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Synthesis of Methyl Tertiary Butyl Ether Catalyzed by Ion-Exchange Resin. Influence of Methanol Concentration and Temperature

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Synthesis and decomposition of methyl t-butyl ether (MTBE) have been carried out in the temperature range of 50–95°C and in the presence of a sulfonic acid resin. A Langmuir–Hinshelwood model rate expression has been selected to interpret results. Relative rate constants and equilibrium constants are given as a function of temperature and the activation energy and reaction enthalpy have been determined. The results are particularly discussed in terms of the effect of methanol concentration. The catalytic activity of the resin is sensitive to the concentration of methanol, and at a given temperature, the variation in the apparent equilibrium constant is mainly due to the variation of methanol activity coefficient as a function of its molar fraction.

INTRODUCTION

The easy elimination of the reaction medium and the possible reutilization of ion-exchange catalysts make them preferable to inorganic acids and bases. Amberlyst 15 macroreticular sulfonic resin, used to catalyze the reaction of synthesis of methyl tertiary butyl ether (MTBE), acts through the intermediary of sulfonic groups bonded to an insoluble macromolecule. It occurs in the form of porous spherical beads containing 4.9 me protons/g.

The catalytic mechanisms occurring in the presence of this resin depend on the polarity of the reaction medium, as pointed out by kinetic studies carried out on dehydration reactions of alcohols such as methanol, tertiary butyl alcohol and isopropyl alcohol (*1*, *2*). At low alcohol concentration, the resin retains a network of hydrogen bonds between the sulfonic groups alone, or between these groups and the alcohol, while at high alcohol concentrations the protons are solvated and the H-bonded network disappears.

This article examines the influence of methanol concentration on the activity of Amberlyst 15 resin to form MTBE, i.e., on the reaction rates, together with the effect of the polarity of the medium on the reaction thermodynamics.

For a given polarity, the influence of temperature on the reaction rate constant helped to determine the activation energy of the MTBE synthesis and decomposition reactions. The effect of temperature on the equilibrium constants served to determine the enthalpy variation during the reaction. No complete thermodynamic study is currently available in the literature, and a kinetic study made by Ancillotti *et al.* (*3*) gave the value of the energy of activation from the initial reaction rates.

EXPERIMENTAL

The reaction was conducted in a stainless-steel double-jacketed reactor in batchwise operation. The reaction medium was agitated at 575 rpm by a magnetic-drive turbine. The temperature was controlled by thermostated water flow through the double jacket. A stainless-steel vessel containing the solid catalyst was bolted to the rotary shaft. The reagents were introduced and samples taken during the experiment through stainless-steel valves. The reagents and the reactor were preheated for 2 h before each experiment. Samples were ana-

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lyzed by gas chromatography on three chromatographs, as specified below.

(1) A Girdel 75 flame ionization detector chromatograph was used to determine MTBE, dimers, and traces of secondary ether, using a GLC capillary column, a 46 m long, 0.25-mm-diameter tube containing a squalane phase and held at 30°C. Nitrogen carrier gas flow rate was 12 ml/min.

(2) An Intersmat IGC 12M catharometer chromatograph was used to determine at 25°C isobutene in the C_4 fraction with a column a 10-m-long, ⅛-in.-diameter tube packed with Chromosorb loaded with β,β'-oxydipropionitrile. Helium carrier gas flow rate was 25 ml/min.

(3) An Intersmat catharometer chromatograph was used to determine at 145°C methanol, tertiary butyl alcohol, the entire C_4 fraction and MTBE with a Porapak Q column 1.2-m long, ⅛-in. diameter. Helium carrier gas flow rate was 18 ml/min.

The detectors of the instruments were connected to an HP integrator or an Iris 50 computer, directly giving the area of the different peaks.

We used inert n-butane (denoted nC_4) as the internal standard to determine the conversion rate of isobutene, F, from chromatographic analyses on β,β'-oxydipropionitrile giving the different butane and butene percentages in the C_4 fraction of the liquid mixture. The conversion rate of isobutene (denoted iC_4) was determined by the equation:

$$F = \frac{\left(\frac{\%\ iC_4}{\%\ nC_4}\right)_0 - \left(\frac{\%\ iC_4}{\%\ nC_4}\right)_t}{\left(\frac{\%\ iC_4}{\%\ nC_4}\right)_0}$$

RESULTS AND DISCUSSION

INFLUENCE OF METHANOL CONCENTRATION

In every experiment, methanol is in large excess with respect to the amount of catalyst since the ratio of moles of methanol to the amount of equivalent proton of the resin is included between 10 and 50. The reaction between methanol and isobutene to give MTBE is always highly selective if the initial methanol/isobutene molar ratio is greater than 1 and if the mixture is devoid of water. In the presence of water, which is more polar than methanol, sulfonic resin preferentially adsorbs water which can react with isobutene to give tertiary butyl alcohol.

The reaction between isobutene and methanol is equilibrated but, at the temperature prevailing in these experiments, the equilibrium is shifted by more than 90% toward the formation of MTBE.

Activity of Amberlyst 15 Resin

A model of the Langmuir–Hinshelwood type was adopted to determine the rate constants. Two assumptions were made to achieve this:

(i) The reaction occurs in a virtually homogeneous manner, in the sense that the isobutene reacts within the resin filled with methanol, always in excess (*4*), and we assume that there is order degeneracy with respect to methanol. The simplified rate equation thus obtained for an equilibrium reaction between isobutene and MTBE in a high methanol concentration medium is expressed as follows:

$$v = \overrightarrow{\mathbf{k}} C_{iC_4} - \overleftarrow{\mathbf{k}} C_{\mathrm{MTBE}} \qquad (1)$$

(ii) The reaction occurs between the methanol adsorbed on the resin and the isobutene in solution according to a Langmuir–Hinshelwood type model (*5*, *6*), and the MTBE must then be desorbed from the resin toward the solution. Thus the equation obtained is expressed as follows:

$$v = \frac{\overrightarrow{\mathbf{k}} C_{iC_4} C_{\mathrm{MeOH}} - \overleftarrow{\mathbf{k}} R C_{\mathrm{MTBE}}}{C_{\mathrm{MeOH}} + R C_{\mathrm{MTBE}}} \qquad (2)$$

The first assumption is valid for the synthesis of MTBE as long as the methanol/isobutene molar ratio is greater than 1. However, a kinetic analysis of the decomposition of MTBE showed that the Langmuir–Hinshelwood type model offers a more accurate picture of what really occurs (7). In conclusion, in order to unify the results, we selected the Langmuir–Hinshelwood type model for all the interpretations. The integrated forms of the rate equations yielding the rate constants are Eqs. (3) and (4) for MTBE synthesis and decomposition, respectively:

$$\frac{\vec{k}t}{F_e} = \frac{F_e}{Y - F_e^2}\left[\frac{Y + F_e(R - 1)}{F_e}\ln\frac{F_e}{F_e - F} + \frac{Y}{F_e}(F_e + R - 1)\ln\frac{Y - FF_e}{Y}\right] \quad (3)$$

$$\frac{\overleftarrow{k}Rt}{C^0_{\mathrm{MTBE}}} = \frac{-F'_e}{2 - F'_e}\left[(R + (1 - R)F'_e)\ln\frac{F'_e - F'}{F'_e} + \frac{F'_e - R}{1 - F'_e}\ln\left(1 + F'\left(\frac{1 - F'_e}{F'_e}\right)\right)\right] \quad (4)$$

To analyze the effect of methanol, hence the polarity of the medium, we used C_4 fractions containing different isobutene concentrations (47.5, 16.6, and 5.5%), and kept the methanol/isobutene molar ratios approximately constant, thus varying the methanol concentration. As an alternative, using a single C_4 fraction (16.6% isobutene), we varied the methanol/isobutene molar ratio. We performed a reaction at 70.7°C with a C_4 fraction containing 47.5% isobutene and with an initial methanol/isobutene molar ratio of 1.33, and the rate constant obtained, denoted $\vec{k}_0$, is taken as a reference for the kinetic analysis.

The results obtained are given in Table 1 in the form of the ratio of rate constants $\vec{k}/\vec{k}_0$ as a function of methanol concentration. For concentrations of methanol higher than 1 to 2 mol/liter, the $\vec{k}/\vec{k}_0$ ratios do not vary as a function of methanol concentration and no more with the methanol/isobutene molar ratio. On the other hand, at concentrations of methanol lower than around 1 mol/liter, the $\vec{k}/\vec{k}_0$ ratios rise substantially.

TABLE 1

Effect of Methanol Concentration on Relative Rate Constants $\vec{k}/\vec{k}_0$ at 70.7°C

% iC_4	$\frac{N^0_{\mathrm{MeOH}}}{N^0_{iC_4}}$	$C^0_{CH_3OH}$ (mole/l)	$\frac{\vec{k}}{\vec{k}_0}$
47.5	1.33	5.3	1
16.6	1.16	2.1	1.1
16.6	0.52	0.9	1.9
5.5	1.17	0.7	1.5

These results suggest that the increasing of rate constants is mainly due to the decreasing of methanol concentration which can modify the proton activity of resin sulfonic groups. Indeed, this effect cannot be due to a competition between isobutene adsorption and methanol adsorption because on the one hand Eq. (3) is always respected and on the other hand no dimers of isobutene have been formed. However, when the methanol/isobutene ratio is equal to 0.52, a small amount of dimer is obtained at a conversion rate higher than 40%, but in this case we calculated the rate constant for the initial period. The increase of resin activity must be related, as suggested by Gates *et al.* (*1*, *2*) and also by Ancillotti *et al.* (*3*, *8*), to the nature and environment of the catalytic site of the sulfonic resin. In fact, in the dry resin network, the sulfonic groups are interlinked by a hydrogen bond and the proton displays a certain activity. In this case Eq. (3) is not suitable, as the reaction is the dimerization of isobutene. The introduction of a great exess of methanol, with respect to equivalent protons, which occurs with liberation of heat, has the effect of dissociating these bonds and solvating the protons. Catalysis occurs by means of protons solvated by several moles of methanol. Consequently the acidity levels off and we have a specific catalysis. Between these two extreme cases, protons can be more or less solvated and the proton activity can be variable.

These considerations suggest that if the methanol concentration is low, extreme care must be exercised in using the experimental results with the rate equations defined above, either because the resin activity varies or because, at very low concentration of methanol, the order with respect to methanol may change.

Conversion Rate at Equilibrium

Expressed in mole fractions, the equilibrium constants for the synthesis of MTBE are expressed by:

$$K_x = \frac{X^e_{\mathrm{MTBE}}}{X^e_{\mathrm{MeOH}} X^e_{\mathrm{iC_4}}} \tag{5}$$

By expressing this constant as a function of the conversion rate of isobutene at equilibrium F_e, the methanol/isobutene molar ratio Y and the factor D which takes account of the dilution of isobutene in the C_4 fraction ($D = N^0_{\mathrm{C_4}}/N^0_{\mathrm{iC_4}}$), we obtain:

$$K_x = \frac{F_e(1 - F_e + Y + D)}{(1 - F_e)(Y - F_e)} \tag{6}$$

As a reference, we use the equilibrium constant denoted K_0 obtained at 70.7°C in the experiment described above (%iC_4 = 47.5%, $Y = 1.33$). The results, presented in the form of ratios of equilibrium constants K_x/K_0, are given in Table 2.

An MTBE decomposition experiment conducted at 70.7°C, using a mixture containing 55 wt% MTBE, 37.5 wt% butane, and 7.5 wt% *cis*-2-butene yielded a K_x/K_0 value of 1.98. This value is determined from the equilibrium constant of MTBE decomposition expressed as follows:

$$K'_x = \frac{F'^2_e}{(1 - F'_e)(1 + F'_e + D')} = \frac{1}{K_x} \tag{7}$$

where $D' = N^0_{\mathrm{C_4}}/N^0_{\mathrm{MTBE}}$.

At 70.7°C the relative value of the equilibrium constant expressed on the basis of mole fractions varies substantially with isobutene dilution, rising from 1 to 3.1 as the isobutene content in the C_4 fraction falls from 47.5 to 5.5%. This considerable variation must be associated with the fact that, whereas the reaction mixture certainly consists essentially of C_4 hydrocarbons, it also contains MTBE and especially methanol which is a polar compound. Figure 1 shows the continuous variation of K_x/K_0 as a function of the methanol mole fraction.

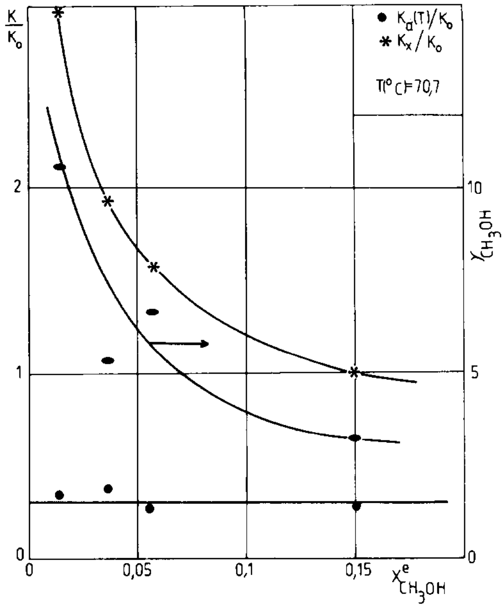

FIG. 1. Relative equilibrium constants dependence on methanol molar fraction.

It should be noted that the equilibrium constant obtained experimentally was expressed as a function of mole fractions. In actual fact, the thermodynamic equilibrium constant, which depends only on the temperature in the liquid phase, must be expressed on the basis of liquid-phase activities by the equation:

$$K_a(T) = \frac{a_{\mathrm{MTBE}}}{a_{\mathrm{iC_4}} a_{\mathrm{MeOH}}} \tag{8}$$

The experimental value can be related to the constant $K_a(T)$ by:

$$K_a(T) = \frac{X^e_{\mathrm{MTBE}}\gamma_{\mathrm{MTBE}}}{X^e_{\mathrm{MeOH}} X^e_{\mathrm{iC_4}}\gamma_{\mathrm{MeOH}}\gamma_{\mathrm{iC_4}}} = \frac{\gamma_{\mathrm{MTBE}}}{\gamma_{\mathrm{MeOH}}\gamma_{\mathrm{iC_4}}} K_x \tag{9}$$

where γ denotes the respective activity coefficients.

TABLE 2

Influence of Activity Coefficients on the Equilibrium Constant at 70.7°C

	% iC_4			%MTBE[a]
	47.5	16.6	5.5	5.5
X^e_{MeOH}	0.1489	0.055	0.0154	0.0354
K_x/K_0	1	1.62	3.08	1.98
γ_{CH_3OH}	3.15	6.575	10.508	5.285
γ_{iC_4}	1.22	1.062	1.037	1.077
γ_{MTBE}	1.001	1.084	1.199	1.029
$\frac{K_a(T)}{K_0}$	0.26	0.25	0.34	0.36

[a] MTBE decomposition.

The Unifac method (*9*), based on the contributions of groups to molecular interactions, together with experimental vapor liquid equilibrium data, helps to determine the parameters introduced into an NRTL method (*10*) used to calculate the activity coefficients of the components of a mixture as a function of the mixture composition and temperature. A method of this type was employed at the Institut Français de Pétrole to calculate the fractionation by distillation of a hydrocarbon mixture containing C_4, methanol, and MTBE, and an experimental distillation was carried out to confirm the forecasts of the predictive methods. Table 2 shows the values calculated, using this method, of the activity coefficients of the equilibrium components, as well as the $K_a(T)/K_0$ values calculated from the above equation. In Fig. 1, the K_x/K_0 and $K_a(T)/K_0$ values are plotted on the ordinate as a function of the molar fraction of methanol, the most polar compound, whose activity coefficient varies considerably with its molar fraction, as also shown in Fig. 1. Since the relative $K_a(T)/K_0$ values are practically equal (0.30), we can conclude that the variation in K_x is essentially due to the variation in the activity coefficient of methanol.

We try to compare experimental thermodynamic constants with the ones obtained through data available in the literature. We found a difference in $\Delta G_L{}^0$ of around 5 kJ/mol. Such a difference can be partly explained by error in calculation of the entropy of isobutene in the liquid phase from data given in the literature for the vapor phase, by experimental errors in the determination of the molar fraction of the different components and also by the precision obtained by the calculation of activity coefficients values. However, the major part of this difference must be due to values of reaction enthalpy which are equal to 42.8 or 43.5 kJ/mol, calculated from heat of combustion or heat of formation data, respectively. Compared with the ΔH values obtained in this work and given later it is evident that a difference in $\Delta G_L{}^0$ of 3 to 5 kJ/mol can be obtained according to the ΔH value chosen.

Consequently calculations from data available in the literature could be error prone to obtain the right values of equilibrium constants K_x which are needed from a practical standpoint. Moreover, since the methanol activity coefficient is strongly dependent on its molar fraction, great care must be taken in calculating conversion rate at equilibrium. For instance, at high isobutene dilution (% iC_4 = 5.5), the conversion rate is actually 10% higher than the conversion rate calculated by Eq. (6) from the results obtained at low dilution (% iC_4 = 47.5). The drop in the conversion rate due to the dilution of reagents is offset by more than 60% by the increasing of the methanol activity coefficient.

INFLUENCE OF TEMPERATURE

To synthesize MTBE, we selected a C_4 fraction containing 47.5% isobutene, and we varied the temperature between 49 and 89°C. The initial methanol/isobutene molar ratio was always greater than 1. Under these conditions, the methanol concentration is sufficiently high for by-products to be negligible. For decomposition of the MTBE, we used an initial mixture containing 72.6 wt% MTBE and 27.4 wt% *cis*-2-

TABLE 3

MTBE Synthesis (iC_4 content 47.5%). Relative Rate Constants Dependence on Temperature

T (°C)	$\frac{MeOH}{iC_4}$ (mol/mol)	$\frac{\vec{k}}{\vec{k}_0}$
49	1.05	0.125
51.5	1.05	0.147
56	1.24	0.286
61.9	1.32	0.464
62.4	1.24	0.684
65.8	1.24	0.893
68.2	1.32	0.725
70.7	1.33	1
73.7	1.32	1.54
75	1.32	1.76
76.7	1.24	1.36
79.3	1.32	1.98
81.7	1.32	1.71
87.3	1.24	3.60
88.6	1.32	4.44

butene, and varied the temperature between 72 and 95°C.

Energy of Activation

MTBE synthesis. The variation in the relative rate constant $\vec{k}/\vec{k}_0$ with temperature serves to determine the energy of activation of the synthesis of MTBE. The values of the relative constants obtained by using Eq. (3) for each experiment are compiled in Table 3. As the temperature rises from 49 to 89°C, the relative rate constant is multiplied by a factor of 35. We obtain the energy of activation by plotting ln $\vec{k}/\vec{k}_0$ versus $1/T$, the slope $-\vec{E}/\mathfrak{R}$ determined by the least squares method (Fig. 2). This gives:

$$\vec{E} = 82.0 \pm 6.7 \text{ kJ/mol}$$

MTBE decomposition. The products $R\overleftarrow{k}$ are determined from Eq. (4). By again selecting the temperature of 70.7°C as a reference, the results are presented in the form $R\overleftarrow{k}/R_0\overleftarrow{k}_0$ in Table 4. The variation in this ratio as a function of temperature serves to determine the thermal increment E of the equation:

$$E = \overleftarrow{E} - \lambda_{MTBE} + \lambda_{MeOH}$$

where $\overleftarrow{E}$ is the energy of activation of MTBE decomposition, and λ_{MTBE} and λ_{MeOH} are the heats of adsorption of MTBE and methanol, respectively (*11*). E is obtained from the slope of the line of the least squares of equation:

$$\ln \frac{\overleftarrow{k}R}{\overleftarrow{k}_0 R_0} = f\left(\frac{1}{T}\right)$$

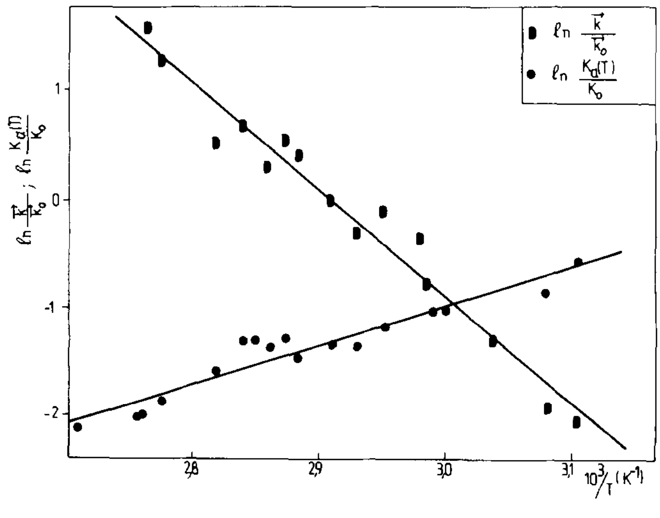

FIG. 2. MTBE synthesis. Influence of temperature on kinetic and thermodynamic constants.

TABLE 4

MTBE decomposition. Relative Rate Constants Dependence on Temperature

T (°C)	$\frac{\overleftarrow{\mathbf{k}}R}{\overleftarrow{\mathbf{k}}_0 R_0}$
94.5	20.51
90.9	8.40
88.3	6.98
85.4	5.70
82.3	4.37
80.1	3.61
77.7	2.26
72.6	1.23

TABLE 5

Activation Energies of MTBE Synthesis

Ref.	$\overrightarrow{E}$ (kJ/mol)	Catalyst	System
a	71.15	Amberlyst 15 resin	Solid/liquid (initial rate)
b	74.08	Amberlyst 15 resin	Solid/liquid (fixed bed continuous flow)
c	87.9	Methyl sulfuric acid	Gas (iC_4)/liquid (methanol)
c	91.2	Methyl sulfuric acid	homogeneous
a	103.4	Paratoluene sulfonic acid	Homogeneous (initial rate)

Note. References: (a) Ancillotti *et al.* (*3*, *8*), (b) Torck (*12*), (c) Beaufils and Hellin (*13*).

which is equal to $-E/\mathfrak{R}$ (Fig. 3). Hence:

$$E = 122.6 \pm 4.2 \text{ kJ/mol}$$

The value of the energy of activation of MTBE synthesis can be compared with those determined in other investigations and presented in Table 5.

First of all, considering the experimental errors giving rise to a range of ±6.7 kJ/mol, the experimental energy of activation agrees satisfactorily with these overall results. The values obtained with Amberlyst 15 sulfonic resin are nevertheless generally lower than those obtained by using an acid in solution in the reaction mixture. This occurrence can be ascribed partly to the fact that diffusion within the pores of the sulfonic resin is more difficult than in solution. The activation energy of diffusion in macroreticular resins is in fact 25 to 42 kJ/mol, compared with 12.5 to 25 kJ/mol in solution (*14*). Furthermore, we can associate this discrepancy with the fact that the resin structure yields a catalytic site and a site environment in which methanol is always in excess, and this is particularly favorable for this reaction by lowering the activation level toward the transition state.

For an equilibrium reaction, the differ-

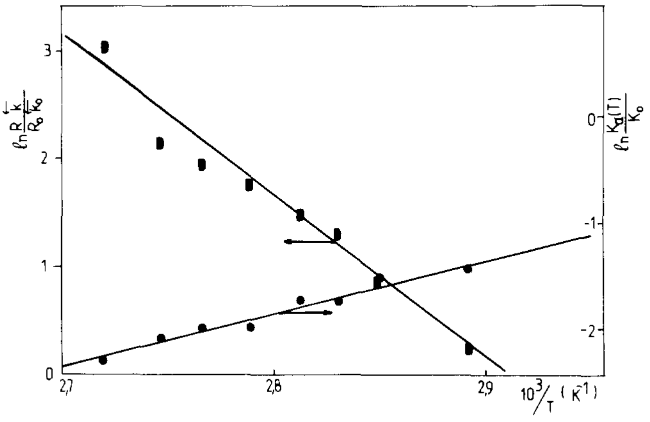

FIG. 3. MTBE decomposition. Influence of temperature on kinetic and thermodynamic constants.

ence $E - \overset{\rightarrow}{\mathbf{E}}$ is equal to the reaction enthalpy. In fact, $v = 0$ at equilibrium. So from Eq. (2):

$$\overset{\rightarrow}{\mathbf{k}} C^{e}_{iC_4} C^{e}_{MeOH} = \overset{\leftarrow}{\mathbf{k}} R C^{e}_{MTBE}$$

$$\frac{\overset{\rightarrow}{\mathbf{k}}}{R\overset{\leftarrow}{\mathbf{k}}} = \frac{C^{e}_{MTBE}}{C^{e}_{iC_4} C^{e}_{MeOH}}$$

$$\mathbf{K}_x = \frac{X^{e}_{MTBE}}{X^{e}_{iC_4} X^{e}_{MeOH}}$$

Since

$$X_i = C_i / \Sigma_i C_i$$

$$K_x = \frac{\overset{\rightarrow}{\mathbf{k}}}{\overset{\leftarrow}{\mathbf{k}} R} \Sigma_i C_i^{e}$$

where: $\Sigma_i C_i^{e} = C^{0}_{iC_4} (1 + Y + D - F_e) = C^{0}_{MTBE} (1 + D' + F'_e)$

$$K_x = \frac{\overset{\rightarrow}{\mathbf{k}}}{\overset{\leftarrow}{\mathbf{k}} R} C^{0}_{MTBE} (1 + D' + F'_e)$$

$$\frac{d \ln K_x}{dT} = \frac{d \ln \overset{\rightarrow}{\mathbf{k}}}{dT} - \frac{d \ln (\overset{\leftarrow}{\mathbf{k}} R)}{dT} + \frac{d}{dT} (1 + D' + F'_e)$$

However:

$$\frac{d}{dT} (1 + D' + F'_e) \simeq 0.03$$

hence:

$$\Delta H = \overset{\rightarrow}{\mathbf{E}} - E$$

The enthalpy of the reaction can therefore be determined from the kinetic results. Thus:

$$\Delta H = -40.6 \text{ kJ/mol}$$

We shall subsequently compare this value with the one determined from the thermodynamic analysis.

Reaction Enthalpy

The MTBE synthesis equilibrium is strongly shifted toward the formation of MTBE, since a conversion yield of 98% can be obtained in some cases, especially at low temperatures. The values of the relative equilibrium constants K_x/K_0 calculated from Eq. (6) are given in Table 6, as a function of temperature. The Unifac computer program calculates the equilibrium constants $K_a(T)$ which depend only on the temperature in the liquid phase. Their relative values are also given in Table 6, and the variation of these constants with temperature is given by the Gibbs—Helmholtz relation

$$-\mathfrak{R} T \log K_a(T) = \Delta G_L{}^0$$

In the temperature range considered, the variation in entropy is not taken into account. Hence the variation in enthalpy during the reaction is obtained from the slope of the line of the least squares of the equation:

$$\ln \frac{K_a(T)}{K_0} = f\left(\frac{1}{T}\right)$$

which is equal to $-\Delta H/\mathfrak{R}$ (Fig. 2).

The results obtained for the decomposition of MTBE are given in Table 7, and the enthalpy is determined by the above method (Fig. 3). The values thus obtained

TABLE 6

MTBE Synthesis (iC_4 content 47.5%). Relative Equilibrium Constants Dependence on Temperature

T (°C)	$\frac{N^0_{CH_3OH}}{N^0_{iC_4}}$	$\frac{K_x}{K_0}$	$\frac{K_a(T)}{K_0}$
49	1.05	3.35	0.566
51.5	1.05	2.46	0.426
60	1.42	1.34	0.359
61.8	1.05	1.92	0.352
65.8	1.24	1.31	0.306
68.2	1.33	1	0.256
70.7	1.33	1	0.258
73.75	1.33	0.88	0.228
75	1.33	1.06	0.274
76.7	1.24	1.06	0.256
78	1.42	0.81	0.27
79.3	1.32	0.80	0.269
81.7	1.32	0.76	0.201
87.3	1.24	0.61	0.155
88.6	1.36	0.50	0.136
89.3	1.05	0.61	0.131
95	1.42	0.41	0.121

TABLE 7

MTBE decomposition. Relative Inverse Equilibrium Constants Dependence on Temperature

T (°C)	$\frac{K_x}{K_0}$	$\frac{K_a(T)}{K_0}$
72.6	1.06	0.233
77.7	0.90	0.199
80.1	0.76	0.175
82.3	0.75	0.174
85.4	0.57	0.135
88.3	0.56	0.136
90.9	0.51	0.123
94.6	0.40	0.100

are −31.3 ± 4 and −39.8 ± 2 kJ/mol from the results of MTBE synthesis and decomposition, respectively. The experimental values obtained from MTBE decomposition are better aligned along the line of least squares than in the case of MTBE synthesis and we consider that the value of the reaction enthalpy:

$$\Delta H = -39.8 \pm 2 \text{ kJ/mol}$$

obtained from the results of MTBE decomposition is more reliable.

A comparison of this last value with the one (−40.6 kJ/mol) obtained from the kinetic study shows a good agreement between the kinetic and thermodynamic results of the MTBE synthesis and decomposition reactions.

CONCLUSIONS

Macroreticular sulfonic ion-exchange resins, such as Amberlyst 15, are ideal catalysts for the synthesis of MTBE due to the great selectivity obtained, even if methanol is present in stoichiometric quantity with respect to isobutene. These resins are quite sensitive to the concentration of methanol, which is preferentially adsorbed and the reaction rates increase sharply when this concentration is low.

The reaction enthalpy has been obtained from the variation in the equilibrium constants with temperature.

The influence of temperature on the reaction rates gives an activation energy which is slightly lower than the value obtained in the homogeneous phase. However, values of activation energies for MTBE synthesis and decomposition allow us to calculate the enthalpy of reaction, which agrees with the value obtained from thermodynamic study.

The calculation of the activity coefficients helps to show that the variation in the apparent equilibrium constant is mainly due to the variation in the activity of methanol as a function of its molar fraction. In fact, the methanol activity increases considerably as its concentration decreases. The higher increasing of activity compared with those for isobutene and MTBE shifts the equilibrium further than is expected from calculation.

APPENDIX: NOMENCLATURE

a_i	liquid phase activity of i
γ_i	activity coefficient of i in liquid phase
C_i^0, C_i, C_i^e	concentration of i at time 0, t, and at equilibrium
D	dilution factor of isobutene (iC_4) in the C_4 fraction (MTBE synthesis)
D'	dilution factor of MTBE in the mixture MTBE + C_4 (others than iC_4) (MTBE decomposition)
$\Delta G_L{}^0$	free energy variation in liquid phase reaction
ΔH	enthalpy variation in reaction
E	thermal increment for MTBE decomposition
$\overrightarrow{\mathbf{E}}$	energy of activation for MTBE synthesis
$\overleftarrow{\mathbf{E}}$	energy of activation for MTBE decomposition
F,F_e	conversion rate of iC_4 at time t and at equilibrium
F',F'_e	conversion rate of MTBE at time t and at equilibrium
$\overrightarrow{\mathbf{k}}$,$\overrightarrow{\mathbf{k}}_0$	direct rate constant at T°C or at 70.7°C
$\overleftarrow{\mathbf{k}}$,$\overleftarrow{\mathbf{k}}_0$	reverse rate constant T°C or at 70.7°C
$K_a(T)$	thermodynamic equilibrium constant
K_x	equilibrium constant in mole fraction
K_0	equilibrium constant in mole fraction at 70.7°C and for $\%iC_4 = 47.5$
N_i^0	initial mole amount of i
R,R_0	ratio of MTBE/CH_3OH adsorption coefficients at T and 70.7°C
$\mathfrak{R}$	gas constant
X_i^e	mole fraction of i at equilibrium
Y	initial CH_3OH/iC_4 molar ratio

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