holds; however, within the series pyrene, anthracene and perylene, neither the final radical concentration nor the rate constants show any *I* dependence. The trends in Table 2 for the reaction between naphthalene and its derivatives with $PtCl_4$ in cyclohexane solvent indicate that reactivities depend more on steric factors than *I*, consistent with other surface adsorption effects of these compounds (*12*, *23*). While no *I* data are available for the chloro- and fluoronaphthalenes, the trend should be similar to the halobenzenes, i.e., naphthalene > fluoronaphthalene > chloronaphthalene. The fact that naphthalene was considerably more reactive than either 1-chloronaphthalene or 2-fluoronaphthalene indicates that steric factors predominate in the charge-transfer interaction. This is confirmed by the observation that neither 1,4-dichloronaphthalene nor octafluoronaphthalene were oxidised.

Reaction Mechanism

The exact nature of the interaction between the polycyclics and $PtCl_4$ is complicated because of the competition involving chlorination and coupling with radical-cation formation. Although quantitative measurements on chlorination and coupling yields were not attempted, it was apparent that the yields from these reactions were considerably greater than the yield of radical cations. Because of the preference for coupling and chlorination, a plausible first step in the reaction is the formation of a covalent complex [species (i)] on the catalyst surface between $PtCl_4$ and the polycyclic hydrocarbon Eq. (III). The complex may be similar to the type described by Aalbersberg *et al.* (*9*). Species (i) may then react in two ways, one leading to the formation of the radical cation, the other yielding chlorination or coupling with the polycyclic [Eqs. (IV)–(V)].



(II)

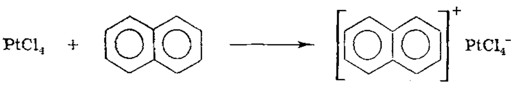


(III)

In this reaction pathway, the observation that naphthalene gives reaction products up to trichloronaphthalene, whereas 1,4-dichloronaphthalene is not oxidized to the radical cation is significant, and indicates that chlorination occurs more readily than one-electron oxidation.

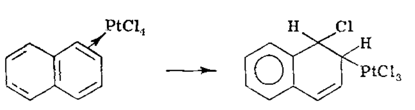
However, there are several difficulties

with this relatively simple reaction scheme. Firstly, from previous EPR adsorption studies with the polycyclics (*1*, *2*, *4*) and also from energetic considerations, formation of the radical ion, initially from a charge-transfer process Eq. (VI), would have been favored, followed by species (i) then chlorination and coupling.



(IV)

A major difficulty with any mechanistic scheme is to explain satisfactorily the observed orientation of chlorine in the α position when naphthalene reacts with $PtCl_4$, especially since in isotope exchange reactions (*14*) involving the deuteration of naphthalene in the presence of $PtCl_4^{2-}$ as catalyst, very severe α-steric effects are observed. These effects have been explained as being due to the difficulty of π–σ conversions occurring with $PtCl_4^{2-}$ and naphthalene in the α position. If similar steric effects occur in the present system with uncharged $PtCl_4$, then to explain α chlorination, it is necessary to propose that general π-complex formation be followed by bond localization and addition of $PtCl_4$ to give the associative intermediate [species (ii)] (Eq. VII). Elimination of HCl and $PtCl_2$ would then give α-chloronaphthalene.



(ii)

(V)

The present work shows that the surface of $PtCl_4$ possesses powerful oxidizing properties. Naphthalene, because of its relatively high oxidation potential (8.12 eV), is difficult to convert to the radical cation, even with sulfuric acid, which readily oxidizes anthracene, perylene and tetracene. However, the naphthalene radical cation has been produced on the surface of catalysts (*24*, *25*) and, as in the present $PtCl_4$ work, chemisorption has a considerable stabilizing effect.

The important conclusion from the present work is that chlorination and coupling appear to occur by a different mechanistic pathway to radical-cation formation in the sense that the radical cations are now intermediates in the redox reaction. An indication of this is the fact that the radical concentration during reaction steadily increases to a constant value. The remaining problem which cannot be answered without further detailed work is the question of the nature of the sites responsible for the two types of reactions. This information will be necessary before the mechanism of the processes can be fully clarified.

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