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The Kinetics of Alkylation of Isobutane with Propylene

J. RANDOLPH LANGLEY and RALPH W. PIKE

Department of Chemical Engineering
Louisiana State University, Baton Rouge, Louisiana 70803

A 17-reaction mechanism model was postulated to describe the alkylation of isobutane with propylene using sulfuric acid as the catalyst. The scheme was based on the Schmerling carbonium ion mechanism with modifications introduced to account for iC_9 and iC_{10} formation. Solving the steady state rate equations for the rate constants a set of 17 equations of the form $k_i = f(r_{C_j}, r_{C_k}, \ldots)/g\,(C_i, C_k, \ldots)$ were obtained. Experimental measurements were made in an ideally mixed, continuous-flow stirred-tank reactor, and the necessary data were obtained to compute the rate constants from 65°F to 135°F. The reaction model was found to be valid in the range of 81°F to 135°F using a 95% sulfuric acid catalyst since the rate constants obeyed the Arrhenius theory. The results obtained at 65°F and 95% sulfuric acid showed significant departure from the model. This was possibly due to a change in reaction mechanism. There was an apparent change in selectivity of the catalyst when the concentration was lowered to 90% sulfuric acid. This resulted in increased rates of formation of iC_9's and iC_{10}'s and decreased rates of formation of iC_5's, iC_6's and iC_8's.

The alkylation of a light isoparaffin with a light olefin in the presence of an aqueous phase catalyst has been the subject of extensive study. Investigations have studied both the effect of process variables on yield and product distribution (*1, 2, 5, 6, 9, 11, 14, 18, 19*) and the possible mechanisms of reactions (*4, 5, 7, 8, 10, 12, 15, 17, 19, 21, 22*). However, the kinetics of the reaction have remained largely unexplored. There appear to be two main reasons for this: (1). the presence of many competing reactions, and (2) two separate phases, hydrocarbon and aqueous. With the aqueous phase being the reaction medium, it is improbable that actual reactant and product concentrations can be measured.

This paper deals with a kinetic study of the alkylation of isobutane with propylene in the presence of a sulfuric acid catalyst. To circumvent problems mentioned above, a modified Schmerling mechanism has been used in conjunction with an analogous nonreacting system and mass transfer relations to derive the mathematical model.

THEORY OF THE ALKYLATION MODEL

As Schmerling's mechanism (*7, 19*) is the most comprehensive one available, it served as the basis for the mathematical model used in this research. The mechanism for the isobutane-propylene reaction as presented by Schmerling describes possible routes of formation of C_3 through iC_8, iC_{10} and iC_{11} saturated hydrocarbon species; they are listed in Table 1. In this table modifications proposed by authors of later works such as Hofmann and Schriesheim (*4, 5*), Kennedy (*10*), and others (*16, 21, 22*) are also included. Specifically, the reaction to form the nonane fraction was a modification made in the light of the knowledge of Schmerling's and others' theories. This is Reaction (1-15) in Table 1. Also, the route of decane formation was tailored to account for the yields of this species over the temperature range investigated. The result is two reactions, one expressing formation of the decyl ion and one expressing its consumption. These are Reactions (1-13) and (1-17) respectively.

The formation of dimethyl-hexane via allylic ions as proposed by Hofmann and Schriesheim (*4, 5*) was considered a modification. However, as experimental information was lacking to discern between this theory and

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Correspondence concerning this paper should be addressed to R. W. Pike. J. R. Langley is with Gulf General Atomic Inc., San Diego, California.

Schmerling's proposed self-alkylation of isobutane (Reactions 1-5 to 1-7 of Table 1) only the latter was retained to account for all octane formation.

RATE EQUATIONS AND MATHEMATICAL MODEL

Rate Equations

For a continuous stirred-tank reactor the overall rates are independent of time when the reactor is operated at steady state. For this heterogeneous system, the reaction rates are in moles per unit volume catalyst per unit time. The concentrations are expressed as moles per unit volume of catalyst per unit time. The concentrations are expressed as moles per unit volume of catalyst. The rate constants are in units that correspond to these. By the usual convention the rate of production of a chemical species is taken as positive.

The rate equations are presented in Table 2 for the chemical reactions listed in Table 1. In Table 2a the reactant consumption rates are given. These are actually material balances on the reactants and are linear combinations of other rate equations. The rate equations in Table 2b serve primarily to relate the product formation rates to the rate equations of Tables 2c and 2d as will be subsequently discussed.

In Table 2c and 2d, the olefinic and ionic rate equations are given. The steady state approximation (*23*) is used for the rates in these equations. These intermediates are present in such small quantities that their rates can never be great after an initial and very short time. Consequently, these rates can be taken to be zero.

The rate equations given in Table 2 comprise the alkylation kinetic model and are used to compute the rate constants from the experimental data. There are a total

TABLE 1. PROPYLENE-ISOBUTANE ALKYLATION REACTION

Initiation reactions

$$C_3^{=} + HX \xrightarrow{k_1} C_3^{+}X^{-} \qquad (1\text{-}1)$$

$$C_3^{+}X^{-} + iC_4 \xrightarrow{k_2} C_3 + iC_4^{+}X^{-} \qquad (1\text{-}2)$$

Primary reactions

$$iC_4^{+}X^{-} + C_3^{=} \xrightarrow{k_{11}} iC_7^{+}X^{-} \qquad (1\text{-}3)$$

$$iC_7^{+}X^{-} + iC_4 \xrightarrow{k_5} iC_7 + iC_4^{+}X^{-} \qquad (1\text{-}4)$$

Self-alkylation reactions

$$iC_4^{+}X^{-} \xrightarrow{k_9} iC_4^{=} + HX \qquad (1\text{-}5)$$

$$iC_4^{+}X^{-} + iC_4^{=} \xrightarrow{k_{10}} iC_8^{+}X^{-} \qquad (1\text{-}6)$$

$$iC_8^{+}X^{-} + iC_4 \xrightarrow{k_6} iC_8 + iC_4^{+}X^{-} \qquad (1\text{-}7)$$

Destructive alkylation reactions

$$iC_7^{+}X^{-} \xrightarrow{k_{12}} iC_7^{=} + HX \qquad (1\text{-}8)$$

$$iC_7^{=} + iC_4^{+}X^{-} \xrightarrow{k_{13}} iC_5^{=} + iC_6^{+}X^{-} \qquad 1\text{-}9)$$

$$iC_5^{=} + HX \xrightarrow{k_{14}} iC_5^{+}X^{-} \qquad (1\text{-}10)$$

$$iC_5^{+}X^{-} + iC_4 \xrightarrow{k_3} iC_5 + iC_4^{+}X^{-} \qquad (1\text{-}11)$$

$$iC_6^{+}X^{-} + iC_4 \xrightarrow{k_4} iC_6 + iC_4^{+}X^{-} \qquad (1\text{-}12)$$

$$iC_7^{+}X^{-} + C_3^{=} \xrightarrow{k_{15}} iC_{10}^{+}X^{-} \qquad (1\text{-}13)$$

$$iC_{10}^{+}X^{-} + iC_4 \xrightarrow{k_8} iC_{10} + iC_4^{+}X^{-} \qquad (1\text{-}14)$$

$$iC_5^{=} + iC_4^{+}X^{-} \xrightarrow{k_{16}} iC_9^{+}X^{-} \qquad (1\text{-}15)$$

$$iC_9^{+}X^{-} + iC_4 \xrightarrow{k_7} iC_9 + iC_4^{+}X^{-} \qquad (1\text{-}16)$$

$$iC_{10}^{+}X^{-} \xrightarrow{k_{17}} iC_5^{=} + iC_5^{+}X^{-} \qquad (1\text{-}17)$$

Ionic species are denoted as $iC_n^{+}X^{-}$ $(C_nH^{+}{}_{2n+1}X^{-})$

Unsaturated species are denoted as $iC_n^{=}$ (C_nH_{2n})

TABLE 2. RATE EQUATIONS FOR THE REACTIONS IN TABLE 1

(a) Material balance on reactants and associated consumption rates

$$\begin{aligned} -r_{iC_4} = F_{iC_4} - P_{iC_4} = {} & k_2 [C_3^{+}X^{-}] [iC_4] \\ & + k_3 [iC_5^{+}X^{-}] [iC_4] + k_4 [iC_6^{+}X^{-}] [iC_4] \\ & + k_5 [iC_7^{+}X^{-}] [iC_4] + k_6 [iC_8^{+}X^{-}] [iC_4] \\ & + k_7 [iC_9^{+}X^{-}] [iC_4] + k_8 [iC_{10}^{+}X^{-}] [iC_4] \qquad (2\text{-}1) \end{aligned}$$

$$\begin{aligned} -r_{C_3^{=}} = F_{C_3^{=}} - P_{C_3^{=}} = {} & k_1 [C_3^{=}] [HX] \\ & + k_{11} [iC_4^{+}X^{-}] [C_3^{=}] + k_{15} [iC_7^{+}X^{-}] [C_3^{=}] \qquad (2\text{-}2) \end{aligned}$$

(b) Product formation equations

$$r_{C_3} = P_{C_3} = k_2 [C_3^{+}X^{-}] [iC_4] \qquad (2\text{-}3)$$

$$r_{iC_5} = P_{iC_5} = k_3 [iC_5^{+}X^{-}] [iC_4] \qquad (2\text{-}4)$$

$$r_{iC_6} = P_{iC_6} = k_4 [iC_6^{+}X^{-}] [iC_4] \qquad (2\text{-}5)$$

$$r_{iC_7} = P_{iC_7} = k_5 [iC_7^{+}X^{-}] [iC_4] \qquad (2\text{-}6)$$

$$r_{iC_8} = P_{iC_8} = k_6 [iC_8^{+}X^{-}] [iC_4] \qquad (2\text{-}7)$$

$$r_{iC_9} = P_{iC_9} = k_7 [iC_9^{+}X^{-}] [iC_4] \qquad (2\text{-}8)$$

$$r_{iC_{10}} = P_{iC_{10}} = k_8 [iC_{10}^{+}X^{-}] [iC_4] \qquad (2\text{-}9)$$

(c) Olefinic intermediate rate equations

$$r_{iC_4^{=}} = 0 = k_9 [iC_4^{+}X^{-}] - k_{10} [iC_4^{=}] [iC_4^{+}X^{-}] \qquad (2\text{-}10)$$

$$\begin{aligned} r_{iC_5^{=}} = 0 = {} & k_{13} [iC_7^{=}] [iC_4^{+}X^{-}] + k_{17} [iC_{10}^{+}X^{-}] \\ & - k_{14} [iC_5^{=}] [HX] - k_{16} [iC_5^{=}] [iC_4^{+}X^{-}] \qquad (2\text{-}11) \end{aligned}$$

$$r_{iC_7^{=}} = 0 = k_{12} [iC_7^{+}X^{-}] - k_{13} [iC_7^{=}] [iC_4^{+}X^{-}] \qquad (2\text{-}12)$$

(d) Carbonium ion rate equations

$$r_{C_3^{+}X^{-}} = 0 = k_1 [C_3^{=}] [HX] - k_2 [C_3^{+}X^{-}] [iC_4] \qquad (2\text{-}13)$$

$$\begin{aligned} r_{iC_4^{+}X^{-}} = 0 = {} & r_{iC_4} - k_9 [iC_4^{+}X^{-}] - [iC_4^{+}X^{-}] [iC_4^{=}] \\ & - k_{11} [iC_4^{+}X^{-}] [C_3^{=}] - k_{13} [iC_7^{=}] [iC_4^{+}X^{-}] \\ & - k_{16} [iC_5^{=}] [iC_4^{+}X^{-}] \qquad (2\text{-}14) \end{aligned}$$

$$\begin{aligned} r_{iC_5^{+}X^{-}} = 0 = {} & k_{14} [iC_5^{=}] [HX] + k_{17} [iC_{10}^{+}X^{-}] \\ & - k_3 [iC_5^{+}X^{-}] [iC_4] \qquad (2\text{-}15) \end{aligned}$$

$$\begin{aligned} r_{iC_6^{+}X^{-}} = 0 = {} & k_{13} [iC_7^{=}] [iC_4^{+}X^{-}] \\ & - k_4 [iC_6^{+}X^{-}] [iC_4] \qquad (2\text{-}16) \end{aligned}$$

$$\begin{aligned} r_{iC_7^{+}X^{-}} = 0 = {} & k_{11} [iC_4^{+}X^{-}] [C_3^{=}] - k_5 [iC_7^{+}X^{-}] [iC_4] \\ & - k_{15} [iC_7^{+}X^{-}] [C_3^{=}] - k_2 [iC_7^{+}X^{-}] \qquad (2\text{-}17) \end{aligned}$$

$$\begin{aligned} r_{iC_8^{+}} = 0 = {} & k_{10} [iC_4^{+}X^{-}] [iC_4^{=}] \\ & - k_6 [iC_8^{+}X^{-}] [iC_4] \qquad (2\text{-}18) \end{aligned}$$

$$\begin{aligned} r_{C_9^{+}} = 0 = {} & k_{16} [iC_5^{=}] [iC_4^{+}X^{-}] \\ & - k_7 [iC_9^{+}X^{-}] [iC_4] \qquad (2\text{-}19) \end{aligned}$$

$$\begin{aligned} r_{C_{10}^{+}} = 0 = {} & k_{15} [iC_7^{+}X^{-}] [C_3^{=}] - k_{17} [iC_{10}^{+}X^{-}] \\ & - k_8 [iC_{10}^{+}X^{-}] [iC_4] \qquad (2\text{-}20) \end{aligned}$$

of 17 independent equations which are solved for the 17 constants. All of the reactions were considered to occur in the acid (catalyst) phase, and the model was derived considering all of the reactants (carbonium ions and unsaturates) and products to be in solution in this phase. The rate constants are given in Table 3 in terms of the reaction rates and concentrations in the catalyst phase. These were obtained by manipulating the equations given in Table 2. The equations given in Table 3 require the concentration of the various species in the catalyst phase. However, the concentrations of the various species were measurable in the hydrocarbon phase only. Thus, mass transfer relationships along with solubility data were used to estimate the acid phase concentrations. The ionic and unsaturate concentrations within this phase were derived assuming proportional relationships among them and their parent species, and this is discussed in the next section.

Estimation of Hydrocarbon Concentrations in the Acid Phase

Isobutane Concentration. The reactant isobutane was considered to saturate the acid phase and its concentration in this phase was independent of that in the hydrocarbon phase. Work by Jernigan, Gwyn, and Cupit (*2*) showed that the mass transfer area and therefore the mass transfer rate reached a maximum when all of the hydrocarbon was emulsified (dispersed). For a large hydrocarbon fraction of isobutane and all other things being equal, this implies that there is a limiting ("saturated") isobutane concentration in the acid. These conditions were met in the experiments conducted.

Propylene Concentration. Propylene, which is very soluble in the acid, would be expected to exhibit concentrations in the acid proportional to the concentration in the feed. Thus, the following model for propylene concentration in the acid was assumed:

$$[C_3]_{\text{acid}} = (\text{constant})\ [C_3{}^{=}]_{\text{feed}} \tag{1}$$

Other Paraffin Concentrations. The acid phase concentration of the remaining paraffins were computed via a steady state mass transfer equation relating concentration driving forces between phases.

$$N_i = K_{mi}\, aV\ ([C_i]_{\text{acid}}\, K_{Di} - [C_i]_{\text{HC}}) \tag{2}$$

TABLE 3. RATE CONSTANT EQUATIONS

$$k_1\ = rC_3/[C_3{}^{=}]\ [HX] \tag{3-1}$$

$$k_2\ = r_{C_3}/[C_3{}^{+}X^{-}]\ [iC_4] \tag{3-2}$$

$$k_3\ = r_{iC_5}/[iC_5X^{-}]\ [iC_4] \tag{3-3}$$

$$k_4\ = r_{C_6}/[iC_6{}^{+}X^{-}]\ [iC_4] \tag{3-4}$$

$$k_5\ = r_{iC_7}/[iC_7{}^{+}X^{-}]\ [iC_5] \tag{3-5}$$

$$k_6\ = r_{iC_8}/[iC_8{}^{+}X^{-}]\ [iC_4] \tag{3-6}$$

$$k_7\ = r_{iC_9}/[iC_9{}^{+}X^{-}]\ [iC_4] \tag{3-7}$$

$$k_8\ = r_{iC_{10}}/[iC_{10}{}^{+}X^{-}]\ [iC_4] \tag{3-8}$$

$$k_9\ = r_{iC_8}/[iC_4{}^{+}\mathrm{X}^{-}] \tag{3-9}$$

$$k_{10} = r_{iC_8}/[iC_4{}^{+}X^{-}]\ [iC_4{}^{=}] \tag{3-10}$$

$$k_{11} = \{r_{iC_7} + r_{iC_{10}} + (r_{iC_5} + r_{iC_6} + r_{iC_9})/2\}/[iC_4{}^{+}X^{-}]\ [C_3{}^{=}] \tag{3-11}$$

$$k_{12} = r_{iC_6}/[iC_7{}^{+}X^{-}] \tag{3-12}$$

$$k_{13} = r_{iC_6}/[iC_7{}^{=}]\ [iC_4{}^{+}X^{-}] \tag{3-13}$$

$$k_{14} = \{r_{iC_5} + r_{iC_6} - r_{iC_9}\}/2[iC_5{}^{=}]\ [HX] \tag{3-14}$$

$$k_{15} = \{r_{iC_5} - r_{iC_6} + r_{iC_9} + 2r_{iC_{10}}\}/2[iC_7{}^{+}X^{-}]\ [C_3{}^{=}] \tag{3-15}$$

$$k_{16} = r_{iC_9}/[iC_5{}^{=}]\ [iC_4{}^{+}X^{-}] \tag{3-16}$$

$$k_{17} = \{r_{iC_5} - r_{iC_6} + r_{iC_9}\}/2[iC_{10}{}^{+}X^{-}] \tag{3-17}$$

The above is a standard mass transfer equation employing K_{Di}, the phase distribution coefficients, to relate the concentrations of the species $[C_i]$ in the two phases. For an acid-hydrocarbon system, K_{Di} for the hydrocarbon species is equivalent to the inverse of the solubility of that species in the acid, since it has infinite solubility in the hydrocarbon phase. Data for the solubility of isobutane in sulfuric acid are all that has been reported in literature. Therefore, the solubilities for the other isoparaffins were taken to be inversely proportional to their molecular weights as compared to isobutane.

To evaluate the mass transfer coefficient in the above equation data from an analogous nonreacting system with similar physical properties was used. The data of Malloy and Taylor (*13*) was for such a system.

Ionic Intermediate Concentrations. Many factors can influence the stability of ionic intermediates and thus their concentrations. However, no data exist on the lighter ones such as encountered in the work. Thus the concentration of the ions has been assumed to be proportional to the concentration of saturated species

$$[iC_i{}^{+}X^{-}]_{\text{acid}} = Z\ [iC_i]_{\text{acid}} \tag{3}$$

where Z is a constant of proportionality.

The above relation was adequate for all ions except the tertiary butyl cation which differs in that it is produced in the initiation reaction [(1-2) of Table 1]. According to the model, the only other time this reaction occurs is in conjunction with octane formation. Equating the rates of consumption and production of the tertiary butyl cation in Reactions (1-2) and (1-5) and using Equations (2 to 13), the following equation is obtained.

$$[iC_4{}^{+}X^{-}]_{\text{acid}} = \frac{k_1}{k_9}\, [C_3{}^{=}]_{\text{acid}}\ [HX] \tag{4}$$

This relates the tertiary butyl cation concentration in the acid phase to the propylene and acid concentrations.

Since the concentration of propylene in the acid phase is proportional to that in the hydrocarbon phase, the relationship between butyl carbonium ions at two different propylene concentrations becomes (*12*)

$$[iC_4{}^{+}X^{-}]_{\text{acid},\,2} = [iC_4{}^{=}X^{-}]_{\text{acid},\,1}\ \frac{[C_{C_3}{}^{=}]_{\text{HC},\,2}}{[C_{C_3}{}^{=}]_{\text{HC},\,1}} \tag{5}$$

where $[iC_4{}^{+}X^{-}]_{\text{acid},\,1}$ was selected as a reference value. The most convenient one for this work was at the lowest concentration. Using Equations (1) and (3) with this reference value, the values of $[iC_4{}^{=}X^{-}]_{\text{acid},\,2}$ for various values of $[C_3{}^{=}]_{\text{HC},\,2}$ are calculated.

Olefinic Intermediate Concentrations. The olefinic intermediates are unique in that they appear in reactions which are very similar. The species $iC_4{}^{=}$ may be used for example. From Equation (2-10), Table 2

$$[iC_4{}^{=}] = k_9/k_{10} \tag{6}$$

Referring to Table 1, Reactions (1-5) and (1-6) are serial, and there is the possibility that either (1-5) or (1-6) is rate limiting. Due to physical limitations of the reaction medium it cannot be readily ascertained if one is limiting. Because of this, the catalyst phase concentration of $iC_4{}^{=}$ would be dependent on temperature alone and independent of the concentration of $iC_4{}^{=}X^{-}$ by Equation (6). However, this is unreasonable to assume as obviously the concentration of any intermediate species should be a function of both its parent and daughter species.

The logic pursued to obtain equations to relate the concentration of these species to measured concentration is intuitive. Referring to Reactions (1-5) and (1-6), there should exist some relationship among the concentration of the species involved (excluding HX whose concentration does not vary significantly). Primarily there should exist a relationship between $iC_4{}^{=}X^-$ and $iC_4{}^{=}$ or

$$[iC_4{}^{=}] = f_1\ ([iC_4{}^{+}X^-]) \qquad (7)$$

Also, since there is only one route for the formation of $iC_8{}^{+}X^-$ Reaction (1-6), the relative concentration of $iC_8{}^{+}X^-$ to the other product ions that is, excluding $iC_4{}^{+}X^-$) should also be a measure of the $iC_4{}^{=}$ concentration.

$$[iC_4{}^{=}] = f_2\ ([iC_8{}^{+}X^-]) \qquad (8)$$

But $[iC_8{}^{+}X^-]$ should be directly related to the fraction of iC_8 in the product (isobutane free) or

$$[iC_4{}^{=}] = f_3\ (Y_{iC_8}) \qquad (9)$$

Considering the above relations, one can conclude that

$$[iC_4{}^{=}] = f_4\ \{[iC_4{}^{+}X^-],\ Y_{iC_8}\} \qquad (10)$$

The simplest form of the function was used in this work, that is,

$$iC_4{}^{=} = Y_{iC_8}\ [iC_4{}^{+}X^-] \qquad (11)$$

Similar reasoning was used for $iC_5{}^{=}$ and $iC_7{}^{=}$. The relations are given below.

$$[iC_5{}^{=}]_{\text{acid}} = \{Y_{iC_5} + Y_{C_9}\}\ \{[iC_7{}^{=}]_{\text{acid}} + [iC_{10}{}^{+}X^-]_{\text{acid}}\} \qquad (12)$$

$$[iC_7{}^{=}]_{\text{acid}} = \{2Y_{iC_6} + Y_{iC_9}\}\ [iC_7{}^{+}X^-]_{\text{acid}} \qquad (13)$$

Further details and justification of the derivation of these equations are given by Langley (*12*).

To summarize, the reaction rate constants can be computed using the rate equations given in Table 3 and the equations derived to relate the acid phase concentrations to the measurable hydrocarbon phase concentrations. The input for these equations are the reactant and product flow rates, hydrocarbon feed and product composition, catalyst concentration, mass transfer coefficients, phase distribution coefficients, and concentrations (estimated) of isobutane and propylene in the acid phase. The test of validity of the model was to determine whether all of the rate constants obeyed the Arrhenius relation. The following section briefly describes the experimental apparatus used to measure the reaction rates used to compute the rate constants. This is followed by a discussion of the results obtained.

EXPERIMENTAL AND ANALYTICAL EQUIPMENT AND PROCEDURES

The experimental data were taken using a small pilot unit shown schematically in Figure 1. At the heart of the unit is a baffled (10%), continuous-flow, stirred-tank reactor using a standard tank configuration as described by Rushton (*24*). The reactor was followed by an emulsion settler. Details of the reactor are shown in Figure 2. The impeller speed used was 1,700 rev./min.

Tracer tests using carbon-14 labeled normal heptane were used to determine the residence time distribution of the reactor under reacting conditions. The results of these experiments showed that the reactor was perfectly mixed (*12*).

As a large portion of the alkylate product was composed of hydrocarbons which are gases at atmospheric pressure and the operating temperatures, the pilot unit was operated under pressures sufficient to keep these compounds in the liquid phase using a nitrogen blanket. The sampling system was custom built (*12*) to obtain representative samples under these conditions. The sampling point was located at reactor exit.

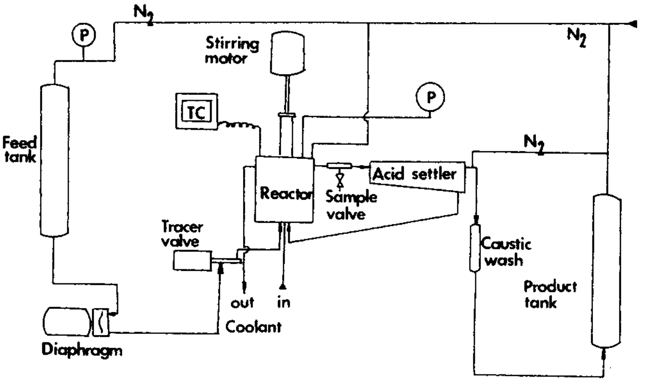

Fig. 1. Pilot unit flow diagram.

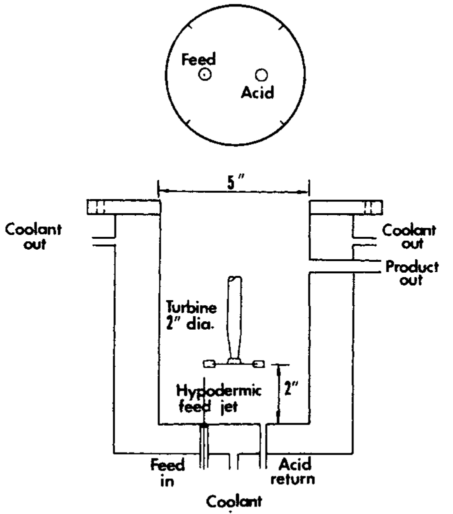

Fig. 2. Continuous stirred reactor.

The feed blends used were mixtures of propylene and isobutane. These chemicals were obtained from the Matheson Company and each had a minimum purity of 99.0%.

Part of this work involved determining the qualitative effects of the catalyst concentration (activity) on the reaction rate constants. To do this the acid had to be diluted with diisobutylene to simulate a degraded alkylation catalyst. This compound has been shown to be a source of octyl cations which are postulated to be a source of organic diluents in the alkylation catalyst (*3*, *20*). All of the sulfuric acid used was Mallinkrodt analytical reagent grade that contained 2.2 to 2.5% water. It was diluted with diisobutylene to 96.0 to 91.0% sulfuric acid such that there would exist no essential differences in catalyst character other than sulfuric acid composition. Typically the acid concentration decreased by 2% with a final catalyst concentration at the end of an experiment of 94% and 89% respectively.

The analytical methods used were gas chromatography and acid base titration. Chromatography was used for analyses of the hydrocarbon samples. Titration was the tool used to determine the sulfuric acid composition in the catalyst.

A Varian Model 1844 gas chromatograph equipped with flame ionization detectors, linear temperature programmer, and a 200 ft. by 0.01 in. open-tubular, squalane-coated column was used to analyze the hydrocarbon samples. Calibration of this instrument involved injecting samples of known composition, and using the resulting chromatograms as standards for subsequent analysis. Quantitative results were obtained directly as peak areas being proportional to mass fraction.

The reactor was run with 60% acid in the acid-continuous emulsion. Prior to each experiment the acid was contacted with pure isobutane (once the turbine power was turned on) so

TABLE 4. THE WEIGHT PERCENT PRODUCT DISTRIBUTION BASED ON GAS CHROMATOGRAPH ANALYSES

Catalyst Conc. % H_2SO_4	95	95	90	90	95	95	90	95	95
Temp., °F	65	65	65	81	81	105	105	120	135
Olefin Space Velocity, hr^{-1}	0.104	0.118	0.101	0.104	0.185	0.131	0.105	0.117	0.104
Run no.	2	9	5	1	6	7	4	8	3
C_3	1.69	1.59	2.40	1.98	3.88	2.83	2.28	2.87	3.20
iC_4	67.75	69.83	79.10	74.85	49.85	67.66	72.22	68.51	76.41
iC_5	0.70	0.97	0.76	0.65	2.66	2.07	1.26	2.20	1.93
23 *DMB*	0.72	0.63	0.46	0.48	1.61	1.01	0.75	1.02	0.69
2 *MP*	0.52	0.42	0.26	0.20	0.84	0.60	0.38	0.65	0.51
3 *MP*	0.16	0.19	0.12	0.09	0.37	0.27	0.16	0.29	0.23
Total C_6	1.00	1.24	0.84	0.77	2.82	1.88	1.29	1.96	1.43
24 *DMP*	5.16	5.24	3.54	4.68	13.95	8.57	7.39	8.20	6.01
23 *DMP*	12.13	10.68	7.19	9.27	13.22	8.13	8.48	7.88	5.16
3 MC_6	0.30	0.37	0.22	0.21	0.67	0.64	0.50	0.87	0.90
Total C_7	17.59	16.29	10.95	14.16	27.84	17.34	16.37	16.95	12.07
224 *TMP*	1.47	1.38	0.85	0.87	2.85	2.35	1.58	2.00	1.31
25 *DMH*	0.56	0.54	0.34	0.42	0.74	0.59	0.45	0.71	0.59
223 *TMP*	0.48	0.54	0.30	0.34	0.78	0.63	0.38	0.74	0.57
234 *TMP*	0.61	0.57	0.37	0.43	0.78	0.68	0.66	0.55	0.37
233 *TMP*	0.59	0.58	0.34	0.39	1.00	0.89	0.67	0.75	0.52
23 *DMH*	0.23	0.23	0.15	0.21	0.39	0.29	0.23	0.31	0.27
24 *DMH*	0.18	0.13	0.17	0.08	0.12	0.07	0.04	0.07	0.14
Other C_8	0.39	0.31	0.16	0.24	0.56	0.31	0.21	0.32	0.41
Total C_8	4.51	4.28	2.58	2.98	7.22	5.81	4.22	5.45	4.18
225 TMC_6	0.30	0.46	0.23	0.31	0.64	0.38	0.27	0.33	0.25
224 TMC_6	Trace	Trace	Trace	Trace	0.01	Trace	Trace	Trace	Trace
234 TMC_6	Trace	Trace	Trace	Trace	0.01	0.01	Trace	Trace	0.01
235 TMC_6	0.04	0.05	0.03	0.04	0.09	0.05	0.04	0.05	0.04
334 TMC_6	0.03	0.06	0.03	0.05	0.05	0.02	0.02	0.03	0.01
Other C_9	1.10	0.80	0.38	0.53	0.50	0.18	0.17	0.12	0.13
Total C_9	1.47	1.37	0.67	0.92	1.30	0.64	0.50	0.53	0.44
2235 TMC_6	0.04	0.13	0.07	0.10	0.13	0.04	0.05	0.03	0.02
224 TMC_7	0.47	0.36	0.23	0.39	0.43	0.14	0.20	0.10	0.07
225 TMC_7	0.24	0.19	0.12	0.25	0.23	0.08	0.19	0.06	0.05
Other C_{10}	4.54	3.75	2.29	3.10	3.77	1.49	1.42	1.31	1.04
Total C_{10}	5.29	4.43	2.71	3.84	4.56	1.75	1.86	1.50	1.18

that the acid would become saturated with this compound at the start of an experiment.

Once the temperature stabilized, the feed pump was started. Feed rates were established by timing known volumes of feed. Product rates were determined in the same manner.

Sampling was deferred until steady state conditions were attained in the continuous-feed stirred-tank reactor used. Sample times were spaced so that the 1 to 2 cc's of hydrocarbon withdrawn would not affect the low flow (less than 12 cc/min) of product to the settler. Typically, steady state was reached after 3 hours of operation and was confirmed by the fact that the product concentration was constant with time.

RESULTS AND CONCLUSIONS

The nine experiments shown in Table 4 were conducted over a temperature range of 65 to 135°F, with olefin space velocities from 0.101 to 0.185 vol olefin/vol catalyst-hr. and catalyst concentrations of 95% and 90% hydrosulfuric acid. These conditions and the corresponding product analyses from the nine experiments are shown in this table. Using this data the rate constant expressions presented previously were evaluated for each experiment. The following values of parameters were used: concentration of isobutane in the acid phase -7.0×10^{-4} lb/lb of H_2SO_4;[*] concentration of propylene for the base case of 12.5% (by wt.) propylene in the feed -1.0×10^{-9} lb-mole/ft^3 of H_2SO_4; Z, the constant in Equation (3) relating the proportion of ion concentration per parent species concentration -1.0×10^{-7}. These values were not arbitrary but were selected so that the first order rate constants in this work were of the same order of magnitude as that reported by Naworski (*17*) who has performed a kinetic study on the most closely related system. The resulting first-order rate constants ranged from 2×10^4 to 1×10^6 s^{-1}, and the second-order rate constants varied from 2×10^5 to 1×10^{18} cc/g-mole-s. (See Table 5.)

Naworski's rate constant was of the order of 1.0×10^4 s^{-1}. However, the reaction he was studying was the polymerization of butene in sulfuric acid; the analogous reaction in this work is

$$C_3^= + HX \xrightarrow{k_1} C_3^+X^- \qquad (1\text{-}1)$$

The value of k_1 was found to be between 2.12×10^5 and 3.09×10^5 cc/g-mole-s in this work.

Validity of the Mathematical Model

It should be obvious that the model used is not the only one possible considering the differences of opinion (and experimental results) as to the true mechanism of alkylation. The authors' only claim is that it is a plausible model which is consistent with accepted theory and experimental results. Consequently, with changes in olefin space velocity and temperature (two recognized major variables in alkylation) if the model obeyed the Arrhenius relation

$$k = k_0 e^{-E/RT}$$

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[*] Data for isobutane solubility in H_2SO_4 indicates a limiting value of 0.001 lb/lb (2). To allow for approximately 30% of the dissolved hydrocarbons being other than iC_4 a value of 0.0007 was used.

in this work it was to be a satisfactory representation of the reacting system.

The experimental values of the rate constants are given in Table 5, and the frequency factors and the activation energies computed from the rate constants are given in Table 6. The frequency factors and the activation energies were positive which is in keeping with the theory. The activation energies obtained for k_2 through k_8 were zero within the limits of experimental error. It may be shown using the assumptions of constant mass transfer coefficient and isobutane concentration that this result was to be expected (*12*). Thus, the rate constants k_2 through k_8 were not a function of temperature. Although this is an approximation, it does point out that these hydride transfer reactions are not a strong function of temperature.

In Figures 3 and 4, the Arrhenius plots of typical values of the experimentally measured rate constants and the associated linear least square line are given. The average absolute deviations of all of the experimental rate constants from least square line was 5.5%, and these deviations ranged from 0.9% to 11.6%.

Predictions with the Mathematical Model

The model was used to make the following predictions from changes in temperature and olefin feed concentration. These results are for temperature from 81°F to 135°F and olefin feed concentration of 12 to 22% (wt).

1. The yield of product increases with increasing temperature and increasing olefin feed concentration.
2. The proportion of the "primary product" iC_7 in the product is insensitive to change in temperature but in-

TABLE 5. RATE CONSTANTS CALCULATED FROM EXPERIMENTS USING A 95% H_2SO_4 CATALYST FOR TEMPERATURE FROM 81 TO 135°F

	Values					
Rate constants	81°F	105°F	120°F	135°F	Rate constant	Values #
$k_1 \times 10^{-5**}$	2.12	2.10	2.40	3.09	$k_2 \times 10^{-11**}$	2.07
$k_9 \times 10^{-4*}$	1.95	2.14	2.26	2.00	$k_3 \times 10^{-10**}$	3.29
$k_{10} \times 10^{-16**}$	5.92	7.53	9.46	10.9	$k_4 \times 10^{-10**}$	4.04
$k_{11} \times 10^{-15**}$	3.81	4.39	5.42	5.21	$k_5 \times 10^{-10**}$	4.20
$k_{12} \times 10^{-5*}$	1.25	1.31	1.41	1.46	$k_6 \times 10^{-10**}$	5.35
$k_{13} \times 10^{-17**}$	2.50	3.78	4.39	6.16	$k_7 \times 10^{-10**}$	6.02
$k_{14} \times 10^{-8**}$	3.38	4.49	4.81	6.10	$k_8 \times 10^{-10**}$	6.68
$k_{15} \times 10^{-15**}$	5.27	5.36	5.62	8.32		
$k_{16} \times 10^{-17*}$	5.25	6.21	5.73	8.53		
$k_{18} \times 10^{-5*}$	3.34	7.14	8.43	12.40		

[*] First-order (sec-1) ** Second-order (cm^3/g-mole-s)

[#] Rate constants k_2 through k_8 were not temperature dependent.

TABLE 6. RESULTS OF THE LEAST SQUARE FITS OF THE RATE CONSTANTS OVER THE RANGE OF 81 TO 135°F AND WITH A 95% H_2SO_4 CATALYST

Reaction rate	Rate law	Frequency factor*	Activation energy #
Initiation			
$C_3^= + HX \rightarrow C_3^+X^-$	k_1AB	1.01×10^7	2.35
$C_3^+X^- + iC_4 \rightarrow C_3 + iC_4^+X^-$	k_2AB	2.07×10^{11}	0.0
Primary			
$iC_4^+X^- + C_3^= \rightarrow iC_7^+X^-$	$k_{11}AB$	1.99×10^{17}	2.36
$iC_7^+X^- + iC_4 \rightarrow iC_7 + iC_4^+X^-$	k_5AB	4.20×10^{10}	0.0
Self-alkylation			
$iC_4^+X^- \rightarrow iC_4^= + HX$	k_9A	3.92×10^4	0.40
$iC_4^+X^- + iC_4^= \rightarrow iC_8^+X^-$	$k_{10}AB$	5.63×10^{19}	4.10
$iC_8^+X^- + iC_4 \rightarrow iC_8 + iC_4^+X^-$	k_6AB	5.35×10^{10}	0.0
Destructive alkylation			
$iC_7^+X^- \rightarrow iC_7^= + HX$	$k_{12}A$	7.49×10^5	1.08
$iC_7^= + iC_4^+X^- \rightarrow iC_5^= + iC_6^+X^-$	$k_{13}AB$	3.64×10^{21}	5.73
$iC_5^= + HX \rightarrow iC_5^+X^-$	$k_{14}AB$	1.62×10^{11}	3.69
$iC_5^+X^- + iC_4 \rightarrow iC_5 + iC_4^+X^-$	k_3AB	3.29×10^{10}	0.0
$iC_6^+X^- + iC_4 \rightarrow iC_6 + iC_4^+X^-$	k_4AB	4.04×10^{10}	0.0
$iC_7^+X^- + C_3^= \rightarrow iC_{10}^+X^-$	$k_{15}AB$	3.72×10^{17}	2.59
$iC_{10}^+X^- + iC_4 \rightarrow iC_{10} + iC_4^+X^-$	k_8AB	6.68×10^{10}	0.0
$iC_5^= + iC_4^+X^- \rightarrow iC_9^+X^-$	$k_{16}AB$	4.26×10^{19}	2.65
$iC_9^+X^- + iC_4 \rightarrow C_9 + iC_4^+X^-$	k_7AB	6.02×10^{10}	0.0
$iC_{10}^+X^- \rightarrow iC_5^= + iC_5^+X^-$	$k_{17}A$	4.45×10^{11}	8.40

[*] cc/g-mole s or s^{-1}.

[#] Kcal/g-mole.

creases with olefin feed concentration.

3. The concentration of the "self-alkylation" product iC_8 decreases with increases in both temperature and olefin feed concentration.

4. The concentration of the "destructive alkylation" products iC_5, iC_6, iC_7, and iC_{10} all increase with increasing olefin feed concentration. Only iC_5 is a strongly increasing function of temperature. These results are shown graphically in (*12*).

Experimental Results at 65°F

Three experiments were carried out at 65°F. The results of these experiments are shown in Table 4 under Runs 2, 5, and 9. In Table 7 a comparison of the measured and computed rate constants are given. The primary difference between the experimental rate constants at 65°F and those predicted by the model are for the iC_9 and iC_{10}'s. These compounds were formed in much greater quantities than were predicted. In fact, they were about the same as the values at 81°F which was run with an olefin feed concentration that was 60% greater than the 65°F experiment. This is contrary to the results of the model which predicts that both the yields of iC_9 and iC_{10} to be strong positive functions of the olefin feed concentration. There appears to be a change in mechanism between the operating temperatures of 81°F and 65°F (*12*). Such a change should not be unexpected; the range of temperatures at which H_2SO_4 catalyzed alkylation takes place is not large—generally between 40°F and 70°F for commercial butene plants. Due to propylene's stronger affinity for the acid cation (*2*) propylene alkylation is generally carried out at higher temperatures. When propylene alkylation was attempted at lower temperatures (50°F) in this work, no alkylation products could be identified on an individual basis—rather greater than half of the product species were concentrated in a nonane-plus fraction which was of a high molecular weight and had a long retention time in the gas chromatograph. In a series of four runs, the catalyst was rapidly degenerated to less than 50% H_2SO_4 showing the propylene's preference for the acid at lower temperatures. These results support the hypothesis of a change in mechanism.

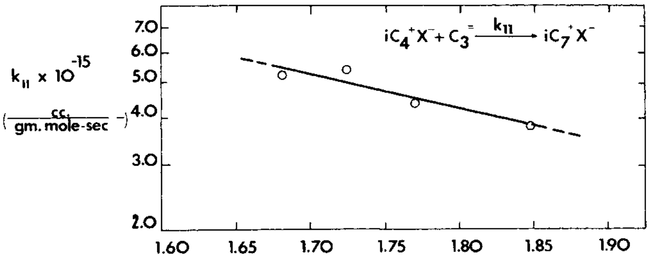

Fig. 3. Arrhenius plot of rate constant k_{11} and the least square line.

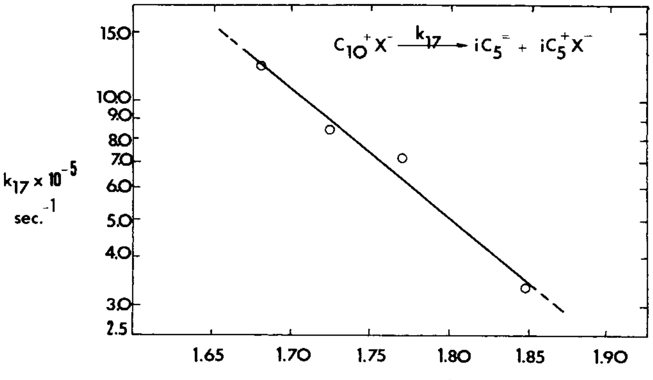

Fig. 4. Arrhenius plot of rate constant k_{17} and the least square line.

TABLE 7. COMPARISON OF EXPERIMENTAL AND PREDICTED VALUES FOR THE RATE CONSTANTS AT 65°F USING A 95% H_2SO_4 CATALYST

Rate constant	Predicted from least squares fit	Obtained from experiment 9
k_1^{**}	1.75×10^5	1.34×10^5
k_2^{**}	2.11×10^{11}	2.11×10^{11}
k_3^{**}	3.47×10^{10}	3.45×10^{10}
k_4^{**}	4.13×10^{10}	4.12×10^{10}
k_5^{**}	4.80×10^{10}	4.79×10^{10}
k_6^{**}	5.47×10^{10}	5.46×10^{10}
k_7^{**}	6.15×10^{10}	6.14×10^{10}
k_8^{**}	6.82×10^{10}	6.81×10^{10}
k_9^{**}	1.98×10^4	1.79×10^4
k_{10}^{**}	4.73×10^{16}	7.43×10^{16}
k_{11}^{**}	3.39×10^{15}	5.56×10^{15}
k_{12}^{*}	1.12×10^5	9.28×10^4
k_{13}^{**}	1.84×10^{17}	3.05×10^{17}
k_{14}^{**}	2.79×10^8	1.55×10^8
k_{15}^{**}	4.25×10^{15}	1.28×10^{16}
k_{16}^{**}	4.42×10^{17}	1.27×10^{18}
k_{17}^{*}	2.27×10^5	2.35×10^5

* First order (sec-1), ** Second order (cm^3/g-mole s).

The Effect of Catalyst Concentration

Three experiments (1, 4, and 5 in Table 4) were run at a nominal 90% acid concentration. These experiments were performed to study the qualitative effects of the catalyst concentration on the reaction rates.

In general, the main effect of the low catalyst concentration was to increase production of iC_9 and iC_{10} at the expense of lighter products. A comparison of rate constants obtained at 90% and 95% H_2SO_4 which is given by Langley (*12*) showed that the formation of the $iC_7^+X^-$ species (that is, k_{11}) was about 25% higher for the 90% acid. Also the formation of the $C_7^=$ (that is, k_{12}) which is largely responsible for the iC_5 and iC_6 species, was about 30% lower for the 90% acid.

As can be seen from Table 4, the effect of increasing temperature to 105°F results in a far superior product, that is, the increased compositions of the desirable iC_7 and iC_8 and the decreased compositions of iC_9 and iC_{10}. It appears that this higher temperature makes up for loss in selectivity of the dilute catalyst.

Comments on Related Research

There were two investigations reported in the literature on the effect of catalyst concentrations on olefin-isobutane alkylation with sulfuric acid catalyst. These were by Schlegeris (*21*) who alkylated propylene and Mosby (*15*) who alkylated butene-1. Schlegeris (*21*) used a 95% catalyst obtained from an American Oil Company commercial alkylation unit for comparison with the results he obtained at 99.3%. He found that conversion decreased with the lower strength catalyst. The decrease in conversion with acid strength was not noted in this work, however. The 95% and 90% catalysts used in this work both had the same character; however, the 99.3% and 95.5% catalysts Schlegeris used did not. The larger amount of organic diluents in this work may have actually aided conversion by promoting the solubility of isobutane more than the corresponding loss of activity upon dilution.

Mosby (*15*) investigated the effect of acid concentration on the alkylation of isobutane with butene-1. The catalyst used was made by blending a used alkylation catalyst similar to that used by Schlegeris with fuming H_2SO_4. Though the olefin was different, some qualitative comparisons can be made. Mosby found that the "C_9 plus" fraction of the product was higher at a concentration of 90-91% than at 94-95%. He also found that the product fraction of iC_5 through iC_7—comparable to iC_5 and iC_6 in this work—decreased with decrease in acid strength. Similar results were noted in this work.

CONCLUSIONS

A 17-reaction, mechanistic model described the alkylation of isobutane with propylene using 95% H_2SO_4 catalyst over the temperature range of 81°F to 135°F. The rate of formation of each species was adequately explained by one reaction path except for iC_5 which required two. Based on predictions of product distributions, low temperatures (down to 80°F) and low olefin feed concentrations (down to 12%) gave the highest concentration of the desired products iC_7 and iC_8 and the lowest concentrations of the undesirables iC_9 and iC_{10}.

For a 95% catalyst concentration, a change in the reaction mechanism, and thus the product distribution, occurred going from 80°F to 65°F. This was thought to be due to either a significant departure in the rate of formation of tertiary-butyl cations or to a change in reaction path. This difference in mechanisms caused increases in the iC_9 and iC_{10} concentrations.

Low acid concentrations, that is, 90%, yielded high concentrations of iC_9 and iC_{10}. The higher iC_9 and iC_{10} concentrations are considered to be a consequence of a change in selectivity to these products. In addition, since iC_7 concentrations were comparable to the yields at 95% H_2SO_4, the increased amount of organic diluents present in the catalyst probably aided conversion since isobutane solubility is thought to be enhanced with increased organic diluent.

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NOTATION

a = mass transfer area per unit volume of emulsion
C_i = saturated hydrocarbon of carbon number i
$C_i^=$ = monounsaturate of carbon number i
C_i^+ = carbonium ion of carbon number i
$[C_i]$ = concentration of species C_i
E = activation energy
F_{C_i} = molal feed rate of component C_i per unit volume of acid in reactor
k_i = reaction rate constant
K_m = mass transfer coefficient
K_{D_i} = phase distribution coefficients of species i
M = molecular weight
N_i = mass transfer rate of species i
P_i = molal product flow rate of species i per unit volume of catalyst
r_{C_i} = rate of formation of species C_i per unit volume of catalyst
S = olefin space velocity—vol. olefin/vol. acid-hr.
V = volume of catalyst in the reactor
W = mass flow rate
X = HSO_4^- ion
Y_{C_i} = mole fraction of component C_i in the hydrocarbon product (isobutane free)
Z = constant of proportionality between concentration of C_i and $C_i^+X^-$

Subscripts

acid = acid phase
HC = hydrocarbon phase
m, n, i = number of carbon atoms in a species

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