ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 3, pp. 357–362. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.B. Arbuzov, V.A. Drozdov, M.O. Kazakov, A.V. Lavrenov, M.V. Trenikhin, V.A. Likholobov, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 3, pp. 372–376.

Liquid-Phase Isobutane Alkylation with Butenes over Aluminum Chloride Complexes Synthesized In Situ from Activated Aluminum and *tert*-Butyl Chloride

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Received October 27, 2011

Abstract—The liquid-phase interaction between isobutane and butenes at 303 K and 2.5–3.0 MPa has been investigated using activated aluminum (Al*)—*tert*-butyl chloride (TBC) model system (TBC : Al* = 0.35–4 mol/mol). It has been demonstrated by attenuated total reflection FT–IR (ATR–FT–IR) spectroscopy that the catalytically active aluminum chloride complexes forming in situ in the hydrocarbon medium vary in composition. Alkylation as such takes place at equimolar proportions of the reactants (TBC : Al* = 1 : 1) and butenes feed mass flow rate of 5 h^{-1} per gram of Al*. According to ATR–FT–IR data, the most abundant aluminum complexes resulting under these conditions are the $AlCl_4^-$ and $Al_2Cl_7^-$ ions and, probably, the molecular complex $AlCl_3 \cdot$ *sec*-C_4H_9Cl. In a fourfold excess of TBC over Al* at butenes mass feed rate of 2.5 h^{-1}, isobutane undergoes self-alkylation. In this case, the $Al_2Cl_7^-$ ion is not detected and the most abundant complexes are $AlCl_4^-$, $Al_3Cl_{10}^-$, and the molecular species $AlCl_3 \cdot$ *tert*-C_4H_9Cl. It is hypothesized that the $Al_2Cl_7^-$ ion plays the key role in the liquid-phase alkylation of isobutane with butenes.

DOI: 10.1134/S0023158412030020

Isobutane alkylation with butenes is among the most important reactions in hydrocarbon processing into environmentally friendly, high-octane components of motor fuels. This reaction was described for the first time by V.N. Ipatieff, who used equimolar amounts of $AlCl_3$ and HCl as the catalyst and conducted the reaction at atmospheric pressure and a temperature of 238 K [1]. The present-day industrial process employs liquid H_2SO_4 and HF, which exert an adverse effect on the environment and on the process equipment. This prompts researchers to develop alkylation technologies using other catalytic systems, including heterogeneous catalysts [2]. The usability of ionic liquids, including those based on aluminum chloride, in this reaction was considered by Nasyrov et al. [3]. The catalytic properties of $AlCl_3$ are commonly associated with the formation of ionic aluminum chloride complexes possibly stabilized by carbenium ions [4, 5] or with the formation of solvated molecular complexes [6]. However, there is no systematic and noncontradictory information concerning their structure and their effect on the hydrocarbon conversion value. Therefore, it is still essential to study this reaction on model catalytic systems by physical methods, including in situ ones.

In an earlier work [7], we reported the formation of aluminum chloride complexes from activated aluminum (Al*) and *tert*-butyl chloride (TBC) in liquid isobutane. Decreasing the TBC : Al* ratio in this system is likely favorable for the formation of polynuclear aluminum chloride complexes. Here, we report how the liquid-phase alkylation of isobutane with butenes depends on the composition of the aluminum chloride complexes forming in situ in the Al*–TBC model system in the hydrocarbon medium at varied molar ratios of the components.

EXPERIMENTAL

Aluminum metal (AD-1 brand, 99.3 wt % Al) was used as 10 × 5 mm plates 2 mm in thickness. The activator was liquid Ga–In eutectic (mp 289 K), which contains 76 wt % Ga. Aluminum was activated at ambient temperature by placing a 20-μL eutectic drop on the plate surface (contact time of 36–38 h) [8].

The other chemicals were TBC (Aldrich, 99.0 wt %), isobutane (99.5 wt %), and butenes (55.7 wt %).

It was demonstrated earlier [7] that the aluminum chloride complexes can be efficiently obtained in isobutane at 333–353 K and a TBC : Al* molar ratio of 0.25–4 just in a laboratory reactor consisting of a titanium autoclave and a dosing system suggested by Lavrenov et al. [9]. Prior to being placed in the autoclave, Al* was mechanically cleaned in argon from the products of its interaction with air and was weighed on an analytical balance with an accuracy of 0.0001 g. Next, the appropriate amount of TBC was added and 40 g of isobutane was introduced under a pressure of 1 MPa. Argon was added to the reaction mixture until the pressure became 1.5–2.0 MPa. The interaction between Al* and TBC was monitored by GLC analysis of the mixture, which was sampled at intervals until the residual TBC concentration was 10^{-2}–10^{-3} wt %.

The reaction between isobutane and butenes was conducted at 303 K after the autoclave was cooled from 333–353 K. Butenes at a pressure of 2.5–3.0 MPa were fed into the autoclave at a mass flow rate of 2.5 or 5 h^{-1} per gram of the initial Al* (ν_m^{Al*}). The reaction mixture was kept under these conditions for 1 h and was then chromatographed, and its attenuated total reflection FT–IR (ATR–FT–IR) spectra were recorded. Reaction parameters—butenes conversion (x), liquid hydrocarbons and n-butane yields per unit weight of the butenes converted (YC_{5+} and Yn-C_4, respectively), isobutane consumption during the reaction (i-$C_4/C_{4=}$), and the fractional composition of the alkylate (wt %)—were derived from the material balance over 1 h. Since Al* was incompletely converted under the given conditions, the preset butenes mass flow rate ν_m^{Al*} was only an apparent value. For this reason, we converted this parameter to the butenes mass flow rate per unit weight of reacted Al* (ν_m^{AlCl}). The isobutane : butenes weight ratio was 14 or above.

Chromatographic analyses were performed on a GKh-1000 chromatograph (Khromos, Russia) in the temperature-programmed mode. The oven temperature was linearly increased from 313 to 393 K at a rate of 4 K/min and from 393 to 503 K at a rate of 10 K/min. The chromatograph was equipped with a DB-1 capillary column 0.25 mm in diameter and 100 m in length and with a flame-ionization detector. Since this type of detector introduces a systematic downward error into the signal from TBC in the reaction mixture, we determined the sensitivity factor for this compound using the TBC–n-hexane model mixture, and this factor was turned out to be 1.43.

The aluminum chloride complexes that deposited on the rector walls during the reaction were removed and were coated onto a ZnSe crystal for ATR–FT–IR spectroscopy. Their ATR–FT–IR spectrum was recorded against the spectrum of a pure ZnSe crystal (4000–400 cm^{-1}, 4-cm^{-1} resolution, 32 scans). All spectra were obtained on a NICOLET-5700 spectrometer (Thermo Fisher Scientific).

RESULTS AND DISCUSSION

Table 1 lists parameters of the liquid-phase alkylation of isobutane with butenes in the presence of aluminum chloride complexes formed in situ in liquid isobutane at different TBC : Al* molar ratios and a temperature of 353 K. Table 1 includes the results of isobutane alkylation with 2-but-2-ene over $AlCl_3$ from two other studies [10, 11]. Both of these studies were carried out in a well-stirred reactor, with the difference that an equimolar amount of HCl was additionally used in one of them [10] according to the presumed reaction mechanism [12].

The data presented in Table 1 suggest that the optimum conditions for domination of the alkylation reaction are a feed flow rate of $\nu_m^{AlCl} = 48$ h^{-1} and TBC : Al* ≈ 1 mol/mol. Under these conditions, the liquid hydrocarbons yield YC_{5+} is 1.77 g/g, which exceeds the value obtained for alkylation over $AlCl_3$ [10, 11] but is below the theoretical value of 2.04 g/g. The i-$C_4/C_{4=}$ ratio, which is 1.35 g/g and is close to 1 g/g (Table 1), indicates that, under the given conditions, isobutane is uninvolved in the self-alkylation side reaction. The fractional composition of the resulting alkylate is dominated by C_8 hydrocarbons (ΣC_8). The C_8 content of the alkylate obtained in this study is lower than is reported by Zhang et al. [11], but is above the value observed in the presence of HCl [10]. The total trimethylpentane content (ΣTMP) of our alkylate is 2 times higher than that of the alkylate obtained using $AlCl_3$ and HCl. The ratio of ΣTMP to the total dimethylhexane content (ΣTMP/ΣDMH) is nearly the same as the ratios reported in [10, 11]. A specific feature of our alkylate is that it contains a high percentage of organochlorine compounds (ΣCCl) mainly represented by unreacted TBC and large amounts of sec-butyl chloride (sec-BC). An alkylate with the same fractional composition was obtained at $\nu_m^{AlCl} = 31$ h^{-1} and TBC : Al* ≈ 0.35. However, increased values of i-$C_4/C_{4=}$ and ΣTMP/ΣDMH were observed in this case. This is evidence that isobutane self-alkylation and "conjunct oligomerization" of isobutene take place as side reactions.

At lower feed flow rates ($\nu_m^{AlCl} = 6$–20 h^{-1}) and a large TBC : Al* molar ratio of ≈ 4, the dominant reaction is isobutane self-alkylation (Table 1). Reducing the ν_m^{AlCl} value leads to total butene conversion. The yield YC_{5+} is almost equal to its theoretical value for alkylation (2.04 g/g) at $\nu_m^{AlCl} = 13$ and 20 h^{-1} and is 2.3 times higher than the theoretical value at $\nu_m^{AlCl} =$ 6 h^{-1}. The parameters i-$C_4/C_{4=}$ and Yn-C_4 are the same at $\nu_m^{AlCl} = 13$ and 20 h^{-1}, but they increase sharply on passing to $\nu_m^{AlCl} = 6$ h^{-1}. At this feed flow rate, they several times exceed the corresponding values for $\nu_m^{AlCl} =$

Table 1. Parameters of liquid-phase isobutane alkylation with butenes over aluminum chloride complexes and the composition of the resulting alkylate

Parameter	Experimental data					Literature data	
						[10]	[11]
TBC : Al*	4.04	4.09	1.01	0.37	0.97	–	–
ν_m^{Al*}, h^{-1}	2.5	5	2.5	2.5	5	–	–
ν_m^{AlCl}, h^{-1}	6	13	20	31	48	–	–
x, %	100	98.2	99.9	72.1	86.8	–	96.0
YC_{5+}, g/g*	4.77	2.13	1.96	1.98	1.77	1.40	1.68
Y*i*-C_4, g/g	0.72	0.51	0.55	0.16	0.13	–	–
i-$C_4/C_{4=}$, g/g	4.97	2.04	1.98	1.52	1.35	–	–
$\Sigma(C_5–C_7)$, wt %	48.0	41.5	29.2	10.7	8.7	37.2	20.2
ΣC_8, wt %	28.7	30.1	40.6	45.3	47.2	23.9	56.2
ΣC_{9+}, wt %	14.2	12.5	10.9	28.5	23.5	39.0	27.0
ΣCCl, wt %	9.1	16.0	19.3	15.5	20.5	0.2	–
ΣTMP, wt %	13.1	26.4	32.0	31.8	30.1	14.5	–
ΣTMP/ΣΔMH	1.1	3.5	3.2	2.8	2.3	2.1	1.9
TBC, wt %	4.8	13.4	18.8	3.7	6.3	–	–
sec-BC, wt %	4.2	2.2	0.5	11.4	13.7	–	–

* YC_{5+} was calculated without taking into account organochlorine compounds.

48 h^{-1}, indicating that isobutane self-alkylation takes place. At ν_m^{AlCl} = 20 h^{-1}, ΣTMP in the alkylate is the same as in the case of ν_m^{AlCl} = 48 h^{-1}, but the ΣTMP/ΣDMH ratio is substantially larger. This is likely due to the conjugate oligomerization of isobutene forming from isobutane.

Figures 1a and 1b show the ATR–FT–IR spectra of the aluminum chloride complexes that form in situ when the alkylation reaction dominates in the system (ν_m^{AlCl} = 48–31 h^{-1}, TBC : Al* ≈ 1–0.35). A comparison of the observed absorption bands with those reported in the literature is presented in Table 2. The $AlCl_4^-$ and $Al_2Cl_7^-$ ions perturbed by cations, as well as structurally different molecular complexes, were identified in the spectra. At ν_m^{AlCl} = 48 h^{-1} and TBC : Al* ≈ 1, the spectrum indicates the presence of the molecular complex $AlCl_3 \cdot$ *sec*-BC (Fig. 1b, curve *2*, absorptions bands at 552 and 567 cm^{-1}). At ν_m^{AlCl} = 31 h^{-1} and TBC : Al* ≈ 0.35, the molecular complex $Al_2Cl_6 \cdot$ TBC was identified (Fig. 1b, curve *1*, absorption bands at 546 and 559 cm^{-1}).

The fact that the band at 529 cm^{-1} in spectrum *2* (Fig. 1a) is broader than the same band in spectrum *1* and the fact that the smoothing of spectrum *2* over 11 points reveals a shoulder at 534 cm^{-1} (Fig. 1b) are likely due to the presence of the $Al_3Cl_{10}^-$ ion.

A band at 586 cm^{-1} is additionally present in the 515–645 cm^{-1} range of both spectra (Fig. 1b). This band is assignable to the stretching vibrations of the $AlCl_4^-$ ion with aluminum in a distorted tetrahedral coordination environment with C_{3v} symmetry [15]. This band is usually observed in the IR reflectance spectra of $Zn(AlCl_4)_2$ melts [15]. Weak bands at 605 and 626 cm^{-1} are also noticeable in this range. According to the literature [16], they are assignable to the molecular species $AlCl_3$ and Al_2Cl_6, respectively. Strong absorption at these wavenumbers was observed for gaseous aluminum chloride at 780 and 453 K, respectively [16].

Figure 2 presents the ATR–FT–IR spectra of the aluminum chloride complexes forming in situ under isobutane self-alkylation conditions. The observed absorption bands and the corresponding data from the

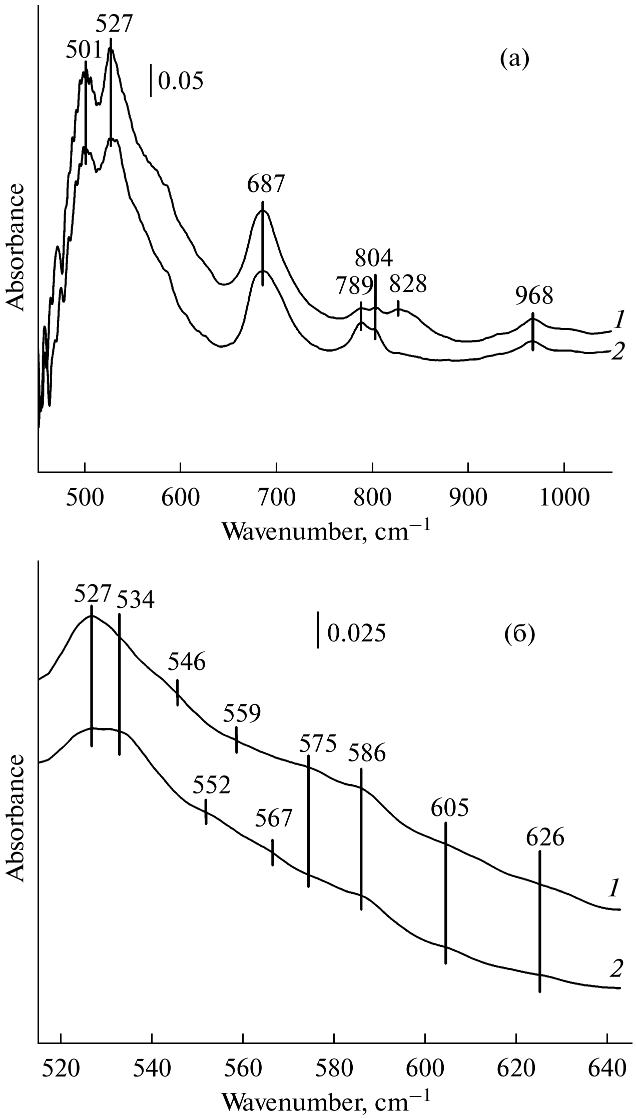

Fig. 1. ATR–FT–IR spectra of aluminum chloride complexes recorded after liquid-phase isobutane alkylation with butenes at ν_m^{AlCl} = (*1*) 31 and (*2*) 48 h^{-1}: (a) region of Al–Cl stretching frequencies, 450–1050 cm^{-1}; (b) 515–645 cm^{-1} range of Al–Cl stretching frequencies after smoothing over 11 points.

literature are listed in Table 2. At ν_m^{AlCl} = 6 and 13 h^{-1} (Fig. 2, curves *1*, *2*), the dominant species are the $AlCl_4^-$ and $Al_3Cl_{10}^-$ ions and the molecular complex $AlCl_3 \cdot$ TBC. By contrast, at ν_m^{AlCl} = 20 h^{-1} the spectrum indicates the presence of the $Al_3Cl_{10}^-$ ion (broad band peaking at 529 cm^{-1}) and the molecular dimer complex $Al_2Cl_6 \cdot$ TBC (Fig. 2, curve *3*, shoulder at 558 cm^{-1}) along with $Al_2Cl_7^-$.

The bands observed at 687 and 692 cm^{-1} were not assigned unambiguously. It was hypothesized by Hvistendahl J. et al. [13] that these bands are due to overtones and/or combined frequencies of the $AlCl_4^-$ and $Al_2Cl_7^-$ ions; however, the authors themselves do not consider this assignment quite satisfactory [13].

Thus, by analyzing the ATR–FT–IR data and the results of the catalytic tests, it was demonstrated that the major aluminum species existing under conditions of liquid-phase isobutane alkylation with butenes is the $Al_2Cl_7^-$ ion, which was not detected in isobutane self-alkylation. This ion likely plays the key role in the alkylation reaction. It can result from the following two thermodynamically allowable processes: coordination between the resulting $Al_2Cl_7^-$ and an $AlCl_3$ ion [17, 18] and $AlCl_4^-$ dissociation [19].

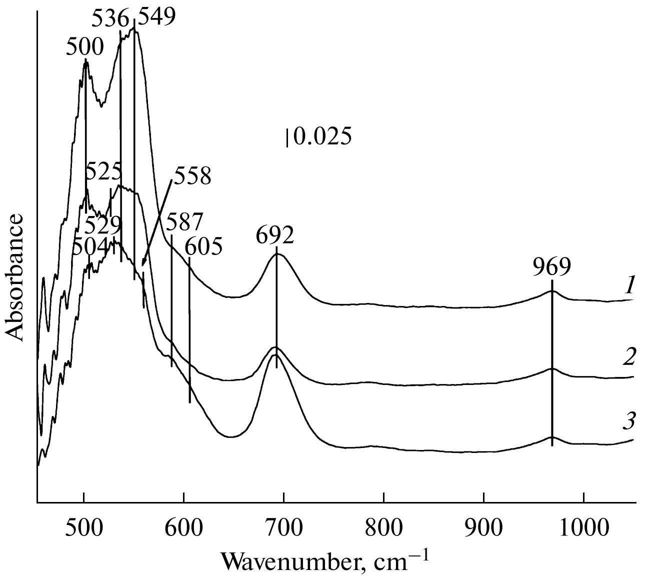

Fig. 2. ATR–FT–IR spectra of aluminum chloride complexes recorded in the region of Al–Cl stretching frequencies (450–1050 cm^{-1}) after liquid-phase isobutane alkylation with butenes at ν_m^{AlCl} = (*1*) 6, (*2*) 13, and (*3*) 20 h^{-1}.

The following interaction can take place in the presence of butenes and HCl: $HCl \cdot [Al_2Cl_7^-] + C_4H_8 + HCl \rightarrow HCl \cdot [AlCl_4^-] + C_4H_9^+[AlCl_4^-]$ (by analogy with the protonation of aromatic hydrocarbons in ionic liquids [20]). Thus, we believe that the observed direction of isobutane alkylation with butenes is due to the

Table 2. Observed absorption bands in the ATR–FT–IR spectra of the aluminum chloride complexes and the corresponding data from the literature [13, 14]

TBC : Al*	ν_m^{Al*}, h^{-1}	ν_m^{AlCl}, h^{-1}	Al–Cl stretching frequencies, cm^{-1}		Aluminum chloride complex
			this study	literature data	
4.04	2.5	6	500 536 549	499, 475 537, 533 540, 550	$AlCl_4^-$ $Al_3Cl_{10}^-$ $AlCl_3 \cdot$ TBC
4.09	5	13	500 536 549	499, 475 537, 533 540, 550	$AlCl_4^-$ $Al_3Cl_{10}^-$ $AlCl_3 \cdot$ TBC
1.01	2.5	20	504 536 529 549, 558	499, 475 537, 533 542, 517, 525 500, 550, 560, 600	$AlCl_4^-$ $Al_3Cl_{10}^-$ $Al_2Cl_7^-$ $Al_2Cl_6 \cdot$ TBC
0.37	2.5	31	501, 804 527, 575, 789 546, 559	475, 802 514, 570, 791 500, 550, 560, 600	perturbed $AlCl_4^-$ perturbed $Al_2Cl_7^-$ $Al_2Cl_6 \cdot$ TBC
0.97	5	48	501, 804 527, 575, 789 552, 567	475, 802 514, 570, 791 551, 563	perturbed $AlCl_4^-$ perturbed $Al_2Cl_7^-$ $AlCl_3 \cdot$ *sec*-BC

The article is based on the materials of the Russian Congress on Catalysis, Moscow, October 3–7, 2011.

presence of the active form of the HCl · [$Al_2Cl_7^-$] complex. However, further studies are necessary to detail the mechanism of this reaction.

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