Thiourea Adduction of Alkylated Polynuclear Aromatic Hydrocarbons and Heterocyclic Molecules

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Thiourea was mixed with an aromatic concentrate of heavy catalytic cycle oil in an attempt to separate, as solid adducts, those molecules having preponderant adductable substituents. Adduction occurred readily; however, examination of the regenerated adductate showed that the postulated substituents had not been the primary cause of adduction. Instead the location of alkyl substituents upon fused nuclei was more important to adduction than was the size or shape of these substituents. The compounds adducted from the cycle oil were identified as alkylated naphthalenes, diphenyls, dibenzofurans, dibenzothiophenes, phenanthrenes, anthracenes, and fluorenes. Several β-methylated naphthalenes and anthracenes were separated from the cycle oil adductate and identified. Compounds which adduct are characterized as kata-condensed molecules and include linearly-fused, β-alkylated polynuclear aromatics and heterocyclics; and phenanthrenes alkylated at ring positions 1, 2, 7, and 8. Thiourea adduction may be utilized in the separation of complex natural and synthetic products.

BOTH THIOUREA and urea form solid complexes with organic compounds of particular structures. A complete review of this adduction phenomena is given by Domask and Kobe (*5*). In general, the hydrocarbon adducts have been characterized as nonstoichiometric complexes in which the urea or thiourea molecules have formed a crystalline solid containing interior channels of such dimensions that *n*-paraffins (urea adducts) and isoparaffins and naphthenes (thiourea adducts) are bound within the channels. Schiessler and Flitter (*12*) empirically established limiting dimensions for adductant hydrocarbon molecules using Fisher-Taylor-Hirschfelder models. Further, these workers established that phenyl groups inhibit adduction by thiourea, although adduction may proceed through the influence of a preponderate adductable substituent.

Teter and Hettinger (*13*) have more recently observed the adduction of durene with thiourea. Durene is apparently the only example of true aromatic adduction reported in the literature.

In connection with the constitution of heavy cycle oil aromatics, the separative potential of thiourea adduction was of interest especially in view of the work of Charlet *et al.* (*4*), who reported the presence of aromatic molecules having individual alkyl substituents of nine carbon atoms. Consequently, thiourea adduction was applied to an aromatic concentrate of heavy cycle oil and to distillate fractions of this concentrate to ascertain whether or not adduction would take place by virtue of the presence of branched alkyl substituents. Adduction with thiourea occurred readily; however, examination of the recovered aromatics indicated that branched alkyl substituents were not important requirements for adduction. The principal adductable components of heavy cycle oil appear to be alkylated and kata-condensed aromatic hydrocarbons and heterocycles in which the location of the alkyl substituent has a more important bearing on the adduction reaction than its size and shape. Several of the cycle oil adductants have been studied in pure form with thiourea to verify this hitherto unreported general reaction.

EXPERIMENTAL

Aromatic Concentrate of Cat Cracker Heavy Cycle Oil. A concentrated mixture of alkylated aromatics and heterocyclics was prepared by extracting heavy cycle oil first with sulfur dioxide, and then re-extracting the extract oil with dimethylsulfoxide. The resultant concentrate contained 95 wt. % of combined aromatics as determined by *n*-pentane elution from silica gel. Other pertinent properties of the concentrate were: boiling range, 470° to 950° F.; API gravity, 2.9°; average molecular weight, 221; and sulfur content, 1.99 wt. %. A portion of this concentrate was carefully fractionated, at 100 mm. pressure, into 28 distillate fractions. The distillation column was a 36-inch Hypercal column of 30-mm. diameter, filled with 0.175-inch Heli-Pak sections. Each fraction represented 2.86 vol. % of the concentrate.

FORMATION OF ADDUCTS. Thiourea-aromatic adducts were formed under conditions similar to those used to form thiourea adducts of naphthenes and isoparaffins. Removal of adductants from the total cycle oil and the 28 distillate fractions was carried out by adding to each slightly more methanol than was necessary for saturation. This was followed by the addition of excess thiourea and stirring of the systems for 24 hours at 75° F. After filtration, the solids were twice slurried with benzene and filtered. Recovery was accomplished by dissolving the solids in water and extracting the hydrocarbons with benzene. Considerable variation in yields was found, although the general trend was for a maximum of 25 to 30 wt. % adducted from fractions boiling in the range 640° to 730° F. The yield from the total concentrate was 7 wt. %. A few illustrative chromatograms of the distillate fractions and the corresponding adductates are presented as Figures 1 and 2.

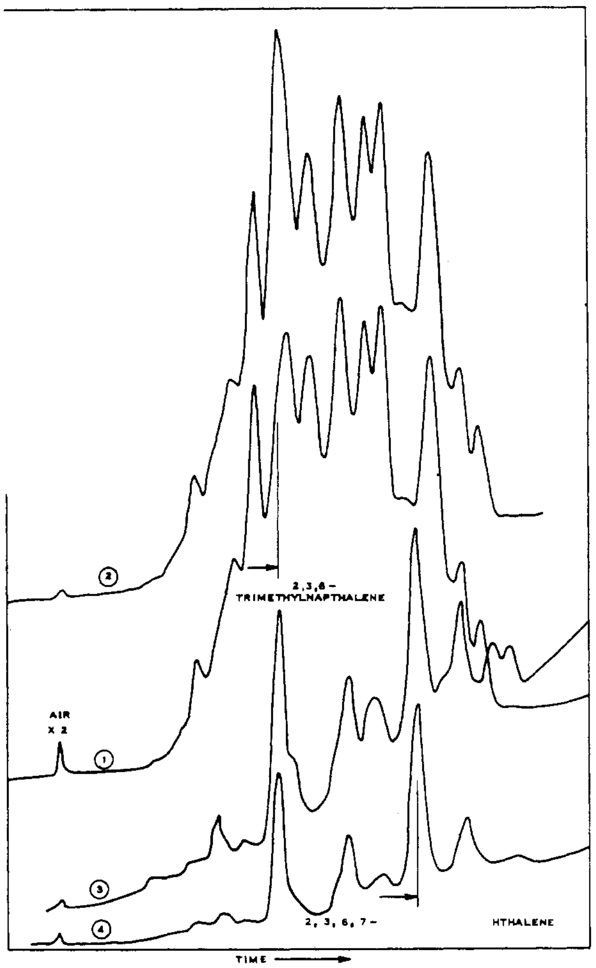

Figure 1. Gas-liquid chromatograms

(Conditions: 200° to 250° C. (limit) at 4°/min., 60 ml. He/min.)

1. Distillate fraction 10, from heavy cycle oil aromatic concentrate
2. Same as No. 1, plus 2-methylanthracene
3. Thiourea adductate of No. 1

The regenerated adductates were yellow-brown solids or semisolids. Adductate from the total aromatic concentrate was found to be 99 wt. % aromatic compounds containing 3.38, 0.12 and 0.5 wt. % of sulfur, nitrogen and oxygen, respectively.

To characterize the structure of the adduct from the entire aromatic concentrate, adduct free of excess thiourea or oil derivatives was prepared for x-ray studies by a two-stage operation. Feed for this second adduction was prepared by dissolving a portion of regenerated adductate in a minimum of benzene. To this solution was added 33 volumes of saturated methanol-thiourea so that the adduct was precipitated free of uncomplexed thiourea. (Large adduct crystals were formed when this system was warmed and slowly cooled.) Recovery of unreacted adductate revealed that only 12% had not adducted from the alcoholic solution. This adduct was assumed to be representative of at least the most stable thiourea-adductant combinations derivable from the cycle oil aromatics. X-ray diffraction powder patterns proved the absence of excess thiourea or oil derivatives, and from the large number of lines observed, it was inferred that the adduct crystals were of low symmetry. The significant feature of the infrared spectra of this adduct and the adductate regenerated from it is the shift (or absence) of the-CH_3 band at 7.25μ.

The adduct of a single, pure aromatic hydrocarbon was also characterized. The adduct of 2,3,6-trimethylnaphthalene, free of excess thiourea or hydrocarbon, was prepared in the manner described for that of the adduct of the total aromatic concentrate. This adduct, too, was examined by x-ray and the diffraction powder pattern indicated the crystals were of low symmetry. A similarly prepared decalin adduct gave a rhombic pattern definitely distinct from that of the aromatic adduct. Again the significant feature of the infrared spectra of the aromatic hydrocarbon and its adduct is the absence of the 7.3μ absorption of the methyl groups in the adduct. This adduct contained 30.5% sulfur, from which a thiourea/hydrocarbon mole ratio of 5.90/1.00 was calculated for the adduct composition.

Separation and Identification of Cycle Oil Components. Pure compounds were separated from the cycle oil adductates by a successive combination of crystallization and gas-liquid chromatography. Each of the adductates from the distillate fractions was repeatedly crystallized from ethanol until no further purification could be achieved. Purity was determined by programmed gas-liquid chromatography.

These chromatographic analyses were performed with a Model 500 F. & M. instrument using a helium carrier gas. The columns were coiled lengths of aluminum tubing 120 × 1/4 inches. The fixed phase was polyethylene glycol (Carbowax 20 M) deposited upon Chromosorb P. Concentrations of 5 and 2% permitted rapid elution with good resolution.

The compounds of the impure crystals, with the exception of 2,6- and 2,7-dimethylanthracene, were separable by chromatography. The eluted components were trapped for infrared examination by the method of Leggon (*8*), or by deposition directly upon potassium bromide plates. For ultraviolet spectra the eluates were trapped in spectral grade cyclohexane. The compounds isolated from the cycle oil are given in Table I and the methods of identification are cited for each. The compounds identified as 2,3,6,7-tetramethylnaphthalene, 2,6- and 2,7-dimethylanthracene, and 2,3,6-trimethylanthracene have spectra consistent with known infrared structural correlations, such as those given by Bellamy (*2*). The paper of Orr and Thompson (*11*) contains a reference spectrum of 2,3-dimethylanthracene.

Determination of Cycle Oil Adductate Ring Systems. It was desirable to characterize the aromatic systems of the adductates because the individual compounds isolated from the cycle oil adductates comprised only a small portion of the total adductates. This characterization was performed through dealkylation of adductate components, followed by quantitative analysis of the unsubstituted polynuclear systems. A substantial volume of adductate was needed for exploratory dealkylations. Since the aromatic concentrate first described was a reference sample the adductate of another concentrate was prepared for dealkylation studies.

The dealkylation feedstock was a fraction of a heavy cycle oil obtained from the same refinery unit as the original aromatic concentrate. This 500° to 700° F. distillate fraction was also sequentially extracted with sulfur dioxide and dimethylsulfoxide. Previous work had shown that aromatics of this boiling range provided large yields of adductates. Except for the boiling range, 500° to 700° F. *vs.* 470° to 950° F., this second concentrate was similar to the reference concentrate first described.

The thiourea adductate of the 500° to 700° F. concentrate, prepared as described under "Formation of Adducts," equalled 24 wt. % of the concentrate; the elemental composition and hydrogen atom distribution were determined. Sulfur and oxygen contents were 2.8 and 0.6%. Analysis

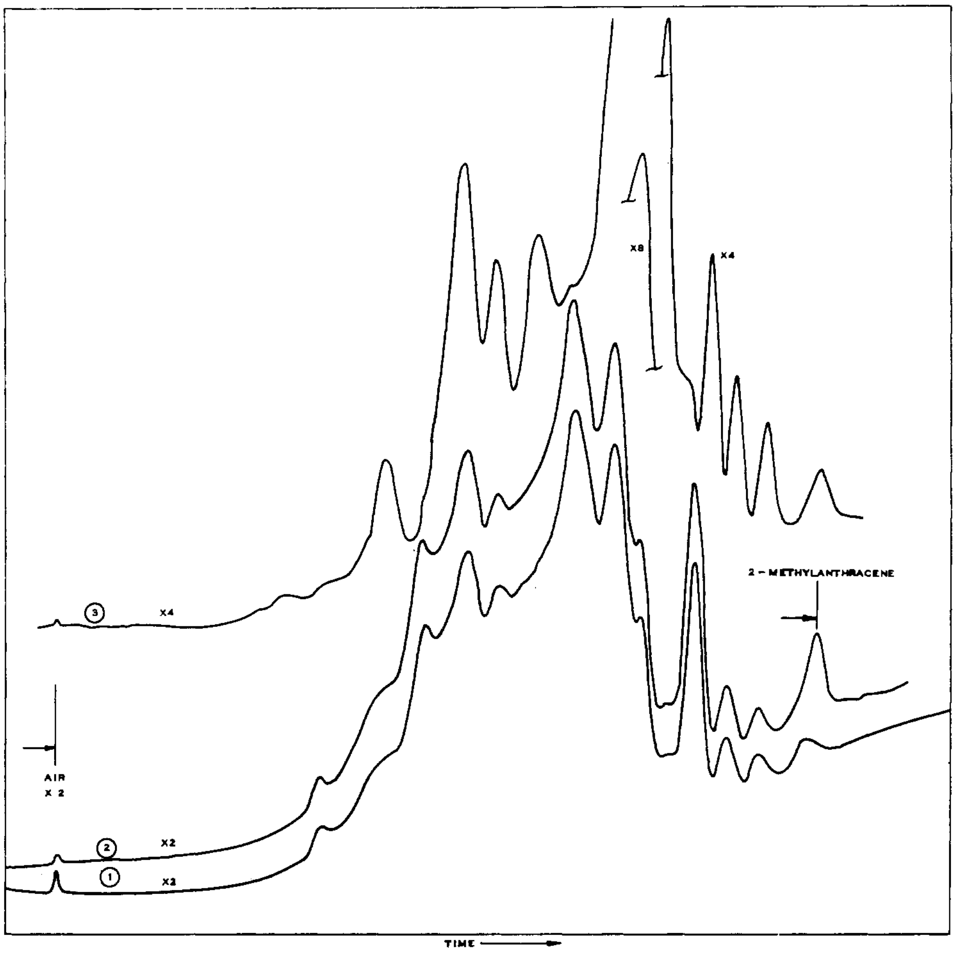

Figure 2. Gas-liquid chromatograms

(Conditions: 200° to 240° C. at 4°/min., 60 ml. He/min.)

1. Distillate fraction 4 of heavy cycle oil aromatic concentrate
2. Same as No. 1, plus 2,3,6-trimethylnaphthalene
3. Thiourea adduct of No. 1
4. Thiourea re-adduct of No. 1

by nuclear magnetic resonance indicated that the average nonmethyl alkyl substituent of the ring systems contained 5.6 carbon atoms. On the average, every molecule was doubly alkylated and three of each four molecules were methylated only. One fourth of these doubly alkylated molecules possessed the indicated 5.6 carbon alkyl in addition to a methyl substituent.

All alkyl substituents present in this adductate were oxidized to carboxyl substituents by using a procedure derived from that of Friedman (*6*). The copper sulfate–quinoline procedure (*9*) was employed to decarboxylate the acids recovered from the oxidation operation. The sulfur content of the resultant mixture of dealkylated nuclei was 3.7% and the theoretical value, which had been calculated from the nuclear magnetic resonance data, was 3.6%. Agreement between these actual and calculated values indicates that the alkylated nuclei were representative of the original alkylated adductants. The composition of the mixture of dealkylated aromatics and heterocyclics is presented in Table II and was determined by gas-liquid chromatography performed as described earlier.

SELECTIVITY OF ADDUCTION

Several commercially available hydrocarbons which had been identified in the cycle oil adductates were used to prepare adducts for study. Because isomers of these hydrocarbons also were available it was possible to observe the selectivity of thiourea adduction. A benzene solution containing 1,2- and 2,7-dimethylnaphthalenes and 2,3,6- and 2,3,5-trimethylnaphthalenes was prepared. A portion of this was equilibrated with a saturated solution of methanol-thiourea, and the precipitated solids were washed with benzene and decomposed. The composition of the adductate and feed mixtures were as tabulated in Table III.

The composition of the adductate was, within analytical error, that which would have been obtained by addition of further 2,3,6-trimethylnaphthalene to the starting mixture. Insufficient thiourea was present to form the less stable adduct of 2,7-dimethylnaphthalene.

In an attempt to verify the observation that the 2,3-dimethylnaphthalene adduct was more stable than that of the 2,6-isomer, adduction of both from a synthetic solution

Table I. Identification of Aromatic Compounds

Compound	G.L.C. Retention Time	IR Spectrum	UV Spectrum	NMR Spectrum	C-H Content Obs.	C-H Content Theor.	Melting Point, ° C. Obs.	Melting Point, ° C. Theor.
2-Methylnaphthalene	X	. . .	X	. . .	. . .			
2,3-Dimethylnaphthalene	X	. . .	X	. . .	. . .			
2,6-Dimethylnaphthalene	X	. . .	X	. . .	. . .			
2,3,6-Trimethylnaphthalene	X	X	X	X	91.8/8.25	92.0/8.00	101	102(*3*)
2,3,6,7-Tetramethylnaphthalene	. . .	Y(*2*)	Y	Y	. . .		195	191(*7*)
2-Methylanthracene	X	X	X	. . .	. . .		205	206(*1*)
2,3-Dimethylanthracene	. . .	X(*11*)	. . .	. . .	. . .			
2,6-Dimethylanthracene	. . .	Y(*2*)	Y	Y	92.9/7.0	93.2/6.85	230	250(*10*)
2,7-Dimethylanthracene	. . .							241(*10*)
2,3,6-Trimethylanthracene	. . .	Y(*2*)	Y	Y	. . .	. . .		. . .

X Matches authentic sample
Y Matches reference
. . . Not determined

Table II. Ring Systems of a Thiourea Adductate Derived from Cycle Oil

Dealkylated Component	Relative Wt. %
Naphthalene	12.4
Diphenyl	0.9
Dibenzofuran	4.1
Dibenzothiophene	21.3
Fluorene	10.4
Phenanthrene	34.2
Anthracene	15.7
Unknown	1.0

Table III. Separation of Trimethylnaphthalenes

Component	Wt. % Feed	Wt. % Adductate
1,2-Dimethylnaphthalene	6.3	3.5
2,7-Dimethylnaphthalene	39.1	16.5
2,3,6-Trimethylnaphthalene	21.4	56.5
2,3,5-Trimethylnaphthalene	33.2	23.5

Table IV. Selectivity between Adductant Isomers

Component	Composition, Wt. % Feed	Composition, Wt. % Mother liquor	Composition, Wt. % Adductate
2,6-Dimethylnaphthalene	5.5	4.5	22.0
2,3-Dimethylnaphthalene	7.7	4.2	48.0
2,3,6-Trimethylnaphthalene	2.0	0.5	12.0
2-Methylfluorene	3.7	2.4	18.0
n-Decane	81.1	88.4	. . .

was carried out. The 2,6-, 2,3-, and 2,3,6-methylnaphthalenes and 2-methylfluorene were added to *n*-decane, in the amounts cited in Table IV as "Feed." Enough saturated methanol-thiourea solution was added to the hydrocarbons to form a second liquid phase and a solid. Additional solid thiourea was added in excess of that needed for adduction. After equilibration, the solids were filtered free of mother liquor, and the adducted substances were regenerated in the manner previously disclosed. Compositions of the mother liquor and the adductate are also given in Table IV.

These data, showing a marked concentration of the 2,3-dimethylnaphthalene in the adduct, verify that the 2,3-dimethylnaphthalene adduct is more stable than the adduct of 2,6-dimethylnaphthalene. The reason for this selectivity has not been established.

The separation of isomeric phenanthrenes through adduction was demonstrated by the selective concentration of 2- rather than 3-methylphenanthrene in an adduct. A benzene solution containing 0.13 gram/ml. of 2,3,6-trimethylnaphthalene and 0.083 gram/ml. of both 2- and 3-methylphenanthrenes was added to 33 volumes of thiourea-saturated methanol. The adduct which formed was separated from the mixture and decomposed. Portions of the regenerated adductate were freed of trimethylnaphthalene by gas-liquid chromatography. Infrared examination of the eluted phenanthrenes of the adductate indicated a greater concentration of the 2- than 3-methylphenanthrene in the adductate. Absorption at 12.0μ is characteristic of 3-methylphenanthrene and 12.3μ absorption is characteristic of 2-methylphenanthrene.

DISCUSSION

The aromatic thiourea adducts are similar in mode of formation and stability to other adducts of thiourea, but structurally are different. By x-ray diffraction patterns, it has been determined that the thiourea component of the aromatic adducts is present in a different cystalline form than that previously reported for other systems. It is probable for the aromatic adducts that, analogously to other thiourea adducts, uniform channels exist within the framework of the thiourea molecules. The aromatic molecules are bound within these channels which are larger in at least one dimension than the channels that have been reported for the adducts characterized by rhombic cells.

The molecular structures of the cycle oil adductants may be utilized to determine the size of the adduct lumen and to characterize other adductants. The identified compounds adducted from the cycle oil were all linearly-fused, polynuclear aromatics methylated at the β-carbon atoms of the nuclei. These symmetrical naphthalenes and anthracenes are of uniquely low solubility as compared to isomeric compounds. Through adduction, these compounds were concentrated to such a level that they crystallized readily from the regenerated adductates. It was possible, by adduction with thiourea, to remove these β-methylated hydrocarbons from synthetic mixtures rich in the α-methylated isomers. From this it may be deduced that alkylation of the α-carbon atoms of the nuclei produces a molecule too large to fit within the thiourea channel. Since the adductants are planar the dimension normal to the plane is of little consequence. If the plane of the nuclei is assumed parallel to the channel formed within the thiourea, it is apparent that the shorter cross-planar dimension is indeed the limiting dimension for adduction. For the linearly fused ring systems this dimension is 7.7A, as determined from Fisher-Taylor-Hirschfelder models. α-Methylation increases this dimension to 8.6A. Larger alkyl groups placed upon the β-atoms of the nuclei may be oriented so as not to exceed 7.7 A. The presence of such large groups in cycle oil adductates was established by nuclear magnetic resonance studies. Among the ring systems found in the cycle oil adductates, only phenanthrene was not linearly fused. (However, acenaphthenes and acenaphthylenes, if present in the adductate, would have been converted to naphthalene by the oxidation-decarboxylation technique used to dealkylate the cycle oil aromatics). Models show a minimum critical dimension of 8.3 A for phenanthrene, and alkylation at positions 1, 2, 7, and 8 does not change this value. Similar relations are true for chrysene and picene. It may therefore be concluded that these new adductants are β-alkylated, linearly fused polynuclear aromatic hydrocarbons and heterocyclic molecules, and phenanthrenes alkylated so as not to exceed a cross-planar dimension of 8.3 A. Katacondensation is common to these ring systems. Although the adduction of suitably alkylated chrysenes and picenes has not been investigated, molecular dimensions suggest that such compounds are adductable.

As thiourea adduction does not occur for nonalkylated polynuclear aromatics, alkylation may be considered a requirement for adduction. Infrared spectra support this conclusion by indicating an interaction of methyl ring substituents with thiourea. In the adducts the infrared absorption at 7.25–7.30μ is shifted to 7.10–7.15μ or is completely absent. For a long chain alkyl substituent the methylene group adjacent to the aromatic ring would function, insofar as adduct formation is concerned, as does the methyl substituent. These figures also show that absorption of the aromatic hydrogen atoms, in the range of 11.0–12.5μ, is unchanged in the adduct. The absence of any development of color during thiourea adduction of these alkylated aromatics may be considered as evidence against complex formation through the π-electrons of the aromatic systems. Thus the evidence is in favor of adduction through the alkyl groups and opposed to adduction through the aromatic systems per se.

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