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CHEMISTRY OF FOSSIL FUEL

Recovery of Isobutylene from Commercial Butane–Butylene Fractions

K. G. Sharonov, A. M. Rozhnov, S. Ya. Karaseva, Yu. B. Myshentseva, V. I. Barkov, and V. I. Alenin

Samara State Technical University, Samara, Russia

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Abstract—A possibility of recovery of isobutylene with high concentration and purity from abgases of petroleum production and oil refining, e.g., from gases released in pyrolysis or catalytic cracking, by reversible reaction of isobutylene with isobutanol was studied.

In recent years, the production of methyl *tert*-butyl ether (MTBE) and methyl *tert*-amyl ether (MTAE) by alkylation of methanol with isoolefins has increased in many countries. These compounds are used as additives to motor fuel.

The hydrocarbon fractions C_4–C_5 of gases released in pyrolysis and catalytic cracking can be used as low-cost raw materials for production of isoolefins. A review of procedures for recovery of isoolefins from hydrocarbon gases was given in [1]. The procedures are based on the high reactivity of the tertiary carbon atom at the double bond in reactions of electrophilic addition. With many reagents (water, alcohols, and acids), such reactions are reversible, which allows recovery of concentrated isoolefins by subsequent decomposition of these products.

Strong acids, such as sulfuric, hydrochloric, organic sulfonic acids, and Friedel–Crafts catalysts can catalyze this reaction. The common drawback of these acids is their high corrosion activity and the low selectivity of the process. The use of weak acids, e.g., phosphoric, is inefficient owing to the low rate of the process. Of most interest as catalysts are sulfonic cation exchangers, allowing the reaction to be performed with high selectivity at low temperatures (85–90°C).

However, the procedure for hydration recovery of isobutylene via trimethylcarbinol (TMC), in which sulfonic cation exchangers are used as catalysts, has significant drawbacks: (1) the use of aqueous solutions decreases the catalytic activity of sulfonic cation exchanger, and (2) concentrated isobutylene-containing fractions (with isobutylene content of no less than 50 wt %) are used.

These drawbacks are lacking in the case of the reaction of isobutylene with aliphatic alcohols C_4–C_5. The reaction yields *tert*-alkyl ethers, which are subsequently decomposed.

The procedure for synthesizing MTBE and MTAE was thoroughly studied and discussed in [1]. As regards synthesis, and especially decomposition of ethers of higher alcohols, a number of problems still remain unsolved. It is well known [2, 3] that the reactivity of alcohols and the equilibrium degree of their conversion in the reaction with isobutylene decrease with increasing molecular weight of alcohol (Table 1). In addition, butyl alcohols do not undergo intermolecular dehydration on sulfonic cation exchanger (contrary to methanol and ethanol) and have higher boiling point. Therefore, the use of butyl alcohols as chemical extracting agents for recovery of isoolefins is of practical interest.

In this work the possibility of recovery of isobutylene from pyrolysis gases by the reaction with isobutanol was demonstrated by calculations and experiments.

Table 1. Rate constants b and equilibrium constants K_c for alkylation of alcohols with isobutylene at 323 K [2, 3]*

Alcohol	b, H^+-equiv mol^{-1} h^{-1}	K_c
Methanol	0.28	12.8 ± 2.0
Ethanol	1.58	76.1 ± 2.0
Propanol	2.63	137.6 ± 1.8
Butanol	3.53	150.3 ± 1.8
Pentanol	5.92	160.6 ± 1.8

* For stoichiometric ratio of the initial components.

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Table 2. Data on the equilibrium of reaction (1) in the liquid phase in the presence of sulfonic cation exchanger KU-23 at molar ratio alcohol : isobutylene = 4 : 1

T, K	Catalyst content, mol %	Number of tests	τ, h	Composition of equilibrium mixture, mole fraction			$K_c = \alpha_{eth}/\alpha_{al}\alpha_{ol}$	Activity coefficient γ_i			$K_a = K_c K_\gamma$ *
				iso-C_4H_8	*iso*-C_4H_9OH	BTBE		*iso*-C_4H_9OH	BTBE	olefin	
343	10–15	13	9–23	0.01360	0.7534	0.2330	2270 ± 0.36	1.079	2.087	1.551	28.46
363	10–15	14	9–15	0.02439	0.7561	0.2195	11.90 ± 0.31	1.073	2.033	1.544	14.64
383	10–12	12	10–17	0.04251	0.7606	0.1968	6.09 ± 0.18	1.066	1.995	1.546	7.37
403	8–10	12	1.5–5	0.06459	0.7661	0.1693	3.42 ± 0.21	1.058	1.965	1.555	4.10
423	8–10	13	0.75–5	0.08946	0.7724	0.1382	2.00 ± 0.13	1.049	1.941	1.568	2.36

* $K_\gamma = \gamma_{eth}/\gamma_{al}\gamma_{ol}$.

Table 3. Concentration equilibrium constants K_c of reaction (1) at various *iso*-C_4H_9OH : *iso*-C_4H_8 molar ratios

T, K	K_a	Molar ratio *iso*-C_4H_9OH : *iso*-C_4H_8									
		1 : 1		2 : 1		5 : 1		10 : 1		20 : 1	
		K_c	K_c'	K_c	K_c'	K_c	K_c'	K_c	K_c'	K_c	K_c'
343	27.66	114.18	140.42	57.46	59.44	28.65	28.65	21.56	21.53	18.46	18.45
363	13.73	47.34	57.21	26.72	27.91	14.27	14.28	10.89	10.88	9.38	9.37
383	7.33	21.75	25.64	13.38	14.00	7.62	7.63	5.90	5.90	5.11	5.11
403	4.17	1–.97	12.54	7.16	7.48	4.32	4.41	3.41	3.40	2.97	2.97
423	2.50	6.00	6.65	4.09	4.98	2.59	2.59	2.07	2.07	1.81	1.81

It has been shown in a number of studies concerned with synthesis of MTBE and MTAB [4, 5] that the concentration equilibrium constant K_c does not correspond to the thermodynamic constant K_a owing to deviation of the system alcohol–ether–isobutylene from ideality. At the same time, at the molar ratio alcohol : isobutylene equal to 3 : 1 and higher the concentration equilibrium constant becomes stable. The equilibrium of the reaction

$$CH_3–CH–CH_2OH + CH_2=C(CH_3)_2 \rightleftarrows CH_3–CH–CH_2–O–C(CH_3)_3 \quad (1)$$

was studied in the liquid phase in the range 343–423 K. The experiments were carried out in hermetically sealed glass ampules in the presence of KU-23 sulfonic cation exchanger as catalyst. For the study, we used isobutylene (99.8 wt %), isobutanol (99.8 wt %), and isobutyl *tert*-butyl ether (ITBE) (98.5 wt %).

Isobutyl *tert*-butyl ether was produced by the reaction of isobutylene with isobutanol, with subsequent rectification. The equilibrium for each temperature was reached for both direct and reverse reactions.

The reaction products were analyzed by gas-liquid chromatography on a KhROM-3.1 device equipped with a flame-ionization detector and temperature programming unit on a 6-m-long column packed with 15% PEG-20M on silanized Chromaton AW-HDMS. The results of the experiments are given in Table 2 listing the activity coefficients γ_i of the mixture components and the thermodynamic equilibrium constants K_a. The values of γ_i were calculated by the UNIFAC technique [6], using the quantitative data for molecular fragments given in [7]. The resulting equilibrium constants K_a are described by the equation

$$\log K_a = -4.08 + 1894/T. \quad (2)$$

With the use of K_a values, we calculated the equilibrium composition of the products of reaction (1) by the scheme

$$K_a \rightarrow \text{(composition)} \rightarrow \text{UIFAC} \rightarrow K_\gamma \rightarrow K_c = K_a/K_\gamma. \quad (3)$$

In doing so, the butane-butylene fraction with isobutylene content of 20 mol % was used as isobutylene-containing fraction. The calculations were carried out for the range 343–423 K and *iso*-C_4H_8 : *iso*-C_4H_9OH molar ratios of 1 : 1, 1 : 2, 1 : 5, 1 : 10, and

Table 4. Material balance of IBTBE synthesis at 333 K and molar ratio isobutanol : isobutylene of 2 : 1

Component	Passed		Obtained			
			liquid phase		gas phase	
	g h^{-1}	wt %	g h^{-1}	wt %	g h^{-1}	wt %
Isobutane	4.1	2.88	0.4	0.44	3.7	7.33
n-Butane	2.6	1.83	0.3	0.33	2.3	4.56
1-Butene	28.0	19.69	4.9	5.34	23.1	45.73
trans-2-Butene	7.9	5.56	0.2	0.22	7.7	15.25
cis-2-Butene	6.2	4.36	0.9	0.98	5.3	10.50
Isobutylene	25.2	17.72	1.2	1.31	1.2	2.38
Butadiene	0.1	0.07	0.01	0.01	0.09	0.18
C_4-acetylene	1.5	1.05	0.05	0.05	1.45	2.87
Isobutanol	66.6	46.84	35.0	38.17	2.07	4.10
IBTBE	–	–	48.1	52.47	3.30	6.54
Isobutene dimers	–	–	0.23	0.25	0.10	0.20
Trimethylcarbinol	–	–	0.30	0.33	0.18	0.36
Total	142.2	100.0	91.69	100.0	50.49	100.0

1 : 20. The value of K_c was determined using approximation procedure by the scheme

$$K_a \rightarrow (\text{composition}, K_\gamma) \rightarrow K_c \rightarrow (\text{composition}, K''_\gamma) \rightarrow K'_c = (\text{composition}, K'''_\gamma) \rightarrow K''_c. \quad (4)$$

The approximation was considered acceptable when the discrepancy in K_c values did not exceed 10 rel. %.

The results of calculations performed by scheme (4), presented in Table 3, suggest that even the first approximation gives K_c constants coinciding with K'_c within 10 abs. %. A plot of the equilibrium conversion of isobutylene against temperature at various alcohol : isobutylene ratios is presented in Fig. 1. The calculations showed that the equilibrium conversion of isobutylene is close to 100% at low temperature andalcohol : isobutylene molar ratio exceeding 5 : 1. The calculations also confirmed that hydrocarbon gases with isobutylene content of approximately 5 wt % are suitable as feed.

The obtained calculated and experimental data were verified on a continuous laboratory setup in a temperature-controlled sectional vertical reactor packed with KU-23 cation exchanger, using butane–butylene fraction from the catalytic cracking installation[1] and isobutanol. The initial isobutanol-containing mixture was fed from the top of the reactor, and the gaseous butane-butylene fraction, from the bottom through a bubbler. The material balance of the synthesis is presented in Table 4. The degree of isobutylene recovery was 90–92%.

[1] "Sintezkauchuk" (Togliatti).

The experimental values of the concentration equilibrium constant K_c for IBTBE synthesis were used to evaluate the equilibrium degree of conversion of ether in its decomposition. The evaluation was carried out for the range 353–403 K and isobutanol : IBTBE molar ratios of 1 : 1, 2 : 1, and 3 : 1. The results of evaluation are represented by lines in Fig. 2. Also

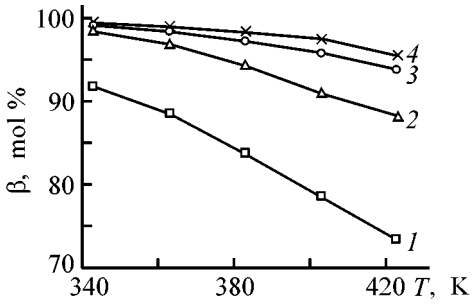

Fig. 1. Equilibrium conversion of isobutylene, β, vs. temperature T in IBTBE synthesis.

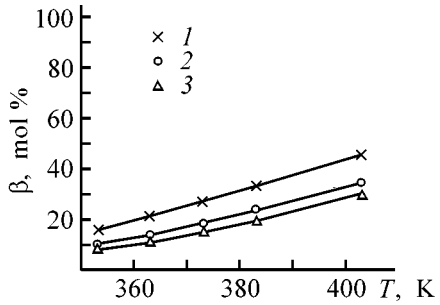

Fig. 2. Equilibrium conversion of IBTBE, β, vs. temperature T in its decomposition. Isobutanol : IBTBE molar ratio: (*1*) 1 : 1, (*2*) 2 : 1, and (*3*) 3 : 1. (*Line*) calculation and (*points*) experimental data.

Table 5. IBTBE decomposition in a flow-type reactor at 363 K and equimolar ratio of the ether and alcohol

v, h^{-1}	Composition of the reaction mass, wt %				IBTBE conversion	Selectivity with respect to isobutylene	Relative error of material balance, %
	iso-C_4H_8	*iso*-C_4H_9OH	IBTBE	isobutylene dimers	mol %		
0.3	2.38	88.33	8.86	0.43	85.24	99.17	0.35
0.5	6.60	82.83	8.48	2.09	85.87	96.11	0.49
1.0	2.16	92.70	5.04	0.10	91.60	99.82	1.09
3.0	4.09	89.52	6.20	0.19	89.67	99.65	1.50
5.0	4.96	86.24	8.57	0.23	85.07	99.55	0.60
8.0	6.02	77.76	16.05	0.17	73.27	99.62	0.34
12.0	8.23	68.23	23.39	0.15	61.04	99.61	0.72

given are the experimental IBTBE conversions (*points*) in IBTBE decomposition at 363 K, isobutanol : IBTBE molar ratio in the feed of 1 : 1, 2 : 1, and 3 : 1, and volumetric flow rate of feed equal to 1 h^{-1}. The results of these experiments showed that removal of isobutylene from the reaction zone increases the IBTBE conversion to 91.6%, compared with the equilibrium value of 21%.

The calculations showed that the optimal dilution is the alcohol : ether ratio of 1 : 1. With increasing dilution, the conversion of the ether decreases. Although the ether decomposition is a high-temperature reaction, the temperature should not be raised above 120°C because of the probable polymerization of isobutylene and degradation of sulfonic cation exchanger.

The experiments on IBTBE decomposition were carried out in the liquid phase in a temperature-controlled flow-type reactor packed with KU-23 cation exchanger. A system of traps was mounted at the outlet of the reactor. The first trap served to collect the liquid reaction mass, and the second trap contained a 0.5 N solution of bromine in acetic acid to absorb the released isobutylene. The reaction mass of the first trap was analyzed on a chromatograph without any pretreatment. The material balance was stricken for each run. The maximum error with respect to material balance was 6.54 rel. %.

The experiments were performed at varied temperature, isobutanol : IBTBE molar ratio, and volumetric feed flow rate v. In each run, we determined the conversion and selectivity of ether decomposition. The results of one of ether decomposition runs are presented in Table 5.

This study allows us to propose the following scheme of isobutylene recovery from the butane–butylene fraction of catalytic cracking or pyrolysis gas: etherification of isobutyle with alcohols C_4 → blowing off of unreacted hydrocarbons from the ether fraction → decomposition of ether to isobutylene → successive washing of isobutylene with alcohol C_4 cooled to 263 K and water. Isobutylene produced by this scheme was of no less than 99.9 wt % purity.

CONCLUSIONS

(1) The equilibrium of synthesis and decomposition of isobutyl *tert*-butyl ether in the presence of sulfonic cation exchanger KU-23 was studied. The equilibrium conversion of isobutylene in synthesis is close to 100% at alcohol : isobutylene molar ratios of 5 : 1 and 10 : 1. An experimental verification of the equilibrium data showed that the isobutylene conversion is 90–92%.

(2) The calculations showed that it is appropriate to carry out the decomposition of isobutyl *tert*-butyl ether in a solution of isobutanol at the optimal alcohol : ether molar ratio of 1 : 1. The ether conversion in a flow-type reactor at 363 K reaches 91% and the selectivity is more than 99% at a volumetric flow rate of feed equal to 1 h^{-1}.

(3) A scheme for recovery of isobutylene from dilute gas mixtures was proposed.

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