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Poisoning Effect of Acid Soluble Oil on Triflic Acid-Catalyzed Isobutane Alkylation

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Abstract—The rate of the isobutane alkylation reaction with secondary butenes catalyzed by trifluoromethanesulfonic acid at –20°C is experimentally found to depend on the concentration of acid soluble oil (ASO), which poisons TfOH. With an increase in the ASO molar fraction from 0.13 to 0.16, the reaction rate decreases by a factor of ten. The Hammett acidity function was determined for TfOH solutions at 25°C in the concentration range from 0 to 0.2 ASO molar fractions. The results obtained suggest that the alkylation reaction rate is proportional to the proton activity in the acid phase determined by the Hammett acidity function.

INTRODUCTION

Liquid-phase isobutane alkylation by olefins is widely used to produce high-octane gasoline components [1, 2]. Liquid Brønsted acids are conventional catalysts, which are gradually deactivated by acid-soluble oil (ASO) [3] formed in the reaction as a byproduct. ASO mainly consists of substituted five-membered rings containing conjugated double bonds [4, 5] and forms complexes with acid catalysts, for example, with trifluoromethanesulfonic acid (TfOH) of composition $2\text{TfOH} \cdot \text{ASO}$ [5].

The purpose of this work was to study the poisoning nature using the isobutane alkylation reaction with butenes in the presence of TfOH as an example.

EXPERIMENTAL

ASO was prepared by the method described in [5]. The composition and purification of reagents are described in [5].

Triethylammonium triflate was synthesized by the reaction of freshly distilled and dried triethylamine with TfOH. The obtained salt was decolorized by activated carbon. The compound was dried until residual water concentration was at most 0.05% in a vacuum desiccator over phosphoric anhydride.

The reagent grade Hammett indicators 2,4-dinitroaniline, 3-chloro-2,4,6-trinitroaniline and 4-nitrotoluene [9] were used not later than one week after recrystallization from boiling ethanol followed by drying as in the case of triethylammonium triflate. The pK_a value for 4-nitrotoluene at 25°C was determined in the $\text{TfOH–H}_2\text{O}$ medium and was equal to 12.09.

The reference solutions of HCl and NaOH were used for acid–base TfOH titration in hexane. The hydrocarbon mixture was analyzed using a HP 5890 chromatograph with an OV-101 50-m column.

Alkylation was performed in a glass setup at a temperature of –20°C and intensive stirring with a rate of 3000 rpm when the reaction was controlled by kinetics. All procedures were carried out in argon.

The determination of the equilibrium TfOH concentration in hexane was carried out as follows. The glass vessel was purged with dry argon and necessary amounts of TfOH and AC (water, triethylammonium triflate or ASO) were added one after another. Then, hexane was introduced. Later, the equilibrium between the acid and hydrocarbon phases was set by shaking for 30 min at 25°C. After phase separation at the same temperature, the hydrocarbon layer was analyzed to determine the acid concentration.

The TfOH concentration in the hydrocarbon phase was determined by titration with a 0.1 N NaOH solution with phenolphthalein indicator in excess water, while strongly shaking the mixture.

The optical density in the UV area was measured with an automatic Hewlett Packard 8451A spectrophotometer using a hermetically closed quartz cell (2 or 10 mm) in argon. For comparison, we used a cell with a solution analogous to the working one but without the indicator.

The calculation of the acidity function based on spectrophotometric data at a known value of pK_a was described in [6].

RESULTS AND DISCUSSION

The dependence of the rate of isobutane alkylation with butenes on the ASO concentration dissolved in TfOH was measured (Fig. 1). The alkylation rate is reduced by an order of magnitude with an increase in

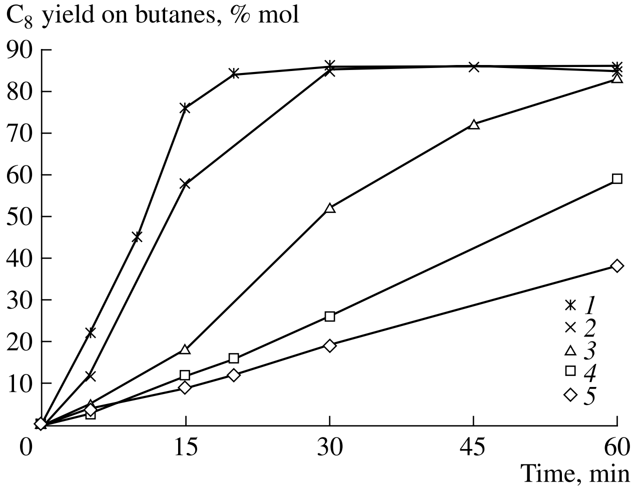

Fig. 1. Dependence of the yield of C_8 hydrocarbons (based on butenes) on time at N_{ASO}: (*1*) 0.132, (*2*) 0.137, (*3*) 0.146, (*4*) 0.154, and (*5*) 0.161 (–20°C, isobutane/butenes = 55 : 1, TfOH/butenes = 5 : 1 mol/mol).

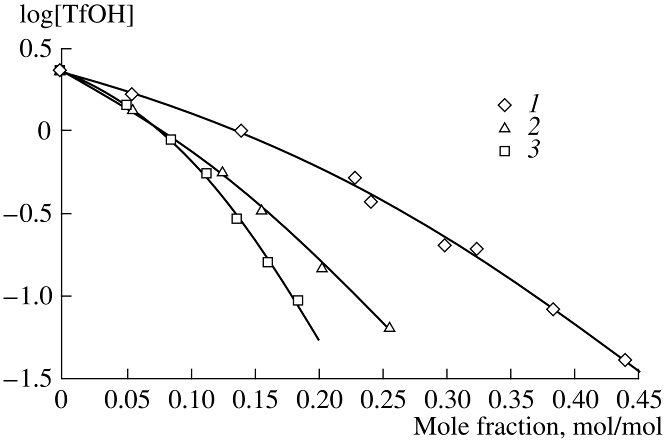

Fig. 2. Dependence of the logarithm of the equilibrium TfOH concentration in the hexane phase on the molar fraction of different acidity controllers in the TfOH phase at 25°C: (*1*) H_2O, (*2*) triethylammonium triflate, and (*3*) ASO.

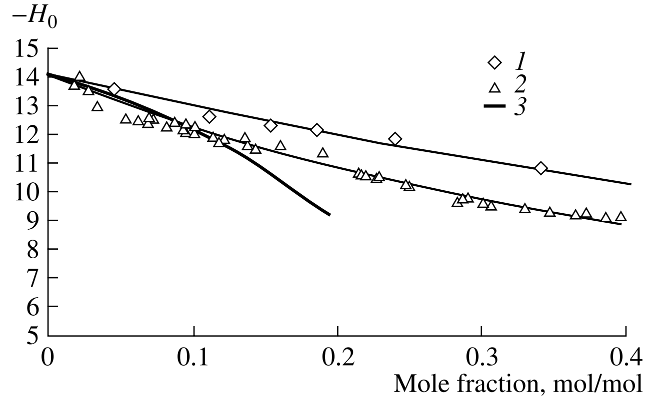

Fig. 3. Dependence of Hammett acidity function on the mole fraction of acidity controller in TfOH at 25°C: (*1*) H_2O, (*2*) triethylammonium triflate, and (*3*) ASO.

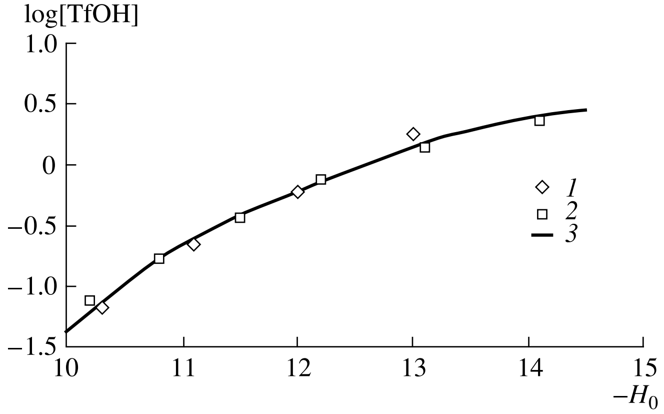

Fig. 4. Dependence of the equilibrium TfOH concentration in hexane on the Hammett acidity function in TfOH solution of acidity controller: (*1*) H_2O, (*2*) triethylammonium triflate, and (*3*) empirical equation.

the ASO mole fraction from 0.13 to 0.16. It is difficult to explain this dramatic effect by conventional site-by-site passivation even taking into account the ASO ability to bind the acid in a 2TfOH · ASO complex.

On the other hand it is well known that the rate of the acid-catalyzed reaction is quite often related to the acidity of the medium, which changes very strongly when adding small amounts of acidity-modifying agents or acidity controllers (AC) such as H_2O [6, 7] or trifluoro acetic acid [8].

The use of Hammett indicators in a study of the effect of ASO on the acidity of triflic acid is difficult since ASO solutions in TfOH have intense colors. Therefore, an alternative method is required to measure the acidity of such mixtures. The approach used in this work is based on the assumption that, for the acidity range relevant to isobutane alkylation, the solubility of TfOH in a hydrocarbon medium in contact with the acid medium directly correlates with the Hammett acidity of the acid.

To check the validity of such an approach, the TfOH concentrations in hexane (see the experimental section) were determined at equilibrium with acid containing water or triethylammonium triflate in various concentrations (Fig. 2). We plotted the H_0 dependence on the AC concentration for H_2O and triethylammonium triflate (Fig. 3: literature data [7] for H_2O; data measured by using Hammett indicators for triethylammonium triflate). In Fig. 4, the equilibrium concentration of triflic acid in hexane at 25°C is plotted against $-H_0$ for two ACs. As shown, the equilibrium concentration of triflic acid in hexane depends on H_0 and is independent of AC.

Consequently, the equilibrium TfOH concentration in hexane can serve as a measure of the acidity of TfOH mixtures. The correlation between H_0 and the solubility of TfOH in hexane at 25°C as shown in Fig. 4 translates into the following empirical equation:

$$-H_0 = 12.63 + 3.12\log[\mathrm{TfOH}] + 0.94(\log[\mathrm{TfOH}])^2,$$

where $-H_0$ is the Hammett's acidity function, log is the logarithm, [TfOH] is the weight percent concentration of TfOH solution in hexane at the equilibrium state.

The following conditions should be met for the solubility method to be useful in acidity determination: (a) the acid should be soluble in a hydrocarbon in the absence of AC, (b) the solubility of the hydrocarbon in the acid phase should be insignificant, and (c) the hydrocarbon should be chemically stable under measurement conditions. The most important condition for use of the method is acid transfer from the AC containing acid phase to the hydrocarbon phase without AC. Hexane proved to be a suitable hydrocarbon for TfOH acidity determinations by the solubility method.

It was determined by UV spectroscopy that ASO and its complex with TfOH [5] are practically absent from the hydrocarbon phase. Using experimental data (Fig. 2) the following equation was derived by the least-squares method for the dependence of the triflic acid concentration in hexane on the molar ASO fraction in the acid:

$$\log[\mathrm{TfOH}] = 0.3674 - 2.767N_{\mathrm{ASO}} - 26.95N_{\mathrm{ASO}}^2,$$

where N_{ASO} is the ASO mole fraction in its TfOH solution.

The dependences of log[TfOH] on N_{ASO} (Fig. 2) and H_0 on log[TfOH] (Fig. 4) resulted in the following empirical correlation between the molar ASO fraction in TfOH and its acidity (Fig. 3):

$$-H_0 = 14.1 - 13.28N_{\mathrm{ASO}} - 62.12N_{\mathrm{ASO}}^2.$$

Using the determined H_0 dependence on the ASO concentration in TfOH, it can be shown that, when the ASO concentration changes by 0.03 mole fractions, the acidity function changes by one unit, which corresponds to a change in the proton activity by one order of magnitude. This agrees with the aforementioned data on the dependence of the rate of isobutane alkylation by butenes (Fig. 1) on the ASO concentration. Therefore, triflic acid is poisoned by ASO because of a decrease in the acidity of the liquid catalyst.

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