Effect of acid / hydrocarbon ratio, temperature and contact time on the isobutane–isobutylene alkylation with trifluoromethanesulfonic acid

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Received 20 March 1996; accepted 26 May 1996

The effect of the acid–hydrocarbon ratio and temperature on the isobutane–isobutylene alkylation with trifluoromethanesulfonic acid was studied over the temperature range of $40°C \geqslant T \geqslant -80°C$. The effect of acid/hydrocarbon ratios and temperature passes through a maximum giving high quality alkylate of approximately 70% branched C_8 products at −30°C, with a catalyst/hydrocarbon ratio of 0.5. The optimum reaction conditions also depend on the induction period and the effect of secondary reactions influenced by contact time. TFSA is a readily recyclable acid without the need for any purification or regeneration.

Keywords: alkylation; isobutane; isobutylene; trifluoromethanesulfonic acid; temperature dependence

1. Introduction

Alkylation of isobutane with various olefins is one of the most important processes in petroleum industry. The catalysts commercially used in alkylation plants have many advantages as well as disadvantages. Hydrogen fluoride is highly toxic, volatile and corrosive, while the sulfuric acid process produces a large amount of spent acid. The modification of HF, using a less volatile pyridinium–poly(hydrogen fluoride) (PPHF) system renders this procedure environmentally safer [1]. Recent reviews [2,3] summarized the topic including efforts to find better catalysts for the alkylation reaction, including solid acid catalysts [4,5]. So far, however, no really suitable industrially applicable solid acid catalyst was found. Different solid superacids, such as sulfated zirconia [6], heteropoly acids [7] etc. were studied, but the fast deactivation hinders practical application.

Previously we described the acidity dependence of the isobutane–isobutylene alkylation using trifluoromethanesulfonic acid modified by water or trifluoroacetic acid [8]. We report now the alkylation of isobutane with isobutylene catalyzed by trifluoromethanesulfonic acid (TFSA) and the effect of operating variables with emphasis on the acid/hydrocarbon ratios, temperature (studied in the range of $40°C \geqslant T \geqslant -80°C$) and the reaction time.

2. Experimental

Isobutane and isobutylene were commercial products (Matheson, purity ⩾99%) and were used without further purification. TFSA was purchased from 3M. Before use, acid was distilled under dry nitrogen stream.

Alkylation reactions were carried out in a 600 cm^3 PARR stainless steel mechanically stirred (400 rpm) batch reactor. In each experiment 35 cm^3 isobutane and appropriate amount of TFSA were premixed before reaction and thermostated at the desired temperature. A previously prepared isobutane/isobutylene mixture (45 cm^3, alkane/alkene mole ratio was 7.5 : 1) was then introduced from a connected vessel into the reactor under nitrogen pressure through a stainless steel tube and liquid/gas inlet. The final pressure in the reactor was 500 psi, with 14 : 1 final mole ratio of isobutane/isobutylene. The reaction was continued for 20 min, except for experiments where the reaction time was varied as indicated. After completion of the reaction excess isobutane was vented off at room temperature. The hydrocarbon phase was then separated from the acid, washed several times with water and kept over KOH pellets.

For temperature dependence measurements always a fresh sample of acid was used. In catalyst recycling experiments the used catalyst was separated from the alkylate and reused while other operating variables were unchanged.

A Hewlett-Packard GC-MS (HP-5890 series II GC coupled with HP-5971 series MSD, 30 m DB-5 capillary column) and a Varian 3400 gas chromatograph with flame ionization detector and same column were used for analysis. Identification of all C_5, C_6, C_7 and C_8 hydrocarbons is based on the comparison with authentic samples. Individual isomers of heavier hydrocarbons except for 2,2,5-trimethylhexane were not identified. The results are given in weight% and the research octane numbers (RON) were calculated as described [9].

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3. Results

3.1. Effect of acid/hydrocarbon volume ratio

A highly desirable goal in acid catalyzed isobutane–isobutylene alkylation is the decrease of overall acid concentration. In studied alkylations involving two-phase heterogeneous systems, the acid composition and other reaction parameters strongly affect the yield and quality of products. First of all, the alkylate composition strongly depends on the acid/hydrocarbon volume ratio. Previously, we reported the effect of acidity of TFSA on the isobutane–isobutylene alkylation [8]. It was shown, that even as low an acid/hydrocarbon volume ratio (as low as 0.003) catalyzes the reaction, however, the quality of alkylate is unsatisfactory, because of the high amount of heavier components (76% C_9 and higher) due to predominant isobutylene oligomerization. When using an acid/hydrocarbon ratio of 1.0 the alkylate contained 64% of light hydrocarbons (C_7 and lower). The acidity of TFSA as determined earlier by Saito and coworkers [10], is on the Hammett acidity scale $H_0 = -14.1$ using a UV-spectrophotometric method and an acid–base indicator. A relationship between the acid strength and cracking activity was established [11].

In our studies it is now shown that the alkylate quality passed through a maximum as a function of the acid/hydrocarbon volume ratio. As it is shown on fig. 1 optimal quality product was obtained in the case of a 0.0625 ratio. This represents very low acid concentration in the system contrasted with acid induced alkylations generally carried out in excess acid systems (H_2SO_4 or HF).

Since the alkylation in the TFSA catalyzed reaction takes place in a two-phase system the role of interface beside the acid strength is very important. The optimal product quality as a function of acid/reactants volume ratio showed the most favourable reaction conditions achieved with minimal acid concentration and related interface of the heterogeneous system. On the basis of these studies three different acid/hydrocarbon volume ratio systems were selected for the study of temperature dependence, which were the 0.025, 0.0625 and 0.50 volume ratios.

We have not, however, studied in our work the effect of variation of stirring speed on the reaction (all reactions were carried out at a stirring speed of 400 rpm). More effective stirring is expected to increase interface reactivity and thus alkylate quality.

3.2. Effect of temperature

The effect of temperature on the TFSA catalyzed isobutane–isobutylene alkylation was studied at the selected acid catalyst/reactants volume ratio, through a fairly wide temperature range. The calculated research octane numbers (RON) of the obtained alkylate are plotted in fig. 2, while the detailed data related to the composition of different samples are tabulated in tables 1 and 2.

The experimental results show that satisfactory alkylation takes place even at −80°C, a temperature much lower than the so far reported minimum temperature for isobutane alkylation with ethylene and propylene of −30°C in the presence of HCl–$AlCl_3$ catalyst [12].

As it can be seen in tables 1 and 2 and fig. 2, at low acid catalyst/hydrocarbons ratio (0.025 and 0.0625) the temperature does not significantly affect the quality of the alkylate formed. In fact, the composition hardly varied, except for the lowest temperatures, where the alkylate quality decreased. In contrast, using a 0.5 volume ratio the C_8-fraction of the alkylate paralleling the RON values passed through a maximum as a function of temperature. The best quality alkylate was formed at −30°C, with a calculated research octane number RON = 86. The amount of heavy ends increased at

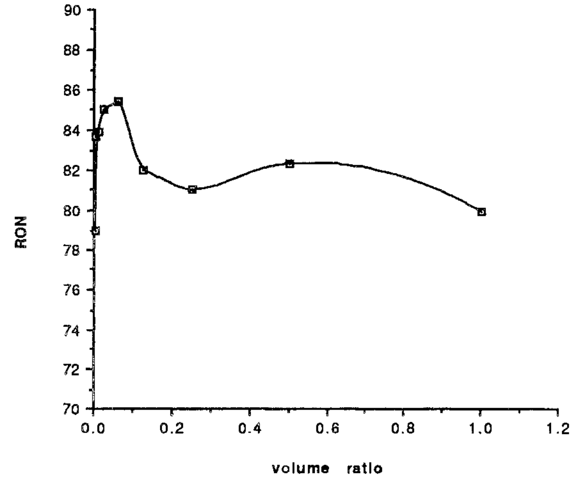


Fig. 1. Effect of the catalyst/hydrocarbon volume ratio on the alkylate quality in the TFSA catalyzed isobutane–isobutylene alkylation at 20°C.

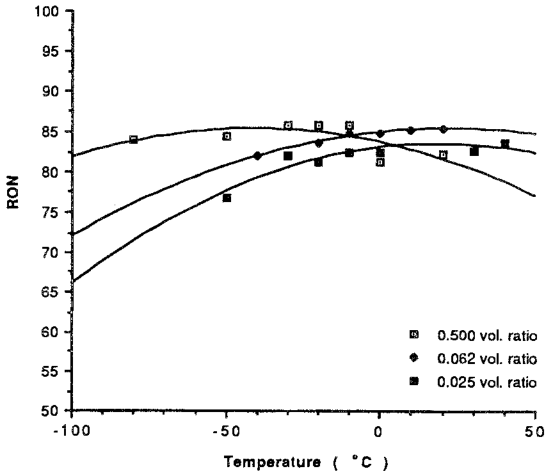


Fig. 2. Effect of temperature on the alkylate quality in TFSA catalyzed isobutane–isobutylene alkylation at various catalyst/hydrocarbon volume ratios.

Table 1
Effect of temperature on the TFSA catalyzed isobutane–isobutylene alkylation (acid/hydrocarbon volume ratio is 0.025)

Products (%)	Temperature (°C)							
	−50	−30	−20	−10	0	20	30	40
C_5	1.0	2.7	2.7	3.3	2.7	4.1	5.1	4.7
C_6	2.4	3.6	3.0	4.1	3.7	5.4	5.3	5.8
C_7	1.4	3.8	3.2	4.3	4.5	6.3	6.1	7.5
C_8	14.0	34.5	31.0	37.5	38.7	37.5	37.8	39.8
2,2,4-TMP	11.2	24.6	22.0	24.0	23.5	21.1	19.7	19.0
C_{9+}	81.2	55.4	60.1	50.8	50.4	46.7	45.7	42.2
RON	76.9	82.0	81.3	82.4	82.5	82.5	82.6	82.6

lower volume ratios, while remaining about the same at 0.5 ratio. The alkylate product distribution (main fractions, and C_8-hydrocarbons) is shown in figs. 3a and 3b.

Fig. 3a shows that the amount of light ends (C_5, C_6 and C_7 products) increases monotonically as the temperature increases, while the change in the heavy ends products shows an opposite trend. The C_8 alkylate content passed through a maximum at −30°C, and decreased rapidly with the raising of temperature. Further important indications are the ratio of trimethylpentanes (TMP-s) and dimethylhexanes (DMH-s), and the isooctane (2,2,4-TMP) in the total amount of TMP-s. These are plotted on fig. 3b. The TMP-s/DMH-s ratio shows an optimum value at −80°C and strongly decreases at higher temperature. At 20°C the ratio is 0.16, which means that the amount of TMP-s formed is very low compare to DMH-s. It is interesting to mention that the 2,2,4-TMP percentage among each TMP-s is practically constant, usually 75–80% independent from the temperature.

3.3. *Effect of residence time*

The residence time is also a most important operating variable, particularly because of the possibility of secondary reactions effecting the alkylation system. To study the influence of secondary reactions such as isomerization or degradation the alkylate composition was measured as a function of reaction time, under the optimal experimental parameters previously established (0.5 acid/hydrocarbon volume ratio, −30°C reaction temperature). The results are summarized in figs. 4a and 4b.

It was found, that the alkylate quality showed a maximum as a function of residence time. The highest amount of isooctane was obtained after 20 min reaction time with relatively low amount of light and heavy ends (fig. 4a). The presence of an induction period is in accordance with literature results [13]. However, the alkylate quality decreases after an optimum residence time, with heavy ends also decreasing because of product degradation. Additionally, the TMP-s/DMH-s ratio is also continuously decreasing with longer residence times (fig. 4b), while the amount of 2,2,4-TMP remaining constant in overall TMP-s in this case too (75–80%) as mentioned before.

3.4. *Catalyst acid recycling*

As recycling of catalyst acid is essential in practical alkylations, we also carried out such a study in our work. Under identical conditions used for alkylation with fresh acid (see experimental section) used catalyst separated from the alkylates was used with new hydrocarbon fuel in the same reactor while stirred at −30°C for 20 min. After the separation of catalyst and alkylate the cycle was repeated several times. The data of consecutive runs are summarized in figs. 5a and 5b.

The results show that reapplied catalyst acid without any purification produces quite good alkylate quality; decrease in quality was observed only after four runs.

Table 2
Effect of temperature on the TFSA catalyzed isobutane–isobutylene alkylation (acid/hydrocarbon volume ratio is 0.5)

Products (%)	Temperature (°C)						
	−80	−50	−30	−20	−10	0	20
C_5	3.4	2.1	1.8	8.4	8.3	12.8	28.1
C_6	2.7	2.6	3.2	7.1	8.0	9.0	16.2
C_7	3.7	3.6	5.3	8.5	12.1	12.1	15.2
C_8	35.9	54.0	68.6	51.2	40.3	33.8	20.4
2,2,4-TMP	24.2	31.7	35.1	21.6	12.1	9.9	1.3
C_{9+}	54.3	37.7	21.1	24.8	31.3	32.3	20.1
RON	83.9	84.5	86.1	85.7	85.7	81.1	82.3

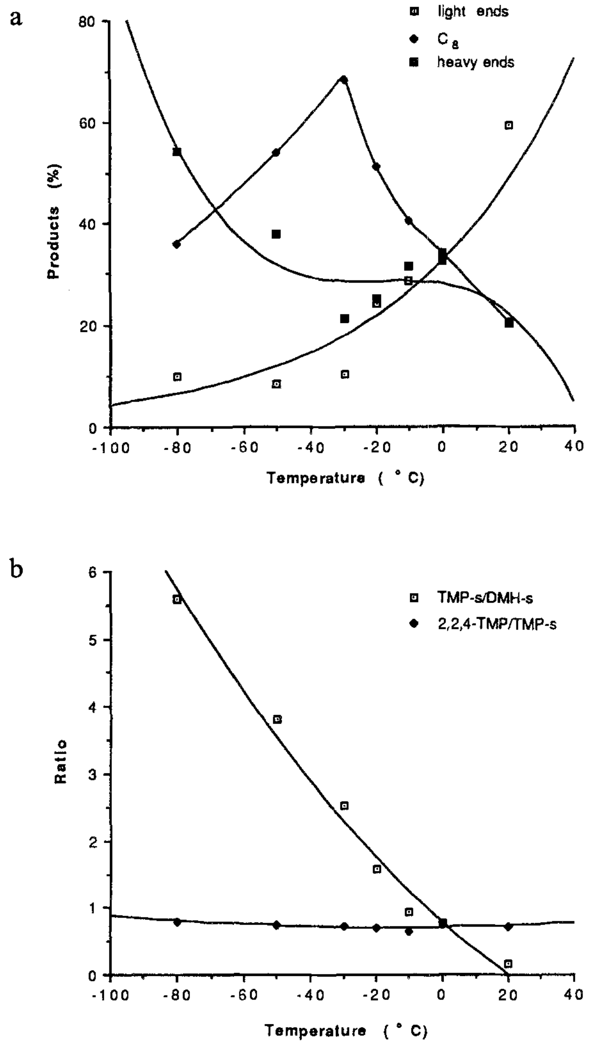


Fig. 3. Effect of temperature on the product distribution of TFSA catalyzed isobutane–isobutylene alkylation at 0.5 catalyst/hydrocarbon volume ratio. (a) Distribution of major fractions; (b) distribution of C_8 fractions.

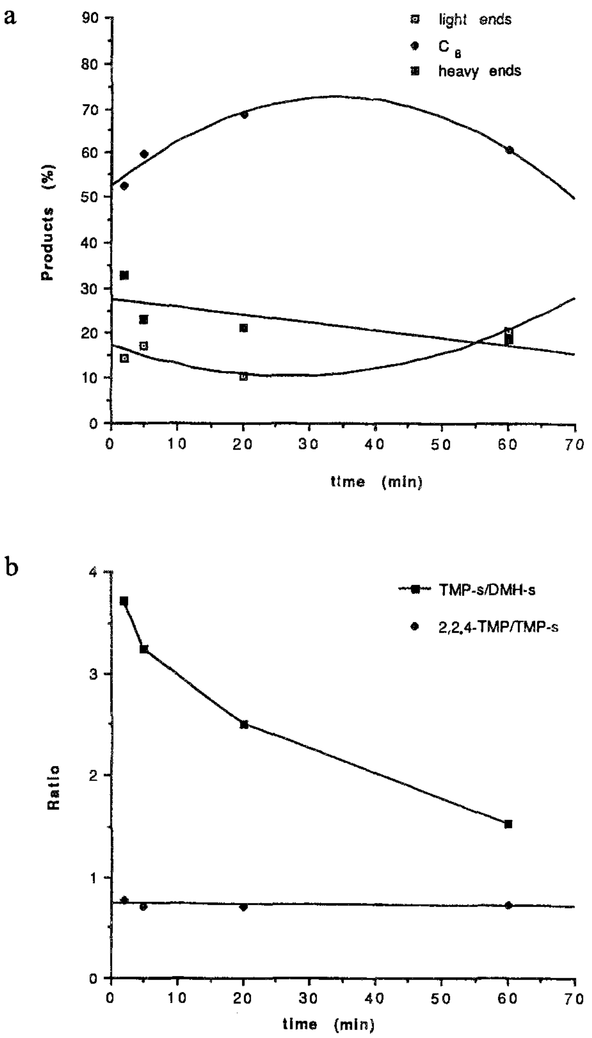


Fig. 4. Effect of residence time on the distribution of major (a) and C_8 (b) fractions in the TFSA catalyzed isobutane–isobutylene alkylation at −30°C and 0.5 catalyst/hydrocarbon volume ratio.

The amount of C_8 hardly changed. However, the amount of light ends strongly decreases, in a fifth run (its combined amount is practically negligible, ≈ 2%). At the same time the heavy ends increase and in a fifth run their amount reaches 44% (fig. 5a).

The results are in accord with slow build up of acid soluble oils (ASO) in recycled acid, decreasing its ability for alkylation. As TFSA is, however, easily purified and can be distilled without decomposition (b.p. 168°C), and readily recyclable.

4. Discussion

The isobutane–isobutylene alkylation catalyzed by trifluoromethanesulfonic acid (TFSA) is similar to that previously studied with modified TFSA catalysts.

Due to the high acidity of TFSA ($H_0 = -14.1$) effective alkylation can take place at temperatures as low as −80°C, which is unprecedented. The alkylate quality, and the C_8, or TMP-s content showed a maximum as a function of temperature, in accord with our previous conclusion concerning an optimal acidity for isobutane–isobutylene alkylation [8]. However, such a significant effect can be observed only at 0.5 acid catalyst/hydrocarbon ratio. At lower ratios (0.025 and 0.0625) temperature does not affect significantly the alkylate composition. In these cases the C_8 and 2,2,4-TMP contents stay quite constant, changes were observed only in the ratio of light and heavy ends. At low temperatures (−40°C to −80°C region) the amount of heavy ends significantly increased independently from the acid/hydrocarbon volume ratio, indicating that the acid strength was less effective in that region. At higher temperature cracking reactions become more important and the amount of light ends greatly increased (59.5% at 20°C, table 2). It should also be mentioned that the freezing point of TFSA is −37°C, which means that below −40°C

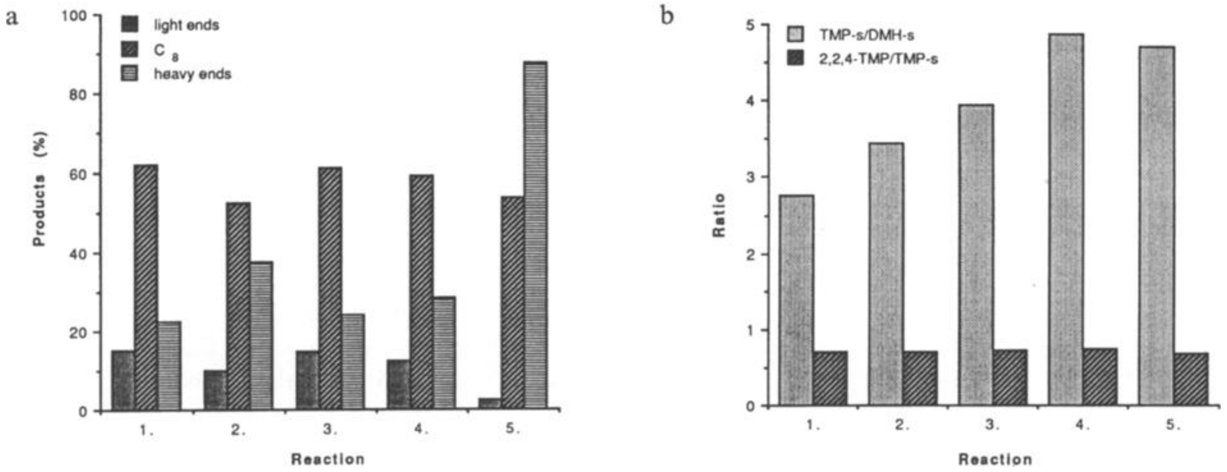


Fig. 5. Effect of catalyst recycling on the composition of major (a) and C_8 (b) fractions in the TFSA catalyzed isobutane–isobutylene alkylation at −30°C and 0.5 catalyst/hydrocarbon volume ratio.

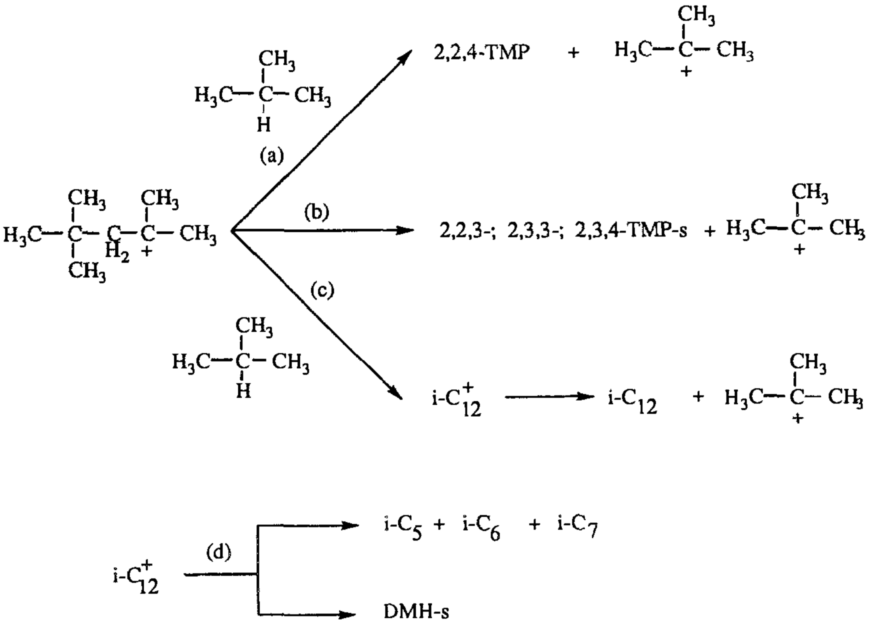
the acid catalyst partly solidify and the effective interface is probably limited.

The effect of residence time on the alkylate quality also shows an optimum at around 20 min, similarly to the results of Li et al. [13], who suggested an induction period for alkylation. At longer reaction times TFSA will act as a strong cracking catalyst even at −30°C. This can be also seen in the change of TMP-s/DMH-s ratio, which continuously decreases with increasing residence time. These results show the important role of secondary reactions.

TFSA catalyst is recyclable in several cycles without any purification or regeneration showing no significant change in alkylate yield and quality. The RON and the C_8 content (with good TMP-s/DMH-s ratio) of alkylates of consecutive reactions is even slightly increased. Further loss of catalyst was negligible. Since in sulfuric acid catalyzed alkylation the formation of large amount of "acid soluble oils" is a significant problem the hydrocarbon content of used catalyst was checked. We found that TFSA contains dissolved hydrocarbon products (oils) in low amounts only after four repeated recyclings.

As discussed experimental parameters affect not only the distribution of major fractions, but the TMP-s/DMH-s ratio, which is an important factor related to alkylate quality. At low temperatures TMP-s are major C_8-products, while at 20°C trimethylpentanes are negligible compared to dimethylhexanes. This is in accord with the mechanism of isobutane–isobutylene alkylation involving intermediacy of the 2,2,4-trimethylpentyl cation (I) [14] (scheme 1).

However, Albright [15] has already emphasized that



Scheme 1.

Table 3
Distribution of alkylates formed in HF, PPHF, H_2SO_4 and TFSA catalyzed isobutane–isobutylene alkylation

Products (%)	Catalyst			
	HF[a]	PPHF[b]	H_2SO_4[c]	TFSA
light ends	5.8	8.6	16.3	10.3
TMP-s	75.1	68.8	35.1	50.2
DMH-s	13.7	11.0	10.3	18.6
methylheptanes	–	–	–	–
heavy ends	5.4	11.6	38.3	21.1
RON	96.7	93.8	82.0	86.1

[a] 200 g HF, 80 ml isobutane : isobutylene mixture (14 : 1 volume ratio), 20°C.

[b] 190 g HF : Py (85 : 15 weight ratio), 80 ml isobutane:isobutylene mixture (14 : 1 volume ratio), 20°C.

[c] 100 ml H_2SO_4 (96%), 80 ml isobutane : isobutylene mixture (14 : 1 volume ratio), 0°C.

secondary reactions such as isomerization and degradation can play an important role. These secondary reactions strongly depend on the experimental conditions and catalyst used. TFSA as a superacid can effectively catalyze the cracking reactions [11]. However, at low temperatures or short reaction times the observed good TMP-s/DMH-s ratio and low amount of light ends (figs. 3 and 4) indicate that the major reaction pathways are (a) and (c). The relatively high amount of heavy ends can be interpreted as due to susceptibility of isobutylene in the formation of oligomeric cations [16].

In order to evaluate results obtained in present work with those observed with conventional acid catalysts, we compared different systems under similar conditions and results are tabulated in table 3.

The results show that the alkylate quality formed with TFSA catalyst is lower than that with HF catalysts (neat HF and PPHF), but it is better than that of sulfuric acid alkylation.

5. Conclusions

Study of the superacidic trifluoromethanesulfonic acid catalyzed isobutane–isobutylene alkylation showed effective alkylation with low catalyst/hydrocarbon volume ratio. Optimal alkylate yield and product composition (indicated by the RON of the product) was obtained at about −30°C. In contrast to sulfuric acid catalyzed alkylation good quality alkylate can be obtained. TFSA is usable in several recycles without any regeneration or purification and the acid can be readily purified.

Acknowledgement

The work was supported by the Loker Hydrocarbon Research Institute. BT thanks the Hungarian National Science Foundation for a postdoctoral fellowship (Grant OTKA W015063).

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