

USE OF THE STRUCTURE-CHEMICAL REACTIVITY DATA FOR  
DEVELOPMENT OF NEW METHODS IN PETROLEUM HEAVY ENDS UPGRADING

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INTRODUCTION

The chemical structure of the heavy ends of petroleum has been studied extensively (1). However, these studies have had little impact on the processes used commercially to upgrade heavy petroleum fractions. Industrial processes involve thermal (high temperature free radical chemistry) or catalytic routes such as catalytic cracking or hydroprocessing at temperatures greater than 300°C.

Low temperature ionic reactions have not been explored extensively for upgrading petroleum heavy ends. We have examined transalkylation, the transfer of alkyl fragments from high molecular weight components to smaller aromatic acceptor molecules in presence of Friedel Craft catalysts. We present results of transalkylation using catalysts consisting of trifluoromethanesulfonic acid as well as aluminum chloride promoted by water (2). Results are presented for transalkylation to native aromatic compounds present in crude petroleum (whole crude transalkylation) as well as to added aromatic molecules (resid transalkylation).

Most molecules in petroleum heavy ends contain 20 to 40 wt. % aliphatic groups substituted to aromatic (or heteroaromatic) rings (3). These aliphatic substituents are:

- normal and iso alkyl groups (we positively identified C<sub>2</sub> to C<sub>16</sub> alkyl chains);
- cycloalkyl groups (we identified cyclopentyl and cyclohexyl substituents but the presence of larger saturated polycyclic groups cannot be precluded);
- methylene groups linking two aromatic rings.

In the presence of Friedel Crafts catalysts these aliphatic groups can be transferred to small aromatic molecules (3). The result of transalkylation is then the formation of new distillable products which contain the small aromatic molecules substituted with normal, iso, and cyclo alkyl groups. Obviously, in such complicated mixtures as the petroleum heavy ends are, under the transalkylation reaction conditions, other reactions will also take place; for example, the dialkyl sulfides form mercaptanes and paraffins, and at long reaction times, alkyl substituents with five or more carbons form hydroaromatic rings by cyclization.

The products of the transalkylation and of secondary reactions are mixtures of petroleum like compounds with molecular weights

(and boiling points) ranging from that of the acceptor (the small aromatic molecule) to that of the resid.

If whole crude oils are treated under the conditions of the transalkylation reaction, alkyl groups from heavy ends are transferred to the light aromatic hydrocarbons present in the crude oil. The result is a change of the boiling point distribution of the whole crude toward medium boiling point fractions.

Very early in our work we realized the lack of literature data concerning the transfer of the alkyl substituents between aromatic rings with different degrees of ring condensation. To gain this information we studied the transalkylation reaction with appropriate model compounds (3,4).

The transalkylation reaction can be applied both to materials soluble in aromatics and to solids as kerogens (3) or coals (5,6) and coal liquefaction products (6).

## RESULTS AND DISCUSSION

The transalkylation reaction can be formulated:



In our discussion  $\text{Ar}^{\text{I}}\text{-Alkyl}^{\text{I}}$  will denote large aromatic molecules from petroleum heavy ends and  $\text{Ar}^{\text{II}}\text{H}$  will be benzene, toluene or o-xylene.

### A. Kinetic and thermodynamic constraints of the transalkylation reaction

We have shown previously (3,4) that the rate of the transalkylation reaction between polyaromatic and monoaromatic rings is:

- independent of the chain length (at least for C<sub>2</sub>-C<sub>10</sub> alkyl chains),
- dependent on the nature of the aliphatic substituent (cycloalkyls transfer faster than n-alkyls),
- dependent on the structure of the polyaromatic moiety involved in the transalkylation reaction (the rate of transfer of the aliphatic substituent increases for systems with increased degree of aromatic ring condensation).

Concerning the thermodynamics of transalkylation, we found that the thermodynamic equilibrium is:

- independent of the structure of the polyaromatic moiety (Table I),
- only slightly influenced by temperature in the 27-227°C interval in which we studied the transalkylation reaction (Table II).

Data in Tables I and II show that the equilibrium constant of the

transalkylation reaction is close to unity (i.e.  $\Delta G = 0$ ) for any pair of donor-acceptor. That means that at donor-acceptor molar ratio of 1:1, the maximum conversion to be expected is 50% for any of the starting materials. Thus, the only way to push a transalkylation reaction in a desired direction is to work with excess of acceptor. For example, for a molar ratio of 1:4 at equilibrium, 80% of donor will be converted at 127°C (400°K).

In the case of conversion of petroleum heavy ends by a transalkylation reaction, the big differences between the molecular weight of the donor (average molecular weight 1000) and of the acceptor (molecular weight ~100) insure an advantageous molar ratio even for a weight ratio resid:aromatic hydrocarbon of 1:1.

These thermodynamic constraints are very important for upgrading whole crude (see Section C following).

While the thermodynamic equilibrium is independent of the degree of aromatic ring condensation of the donor, the rates of the transalkylation reaction are faster for transfer of aliphatic groups from more to less condensed aromatic systems. The transfer in the opposite direction necessitates larger acid (catalyst) concentration (4), which in turn favors some secondary reactions.

#### B. Transalkylation reactions of vacuum resids

Some transalkylation reactions between Arabian Light vacuum resid and toluene or o-xylene are given in Table III. Typical composition of the distillate is shown in Figure 1 for an Alaskan resid. Some properties of the dealkylated resids are given in Table IV. In general, 60-80% of the initial resid remains as dealkylated resid.

If the dealkylated resid is hydrotreated in the presence of Co-Mo catalysts (Table V), the hydrogen consumption is similar to that for the untreated resid, but the degree of desulfurization is somewhat higher (72% for the dealkylated resid than for the untreated resid (65% desulfurization). It should be observed that the dealkylated resid (76% of the initial resid) was distilled to a lower average molecular weight (620) than that of untreated resid (average molecular weight 1100).

The saturated hydrocarbon fraction in the hydrotreated vacuum resid (for the hydrotreating condition see Table V) represents 20.5% of the product and has an average molecular weight of ~1000. In the hydrotreated dealkylated resid the saturated hydrocarbons represent 24.5% of the product and their average molecular weight is only 386.

#### C. Transalkylation reactions of whole crude oils

The transfer of aliphatic substituents from the big molecules to lower molecular weight aromatics of a crude oil can be achieved under mild conditions in the presence of a Friedel-Crafts catalyst (Table VI). We used topped (80°C+) crude oils because the lowest boiling point acceptor in crude oils is benzene

(b.p. ~80°C). Work with model compounds (4) indicated that the transfer of substituents is easier from polyaromatic to monoaromatic rings. This favors the redistribution of aliphatic substituents in whole crudes in the desired direction.

In the case of aromatic crudes (for example the Alaskan crude in Table VI), there are enough low molecular weight natural acceptors in the crude to achieve a substantial transfer. In the case of a paraffinic crude (North Sea crude), the addition of some small aromatic molecules can be helpful (Table VI).

The net result of the internal transalkylation is a redistribution of boiling points in the crude with an increase in the quantity of medium range products.

D. Chemical composition and mechanistic limitations of upgrading petroleum heavy ends by the transalkylation reaction

The petroleum heavy ends contain large amounts of aliphatic substituents on polyaromatic rings. This makes the use of the transalkylation reaction an attractive alternative for their upgrading.

One element of structure which poses a problem is the presence of basic compounds, especially basic nitrogen compounds in petroleum heavy ends. The basic nitrogen compounds react with the acidic catalysts and form salts.

Another limitation for the use of the transalkylation reaction is the effect of acid concentration on the reaction rate. Our work with model compounds (4) has shown that the concentration of acid must exceed a certain threshold to obtain an acceptable rate of reaction.

Understanding of the quantitative relationship between the chemical structure of the reactants and the concentration of acid is new chemistry and our initial results (4) are only a beginning. Certainly, more research in this area is needed because it is likely to be relevant to other acid catalyzed reactions besides transalkylation.

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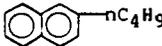
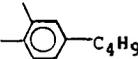
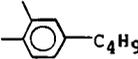
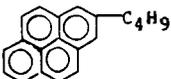
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TABLE I

Equilibrium Constants at 400°K (127°C) for  
Several Transalkylation Reactions



Aryl <sup>I</sup> -Alkyl <sup>I</sup> donor	Aryl <sup>II</sup> H acceptor	ΔG° 400°K Kcal/mole	K <sub>400°K</sub>
		-0.11	1.15
		-0.11	1.15
		0	~1
		+0.11	0.87
		0	~1

ΔG° values for 2-n-butyl naphthalene, benzene and o-xylene are experimental values (7), those for 1,2-dimethyl 4-n-butyl benzene and 2-n-butyl pyrene are calculated by the method of "group additivity" (8,9).

TABLE II

The Influence of Temperature on Thermodynamical  
Equilibrium of the Transalkylation Reaction\*



Equilibrium Constant at:

300°K (27°C)	400°K (127°C)	500°K (227°C)
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1.03	1.15	1.21
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\*All values are experimental values (7).

TABLE III

Conditions of the Transalkylation Reaction

Vacuum Resid (1050+F) a	Aromatic Hydro-carbon b	Catalyst c	Wt. Ratio a:b:c	Temp. °C	Time Hrs.	Wt. % Distillate <sup>a</sup> (based on resid)
1. Arabian Light	toluene	AlCl <sub>3</sub>	1:6.5:0.5	20	18	10
2. Arabian Light	o-xylene	AlCl <sub>3</sub>	1:0.86:0.5	144	3	15.3
3. Dealkylated Resid Exp. 2	o-xylene	AlCl <sub>3</sub>	1:1.7:0.5	144	6	25
4. Arabian Light	o-xylene	CF <sub>3</sub> SO <sub>3</sub> H	1:2.6:0.4	144	6	34

<sup>a</sup>This % includes the light aromatics incorporated by transalkylation.

TABLE IV

Properties of Dealkylated Resids

	C	Wt. %		MW VPO/Toluene	% ar H
		H	S		
Arabian Light	85.1	10.4	4.0	1100	5.6
Dealkylated Resid exp. 2 Table IVII	86.5	9.6	4.1	620	~11 <sup>a</sup>
Dealkylated Resid exp. 3 Table III	87.3	8.7	3.7	503	--

<sup>a</sup>The value of % ar H (<sup>1</sup>H NMR) is from a similar transalkylation run.

TABLE V

Chemical and Structural Properties of Hydrotreated Arabian Light Vacuum Resid and Hydrotreated Dealkylated Arabian Light Resid

Hydrotreating Conditions: wt. ratio resid:o-xylene:CoMo (HDS1441) catalyst 1:344:0.5; t = 340°C; 1000 psi H<sub>2</sub>, 1 h

Material	% ar H	Elem. Analysis Wt. %			Av. M <sub>w</sub> (VPO Toluene)
		C	H	S	
1. Arabian Light Vac. Resid	5.6	85.1	10.4	4.0	1110
2. Hydrotreated 1 (yield 90% of 1)	1.6	86.5	11.7	1.4	1000
3. Dealkylated (AlCl <sub>3</sub> catalyst) Arabian Light Vacuum Resid (76% of initial material)	9.8	84.9	9.1	3.6	620
4. Hydrotreated 3 (yield 90% of 3)	6.8	88.2	10.5	1.0	477

TABLE VI

Boiling Point Distribution of Topped Whole Crude Oils  
Before and After Transalkylation in the Presence of  
Trifluoromethanesulfonic Acid\*

	Boiling Points, °C			
	80-215	215-344	349-426	426+
<u>Topped Alaskan Crude</u>				
Initial	7.9	26.9	17.0	48.2
After transalkylation	<u>9.3</u>	<u>32.0</u>	<u>19.7</u>	<u>39.0</u>
	+1.4	+5.1	+2.7	-9.2
<u>Topped North Sea Crude</u>				
Initial	10.5	35.1	22.0	32.4
After transalkylation	<u>11.7</u>	<u>37.1</u>	<u>24.1</u>	<u>27.1</u>
Δ	+1.2	+2.0	+2.1	-5.3
<u>Topped North Sea Crude 5% o-Xylene</u>				
Initial	15.5	33.4	21.0	30.8
After transalkylation	<u>12.6</u>	<u>40.2</u>	<u>26.3</u>	<u>20.9</u>
Δ	-2.9	+6.8	+5.3	-9.9

\*Typical transalkylation conditions: wt. ratio oil :  $\text{CF}_3\text{SO}_3\text{H}$  10:1, reaction temperature  $\sim 100^\circ\text{C}$ , reaction time  $\sim 4$  h. After reaction, the mixture was quenched with aqueous NaOH, the organic layer was separated and dried over  $\text{MgSO}_4$ . The boiling point distribution in the initial material and products was determined by flash distillation over chromosorb followed by simulated distillation by gas chromatography.

FIGURE 1.

GAS CHROMATOGRAM OF THE TRANSALKYLATED PRODUCTS FROM  
THE REACTION BETWEEN AN ALASKAN VACUUM RESID AND o-XYLENE

