Catalysis Letters 61 (1999) 105–110

Acid-catalyzed isobutane–isobutylene alkylation in liquid carbon dioxide solution

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Received 1 July 1999; accepted 9 July 1999

Liquid carbon dioxide was studied as a solvent for the isobutane–isobutylene alkylation. The acid catalysts in the reaction were anhydrous HF (AHF), pyridinium–poly(hydrogen fluoride) complex (PPHF), concentrated sulfuric acid and trifluoromethanesulfonic acid (TFSA). The effect of the acid–hydrocarbon volume ratio, temperature and residence time on the alkylate quality were studied over the temperature range of $50 \geqslant T \geqslant 0\,^\circ$C. Carbon dioxide as a competing weak base decreases the acidity of the system which parallels the alkylate quality. In the case of HF and TFSA catalysts, solvent CO_2 increased the octane number of the alkylate product (RON 95.6 for HF- and 88.0 for TFSA-catalyzed alkylation with CO_2 solvent).

Keywords: alkylation, isobutane, isobutylene, HF, PPHF, H_2SO_4, trifluoromethanesulfonic acid, liquid CO_2

1. Introduction

Carbon dioxide has been used as a subcritical as well as supercritical solvent in stoichiometric as well as heterogeneous and homogeneous catalytic reactions [1–7]. Since the critical parameters of carbon dioxide ($T_c = 31\,^\circ$C, $P_c = 72.9$ atm) [8] are not extreme, supercritical CO_2 is one of the easiest supercritical fluids to handle. The nonpolar character of CO_2 makes it a good candidate as a solvent for many organic transformations.

Alkylation of isobutane with various olefins is a major process in petroleum industry. Acid catalysts commercially used in alkylation plants are anhydrous hydrogen fluoride (AHF) and sulfuric acid. HF-based catalysts are highly toxic and corrosive, while the sulfuric acid process produces large amounts of spent acid and acid soluble oils. Modified HF in the form of onium polyhydrogen fluorides, such as pyridine poly(hydrogen fluoride) (PPHF), which contains a small amount of HF in equilibrium acting as the catalyst, were developed to alleviate the volatility and toxicity of anhydrous HF [9]. This field was extensively treated by recent reviews [10,11] concerning efforts to find safer, environmentally more friendly and stable catalysts for the alkylation reaction, including several solid acids [12]. Various solid superacidic catalysts, such as sulfated zirconia [13], heteropoly acids [14], etc., were studied, but because of their fast deactivation they are not industrially applicable. No data is available in the scientific literature using solvents in alkylation reaction. The patent literature contains some information, such as on the use of sulfolane. Relatively nucleophilic and high-boiling solvents, however, have serious limitations.

We recently reported the effect of acidity, temperature and residence time on the isobutane–isobutylene alkylation with modified as well as neat trifluoromethanesulfonic acid catalysts [15a,b]. There are two recent reports on the use of supercritical CO_2 as a solvent in the butenes/isobutane alkylation over solid acid catalysts [15c,d]. However, thus far no credible solid acid catalyst is available for butenes/isobutane alkylation. In continuation of our work, we now report the alkylation of isobutane with isobutylene catalyzed by different liquid acids (HF, PPHF, H_2SO_4, TFSA) in CO_2 as a solvent. The study emphasizes the effect of acid/hydrocarbon volume ratios as well as the effect of temperature (studied in the range of $50 \geqslant T \geqslant 0\,^\circ$C) and residence time.

2. Experimental

Isobutane and isobutylene (Matheson, ⩾99% purity) were used without further purification. Anhydrous HF (AHF) (Matheson) was liquefied in an acetone–dry ice bath and was used in liquid form. Pyridinium–poly(hydrogen fluoride) (PPHF) with 90 : 10 HF/pyridine ratio was prepared from pyridine (Aldrich) and HF, as previously described [9]. Trifluoromethanesulfonic acid (TFSA) from 3M was distilled before use under dry nitrogen. Sulfuric acid (Mallinckrodt, 96%) was used as received. Carbon dioxide (Matheson Coleman grade, 99.99%) was obtained from the pressure cylinder equipped with a suitable valve allowing withdrawal of liquid CO_2.

Alkylation reactions were carried out in a 600 ml PARR stainless-steel mechanically stirred (400 rpm) batch reactor. In each experiment, the appropriate amount of the acid and 80 ml isobutane and isobutylene in a 14/1 mole ratio was introduced into the pressure vessel. Subsequently, liquid carbon dioxide was introduced from a connected cylinder at room temperature through a stainless-steel tube and liquid/gas inlet with 5574 kPa final pressure (about 120 g).

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The reactor was then heated to the desired temperature using a thermostat/heater. 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 and carbon dioxide was vented off carefully into a cold trap (dry ice–acetone) at room temperature. The hydrocarbon phase was then separated from the acid, washed several times with water and kept over potassium hydroxide pellets. The condensed gases contained insignificant amount of alkylation products.

Control experiments without carbon dioxide were carried out under the same experimental conditions but without CO_2. In these experiments, high-purity nitrogen was used to keep the system pressurized at 3447 kPa so that all reactants were in the liquid phase.

The products were analyzed with a Hewlett–Packard GC-MS (HP-5890 series II GC coupled with HP-5971 series MSD, 30 m DB-5 capillary column), while a Varian 3400 gas chromatograph with flame ionization detector and same column was used for quantitative analysis. Identification of individual C_5, C_6, C_7 and C_8 hydrocarbons was 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 wt% and the research octane numbers (RON) were calculated as published [16].

3. Results

3.1. Effect of acid/hydrocarbon ratio

The yield and quality of alkylate strongly depends on the acidity, acid/hydrocarbon ratio, besides such other parameters as temperature, rate of mixing, residence time, etc. TFSA-catalyzed isobutane/isobutylene alkylation [15] was studied and optimum conditions were established as a function of the acid/hydrocarbon ratio. It was shown [15] that even very low amounts of TFSA (as low as 0.003 acid/hydrocarbon volume ratio) can catalyze the reaction. The quality of alkylate, however, is unsatisfactory because of the high amount of heavier compounds formed due to the fact that under low acid concentration isobutylene oligomerization becomes the predominant reaction.

In this study using CO_2 as a co-solvent, alkylations with acids such as sulfuric acid, HF, modified HF, i.e., HF containing pyridinium–poly(hydrogen fluoride) (PPHF), and trifluoromethanesulfonic acid (TFSA) catalysts were investigated. Alkylations, for comparison purposes, were also carried out without CO_2 but under nitrogen pressure. In the study of the dependence on acid/hydrocarbon volume ratio only liquid CO_2 served as the co-solvent as the reaction temperature of 20 °C was well below the critical temperature of carbon dioxide. However, in these studies we could not ascertain the extent of inhomogeneity of reaction mixture. The obtained results are summarized in tables 1–5.

From the results of table 1 with sulfuric acid as a catalyst it is evident that the alkylate quality is significantly lower with CO_2 solvent present. The selectivity toward the formation of C_8 fraction and, especially, 2,2,4-trimethylpentane (2,2,4-TMP) is very low paralleled by the increased formation of oligomers. Decreasing the amount of acid results in an increase in the percentage of C_9 and related higher hydrocarbons. Using a 1 : 8 acid/hydrocarbon volume ratio, the amount of C_9 and higher fractions is excessive (84.2%).

The effect of liquid CO_2 on the TFSA-catalyzed alkylations was investigated at 0 °C and at room temperature (20 °C). The results obtained at 0 °C with TFSA (table 2) show a similar trend to sulfuric acid at lower acid/hydrocarbon volume ratios (ratio <0.5) with carbon dioxide as a solvent. However, at a 0.5 acid/hydrocarbon volume ratio the alkylate quality is significantly better than that obtained in the solvent-free reaction. More than 20% increase was observed in the amount of C_8 fraction and 2,2,4-TMP (table 2). The research octane number (RON) becomes maximum in the case of the reaction with carbon dioxide as a co-solvent. Another important measure concerning the alkylate quality is the ratio of trimethylpentanes and dimethylhexanes (TMP/DMH ratio). Under solvent-

Table 1
Effect of acid/hydrocarbon volume ratio on the H_2SO_4-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solvent and in CO_2-free systems at 0 °C.

	Volume ratio							
	Without CO_2				With CO_2 solvent			
	0.12	0.31	0.63	1.25	0.12	0.31	0.63	1.25
Products (%)								
C_5	1.5	3.2	1.6	1.0	1.3	2.9	2.8	1.6
C_6	3.6	5.1	4.3	3.2	2.8	4.1	4.5	3.8
C_7	4.2	5.7	5.4	4.7	2.9	4.0	4.8	3.3
C_8	21.5	31.7	38.9	48.1	8.8	11.1	14.3	22.9
2,2,4-TMP	8.4	12.8	15.9	19.8	3.0	3.8	5.1	9.5
C_9 and higher	69.2	54.3	49.8	43.0	84.2	77.9	73.6	68.4
RON	78.9	82.1	84.0	82.1	75.0	76.8	77.6	79.0
TMP/DMH	3.3	4.1	4.7	4.1	1.3	1.7	1.9	3.5

Table 2
Effect of acid/hydrocarbon volume ratio on the TFSA-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solvent and in CO_2-free systems at 0 °C.

	Volume ratio									
	Without CO_2					With CO_2 solvent				
	0.06	0.13	0.31	0.50	1.00	0.06	0.13	0.31	0.50	1.00
Products (%)										
C_5	5.6	6.5	9.0	12.8	12.4	3.8	3.6	3.8	6.3	12.1
C_6	6.2	6.4	8.4	9.0	9.4	4.1	4.0	4.8	6.7	10.0
C_7	7.5	7.4	9.6	12.1	12.2	5.0	3.0	4.8	7.1	11.9
C_8	51.4	43.9	48.7	33.8	38.5	23.2	23.8	35.7	51.4	36.4
2,2,4-TMP	25.9	20.0	19.4	9.9	10.6	15.4	16.2	21.3	30.2	14.1
C_9 and higher	29.3	35.8	24.3	32.3	27.5	63.9	65.6	50.9	28.5	29.6
RON	85.6	84.7	83.2	81.1	82.7	76.8	80.5	84.0	88.0	86.3
TMP/DMH	2.7	2.1	1.5	0.9	0.8	4.9	5.1	3.7	4.0	1.3

Table 3
Effect of acid/hydrocarbon volume ratio on the TFSA-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solvent at 20 °C.

	Volume ratio		
	0.12	0.31	0.50
Products (%)			
C_5	3.4	3.9	7.5
C_6	4.4	5.3	8.0
C_7	4.0	5.9	9.4
C_8	27.3	39.0	47.0
2,2,4-TMP	17.7	21.8	22.6
C_9 and higher	60.9	45.9	28.1
RON	81.1	83.1	86.3
TMP/DMH	4.3	3.1	2.3

free conditions the TMH/DMH ratio decreases monotonously with increasing acid/hydrocarbon volume ratio. In contrast, in the presence of carbon dioxide this ratio is twice as high using low amount of catalyst than in the solvent-free reaction, and it remains high up to a volume ratio of 2.

At 20 °C (results in table 3), a similar maximum was observed in RON as a function of acid/hydrocarbon volume ratio. However, the overall alkylate quality is lower than at 0 °C. A significant difference was observed in the product distribution with light hydrocarbons being formed in higher amounts, which is paralleled with a decrease in the amount of higher hydrocarbons (due to accompanying cracking reactions). The best alkylate quality was obtained at 0.5 acid/hydrocarbon volume ratio, as was the case at 0 °C. At room temperature the TMP/DMH ratio decreases with increase in acid/hydrocarbon volume ratios.

In industrial alkylations, besides sulfuric acid, anhydrous hydrogen fluoride is the most widely used catalyst that produces high quality alkylate. Using HF alone in control experiments (table 4) we observed the formation of a high octane alkylate as expected. The alkylate quality increases with increasing amount of HF, although a good RON alkylate is even obtained at 0.1 acid/hydrocarbon volume ratio, although the amount of higher oligomers formed is 34%. The changes in the amount of C_8 and 2,2,4-TMP show a similar tendency, increasing the alkylate quality up to RON 94.2. With liquid carbon dioxide co-solvent we observed the same behavior as in the case of trifluoromethanesulfonic acid. The RON values (table 4) show a maximum at an acid/hydrocarbon volume ratio of 2 and the quality of alkylate (RON = 95.6) is excellent. Similar to TFSA results, the TMP/DMH ratios are higher in carbon-dioxide-containing systems than in the solvent-free experiments.

The modified HF, i.e., pyridinium–poly(hydrogen fluoride) (PPHF) complex which is considerably less volatile and thus environmentally safer than neat liquid hydrogen fluoride, produces high quality alkylate. Using the 90/10 HF/pyridine system both as a reaction medium and as a catalyst (there is always a small concentration of HF present in equilibrium with the complex), as seen in table 5 the octane number of alkylate is only slightly lower than with neat HF under solvent-free conditions. However, using carbon dioxide as the solvent the amount of oligomeric hydrocarbons formed is significantly higher. The amount of TMP in the C_8 fraction is approximately the same in both cases, the TMP/DMH ratios being about 8 independent of the solvent.

3.2. Effect of temperature and residence time

The effect of temperature on the isobutane/isobutylene alkylation was also studied using sulfuric acid, TFSA, and PPHF in the temperature range from 0 to 50 °C. The calculated research octane numbers (RON) and the product composition of alkylates are shown in table 6.

The experimental results show that the alkylate quality passes through a maximum using TFSA at 0 °C, while the octane numbers increase with raising temperature with PPHF and sulfuric acid. At 50 °C wherein carbon dioxide is in supercritical phase the alkylation results were poor with TFSA, while the other acids gave approximately the same quality alkylate as obtained under solvent-free conditions.

The reaction or residence time also affects alkylate composition. In acid-catalyzed alkylations besides oligomerizations secondary reactions such as isomerization or cracking can occur, and these reactions can modify the product com-

Table 4
Effect of acid/hydrocarbon volume ratio on the HF-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solvent and in CO_2-free systems at 20 °C.

	Volume ratio							
	Without CO_2				With CO_2 solvent			
	0.10	0.68	1.05	2.50	0.19	0.86	2.00	3.18
Products (%)								
C_5	0.8	1.3	1.7	1.1	1.6	2.2	2.2	2.8
C_6	2.1	1.8		1.8	2.0	2.4	1.7	4.3
C_7	3.3	2.6	1.6	2.9	2.2	2.6	2.2	7.6
C_8	59.8	68.9	53.5	88.3	44.6	67.9	85.8	59.0
2,2,4-TMP	38.0	45.5	31.5	54.2	32.0	48.7	58.8	30.8
C_9 and higher	34.0	25.4	43.2	5.9	49.6	24.9	8.1	26.3
RON	87.7	91.2	86.9	94.2	84.5	91.0	95.6	87.2
TMP/DMH	7.2	10.5	7.3	6.8	8.4	11.3	11.4	3.2

Table 5
Effect of acid/hydrocarbon volume ratio on the PPHF (9 : 1)-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solvent and without CO_2 at 20 °C.

	Volume ratio					
	Without CO_2			With CO_2 solvent		
	0.63	1.49	2.38	0.80	1.40	2.43
Products (%)						
C_5	2.0	0.9	8.6	1.8	1.7	
C_6	2.9	1.6	2.7	2.4	2.6	1.9
C_7	3.8	2.2	4.0	3.8	3.3	2.8
C_8	71.1	61.5	76.8	35.1	57.9	61.2
2,2,4-TMP	45.3	38.2	49.4	22.8	38.5	40.9
C_9 and higher	20.2	33.8	14.8	57.7	34.5	34.1
RON	91.3	87.0	72.0	81.7	87.0	86.7
TMP/DMH	8.2	8.1		6.5	8.0	8.7

Table 6
Effect of the temperature on the H_2SO_4, CF_3SO_3H, and PPHF (9 : 1)-catalyzed isobutane–isobutylene alkylation with CO_2 as a solvent.

	PPHF (9 : 1) in CO_2		H_2SO_4 in CO_2[a]		CF_3SO_3H in CO_2[b]		
	25 °C[c]	45 °C[d]	25 °C	50 °C	0 °C	20 °C	50 °C
Products (%)							
C_5	1.7	2.7	1.6	5.7	6.3	7.5	20.0
C_6	2.6	3.7	3.8	8.1	6.7	8.0	13.8
C_7	3.3	4.7	3.3	10.1	7.1	7.4	14.9
C_8	57.9	55.3	22.9	32.7	51.4	47.0	33.0
2,2,4-TMP	38.5	33.7	9.5	8.0	30.2	22.6	8.6
C_9 and higher	34.5	33.6	68.4	43.4	28.5	28.1	18.3
RON	87.0	87.1	79.0	81.3	88.0	86.3	81.8
TMP/DMH	8.0	5.4	3.5	1.39	4.0	2.3	0.7

[a] 100 ml H_2SO_4 (volume ratio 1.25).
[b] 40 ml CF_3SO_3H (volume ratio 0.5).
[c] 112 ml of PPHF (volume ratio 1.4).
[d] 80 ml of PPHF (volume ratio 1.0).

position. These reactions are strongly dependent on the reaction time and the acidity.

In order to study the effect of secondary reactions on the alkylate quality we studied the effect of residence time on the trifluoromethanesulfonic-acid-catalyzed isobutane–isobutylene alkylation using liquid CO_2 as the solvent. The data are shown in table 7.

The results show that good quality alkylate (RON $=$ 88.0) was obtained with 20 min reaction time. The recognized induction period [17] was shorter than 2 min. At

Table 7
Effect of residence time on the TFSA-catalyzed isobutane–isobutylene alkylation at 0.5 acid/hydrocarbon volume ratio and at 0 °C in liquid CO_2.

	Residence time (min)		
	2	20	60
Products (%)			
C_5	4.3	6.3	4.7
C_6	5.3	6.7	6.9
C_7	4.5	7.1	10.6
C_8	52.9	51.4	37.7
2,2,4-TMP	33.7	30.2	13.1
C_9 and higher	33.0	28.5	40.1
RON	86.9	88.0	83.0
TMP/DMH	4.8	4.0	1.2

60 min the alkylate quality decreases as does the TMP/DMH ratio (1.2), indicating secondary cracking/oligomerization reactions.

4. Discussion

The purpose of our study was to investigate the effect of liquid carbon dioxide on acid-catalyzed isobutane–isobutylene alkylation. Sulfuric acid, trifluoromethanesulfonic acid, anhydrous hydrogen fluoride and pyridinium–poly(hydrogen fluoride) were used. TFSA is of superacidic nature ($H_0 = -14.1$) [18], while the H_0, Hammett constant, of HF and concentrated H_2SO_4 is lower ($H_0 = -11$ to -12). The acidity of anhydrous HF was determined to be $H_0 = -15.1$ by Gillespie [19]. However, even very small amounts of water impurity decrease the acidity to $H_0 = -11$, which is the practical acidity of anhydrous HF.

The experimental results show that solventless alkylations were similar to those previously reported [15,20]. Using CO_2 as a solvent the alkylate quality decreased in the sulfuric-acid-catalyzed reaction. In case of alkylations with PPHF at low acid/hydrocarbon ratios the amount of heavy ends, i.e., C_9 and higher fractions, strongly increased, whereas the C_8 fraction and, especially, the amount of 2,2,4-TMP decreased. With an acid/hydrocarbon volume ratio of 1.4, however, satisfactory alkylate (RON = 87.0) was obtained.

The changes observed using HF and TFSA are similar. With both acids with CO_2 as a solvent a maximum in alkylate quality as a function of acid/hydrocarbon ratio is observed. The optimum RON values obtained are better than those in the neat acids (tables 2 and 4). Moreover, in these reactions considerably less acid catalyst is needed to produce higher quality products than in solvent-free systems. Another additional advantage is the increased formation of 2,2,4-TMP and other trimethylpentanes compared to dimethylhexanes in the CO_2 solvent systems. Using carbon dioxide in the supercritical state (i.e., above the critical temperature) resulted in decrease of the octane values in TFSA-catalyzed reactions, while the alkylate quality with PPHF and H_2SO_4 gave similar or increased octane values as compared to the solvent-free systems.

According to the generally accepted mechanism of the isobutane–isobutylene alkylation [20,21], the formation of higher amounts of heavy ends obtained in alkylations with CO_2 indicates increased oligomerization due to lowering of the overall acidity of the systems. Thus, CO_2 acts as a weak base attenuating the overall Brønsted acidity.

5. Conclusion

Study of the acid-catalyzed isobutane–isobutylene alkylation in liquid CO_2 solution showed that carbon dioxide can also act as a weak base and thus lowers the acidity of the systems resulting in decrease of alkylate quality. However, in cases wherein the acidity of the system is higher, the alkylate quality and, especially, C_8 and 2,2,4-TMP selectivity increased producing higher octane products compared to solvent-free systems again due to attenuation of the acidity. The use of CO_2 as a solvent allows substantial decrease of the overall amount of liquid acid needed for the alkylation. This helps to alleviate the environmental and safety hazard caused by the use of large amounts of acids serving not only as catalysts but as the reaction media.

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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