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Ultrapurification of Aromatic Hydrocarbons through Liquid–Liquid Extraction with Sulfuric Acid

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Abstract

Sulfuric acid is shown to be a selective extractant that will successfully remove trace amounts of anthracene from cyclohexane solutions of phenanthrene; high yields of ultrapure phenanthrene were obtained easily and inexpensively. The method also appears to be successful in the purification of 2-phenylnaphthalene. The effects of acid concentration, hydrocarbon concentration, phase volume, and contact time have been investigated; in general, nonconstant distribution coefficients were obtained, indicating that equilibrium is not established during the separation time. Spectrophotometric studies of the sulfuric acid layer suggest that while protonation may be the initial step in the extraction, slow sulfonation of the hydrocarbon is the ultimate cause of the inability to attain equilibrium rapidly.

Several methods have been proposed for the separation and purification of aromatic hydrocarbons (*1*, *2*), but these are usually tedious and expensive. Ultrapure hydrocarbons are difficult to obtain commercially because they are often contaminated with one or more hydrocarbons closely related to the compound of interest. Reported herein is a rapid, inexpensive method for the purification of some hydrocarbon mixtures through liquid–liquid extraction of cyclohexane solutions of these hydrocarbons with sulfuric acid. In the cases cited below, the products obtained by this method are comparable in purity to any method hitherto reported.

Differences in hydrocarbon reactivity with sulfuric acid are well known. Some workers have attributed these differences to the basicity of the hydrocarbons with respect to protonation by H_2SO_4 (*3*). Others have related the differences in reactivity to the potential at which the hydrocarbon undergoes oxidation (*4*). Therefore, to separate on the basis of reactive extraction with H_2SO_4, the contaminant extracted into the acid layer should either protonate more readily or oxidize at more negative potentials than the principal component in the mixture.

Both these conditions hold for a sample of phenanthrene contaminated with anthracene. It has been estimated that the K_b for anthracene is 10^6 that of phenanthrene (*5*); in addition, anthracene is known to oxidize at potentials more than 0.35 V negative of phenanthrene oxidation (*6*). Moreover, anthracene is a common contaminant of phenanthrene. Commercially available samples of phenanthrene usually contain a 1–2% anthracene impurity which has proved difficult to remove for photochemical studies (*7*) or studies of the conductivity of phenanthrene crystals (*8*).

Separation in these studies was effected only through reaction with maleic anhydride or through repeated zone refining. Therefore, the removal of anthracene from phenanthrene was selected as the means to test the utility of the technique in a difficult, yet practical, separation problem. The detailed results of these experiments, together with less detailed examples of the method, are reported below.

EXPERIMENTAL

Apparatus

Absorbance spectra of all species in cyclohexane and H_2SO_4 were obtained with a Bausch and Lomb Model 505 recording spectrophotometer. Concentration studies were performed with a Cary Model 15 recording spectrophotometer operated at fixed wavelength. Fluorescence studies were conducted with an Aminco-Bowman Spectrophotofluorometer. A Varian Model E-3 ESR Spectrometer was used to detect the presence of hydrocarbon radical cations in the H_2SO_4 layer.

Reagents

The sulfuric acid used was Mallinckrodt analytical reagent grade. Titration with standard NaOH gave an original concentration of 96 ± 1% for each sample; lesser concentrations were prepared by dilution. Higher concentrations were prepared from Mallinckrodt 100% H_2SO_4. Cyclohexane solvent was Fisher certified ACS quality. Spectral interference from the solvent over the wavelength range studied in the experiments was negligible. Phenanthrenes (98+%, mp 98–99°C) from Eastman Organic Chemicals (containing a measured 0.21% anthracene impurity) and from Aldrich Chemical Co. (containing 1.16% anthracene) were used in the various experiments. Fluorescent-grade anthracene was also purchased from Aldrich. Other hydrocarbons were 97% 2-phenylnaphthalene (Aldrich) and 99+% 9,10-diphenylanthracene (Aldrich Gold Seal). Anthracene-2-sulfonic acid was prepared in our laboratories.

A modification of the method originally used by Gold and Tye (*3*) was employed to study the separation. The hydrocarbon solutions were prepared by appropriate dilution of a 10^{-1} or 10^{-2} M mixture of the hydrocarbon in cyclohexane. A measured volume of this solution was placed in a beaker with a measured volume of acid of the desired concentration. The mixture was stirred for a known period of time, transferred into a separatory funnel, and separated; each phase was retained. The anthracene concentration in the cyclohexane phase was determined by its fluourescence emission at 400 nm upon excitation at 365 nm. Phenanthrene concentration in the cyclohexane was monitored by its absorption at 290 nm (log $\varepsilon = 3.8$) because anthracene interference prohibited the fluorometric determination of phenanthene.

Studies were also conducted on the sulfuric acid phase. Species present in the acid phase after the extraction were observed by UV and visible spectrophotometry. Radical entities were observed by ESR spectrometry. In some cases the acid phase studies required that the optical path length be shortened to extend the detectable concentration range of the spectrophotometer. The hydrocarbon systems other than phenanthrene-anthracene reported herein were studied in a similar manner but in much less detail.

RESULTS

Experiments conducted to determine the effect of H_2SO_4 concentration show that only a small fraction of anthracene is removed by dilute acid ($< 90\%$), but that the fraction extracted by acid of concentration above 90% rapidly approaches unity. However, the fraction of phenanthrene extracted also increased with increasing H_2SO_4 concentration. Because this was deemed unsatisfactory for separations, all subsequent studies were conducted with 96% (stock) H_2SO_4.

Studies were also conducted to determine the effect of time of stirring upon the extraction. These experiments show that the amount of anthracene remaining in solution decreases rapidly with continuous stirring for up to 5 min, but that stirring for greater periods of time produces little change in the amount of anthracene extracted. Phenanthrene exhibits a different type of behavior; over a 60-min period it is continuously extracted. Changing the volume ratio of H_2SO_4 to C_6H_{12} or the concentration of the solution has no great effect on this generalization. Thus the maximum amount of anthracene is extracted in a short time, while relatively small amounts of phenanthrene are extracted in the same time.

Even though these studies indicate that a true equilibrium state is not achieved during the first hour of mixing, an apparent distribution coefficient (K_{app}) was calculated for both compounds under various experimental conditions after 10 min of mixing. This was determined by

$$K_{\text{app}} = \frac{(W_0 - W)/V_{\text{H}_2\text{SO}_4}}{W/V_{\text{C}_6\text{H}_{12}}}$$

where V is the phase volume for the phase specified, W_0 is the initial weight of starting material, and W is the weight remaining in the cyclohexane after 10 min of mixing. Values for K_{app} for both compounds are shown in Table 1. No two values of K_{app} are the same for the same compound, as would be expected in an equilibrium situation.

Two trends are evident in Table 1. First, the value of K_{app} (and hence the fraction extracted) for anthracene increases with decreasing anthracene

TABLE 1

Apparent Distribution Coefficients[a]

Compound	Initial concentration in C_6H_{12} (M)	Volume ratio of H_2SO_4 to C_6H_{12}[b]				
		0.20	0.33	1.0	3.0	5.0
Anthracene	1.0×10^{-3}	68 (6.8)	75 (3.8)	83 (1.2)	104 (0.32)	165 (0.12)
	5.0×10^{-4}	68 (6.8)	83 (3.5)	99 (1.0)	128 (0.26)	200 (0.10)
	1.0×10^{-4}	109 (4.4)	100 (2.9)	99 (1.0)	184 (0.18)	334 (0.06)
	1.0×10^{-5}	132 (4.0)	135 (2.2)	147 (0.68)	—	—
Phenanthrene	1.0×10^{-1}	1.8 (73.5)	1.6 (65.3)	2.6 (27.8)	2.4 (12.2)	2.9 (6.5)
	5.0×10^{-2}	1.3 (79.5)	0.92 (76.3)	1.8 (35.8)	1.7 (16.4)	1.9 (9.5)
	1.0×10^{-2}	1.7 (74.5)	0.86 (77.9)	1.3 (43.5)	1.8 (15.6)	2.1 (8.7)
	1.0×10^{-3}	0.42 (92.8)	0.57 (84.0)	0.66 (60.0)	2.3 (12.7)	1.8 (10.0)

[a] Determined after 10 min of mixing.

[b] Quantities in parenthesis show percent unextracted by H_2SO_4.

concentration; for phenanthrene it decreases. This trend indicates that the extent of separation might be increased by dilution with cyclohexane; of course, the added cyclohexane would introduce another separation problem. Second, the value of K_{app} generally increases with increasing H_2SO_4:C_6H_{12} volume ratio for both compounds. While much of the anthracene impurity in a sample of phenanthrene would be extracted if the H_2SO_4:C_6H_{12} ratio were high, much of the phenanthrene would also be removed. This trend suggests that higher yields of purified phenanthrene could be obtained through multiple extractions with small relative volumes of H_2SO_4. Under these conditions, more than 90% of the anthracene present may be extracted in a single extraction at a cost of only 10% loss of phenanthrene.

Table 2 shows the results of a separation performed with a multiple extraction technique. The initial solution was a 0.10-*M* phenanthrene sample contaminated with 1.16% anthracene. The degree of separation compares favorably with previously reported work (*1*, *2*); the yield of pure phenanthrene appears to be higher.

Phenanthrene purity was assured by UV spectrophotometry, fluorometry, and melting point determination. Appropriately diluted samples of the cyclohexane layer exhibited identical UV spectra at all stages of a 60-min extraction with H_2SO_4. Fluorometry of the same solutions revealed changes only in the fluorescence behavior of the anthracene impurity. Studies of spectroquality cyclohexane after extended contact with H_2SO_4 disclosed the appearance of a weakly absorbing band in the UV spectrum at 255 nm; purified phenanthrene crystals (mp 98°C) recovered directly from the

TABLE 2

Phenanthrene Purification by Multiple Extractions with H_2SO_4[a]

Extraction	Phenanthrene[b] yield (%)	Anthracene impurity (%)
0	100	1.16
1	98	0.316
2	94	0.0851
3	95	0.0253
4	94	0.0098
5	91	0.0037
6	91	0.0015

[a] Volume ratio H_2SO_4/C_6H_{12} = 0.20. Mixing time = 3 min. Initial phenanthrene concentration = 0.10 *M*.

[b] Determined prior to recrystallization or sublimation.

C_6H_{12} layer may have been contaminated by this unidentified component. When these crystals were recrystallized from ethanol or vacuum sublimed, their melting point (99.0 °C, calibrated thermometer) agreed favorably with published results for ultrapure phenanthrene (*1*).

An even more efficient separation is possible in the H_2SO_4 purification of 2-phenylnaphthalene. This compound is commercially available contaminated either with anthracene or an anthracene derivative; this is evident from the fluorescence emission spectra of a 1.0×10^{-2} *M* cyclohexane solution of 2-phenylnaphthalene (as received) obtained from excitation at either 304 or 365 nm (Fig. 1, Curves *a* and *b*, respectively). After only two 5-min extractions with equal volumes of H_2SO_4, the spectra shown in Curves *c* and *d* were obtained from this solution; these spectra indicate an essentially complete removal of the anthracene impurity at a cost of very little extraction of 2-phenylnaphthalene. Quantitatively, 3-min H_2SO_4 extractions removed no more than 2% of the 2-phenylnaphthalene present in several samples run at different initial concentrations; in no case in these extractions was less than 99.4% of the anthracene impurity

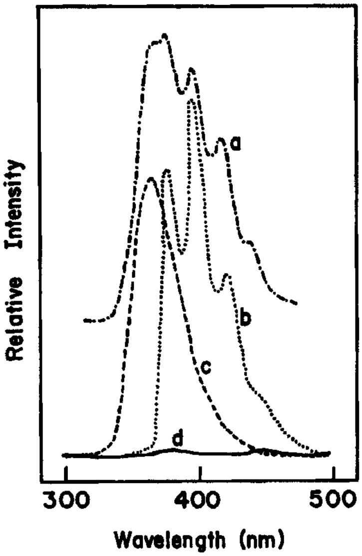

FIG. 1. Fluorescence studies of 10 m*M* 2-phenylnaphthalene in cyclohexane. Curves *a* and *b* were obtained prior to H_2SO_4 extraction; Curves *c* and *d* were obtained after two 5-min extractions. In *a* and *c*, the excitation wavelength was 304 nm; in *b* and *d*, 365 nm.

extracted. Values of K_{app} obtained in the vicinity of 0.02 for 2-phenylnaphthalene suggest that this compound resists H_2SO_4 extraction better than phenanthrene. Concentration-dependent values of K_{app} in the range 165 to 665 obtained for the fluorescent impurity in 2-phenylnaphthalene indicate that it is a more readily extracted derivative of anthracene than anthracene itself.

Experiments conducted with 9,10-diphenylanthracene showed that cyclohexane solutions of this compound were highly resistive to H_2SO_4 extraction, yielding K_{app} values less than 0.02. Since this compound is frequently used as a standard in luminescence studies (*9*, *10*), it is often important that it be obtained free of minor contaminants. Thus this result suggests that one effective step in the purification of 9,10-diphenylanthracene might be extraction of contaminants with H_2SO_4.

In an attempt to elucidate the mechanism of the anthracene extraction process, a spectrophotometric study of the separated H_2SO_4 layer was undertaken. Initially, spectra of the products extracted into the H_2SO_4 from spectroquality cyclohexane in the absence of anthracene were obtained; these are shown in Curves *a* and *b* of Fig. 2 following 5 and 95 min of mixing, respectively. At low anthracene concentrations the absorbance of this component in a 1-cm cell was sufficient to interfere with these mechanistic studies. At anthracene concentrations above 10^{-4} *M*, however, the path length had to be lowered to 0.10 cm. The absorbance of the component extracted from cyclohexane was negligible at this path length (Curves *c–f*). Thus it seems possible that the absorbance band at 300 nm previously attributed to anthracene in H_2SO_4 (*11*) was due to an impurity extracted in a similar manner from cyclohexane.

The absorbance of the anthracene extracted from a $1.0 \times 10^{-4} M$ cyclohexane solution with an equal volume of H_2SO_4 after 10 min of mixing is shown in Curves *c–f* at various times after separation. Under these conditions, essentially all of the anthracene is extracted so that the total anthracene concentration in the H_2SO_4 approaches that present initially in C_6H_{12}. The decreasing peak at 420 nm has been noted previously (*11*) and attributed to the proton complex of anthracene (*12*), but its specific time dependence was not noted at that time. The increasing peak at 260 nm has not been previously identified. It occurs at the same wavelength as the maximum in the absorbance spectrum of 1.0×10^{-5} *M* anthracene-2-sulfonic acid in H_2SO_4 shown in Curve *g*. In fact, in the limit of long time, the peak at 260 nm in the extracted anthracene solution approaches but does not exceed that predicted for a solution of pure anthracene-2-sulfonic acid ($\varepsilon = 7.1 \times 10^4$ l/mole cm). Since this result was obtained

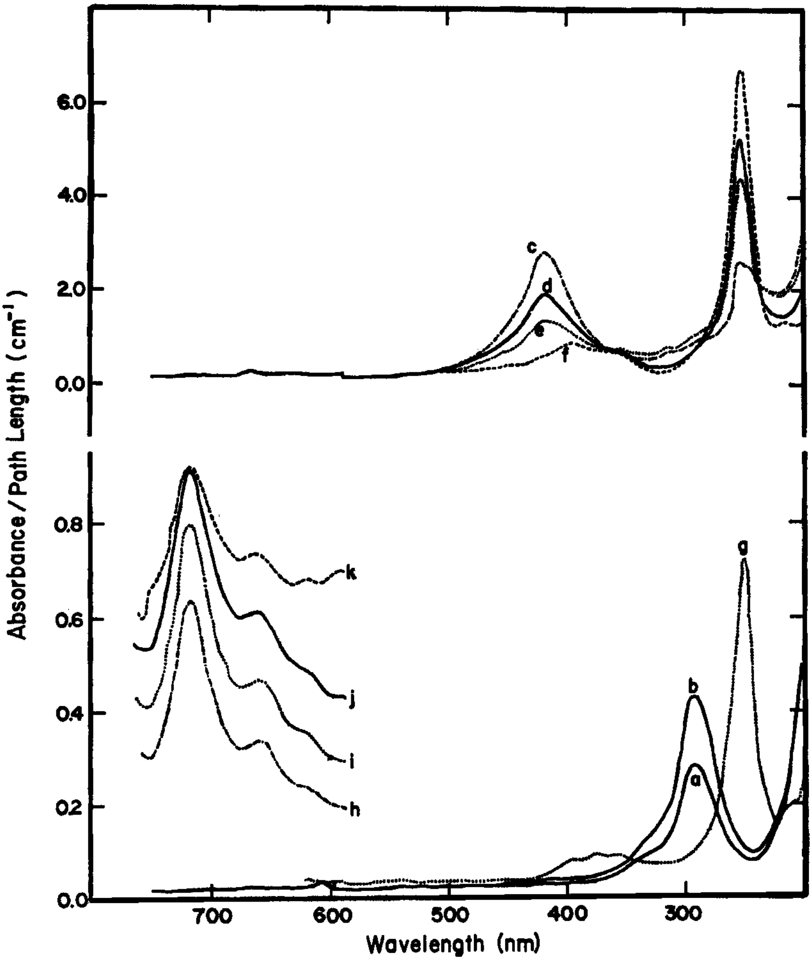

FIG. 2. Spectrophotometric studies of the sulfuric acid layer. Curves *a* and *b* show products extracted from spectroquality cyclohexane in 5 and 95 min of H_2SO_4 contact, respectively. Curves *c*–*f* show the time dependence of anthracene extracted from 0.10 m*M* cyclohexane solution in 10 min of contact; *c*, 5 min after phase separation; *d*, 20 min; *e*, 35 min; and *f*, 95 min. Curve *g* shows the absorbance spectrum of 0.01 m*M* anthracene-2-sulfonic acid. Curves *h*–*k* show the time dependence of anthracene extracted from 5 m*M* cyclohexane solution in 10 min of contact; *h*, 5 min after phase separation; *i*, 20 min; *j*, 35 min; and *k*, 95 min.

with three different anthracene solutions of different concentrations, it seems reasonable to conclude that the sulfonated species is the ultimate product in the extraction of anthracene. This conclusion is contrary to that of Gold and Tye (*12*), but they failed to record the anthracene spectrum below 280 nm, so they did not know of the existence of the absorbance at 260 nm. Kinetic studies of this system reveal that the pseudo-first-order lifetime of the proton complex (as determined from a log A vs t plot) is 130 min; that for the appearance of the peak at 260 nm (as determined from a log $[A_{max} - A]$ vs t plot) is 96 min. This indicates either that the proton complex is not the sole precursor of the sulfonated species or that it is being formed from another anthracene species even as it undergoes sulfonation.

A possible source for the additional anthracene sulfonic acid appears in the visible spectra of anthracene solutions extracted at concentrations higher than 1.0×10^{-3} *M*. Shown in Curves *h–k*, this band at 720 nm undergoes an apparent increase in absorbance following separation; this appears to be due primarily to an increase in background absorbance at this wavelength. Solutions absorbing in this region are green and exhibit the characteristic ESR spectrum of the anthracene cation radical. Kinetic studies of the ESR spectrum of a solution containing 1.0×10^{-3} *M* anthracene revealed that the radical disappeared with a pseudo-first-order lifetime of 77 min. Present in small quantities in equilibrium with the proton complex, the anthracene radical cation could react rapidly enough to produce some of the anthracene sulfonic acid formed.

CONCLUSION

Sulfuric acid has been shown to be a selective extractant that will successfully remove trace amounts of anthracene from phenanthrene. In addition, it has been shown to remove what has been fluorometrically identified as an anthracene derivative from commercial 2-phenylnaphthalene. In each of these separations the more easily oxidized compound was extracted more readily; this tends to support the contention that the extent of extraction depends upon the ease with which H_2SO_4 induces oxidation. On the other hand, the fact that 9,10-diphenylanthracene is not readily extracted by H_2SO_4, even though the potential at which it is oxidized is essentially identical to that of anthracene (*13*), tends to support the position that the formation of the proton complex is essential in this extraction; apparently the presence of the phenyl groups at these positions on the anthracene nucleus prohibits the formation of the proton complex.

Equilibrium is not quickly established, however, and the kinetic studies reported above indicate that the rate of sulfonation of the extracted entity may ultimately control the extent of extraction.

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