Hydration of Isopentenes in an Acetone Environment over Ion-Exchange Resin: Thermodynamic and Kinetic Analysis

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2-Methyl-2-butanol was synthesized in the 60–103°C temperature range over sulfonic acid resin as the catalyst and in the presence of a sufficient quantity of acetone to obtain a single liquid phase. Equilibrium constants and rate constants are given as a function of temperature, and the reaction enthalpy and activation energy were determined. The activity of Amberlyst 15 is compared to that of other catalysts. Reactivities of isopentenes are compared to that of isobutene. The UNIFAC predictive method was used to determine activity coefficients so as to describe the non-ideality of the liquid phase and to compare experimental and thermodynamic constants. Since the isomerization of the double bond occurs during hydration, the mechanism of hydration can be discussed. © 1987 Academic Press, Inc.

INTRODUCTION

2-Methyl-2-butanol is formed by the reaction of 2-methyl-1-butene or 2-methyl-2-butene with water in the presence of an acid catalyst. Such a hydration can be valuable for the production of stable gasoline–alcohol fuel mixtures from high olefin fractions such as C_5 cracking gasoline cuts (*1*). On the other hand, 2-methyl-2-butanol can easily be dehydrated in pure isopentenes which are useful as petrochemical intermediates. Such hydration/dehydration processes have been industrialized for the production of pure isobutene (*2*).

This reaction can be catalyzed by acid ion-exchange resins. Such catalysts have some advantages over aqueous sulfuric acid solutions which give rise to various drawbacks such as corrosion, side reactions, and environmental problems (*3*). Moreover, these resins can be used as a fixed bed in an industrial reactor.

The mutual insolubility of water and hydrocarbons results in low isoolefin conversion, except when a high water-to-isopentene ratio is used. Mutual phase solubility can be increased by the use of a solvent such as a glycol ether (*4*), acetic acid (*5*), or acetone (*6*).

This paper presents a thermodynamic and kinetic analysis of the liquid-phase hydration of 2-methyl-1-butene and 2-methyl-2-butene in a solvent environment and catalyzed by sulfonic resins. This analysis was used to determine thermodynamic and kinetic constants that are useful for designing a continuous-flow reactor.

Acetone was chosen as a solvent because it is inert with respect to olefins as well as to itself in the presence of water. A sufficient quantity was used to have a single liquid phase so as to properly determine thermodynamic data for the liquid-phase hydration of isopentenes. Such data are not available in the literature. Thermodynamic constants were calculated from thermochemical data and compared to values obtained by the measurement of the equilibrium composition in this single liquid phase.

Since the isomerization of the double bond of isopentenes occurs during hydration, the mechanism of olefin hydration can be discussed on the basis of experimental observations concerning this isomerization.

EXPERIMENTAL

The ion-exchange resin used as a catalyst is a macroreticular sulfonic acid resin, sold by Rohm & Haas under the name Amberlyst 15 (surface area: 42 m^2/g, porosity 0.25 cm^3/g, acidity 4.8 meqH$^+$/g). Thermo-

dynamic and kinetic analyses were performed in a stainless-steel jacketed reactor (0.2 liter) in a batchwise operation. A stainless-steel punch-vessel containing Amberlyst 15 (4 g) was bolted to the rotary shaft of a magnetic-drive stirrer running at 2000 rpm. A thermocouple was submerged in the liquid phase in the reactor. Temperature was controlled within ±0.2°C by thermostated water flow through the jacket. Jacketed gauging-glass cylinders were used to feed reagents into the reactor and to control that the mixture of water, hydrocarbons, and acetone produced a single liquid phase at the reaction temperature. 2-Methyl-1-butene (denoted A1) or 2-methyl-2-butene (denoted A2) containing a small initial amount of the respective isomer (1.2 wt% of A2 in A1, 0.52 wt% of A1 in A2) was used in a mixture with 2,3-dimethylbutane.

The reagents and solvent were preheated for 2 h before starting the experiment. Water and part of the acetone were placed in the reactor. Methylbutene, dimethylbutane, and the remainder of the acetone were placed in the gauging-glass cylinder. At time zero the mixture contained in the glass cylinder was fed into the reactor with the stirrer running. A typical initial composition of the mixture (151.6 g) was (P_i^0 in wt%): 80% acetone, 7.65% water, 6.6% dimethylbutane, 5.68% A1, and 0.07% A2. In such a case the initial water-to-isopentenes molar ratio, Y, and the initial molar ratio of inerts (acetone + dimethylbutane) to isopentenes, Z, are, respectively, equal to 5.17 and 17.7.

The composition of the liquid phase was analyzed by taking liquid samples via valves at successive intervals until a steady composition was reached. Samples were collected in liquid form in a chilled test tube with a self-sealing cap, and then they were analyzed by gas chromatography. 2-Methyl-2-butanol (MBA), water, acetone, dimethylbutane, and isopentenes (A1 and A2) were determined at 35°C using a GLC capillary column, a tube 46 m long and 0.25 mm in diameter, containing a squalane phase kept at 35°C. The flow rate of the nitrogen carrier gas was 25 ml/min. The chromatographic response was calibrated for each component (7).

Figures 1a and b show continuous variations in time of the weight percentage of MBA and isopentenes in the reaction mixture. During the formation of MBA, 2-methyl-1-butene was isomerized into 2-methyl-2-butene to a great extent since the A2/A1 equilibrium ratio was equal to 6. On the other hand, isomerization was much less when the reagent was 2-methyl-2-butene (Fig. 1b) and then the value of this ratio equal to 9 was higher than in the preceding case, suggesting that equilibrium is not attained in Fig. 1a. At higher temperatures (Fig. 1c) a maximum was observed for the formation of MBA, and a chromatographic analysis showed that this maximum did not result from the formation of dimers.

2,3-Dimethylbutane (denoted B) was used as an internal standard to determine, by chromatographic analyses, conversions F_i, F_1 of 2-methyl-1-butene and F_2 of 2-methyl-2-butene, and the conversion F of both isopentenes (A + I) by the equations:

$$F_i = \frac{\left(\frac{\%Ai}{\%B}\right)_0 - \left(\frac{\%Ai}{\%B}\right)_t}{\left(\frac{\%Ai}{\%B}\right)_0} \qquad (1)$$

$$F = \frac{\left(\frac{\%A + I}{\%B}\right)_0 - \left(\frac{\%A + I}{\%B}\right)_t}{\left(\frac{\%A + I}{\%B}\right)_0}. \qquad (2)$$

The formation of the isomer (I) of one isopentene is defined, with respect to the amount obtained at equilibrium (e), by the equation:

$$D = \frac{\left(\frac{\%I}{\%B}\right)_t - \left(\frac{\%I}{\%B}\right)_e}{\left(\frac{\%I}{\%B}\right)_e}. \qquad (3)$$

The corresponding values at equilibrium are expressed, respectively, by F_1^e, F_2^e, F^e, and D^e.
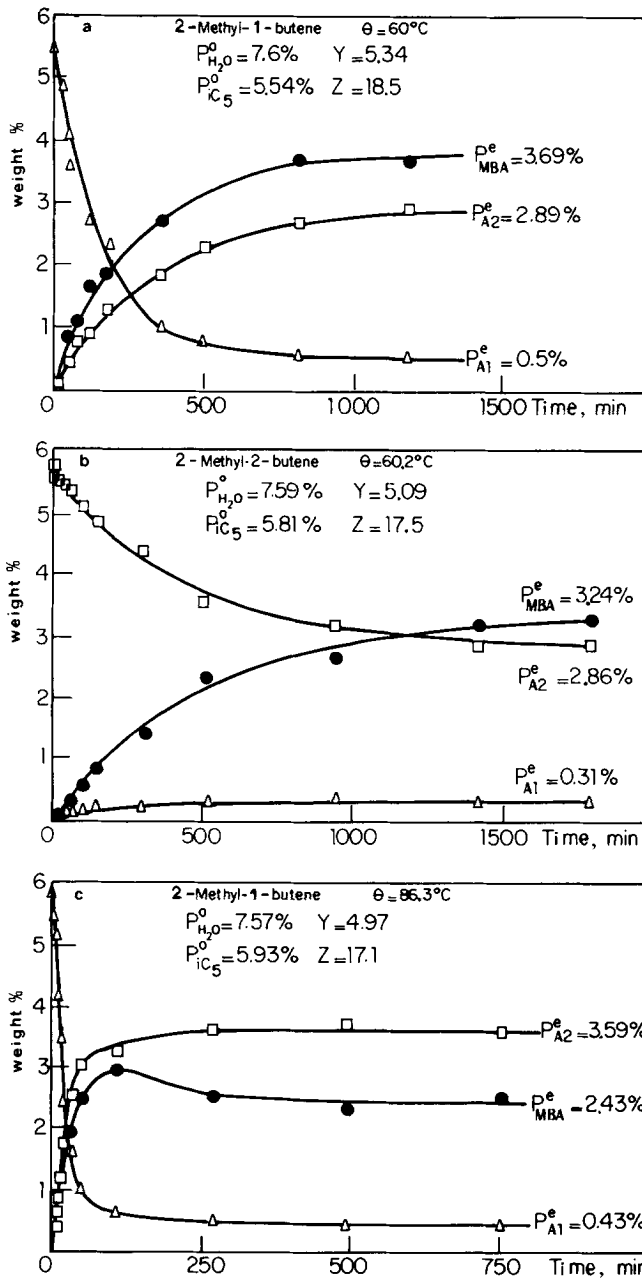
FIG. 1. Variation of mixture composition with time (solvent: acetone).

RESULTS

Thermodynamics of the Liquid-Phase Hydration of Isopentenes

Experimental equilibrium constants. Equilibrium constants for the liquid-phase hydration of isopentenes and for double-bond isomerization are related to the molar fractions in the liquid phase of each component of equilibrium X_i^e by the equation:

$$K_{(1 \text{ or } 2)} = \frac{X_{MBA}^e}{X_{H_2O}^e X_{A(1 \text{ or } 2)}^e} \qquad (4)$$

$$K_1 = \frac{X_{A2}^e}{X_{A1}^e}. \qquad (5)$$

TABLE 1

Influence of Temperature on Equilibrium Constants

θ (°C)	$10^2 F_i^e$	$10^2 F^e$	$10^2 X_i^e$				K_1	K_2	K_I
			H_2O	Al	A2	MBA			
2-Methyl-1-butene					$\Delta H_1 = -30.1$ kJ/mol				
60	91.3	41.2	17.79	0.3784	2.187	2.222	33.0	5.71	5.78
72.7	92.7	40.6	20.76	0.2876	2.213	1.678	28.1	3.65	7.70
80.2	90.3	31.3	20.74	0.3676	2.213	1.591	20.9	3.47	6.02
86.3	92.6	31.8	20.39	0.3178	2.653	1.429	22.0	2.64	8.33
93.5	88.5	20.5	21.56	0.4155	2.500	0.9164	10.2	1.70	6.02
102.6	86.2	23.7	21.66	0.4000	2.431	1.197	13.8	2.27	6.08
2-Methyl-2-butene					$\Delta H_2 = -25$ kJ/mol				
60.2	51.2	45.6	20.0	0.2303	2.124	1.915	41.6	4.51	9.22
69.9	47.4	41.3	20.1	0.3040	2.366	1.587	26.0	3.34	7.78
76.6	40.4	34.0	19.9	0.2893	2.537	1.393	24.2	2.76	8.77
88.6	39.0	30.0	20.7	0.4199	2.726	1.032	11.9	1.83	6.50

The X_i molar fractions can be obtained by the chromatographic analysis of each component of the mixture.

The effect of the reaction temperature was investigated in the 60 to 103°C range using 2-methyl-1-butene or 2-methyl-2-butene as the reagent. As shown in Table 1, at equilibrium the conversion of both isopentenes F^e to alcohol varies from 23.7% at 102.6°C to 46% at 60°C for an initial water-to-olefin molar ratio Y equal to 5.2. Since 2-methyl-1-butene is also isomerized during hydration, its conversion is much higher, i.e., in the range of 86 to 90%. The molar fraction of each equilibrium component and equilibrium constants K_1, K_2, and K_I are given in this table for each temperature. For isopentenes, since equilibrium conditions are more favorable for 2-methyl-2-butene, K_1 is always higher than K_2, and the K_1/K_2 ratio equal to K_I is in the range of 6 to 9. Concerning K_2 values, it can be seen that the results obtained with 2-methyl-1-butene as the reagent are, in all cases, slightly higher than those obtained with the hydration of 2-methyl-2-butene.

These equilibrium constants can be compared to the ones obtained for the liquid-phase hydration of isobutene in the same solvent (8). Whereas K_1 has practically the same value as the isobutene equilibrium constant which is equal to 28.7 at 80°C, the K_2 value, on the other hand, is around tenfold lower, thus showing that, considering isopentenes altogether, alcohol formation is less favorable than for isobutene.

Influence of temperature. The variation of equilibrium constants with temperature is given by the Gibbs–Helmholtz equation:

$$-RT \ln K_a = \Delta G_T^\circ. \qquad (6)$$

In the temperature range considered, since the variations of entropy and enthalpy with temperature are not taken into account, the variation of enthalpy of the reaction is obtained from the slope of the line of the least square of the equation $\ln K = f(1/T)$. These variations of $\ln K_1$, $\ln K_2$, and $\ln K_I$ are illustrated as a function of reciprocal temperature in Fig. 2. For instance, the equilibrium constant for the liquid-phase hydration of 2-methyl-2-butene is related to the temperature by the equation:
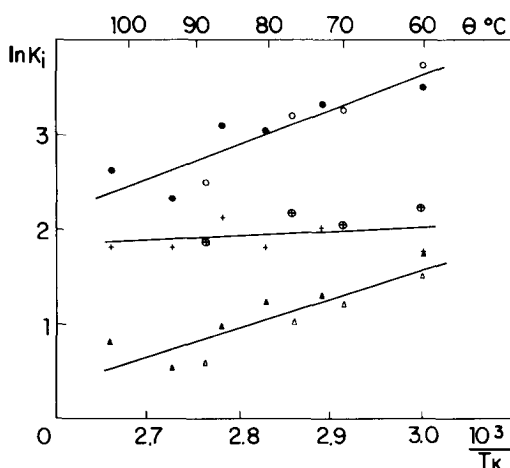
$$\ln K_2 = \frac{3009}{T} - 7.462. \qquad (7)$$

FIG. 2. Dependence of equilibrium constants on temperature. Reagents: A1 (●, ln K_1; ▲, ln K_2; +, ln K_1) and A2 (○, ln K_1; △, ln K_2; ⊕, ln K_1).

Variations of enthalpy of the hydration of isopentenes and of isomerization can be calculated from the slope of the lines obtained. The enthalpy change for 2-methyl-1-butene, which is equal to −30.1 kJ/mol, is higher than for 2-methyl-2-butene, which is equal to −25 kJ/mol. As expected, the variation of the enthalpy of isomerization, i.e., −5 kJ/mol, is equal to the difference between ΔH_1 and ΔH_2.

Comparison with thermodynamic data. These experimental values of equilibrium constants and reaction enthalpy change should be compared to the ones that can be calculated from the thermochemical data of

heat of formation ΔH_f^o and entropy S^o in the liquid phase, as shown by the literature and Table 2. Calculations of ΔH^o and ΔS^o permit the computation of thermodynamic constants at different temperatures. K_a values at 80°C for isopentene hydration and isomerization are given in this table.

Whereas enthalpy variations for hydration and isomerization and the K_1(80°C) experimental value for isomerization are in satisfactory agreement with the ΔH^o values and with K_a(80°C), it is amazing to find that the experimental values for K_1 and K_2 are quite different from the K_a thermodynamic constant. Indeed, at 80°C K_1 and K_2 are, respectively, 28 and 42 times higher than the corresponding K_a(80°C) values.

It should be noted that the equilibrium constant obtained experimentally was expressed as a function of mole fractions by Eqs. (4) and (5). Actually, the thermodynamic equilibrium constant, which depends only on the temperature and is defined by Eq. (6), must be expressed on the basis of liquid-phase activities by the equation:

$$K_a(T) = \frac{X_{MBA}^e \gamma_{MBA}}{X_{H_2O}^e X_A^e \gamma_{H_2O} \gamma_A} = K K_\gamma \quad (8)$$

where the activity of a component i is related to its mole fraction by the activity coefficient γ_i by the equation:

$$a_i = X_i \gamma_i. \quad (9)$$

Since it is particularly difficult to obtain a

TABLE 2

Thermodynamic Data for Liquid-Phase Hydration and Isomerization of Isopentenes

	ΔH_f^o (kJ/mol)	S^o (J/K · mol)	ΔH^o (kJ/mol)	ΔS^o (J/K · mol)	K_a(80°C)
Water	−285.83[a]	69.91[a]			
2-Methyl-2-butanol	−379.32[b]	229.28[b]			
2-Methyl-1-butene (A1)	−60.96[c]	254.0[c]	−32.53	−94.63	0.743
2-Methyl-2butene (A2)	−68.07[c]	252.1[c]	−25.42	−92.73	0.083
A1 ⇌ A2			−7.11	−1.9	8.97

[a] Ref. (9).
[b] Ref. (10).
[c] Ref. (11).

TABLE 3

Equilibrium Constant Computation by the
UNIFAC Method

θ (°C)	γ_{H_2O}	γ_{AI}	γ_{A2}	γ_{MBA}	K_{u1}	K_{u2}	K_{uI}
2-Methyl-1-butene							
60	3.483	3.246	3.329	1.504	4.39	0.741	5.93
72.7	3.219	3.345	3.446	1.478	3.86	0.486	7.93
80.2	3.205	3.306	3.414	1.473	2.90	0.465	6.22
86.3	3.285	3.169	3.279	1.445	3.05	0.354	8.62
93.5	3.170	3.220	3.342	1.448	1.45	0.232	6.25
102.6	3.172	3.128	3.252	1.420	1.97	0.312	6.32
2-Methyl-2-butene							
60.2	3.266	3.410	3.500	1.505	5.62	0.593	9.46
69.9	3.295	3.299	3.397	1.479	3.43	0.441	8.01
76.6	3.323	3.225	3.328	1.467	3.31	0.366	9.05
88.6	3.283	3.146	3.259	1.438	1.66	0.246	6.73

single liquid phase in acetone with water and hydrocarbons, these components can be expected to form very non-ideal solutions. Consequently, the differences observed must be related to the activity coefficients of the components in the mixture.

Activity coefficient and K_γ computation by the UNIFAC method. Such differences between experimental and thermodynamic equilibrium constants were also found for the liquid-phase hydration of isobutene in various solvents (*7, 8*). We were able to explain these differences in such cases by introducing K_γ values calculated by the UNIFAC method. This method is based on the contribution of groups to molecular interactions in nonelectrolytic liquid mixtures. It can be used to determine the activity coefficient of the component of a mixture as a function of the mixture composition and temperature (*12, 13*). Activity coefficients were calculated using a computer program by introducing the temperature and molar fraction of each component, i.e., acetone, water, MBA, and isopentenes (Table 3). The activity coefficients are particularly high for water and isopentenes, and consequently $K_\gamma = 0.13$ for isopentene hydration is small, as found in various other cases (*7, 8, 14*).

These K_γ values were used to calculate the K_{u1}, K_{u2}, and K_{uI} equilibrium constants by equations such as

$$K_{uI} = K_{\gamma I}K_I. \tag{10}$$

The K_u values given in Table 3 should have been the same as the K_a thermodynamic values, as was found for isobutene hydration (*7, 8*). As a matter of fact, the experimental equilibrium constants were strongly decreased by applying the activity coefficient correction. However, their values are still higher than those of K_a. Indeed, at 80°C K_{u1} and K_{u2} are, respectively, 3.9 and 5.6 times higher than the corresponding K_a values. This disagreement may be due to some uncertainty in thermochemical data for isopentenes or MBA. The lack of agreement may also be attributed to the fact that equilibrium between the alcohol and the two isopentenes is difficult to attain. Isomerization occurs in some cases to the detriment of the alcohol formed because a maximum appears in the formation of alcohol. A constant determined with the mole fractions obtained at this maximum would thus have a higher value than expected.

Kinetic Analysis

Kinetic model. Macroreticular sulfonic resins such as Amberlyst 15 adsorb polar compounds, in particular water, in preference to hydrocarbons. In the presence of a mixed solvent like water–acetone, and because the water/isopentenes mole ratio is high, equal to 5, the reaction is considered to occur almost homogeneously (*15*) inside the resin, with water always being in excess in relation to the olefin. If we thus consider that the reaction between isopentenes and 2-methyl-2-butanol is in equilibrium, with a degeneration in reaction order with respect to water and assuming a first order with respect to these reagents, the equation for the rate of MBA formation is given by the equation:

$$v = \vec{k}C_{iC_5} - \overleftarrow{k}C_{MBA}. \tag{11}$$

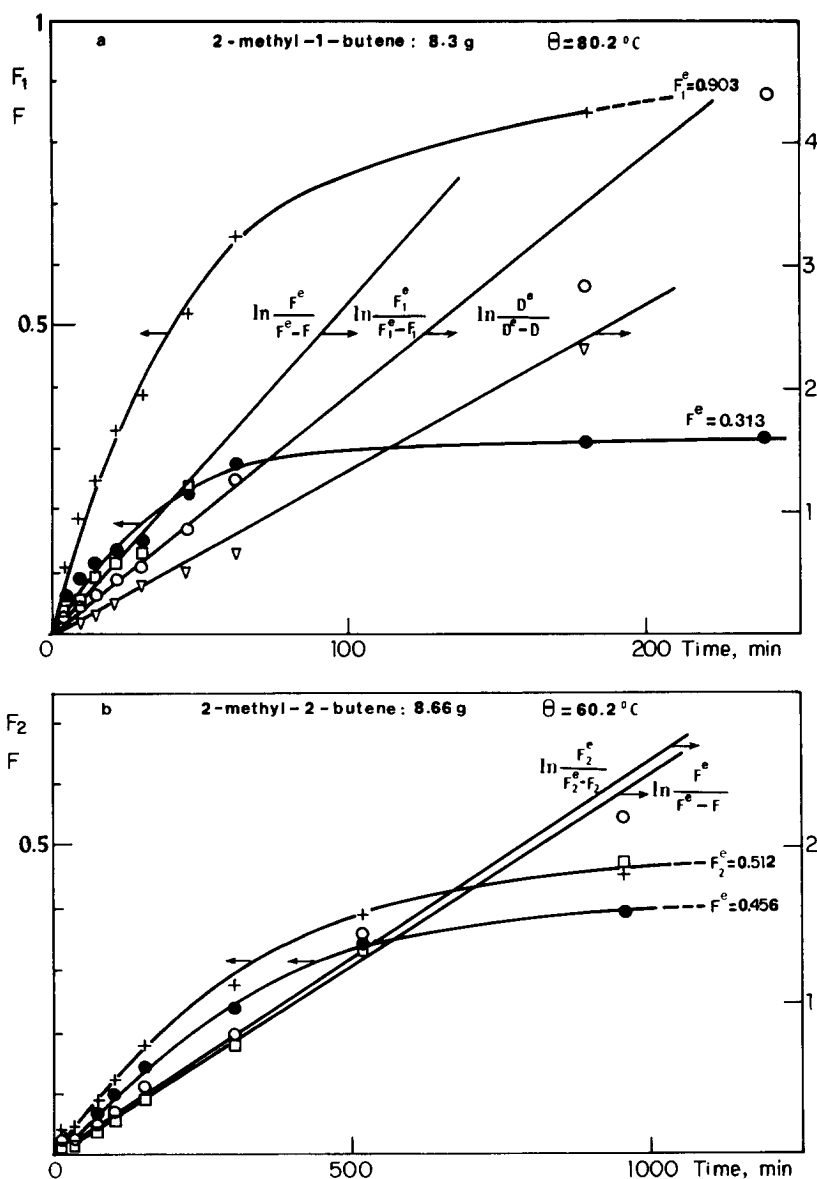The integrated form of this rate equation,

FIG. 3. Conversion variation with time and control of rate equation (acetone 120.8 g, 2,3-DMB 10.1 g, H_2O 11.5 g).

enabling the disappearance rate constant of the both isopentenes together to be obtained, $\vec{k}_{A+I}$ is given by the equation:

$$\ln \frac{F^e}{F^e - F} = \frac{\vec{k}_{A+I}}{F^e} \, t. \qquad (12)$$

$\vec{k}$, which is a first-order kinetic constant, is expressed as the inverse of time, but for taking into account the influence of the catalyst and the effect of the relative amount of reactant to catalyst, it is expressed in $min^{-1} \cdot mol$ isopentene/eq H^+.

The results given in Figs. 3a and b show that, starting with 2-methyl-1-butene or 2-methyl-2-butene, this equation is valid up to nearly 90% of the progress of the reaction, and so the assumptions made are borne out. The values of the rate constants

that can be calculated from the straight lines obtained are, respectively, equal to 5.31 and 0.72 × 10^{-2} min^{-1} · mol/eq H$^+$.

Since the disappearance of the olefin used and the formation of its isomer can also be followed at the same time, two other constants are defined, respectively, $\vec{k}_A$ and $\vec{k}_I$, which are obtained to a first approximation by the equations:

$$ln \frac{F_i^e}{F_i^e - F_i} = \frac{\vec{k}_A}{F_i^e} t$$

$$(i = 1 \text{ or } 2 \text{ for A1 or A2}) \quad (13)$$

$$ln \frac{D^e}{D^e - D} = \frac{\vec{k}_I}{D^e} t. \quad (14)$$

The good linearity also obtained in the graphic representations (Figs. 3a and b) shows that these simplified assumptions are valid for obtaining rate constants that are representative of both the disappearance of the olefin and the isomerization. For example, when 2-methyl-1-butene is the reactant, the rate constant for olefin disappearance $\vec{k}_A$, equal to 10.8 × 10^{-2} min^{-1} · mol/eq H$^+$, is 2.03 times higher than the disappearance constant of both isopentenes $\vec{k}_{A+I}$ = 5.31 × 10^{-2} min^{-1} · mol/eq H$^+$, whereas the rate constant for isomer formation, equal to 8.58 × 10^{-2} min^{-1} · mol/eq H$^+$, is of the same order of magnitude, although slightly lower than the constant of olefin disappearance.

Influence of temperature. Several experiments were performed at different temperatures in acetone and in the presence of 4 g of Amberlyst 15 (i.e., 0.01924 eq H$^+$). Excess water is always present because the initial water/isopentene mole ratio Y is equal to 5.2.

The activation energies for olefin disappearance E_A, for alcohol formation E_{A+I}, and for isomerization E_I were determined by plotting ln k as a function of $1/T$ using the slope $-E/R$ of the straight line obtained by the least-squares method. The values are given in Table 4. E_A is higher than E_{A+I}, probably because the activation energy for

TABLE 4

Kinetic Constants[a] and Activation Energies[b]

Solvent: acetone					
Amberlyst 15 = 4 g $p_{H_2O}^0$ = 7.58% Y = 5.19					
m_T = 151.6 g $p_{iC_5}^0$ = 5.64%					
θ (°C)	100 F^e	100 F_i^e	10^2 $\vec{k}_{A+I}$	10^2 $\vec{k}_A$	10^2 $\vec{k}_I$
2-Methyl-1-butene		E_{A+I} = 73.1	E_A = 82.8	E_I = 89.7	
60	41.2	91.3	1.29	2.55	2.29
72.7	40.6	92.7	4.83	5.8	2.87
80.2	31.3	90.3	5.31	10.8	8.58
86.3	31.8	92.6	6.35	28.4	19.2
93.5	20.5	88.5	11.2	29.6	34.7
102.6	23.7	86.2	37.2	71.3	64.9
2-Methyl-2-butene		E_{A+I} = 84.4	E_A = 90.3	
60.2	45.6	51.2	0.72	0.83	
69.9	41.3	47.4	1.89	1.85	
76.6	34.0	40.4	2.54	2.84	
88.6	30.0	39.0	8.71	11.1	

Note. m_T, total mass of mixture; $p_{H_2O}^0$ or $p_{iC_5}^0$, initial weight percentage of water or isopentenes.

[a] Kinetic constants in min^{-1} × $\frac{\text{moles iC}_5}{\text{eq. H}^+}$.

[b] Activation energies in kJ/mol.

isomerization, equal to 89.7 kJ/mol, is relatively high. Actually, the values obtained with 2-methyl-1-butene are composite, and the most representative value of the activation energy for hydration is the one obtained starting from 2-methyl-2-butene since isomerization is less in this case, i.e.,

$$E_{A+I} = 84.4 \text{ kJ/mol.}$$

This value is almost equal to the one obtained for isobutene hydration in acetone $(E = 84 \text{ kJ/mol})$ (7).

DISCUSSION

The results in Table 4 show that the rate constants for the disappearance of 2-methyl-1-butene are greater than those for isomerization. Indeed, the isomer and alcohol are formed in parallel, as shown in Fig. 1. Figure 1c also shows that, starting from 2-methyl-1-butene at higher temperatures, a maximum is observed in alcohol formation, and beyond this 2-methyl-2-butene is formed from the alcohol.

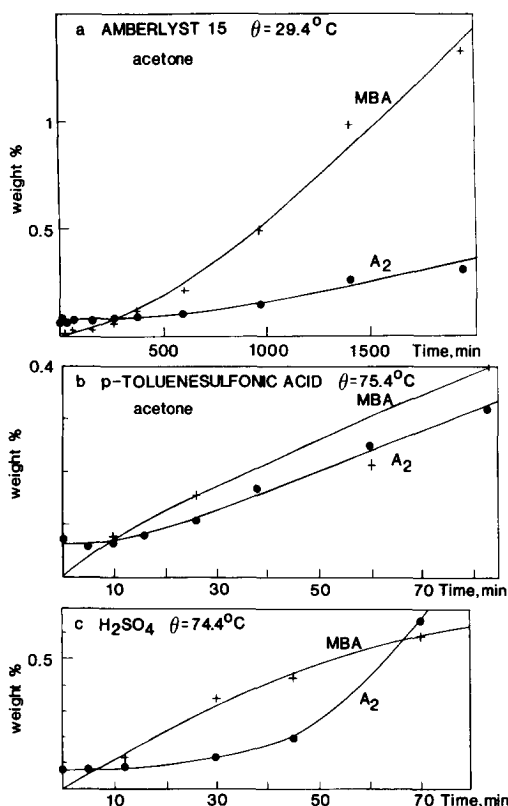Experiments carried out specially at low temperature and with a high ratio of water
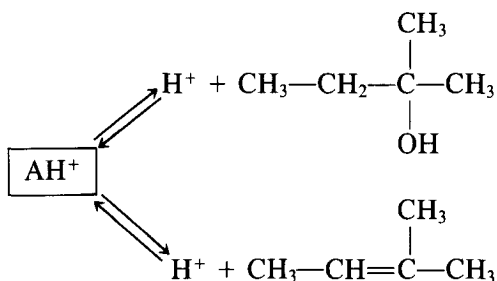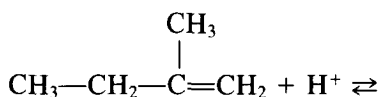
FIG. 4. Initial appearance of olefin isomer during hydration of 2-methyl-1-butene with three different catalysts, (a) Amberlyst 15, (b) p-toluenesulfonic acid, (c) H_2SO_4.

Levy *et al.* (*16*) based their conclusions on the fact that there is no isomerization of 2-methyl-1-butene into 2-methyl-2-butene to reject the hypothesis of going via a free carbonium ion according to a fast and not very advanced equilibrium. According to this mechanism, isopentenes should be at thermodynamic equilibrium very quickly before being hydrated. In our research and under different operating conditions, isomerization occurs, but the isopentenes should at all times be in thermodynamic equilibrium if the 2-methyl-1-butene is in fast equilibrium with a free carbonium ion.

Other research projects (*17–19*) on the hydration of olefins catalyzed by acids have reached the conclusion that the rate determining step is the proton transfer on the double bond of the olefin. Therefore, we suggest that the hydration and isomerization of methylbutenes occur according to a triangular mechanism by reversible reactions going via a protonated intermediary state as indicated by the mechanism:

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3-CH_2-C{=}CH_2 + H^+ \rightleftarrows
\end{array}
$$

to 2-methyl-1-butene ($Y = 23$) show that, during the initial period, the rate at which 2-methyl-2-butene appears increases with alcohol formation (Fig. 4a). The same induction period in the formation of the isomer also appears with *p*-toluenesulfonic acid (APTS) (Fig. 4b) or with the sulfuric acid (Fig. 4c) used as a catalyst in place of Amberlyst 15. Therefore, the isomer seems to be formed directly from the olefin as well as from alcohol.

These findings as a whole show that all the reactions are reversible according to a triangular mechanism, and, since they are catalyzed by the proton, it can be assumed that they occur via a protonated intermediate. In research performed in a dilute medium in aqueous solutions of sulfuric acid,

Comparison of the reactivity of olefins and sulfonic resin to other catalysts. Table 5 give various significant results interpolated at 75°C, as obtained with isopentenes and for comparison with isobutene (*7*), using sulfonic resin, *p*-toluenesulfonic acid, or sulfuric acid as a catalyst. In the latter case, the experiment was performed with two liquid phases and without acetone (*7*).

TABLE 5

Comparison of Olefins and Catalysts Activities

Catalyst	Solvent: acetone $\theta = 75°C$		$10^2 \bar{k}_{A+I}{}^a$	$10^2 \bar{k}_A{}^a$
	eq. H$^+$	Isoolefin		
Amberlyst 15	0.0192	Isobutene	19.08	19.08
Amberlyst 15	0.0192	2-Methyl-1-butene	4.13	8.27
Amberlyst 15	0.0192	2-Methyl-2-butene	2.62	3.02
APTS	0.0192	Isobutene	0.757	0.757
APTS	0.0192	2-Methyl-1-butene	0.77	1.086
APTS	0.0958	2-Methyl-1-butene	1.44	5.36
H$_2$SO$_4$[b]	0.105	2-Methyl-1-butene	0.092	0.0785

^{a} In min^{-1} $\times \dfrac{\text{moles olefins}}{\text{eq. H}^+}$.

^{b} Two liquid phases without solvent.

By comparison of the rate constants for olefin disappearance, isobutene is 2.3 times more reactive than 2-methyl-1-butene which in turn is 2.7 times more reactive than 2-methyl-2-butene when the catalyst is sulfonic resin, whereas in the homogeneous phase, by using p-toluenesulfonic acid as the catalyst, isobutene is 0.6 times less reactive than 2-methyl-1-butene. This last result is in agreement with what was found in the homogeneous phase in sulfuric acid (*17*). The greater reactivity of isobutene can be attributed to a higher stationary concentration inside the resin grain for isobutene than for isopentenes.

The results in Table 5 show, furthermore, that the use of acetone as the solvent leads to disappearance rates of 2-methyl-1-butene greater than the one obtained with H$_2$SO$_4$ as the catalyst. Likewise, a comparison between sulfonic resin and p-toluenesulfonic acid, which sites identical to those of the resin, shows that, for the same equivalent proton number, the sulfonic resin is 7.6 times more active than p-toluenesulfonic acid for the hydration of 2-methyl-1-butene and that it is 25 times more active in the case of isobutene. The greater activity of the sulfonic resin, which must be due to the fact that the sulfonic groups are locally concentrated, nevertheless depends on the nature of the olefin.

CONCLUSION

Amberlyst 15 resin proves to be a good hydration catalyst for isopentenes because its activity is greater than that of p-toluenesulfonic acid or sulfuric acid. Likewise, it can be used in a fixed bed, especially when a solvent such as acetone is employed to make water and isopentenes miscible. The reaction enthalpy and the activation energy of hydration were determined from variations in the temperature of the equilibrium constants and the rate constants. The relative activities of the two isopentenes were determined at different temperatures and compared to those of isobutene.

The experimental equilibrium constants were compared to the ones calculated from thermochemical data found in the literature. The deviations obtained, which cannot be explained solely by the activity coefficients determined by the UNIFAC method (as in the case of isobutene), suggest that the MBA/isopentene mole ratios found experimentally are higher than expected. This is supported by the fact that the isomerization of the double bond occurs partly as the result of alcohol formation.

NOMENCLATURE

A1, A2   2-methyl-1-butene, 2-methyl-2-butene

A + I   isopentene and its isomer formed during the reaction

a_i liquid-phase activity of i

c_i concentration of i at time t

γ_i activity coefficient of i in liquid phase

D   isomer produced with respect to the amount at equilibrium (D^e)

ΔG_T° free energy variation

$\Delta H_{1\,or\,2}$ enthalpy variation of isopentene hydration

ΔH_I enthalpy variation of isomerization

ΔH_f° standard heat of formation

ΔS° entropy variation

E_I activation energy of the isomerization

E_A activation energy of the disappearance of the olefin

E_{A+I} activation energy of the alcohol formation

F, F^e conversion rate of the both olefins at time t and at equilibrium

F_1, F_1^e conversion rate of 2-methyl-1-butene

F_2, F_2^e conversion rate of 2-methyl-2-butene

iC_5 isopentenes

I isomer

K experimental equilibrium constants in mole fraction

$K_a(T)$ thermodynamic equilibrium constants

K_γ ratio of activity coefficients

K_u equilibrium constants computed by the UNIFAC method

$\vec{k}_{A+I}$ direct rate constants of the alcohol formation

$\vec{k}_A$ direct rate constants of the olefin disappearance

$\vec{k}_I$ direct rate constants of isomerization of 2-methyl-1-butene

m_T total mass of the reaction mixture

p_i^0, p_i^e initial and at equilibrium weight percentage of i

R gas constant

S° entropy

T temperature, Kelvin

θ temperature, degree Celsius

X_i^e mole fraction of i at equilibrium

Y initial H_2O/iC_5 molar ratio

Z initial molar ratio of inerts (acetone + dimethylbutane) to isopentenes

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