The two-step alkylation of isobutane with butenes using sulfuric acid as a catalyst

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Alkylation of Isobutane with C$_4$ Olefins. 3. Two-Step Process Using Sulfuric Acid as Catalyst

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Operating conditions for both the first step and the second step of the two-step process greatly affect alkylate quality and yields; statistical analyses indicate preferred conditions. With *n*-butenes as olefins, alkylates with research octane number (RON) values in the 99–100.5 range can be produced at operating conditions that are unacceptable in a one-step process. The isoparaffins in the alkylates are produced by three chemical mechanisms, and the relative importance of each differs with the RON of the alkylate.

When isobutane and *sec*-butyl sulfates react in the presence of sulfuric acid, alkylates (C$_5$–C$_9$ isoparaffin mixtures) are formed with research octane numbers (RON's) frequently as high as 98–100 (Ferman, 1972; Doshi, 1975; Ewo, 1977; Albright et al., 1977). Because of the glass reactors used earlier, only atmospheric pressure was investigated, which limited temperatures to –10 °C or less; at higher temperatures, unreacted isobutane vaporizes. Molar ratios of isobutane to *n*-butenes were investigated to as low as 1.5, and even then, alkylate qualities as high as 98 RON were obtained. The rates of alkylate formation were low at molar ratios of acid to butyl sulfate of less than 5. Yields of alkylate frequently approached 100% (or 204 weight of alkylate per 100 weight of *n*-butene used to prepare the butyl sulfate).

In current commercial processes when isobutane and olefins are reacted to form alkylates in the presence of either sulfuric acid or HF, only a single reactor is needed. Several potential advantages occur with a two-step (or two reactor) process in which butyl sulfates or butyl fluorides are formed in the first step and alkylate is produced in the second step. Higher alkylate qualities may be possible at lower operating costs. Optimum operating conditions (temperature, acid composition, ratio of isobutane to olefin, etc.) likely differ substantially in the two reactors. Advantage may also be taken of the fact that the exothermicities of alkylation occur mainly in the first-step reactions.

Attempts to date to produce *tert*-butyl sulfates by reacting isobutylene and sulfuric acid have been unsuccessful (Ferman, 1972; Doshi, 1975; Albright et al., 1988b). The isobutylene instead reacts rapidly to form mainly low polymers in the C$_8$–C$_{20}$ range. These low polymers react with isobutane in the presence of sulfuric acid to form mediocre-quality alkylates with RON's of about 90–94. In conventional one-step processes, isobutylene produces alkylates of similar quality and composition, whereas much higher quality alkylates are produced from *n*-butenes (Albright, 1966; Li et al., 1970). In the case of isobutylene, the less desired isoparaffins (which are dimethylhexanes, light ends, and heavy ends) are produced to a greater degree, whereas the desired trimethylpentanes are produced to a lesser degree.

The alkylation mechanism proposed by Schmerling (1945, 1946) many years ago and widely accepted fails to

explain the following features of isobutane alkylations when H$_2$SO$_4$ is used as catalyst:

(a) Olefins react faster than isobutane, while according to Schmerling these rates are equal.

(b) Dimethylhexanes are produced, but not in the manner predicted by the mechanism.

(c) Alkylates produced from isobutylene and *n*-butenes differ in a way not expected from this mechanism.

The modified mechanism proposed by Albright (1977) explains all known alkylation results. In the proposed mechanism, butyl sulfates, C$_8$–C$_{20}$ olefins, and conjunct polymers all have key roles in the complicated sequence of events. This modified mechanism was developed in part using the tagged carbon results of Hofmann and Schriesheim (1962a,b) who proposed the production of light ends and dimethylhexanes from a common intermediate. The importance of agitation is also emphasized.

Further study of the two-step approach is needed to investigate both. The present results indicate that high-quality alkylates can be produced by use of rather high temperatures for first-step reactions. The two reactors described by Spalding (1985) and Albright et al. (1988a) were used in this investigation. A calibrated gas chromatographic unit served for analysis of the alkylate product.

Alkylation Runs in Glass Reactor

Liquid mixtures of isobutane and *n*-butenes were added to the glass reactor, and the temperature was then adjusted to either –40 or –30 °C. Acid was slowly added to obtain a mole ratio of acid to olefin (A/O) of 2; most *n*-butenes reacted to produce *sec*-butyl sulfate, but trace amounts of heavy ends, 2,2,3- and 2,3,4-trimethylpentanes (TMP), and 2,2,5-trimethylhexane (2,2,5-TMH) were detected in the hydrocarbon mixture that was predominantly isobutane. The rate of alkylate formation was very low until sufficient acid had been added to obtain an A/O of 5 or greater. At –40 and –30 °C, yields and compositions of the alkylate were identical upon completion of the reactions. Both 1-butene and 2-butenes gave similar results (Ferman, 1972).

Figure 1 indicates a typical S-shaped curve of alkylation yield versus time for a batch run in which butyl sulfates react with isobutane. The increasing rates of alkylate formation during the initial stages of a run are caused by
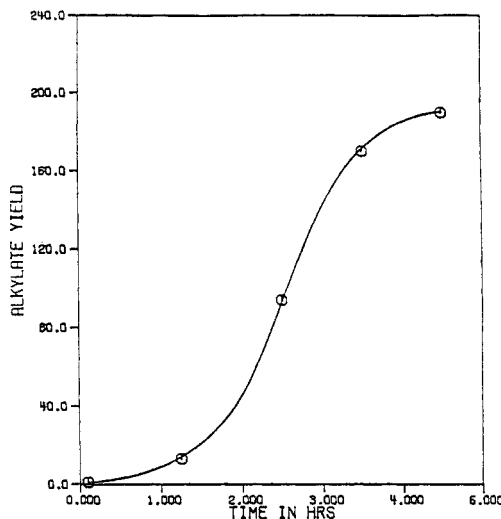
Figure 1. Alkylate yield versus time for second-step batch run: -14 °C, 96.2% H_2SO_4, I/O = 5, A/O = 5.
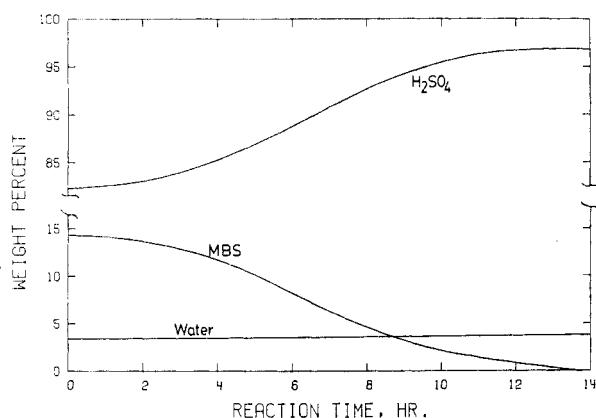

Figure 2. Sulfate-phase composition of second-step run at A/O = 10 and -20 °C.

the increasing acidity of the acid phase since acid is regenerated. Figure 2 indicates the increase in acid concentration for a run with A/O = 10 and at -20 °C. Even greater increases of acid concentration occur when A/O = 5, such as for the run of Figure 1. The decreasing rates of alkylate formation during the last stages of a run are caused by reduced amounts of butyl sulfates. Since the yields of alkylate obtained in several runs were essentially theoretical, most heavy ends, thought to be low polymers, eventually reacted to form alkylate. The rates of alkylate formation increased significantly as the temperature was increased from -40 to -14 °C (the highest temperature used with the glass reactor).

The volumes of the acid and hydrocarbon phases changed as alkylate was produced. Initially the mono-sec-butyl sulfate was present primarily in the acid phase, and the hydrocarbon phase was mainly isobutane. As the run progressed, alkylate migrated to the hydrocarbon phase, causing an increase of its volume. The acid phase decreased in volume because the sec-butyl sulfates reacted forming sulfuric acid. As A/O increased from 5 to 15, the RON of the alkylates of three comparative runs increased by 3.8, resulting in an alkylate with RON over 100. These specific runs were made with 96.2% fresh acid and with I/O = 5. Almost 90% of the RON increase occurred as A/O increased from 5 to 10. For two runs made with I/O = 10, the RON increased by 0.4 as the A/O increased from 10 to 15.

Increasing I/O from 5 to 10 for two comparative runs resulted in an increase in alkylate quality of 0.4 even

Table I. Alkylate Yields and RON's for Composite Runs at I/O = 5, A/O = 10, and 96.4% Sulfuric Acid

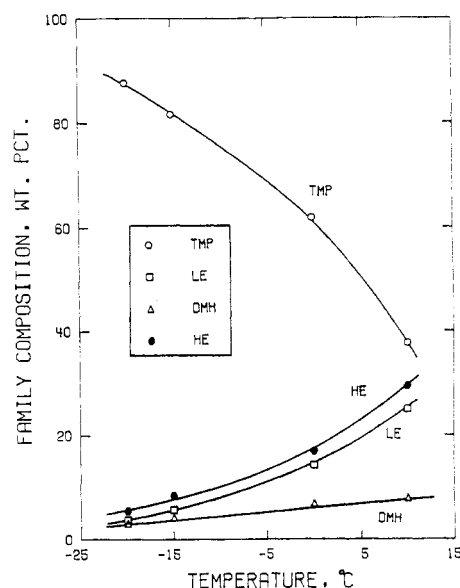| T, °C	yield	RON
-20	188	100.6
-15	201	99.4
0	175	96.0
10	127	92.6

Figure 3. Family contents as a function of temperature for runs at I/O = 5, A/O = 10, and 96.4% sulfuric acid.

though the alkylate quality was high (the RON was over 100). Earlier results (Albright et al., 1977) indicate that the biggest increases in alkylate quality occur when this ratio is increased at lower ratios, such as from 1.5 to 5. Alkylates of 98 RON have been obtained with I/O as low as 2.

Composite Two-Step Alkylation Runs

Composite runs are those runs made with the same temperature and I/O for both the first- and second-step reactions but the A/O is increased for the second step. Seven composite runs were made at I/O = 5 and A/O = 10 in the stainless steel reactor to investigate the effect of temperature and acid composition over the following ranges:

temp, °C	-20 to 10
acid composition, wt %	
H_2SO_4	90.7-96.4
H_2O	1.0-4.4
conjunct polymers (CP)	0-6.1
dissolved SO_2	0-0.6

As shown in Table I, the alkylate quality decreased from 100.6 to 92.6 as the temperature increased from -20 to 10 °C for four runs employing 96.4% fresh acid. As the temperature increased, the rate of alkylate formation, however, increased significantly; the time to complete alkylation decreased from approximately 14 to 0.7 h. At -15 °C, the yield of alkylate was essentially equal to the theoretical yield. Furthermore, the final acid of this run had the same composition as that of the starting acid used for the first-step reaction. At -20 °C, not all sec-butyl sulfates had reacted after 14 h; hence, the yield was less than theoretical. The rather low yields at 0 and 10 °C are caused by oxidative side reactions that produce acid-soluble hydrocarbons (conjunct polymers) and sulfur dioxide. The final acids for the latter two runs contained 0.34 and

Table II. Family Compositions for Composite Runs at I/O = 5, A/O = 10, and 96.4% Sulfuric Acid and 1-Butene

	temp, °C			
	-20	-15	0	10
	LE's			
isopentane	25.8	25.2	33.9	39.8
2,3-DMB	38.1	32.6	29.7	26.6
2-MP	3.7	6.8	5.0	6.5
3-MP	2.9	2.8	3.1	3.7
2,4-DMP	14.6	16.5	14.1	10.7
2,2,3-TMB	2.4	2.3	1.6	1.3
2,3-DMP	12.5	13.0	11.8	10.2
2- and 3-MH	0.0	0.8	0.8	1.2
	TMP's			
2,2,4-TMP	32.5	37.1	35.8	41.2
2,2,3-TMP	2.6	2.6	2.0	2.8
2,3,4-TMP	35.6	30.2	31.4	30.2
2,3,3-TMP	29.3	30.1	30.8	25.8
	DMH's			
2,5-DMH	29.5	32.0	41.0	40.9
2,4-DMH	21.3	24.5	26.3	28.3
2,3-DMH	43.6	38.0	28.7	25.6
3,4-DMH	5.6	5.5	4.0	5.2
	TMH's			
2,2,5-TMH	87.4	86.3	80.2	83.5
2,2,4-TMH	0.0	0.0	0.0	trace
2,4,4-TMH	0.0	1.0	1.5	0.9
2,3,5-TMH	12.6	12.7	18.3	15.6

0.52 wt % conjunct polymers, respectively, plus dissolved sulfur dioxide.

The compositions of the alkylates of these four runs are plotted as a function of temperature in Figure 3. The alkylation quality decreased with increased temperature because of the large decrease in the trimethylpentane (TMP) content. The percentages of the less desired light ends (LE's or C_5–C_7 isoparaffins), dimethylhexanes (DMH's), and heavy ends (HE's) all increased with increased temperature. The HE's were almost entirely trimethylhexanes (TMH's).

The compositions of each of these four families are shown in Table II. The relative importance of the following isoparaffins increased in general in their specific family with temperature: isopentane; 2,2,4-TMP; 2,5-DMH; 2,4-DMH, and 2,3,5-TMH. Those whose importance decreased with temperature include 2,3-dimethylbutane (2,3-DMB); 2,3,4-TMP; 2,3-DMH; and 2,2,5-TMH. Albright et al. (1977) had noted similar trends for the LE and TMP families, but their analytical equipment had not been able to make comparisons for the DMH or TMH family.

Excellent quality alkylates were produced with almost theoretical yields in runs at -15 °C for four acids of quite different composition, as shown in Table III. Two of the acids (acids 1 and 2) were the used (or reject) acid from a commercial alkylation unit. The third acid (acid 3) was a synthetic used acid produced by bubbling 1-butene through a concentrated sulfuric acid, as described earlier (Albright et al., 1988b). Acids 1, 2, and 3 were acids used in the conjunct polymer investigation (Albright et al., 1988a). Acid 3, which produced the highest quality alkylate, had a composition essentially identical with the acid that gave the highest quality alkylate in a conventional, continuous-flow, one-step process (Albright et al., 1972).

The compositions of the four major families in alkylate are compared in Table IV for runs with different acids. Major differences were noted for the TMP and TMH families for runs with used acids as compared to those with the fresh acid. The DMH composition of the run using acid 3 is much different than those of the other three runs.

Table III. Comparison of Alkylate Produced Using 96% Fresh Acid and Three Used Acids in Composite Runs: -15 °C, I/O = 5, and A/O = 10

	fresh acid	used acids		
		acid 1	acid 2	acid 3
acid composition, wt %				
H_2SO_4	96.4	91.7	90.7	96.0
H_2O	3.6	4.4	2.6	1.0
conjunct polymers		3.6	6.1	2.6
SO_2		0.3	0.6	0.4
time, h	3.1	5.0	7.5	2.5
alkylate yield	201	201	192	198
alkylate RON	99.4	99.3	99.4	100.2
alkylate composition				
LE's	5.7	4.3	4.2	4.1
TMP's	81.7	85.2	85.2	88.1
DMH's	4.2	5.1	5.0	3.7
HE's	8.4	5.4	5.6	4.1

Table IV. Family Compositions for Composite Runs Using Spent Acids at I/O = 5, A/O = 10, and -15 °C

	acid type			
	96.4% fresh	acid 1 (used)	acid 2 (used)	acid 3 (synthetic used)
	LE's			
isopentane	25.2	27.5	28.4	26.7
2,3-DMB	32.6	35.7	34.4	35.8
2-MP	6.8	4.2	4.0	3.5
3-MP	2.8	2.8	3.0	2.8
2,4-DMP	16.5	14.7	14.3	16.5
2,2,3-TMB	2.3	2.1	2.1	2.2
2,3-DMP	13.0	13.0	13.8	12.5
2- and 3-MH	0.8	0.0	0.0	0.0
	TMP's			
2,2,4-TMP	37.1	35.4	33.8	36.8
2,2,3-TMP	2.6	0.9	1.2	2.6
2,3,4-TMP	30.2	39.8	42.2	39.2
2,3,3-TMP	30.1	23.9	22.8	21.4
	DMH's			
2,5-DMH	32.0	38.9	35.6	12.6
2,4-DMH	24.5	23.4	23.7	37.0
2,3-DMH	33.0	33.9	37.0	45.3
3,4-DMH	5.5	3.8	3.7	5.1
	TMH's			
2,2,5-TMH	86.3	80.6	79.8	81.4
2,2,4-TMH	0.0	0.0	0.0	0.0
2,4,4-TMH	0.0	0.0	0.0	0.0
2,3,5-TMH	12.7	19.4	20.2	18.6

Acid 3 was saturated with sulfur dioxide to increase the sulfur dioxide concentration; this modified acid resulted in an alkylate with RON = 100.6, which is slightly higher than that of the alkylate produced with acid 3. Both acid 3 and its modification resulted in faster rates of alkylate formation than with the other acids.

Two composite runs were made at -15 °C with a fresh acid containing 98% acid. The alkylate quality was excellent, RON = 100.2 in both cases, but yields of only 160–170 were obtained because of conjunct polymers and SO_2 production. Ninety-eight percent acid is apparently a better oxidant than the other acids used. In commercial units, fresh acids containing 98–99% H_2SO_4 always result in the rapid formation of 1–2% conjunct polymers. When this acid is recycled, conjunct polymers then form less rapidly.

Importance of First-Step Operating Variables

The results of 23 runs were statistically analyzed to determine how first-step operating conditions affect the alkylate yields and quality in second-step reactions. 1-Butene was employed in all runs. The ranges of first-step

conditions investigated were as follows:

temp, °C	-15 to 30
A/O, mol acid/mol olefin	0.4-1.5
I/O, mol isobutane/mol olefin	0-5
agitation, rpm	1300 or 1750
acids	same as those used for composite runs

The second-step reactions were conducted in all cases at -15 °C, A/O = 10, I/O = 5, and 1750 rpm.

During a batch run, once alkylate yields of 20 were reached, quality and composition remained essentially unchanged during the rest of the run. For statistical analysis, the RON values selected were those at the end of the run. The results of several sets of replicate runs were used to estimate run-to-run error. Gas chromatographic error was estimated from sets of duplicate analyses. Since some runs had more chromatographic analyses than others, a weighting factor was developed for the reduction of total error due to multiple analyses; the variance contribution is inversely proportional to the number of analyses of a specific run. The weighting of the response is inversely proportional to the combined variance of the run and chromatographic analyses. A stepwise regression procedure was conducted, with each run appropriately weighed, and using all variables, the square of each, and all two-factor interactions (cross products). The following model contains the factors which are significant at the 95% level, and it indicates that the amounts of conjunct polymer (CP) and of water (H_2O) in the acid phases are significant:

$$RON = 99.73 + 0.40(\% \ CP) - 0.039(\% \ CP)^2 - 0.14(\% \ H_2O) - 0.0835(\% \ CP)(\% \ H_2O) + 1.14(A/O) + 0.165(I/O) - 0.283(A/O)/(I/O) \quad (1)$$

This equation predicts that the best quality alkylates would be produced with acids containing about 4-6% conjunct polymers and 1.0-1.5% water. Essentially identical acids were reported by Albright et al. (1972) as preferred for one-step alkylations. However, the RON values as predicted by eq 1 are much higher than those for the one-step process. A continuous-flow system for two-step alkylations could result in somewhat altered predictions.

Over 15 runs were made with a first-step temperature of 30 °C. Such a temperature is 15-22 °C higher than temperatures commonly used in commercial units; previously 30 °C was considered as unacceptable because of low alkylate qualities and low yields. Yet the first-step temperature was found to have an insignificant effect on alkylate quality (but not yield, as will be discussed later). Higher temperatures for first-step reactions would reduce refrigeration costs significantly.

In several batch runs of this investigation, some sec-butyl sulfates were unreacted at the end of the run, and alkylate yields as reported are hence lower than those that could have been obtained with an extended time of operation. Nevertheless, a stepwise regression analysis was made of the results of 16 runs in which alkylate yields appeared to be close to the obtainable yields. The following relation resulted:

$$yield = 162.8 + 14.0(A/O) + 0.4(I/O) + 0.11t - 1.32(A/O)t + 0.17(I/O)t \quad (2)$$

where t is in °C. For the four acids investigated, acid composition had no appreciable effect on the alkylate yields. Lower yields of alkylate were obtained with the increased temperature and decreased I/O in the first step. The reduced yields were caused by increased production

of conjunct polymer, sulfur dioxide, and water because of oxidative reactions with H_2SO_4. Any acid that is a strong oxidant, such as 98-99% fresh acids, may however result in lower yields than predicted by eq 2. This conclusion is based on both the results of this investigation and those of Albright et al. (1977).

Several runs were also made in which 30 °C was employed for the first-step reactions but the temperatures for the second-step reactions were varied from -10 to 10 °C. Higher second-step temperatures resulted in decreased quality alkylates similar to those reported in Table I. Since agitation speeds were found to have an insignificant effect on the first-step reactions, mass transfer between the liquid phases was not a rate-controlling step in this investigation.

Two-Step Alkylations with Isobutylene

Alkylations with isobutylene differ appreciably from those with n-butenes. Such findings are not surprising since low polymers are the intermediates produced from isobutylene. Table V summarizes the results for the isobutylene runs. The following differences occurred in comparing the isobutylene results with those with n-butenes:

(a) Alkylates were formed at lower A/O values. When the same A/O was employed, alkylation reactions were completed in less time.

(b) Alkylate yields were significantly lower since more conjunct polymers were produced.

(c) Alkylate qualities were much lower with RON values in the 89-92 range common. These two-step alkylations with isobutylene result in alkylates with qualities similar to those obtained by one-step processes.

Detailed analyses of the LE, TMP, DMH, and HE families of isoparaffins are appreciably different than those obtained for n-butenes (Spalding, 1985).

Three Alkylation Mechanisms

The results of this investigation indicate that alkylate isoparaffins are produced by three distinct mechanisms. To aid in discussing these mechanisms, Figure 4 presents alkylate composition data for alkylates prepared from n-butenes with RON's varying from about 90 to 101. The following features are important:

(a) The weight percentage of the TMP's extrapolates to 100% at about RON = 103 (the expected value for TMP), while the weight percentages of the LE's, DMH's, and HE's all extrapolate essentially linearly to zero. Excluding TMP's, the relative amounts of these latter three families are essentially constant in the range 99-101 RON, the upper range of available data. This finding suggests at high RON that all three families are formed from the same intermediate(s). Hofmann and Schriesheim (1962a,b) had early reported evidence indicating that LE's and DMH's were formed from common intermediates.

(b) Somewhat different correlations occur for alkylates obtained in runs with fresh acids as compared to those with used acids (or acids initially containing at least 2% conjunct polymers). Such differences occur for the TMP, LE, and HE families. The differences, if any, are small for DMH's, and only a single DMH curve was drawn in Figure 4.
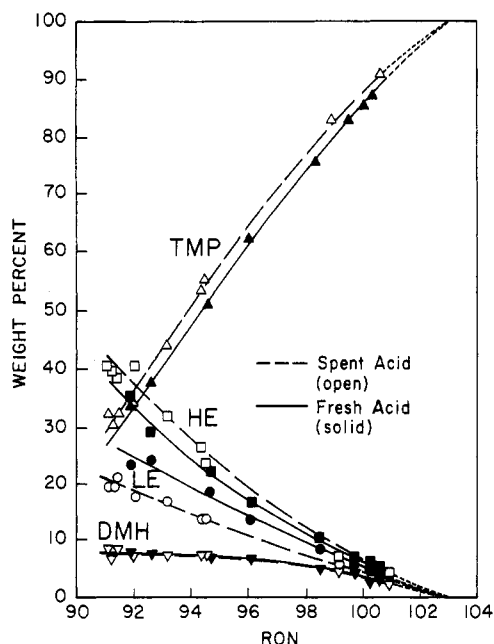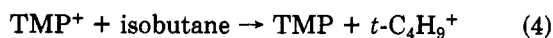
Table V. Iodine Numbers, RON's, and Yields for First-Step Runs Using Isobutylene and 96.4% Sulfuric Acid at -20 °C

A/O	I no.	RON	yield
0.05	175	87.1	100
0.5	155	87.9	98
1.2	88	88.5	97
8.0	42	89.7	91

Figure 4. Alkylate composition relative to four major families as a function of research octane number.

Mechanism 1. Trimethylpentanes only are formed as indicated by the following simplified reactions:

$$t\text{-}C_4H_9^+ + \text{2-butene or isobutylene} \rightarrow TMP^+ \quad (3)$$

$$TMP^+ + \text{isobutane} \rightarrow TMP + t\text{-}C_4H_9^+ \quad (4)$$

Equation 4 is an oversimplification since conjunct polymers are an excellent source of hydride ions (Albright, 1977). The hydride ion is often transferred to the TMP^+ from the conjunct polymers to produce TMP. Later a hydride ion transfers to the conjunct polymer from isobutane, and $t\text{-}C_4H_9^+$ is produced. The increased amounts of TMP's and the faster rates of alkylate formation such as occurred in this investigation with the synthetic used acid can thus be explained by improved and faster hydride ions transfer.

In two-step alkylations, the sec-butyl sulfates decompose in the presence of H_2SO_4 to free 2-butenes and regenerate more H_2SO_4. The 2-butene is released relatively slowly especially at lower temperatures so that there is high probability of forming TMP^+ and then TMP. There is likewise less probability of polymerization reactions that lead to formation of LE, DMH, and HE isoparaffins. DMH's are not produced in significant amounts in two-step alkylations by reactions between 1-butene and $t\text{-}C_4H_9^+$ forming DMH^+ (and eventually DMH). If such a reaction were significant, the DMH curve of Figure 4 would not extrapolate to zero at RON = 103.

In conventional or one-step alkylations, some DMH's may be formed by reactions involving 1-butene if the isomerization of 1-butene to 2-butenes is incomplete. The results of Albright et al. (1988b), however, indicate that sec-butyl sulfates are formed as intermediates during n-butene isomerizations. Since Li et al. (1970) reported essentially identical yields and composition of the high-quality alkylates from both 1-butene and 2-butenes in their one-step process, 1-butene was obviously isomerized to at least equilibrium values in that investigation. Hence, for a one-step alkylation process producing high-quality alkylates from n-butenes, sec-butyl sulfates are important intermediates, 2-butenes account for most TMP's produced, and 1-butene accounts for little or no DMH's.

Mechanism 2. All LE's, some TMP's, most if not all DMH's, and some HE's are produced by mechanism 2.

These are produced from common intermediates as proposed by Hofmann and Schriesheim (1962a,b) and Albright (1977). The intermediates include C_{12}-C_{20} olefins that protonate in the acid medium to C_{12}^+-C_{20}^+. Fragmentation, such as by β-scission, leads to fragments that form C_4-C_9 isoparaffins plus heavier isoparaffins. Since isobutylene polymerizes readily in the presence of H_2SO_4, as was again demonstrated in the present investigation, mechanism 2 is of major importance with alkylations using isobutylene. It is, however, of lesser importance with n-butenes that polymerize less readily. Formation of C_{12}-C_{20} olefins (and cations) is promoted by decreased I/O ratios, higher temperatures, and lower levels of agitation.

Mechanism 3. Only HE's (C_9 and heavier isoparaffins) are produced by this mechanism which is highly important when very low-quality alkylates are produced. The olefin first polymerizes to form heavy cations; hydride ions then transfer to the resulting cations to form the heavy isoparaffins as shown:

$$C_9^+ \text{ and heavier cations} + H^- \rightarrow$$
$$C_9 \text{ and heavier isoparaffins} \quad (5)$$
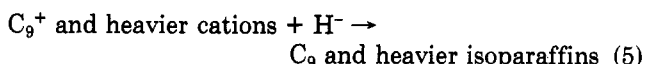
The hydride ion is obtained from conjunct polymer, isobutane, or other isoparaffins as already discussed for mechanism 1.

The four curves of Figure 4 were extrapolated to RON = 87 using the data obtained for alkylates produced from isobutylene (Spalding, 1985) and obtained by the decomposition of sec-butyl sulfates (Albright et al., 1988a). The LE and DMH contents of the alkylate pass through maxima at about RON = 90. At RON values less than 89, the LE, DMH, and TMP contents all extrapolate almost linearly to zero at RON = 87, which is the approximate RON value for heavy ends (Innes, 1977). The heavy end content also extrapolates well to 100% at RON = 87. Conditions that promote polymerization and simultaneously promote rapid hydride transfer (to form HE's) favor mechanism 3. With a less rapid hydride transfer, mechanism 2 is favored.

The following equation was developed to predict the relative importance of mechanism 1 during the production of an alkylate:

$$\% \text{ alkylate produced by mechanism 1} =$$
$$(\% \ TMP\text{'s}) - 0.5(\% \ LE\text{'s}) \quad (6)$$

In the above equation, the last term is the predicted amount of TMP's produced by mechanism 2; it is based on the finding that the ratio of TMP/LE as produced by mechanism 2 is approximately 0.5. This value is based on the experimental finding that the ratio averaged about 0.53 when sec-butyl sulfate or its sodium salt decomposed (Albright et al., 1988a). The ratio was, however, about 0.45 when two-step alkylation runs were made with isobutylene. In these cases, mechanism 1 was obviously of no importance. It seems as if the ratio is slightly higher when n-butenes are used as olefins (to produce sec-butyl sulfate) as compared to isobutylene runs. The TMP/LE ratio of 0.5 was assumed to be constant as the operating conditions varied; experimental evidence is, however, needed to test this postulate.

An equation for mechanism 3 was developed using similar assumptions:

$$\% \text{ alkylate produced by mechanism 3} =$$
$$(\% \ HE\text{'s}) - 1.4(\% \ LE\text{'s}) \quad (7)$$

The last term of eq 7 is an estimate of the amount of HE's produced by mechanism 2. The coefficient 1.4 is the ratio of HE/LE as the alkylate quality approaches RON = 103,

Table VI. Approximate Importance of Three Mechanisms That Produce Isoparaffins: Percentage of Alkylate Produced

RON alkylate	mech. 1	mech. 2	mech. 3
103	100	0	0
100	85	15	0
98	72	28	0
96	57	42	1
94	40	58	2
92	23	72	5
90	9	74	17
88	1	42	57
87	0	0	100

as shown in Figure 4; mechanism 3 is of no importance at such a high RON.

The relative amounts of alkylate produced by mechanisms 1 and 3 are estimated by the above equations and the results of Figure 4. The amount produced by mechanism 2 is the remainder. As indicated by Table VI, mechanism 1 is the predominant mechanism at RON values above about 96. For alkylates of approximately 90–94 RON, mechanism 2 is predominant accounting for about 72% of the alkylate at RON = 92. Mechanism 3 is of minor importance at RON values of 92 or more. It becomes the predominant mechanism at RON values less than 88. The relative importance of the three mechanisms of course depends to some extent on the acid composition, temperature, and feed olefin.

The LE, TMP, DMH, and HE contents of the alkylate produced by mechanism 2 were estimated using the results of Figure 4 and eq 6 and 7. For total alkylates in the range 96–103 RON, the alkylate produced by mechanism 2 contained about 28% LE's, 14% TMP's, 17% DMH's, and 41% HE's. On the basis of this composition, the RON value was about 86.4. When the RON of the total alkylate varied from 92 to 94, the alkylate produced by mechanism 2 contained slightly more LE's, TMP's, and HE's, but the DMH content was about 12%. As a result of the lower DMH content, the RON of the mechanism 2 portion of the total alkylate was then higher, about 87.5. Relatively small variations in the composition and RON values of the mechanism 2 alkylate are to be expected because the characteristics and type of fragmentation of C_{12}–C_{20} cations (or olefins) vary with at least he following factors: specific olefin used, acid used, composition of the acid, and operating conditions. For example, the compositions of the alkylate are affected by temperature and acid composition, as shown in Tables II and IV, respectively.

On the basis of the calculations made, the RON values of the alkylates produced by mechanisms 2 and 3 were similar and much smaller than those of alkylates produced by mechanism 1. In the present investigation, essentially pure trimethylpentanes were produced by mechanism 1, and they had an average RON value of about 103. If, however, propylene is used as olefin, mechanism 1 would produce significant amounts of dimethylpentanes. When HF is used as a catalyst with 1-butene as the olefin, DMH's are produced by mechanism 1. In these latter two cases, the alkylate produced by mechanism 1 is of lower quality than 103 RON.

Two-Step Processes

A two-step alkylation process offers significant commercial promise, as the results of the present investigation indicate. Relative to alkylate yields, the design and operation of the first-step reactor is of major importance. Only a batch reactor operated with a rather long residence time has been investigated to date. If the first-step reactor

was operated with short residence times, side reactions that produce conjunct polymers would likely be greatly reduced and subsequent alkylate yields increased. A flow reactor with good temperature control and with high rates of agitation likely will result in increased yield. In such a reactor, relatively high alkylation temperatures such as 20 °C or even higher should be investigated. The cost of controlling temperature would then be reduced as compared to conventional alkylation processes that operate at about 10 °C. Such a conclusion is based on the fact that first-step reactions are much more exothermic than second-step reactions. Relatively low temperatures in the second-step reactor likely will, however, be needed in order to obtain superior quality alkylates. The preferred olefin feed should be almost exclusively n-butenes with little isobutylene being present.

In the present investigation, the second-step reactions were investigated using mono-sec-butyl sulfate dissolved in excess H_2SO_4. As indicated by Albright et al. (1988b), di-sec-butyl sulfate can also be produced. This sulfate could be transferred to the second-step reactor as either a relatively pure material or dissolved in either isobutane or other hydrocarbons. There is a need to determine if di-sec-butyl sulfate as a feed to the second-step reactor would offer any advantages; in such a case, different composition acids could be used if desired in the two different reactors.

In a commercial second-step reactor, the acid phase should probably always contain sufficient dissolved mono-sec-butyl sulfate to maintain a rapid rate of alkylate formation. Possibly the acid recycled from the second-step reactor to the first-effect reactor should contain appreciable dissolved butyl sulfates. The importance of agitation in the second-step reactor still needs to be determined, especially at 10 °C or higher temperature.

Acknowledgment

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Application of Size Exclusion Chromatography with Inductively Coupled Plasma Emission Spectrometric Detection to Residual Oil Hydrodesulfurization (HDS) and Hydrodemetalization (HDM) Studies

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Size exclusion chromatography with inductively coupled plasma optical emission detection (SEC-ICP) has been applied to the study of the hydroprocessing of residual oils for vanadium (HDV) and sulfur (HDS) removal. SEC-ICP and kinetic studies show that in many residual oil feeds HDV appears to follow parallel, first-order kinetics with fast- and slow-reacting vanadium molecules. Application of parallel, first-order kinetics suggests that kinetics and not reactor hydrodynamics may explain deviations from ideal plug flow, first-order kinetic models observed for many hydrotreating reactions. Adequate comparison of residual oils for relative HDS activities is not accomplished by SEC alone. Desulfurization of large sulfur molecules is a combination of size reduction and removal of thiophenic sulfur.

Residual oils or petroleum fractions boiling above 616 K are becoming increasingly more important in the refining industry. These residuum fractions are often hydrotreated to remove undesirable elements such as sulfur, nitrogen, nickel, and vanadium. Hydrodesulfurization (HDS) and hydrodemetalization (HDM) reactions have been recognized to be strongly influenced by the rate of diffusion of the reactant through the liquid-filled catalyst pores. Spry and Sawyer (1975) proposed a functional relationship between the effective diffusivity and the ratio of the reactant diameter to the catalyst pore diameter, applicable to those situations where the reactant molecular diameter is greater than one-tenth the pore diameter. Other investigators have applied this concept to "hindered or configurational" diffusion to develop kinetic models which relate feed molecular size distributions with catalyst activity (Shimura et al., 1982; Rajagopaian and Luss, 1979; Jaffe, 1981). Thus, it is not surprising that size exclusion chromatography (SEC) has been a useful tool for investigation of heavy oil hydroprocessing (Richardson and Alley, 1975; Bridge and Green, 1979). Most notably, Hall and Herron (1981) used analytical- and preparation-scale SEC to examine six different feeds and a number of hydrotreated products. Elemental analyses were performed on the five fractions from the preparation-scale SEC. Hausler (1985) reported the use of an inductively coupled plasma emission spectrometric detector to give continuous elemental analysis of analytical-scale SEC effluent (SEC-ICP). Recently Reynolds and Biggs (1985) used this technique to compare the effects of process severities on sulfur and vanadium molecular size profiles for thermal and catalytic hydroprocessing. Our work reports the application of SEC-ICP to compare hydrodesulfurization and hydrodemetalization of vanadium (HDV) for different atmospheric residual oils.

Table I. Atmospheric Residua

feed	S, wt %	V, ppm	API gravity, 60 °F	C Res.,[a] wt %
Arabian Heavy	4.5	136	11.6	12.7
Arabian Light	3.0	24	16.4	16.4
ARDS[b]	1.8	35	16.6	6.7
Flotta	2.2	25	16.8	5.5
Hondo[c]	5.4	256	16.4	11.2
Maya[c]	3.7	302	14.5	12.1
North Slope	1.8	51	13.9	7.6
Oriente	1.7	174	12.9	11.9

[a] Ramsbottom carbon residue—ASTM D 524-76. [b] Feed sample taken at refinery. [c] These residua are 478+ K distillation fractions.

Experimental Work

The feeds or residual oils in this study are shown in Table I along with their bulk analytical properties. The residual oils were prepared by first desalting and then fractionating whole crudes. The whole crude was fractionated in a batch fractionator at 0.02 kg/cm² and 477 K to produce a 616+ K equivalent atmospheric resid. Some of the crude oils were batch fractionated at 0.272 kg/cm² and 429 K to produce a 478+ K equivalent atmospheric resid. An 840+ K, Arabian Heavy resid was produced in a Pope wiped-film still at 0.06 kg/cm² and 530 K. The catalyst used throughout this study was a cobalt–molybdenum on alumina catalyst with a relatively high surface area of over 200 m²/g. It was presulfided with a 10% H_2S/H_2 mixture over the temperature range from 477 to 644 K. The catalyst was then cooled and the hydrocarbon feeds were introduced into the reactor at temperatures near 422 K. All reactor tests were made under isothermal conditions and at a pressure of 158.2 kg/cm².

The reactor experiments were made in an automated