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Kinetics of Diacetone Alcohol Conversion to Mesityl Oxide Catalyzed by Ion Exchange Resin

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The liquid phase formation of mesityl oxide from diacetone alcohol was studied. This involves a system of three parallel reactions. Differential reactor data was used to obtain kinetic equations of the Langmuir-Hinshelwood type by means of nonlinear regressions. Calculated conversions from these kinetic equations fitted integral reactor data very well.

INTRODUCTION

The use of ion exchange resins as catalysts has increased significantly in recent years. This is mainly due to the high activity and selectivity which is usually shown by this material. Many reviews have been published on this subject (*1–5*) as well as annual reports (*6, 7*).

Other advantage of the use of ion exchange resins as catalysts is related to those consecutive reactions which alternatively need an acid and a basic medium in its different steps to obtain the final product. With the conventional homogeneous catalysis, more than one reactor would be necessary; while by using a mixed bed of acid and basic resin, only one reactor could be set up (*8*). This would be a good way of obtaining mesityl oxide from acetone since the first step would be the reaction of acetone to diacetone alcohol, which is catalyzed by a basic catalyst, and the second step would be the reaction of diacetone alcohol to mesityl oxide, which is catalyzed by an acid catalyst.

There are many studies regarding the first reaction and its reverse (*9*); on the contrary the second step has been very scarcely studied. A review on this matter has been done elsewhere (*10*). The only reference on a kinetic study of the formation of mesityl oxide is that of Klein (*11*) who used acetone as reactant and the acid form of "Dowex-50" microporous exchange resin as a catalyst.

However, the introduction of the macroporous ion exchange resins has led to a significant increase of the application of these resins as catalysts since they show a greater accessibility to their internal active sites and, specially for big molecules in nonpolar solvents, a higher adsorption rate.

We have studied here the liquid phase dehydration of diacetone alcohol catalyzed by a macroporous ion exchange resin, analyzing the influence of composition and temperature on reaction rate. The main reaction is accompanied by secondary reactions which were also studied.

NOMENCLATURE

a_1, a_2	parameters in Eq. (7)
E	apparent activation energy (kcal/g-mole)
F	molar flow (g-mole/hr)
j	number of components in multicomponent mixture
k	reaction rate constant per g-eq of H^+
K	equilibrium constant
K_i	adsorption equilibrium constant of component i
M	parameter defined in Eq. (6)

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m	mass (g)
n	number of moles (g-mole) or equivalents (g-eq)
P	mass percentage
PM	molecular weight (g/g-mole)
r	reaction rate (g-mole/min g-eq H^+)
S	sum of squares of errors
s	standard error of coefficients
t	time (min)
t_c	ratio between acid g-equivalents of resin and molar flow (min g-eq H^+/g-mole)
T	temperature (°C)
x	conversion
y	molar fraction

Suffixes

A	acetone
c	resin
D	diacetone alcohol
F	phorone
i	general component
m	sample
M	mesityl oxide
0	initial
W	water
1, 2, 3	first, second, and third reaction, respectively

EXPERIMENTAL PART

Equipment

The study was mainly done in a plug flow differential reactor; some tests were also performed in a plug flow integral reactor. A schematic representation of the equipment is given in Fig. 1. The reaction mixture (diacetone alcohol and water or acetone or mesityl oxide) was fed from flask (A), whose air admission tube (B) contained anhydrous sodium carbonate to prevent water contamination. The reaction mixture flowed through stopcock (C) and flow controller (D) (a 1-mm i.d. and 30-cm length tube with a sliding stainless steel wire inside); then to the manometric flowmeter (E); and finally to the reactor unit (G). The reactor unit was preceded by the preheating coil (F) and a 15-cm length packed bed of 3-mm diameter glass beads. Furthermore, (I) indicates the 0.1°C thermometer, (J) the stirrer, (K) the heating electrical resistances and (L) the thermoregulator.

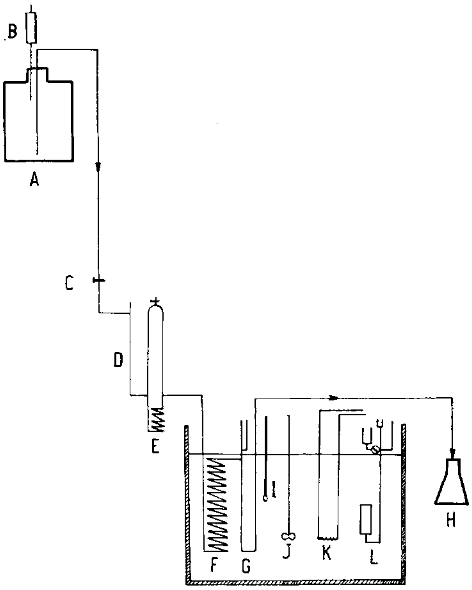


FIG. 1. Schematic flow diagram.

The mixture flowing from the reactor exit was recovered in an erlenmeyer (H) inmersed in a bath at 0°C.

The reactor consisted in a U-tube 10-mm inside diameter containing the catalyst bed diluted with glass beads of the same size of the resin. The bed was supported by glass wool and over it there was other bed of glass beads used to develop the descending liquid flow. The reactor had two openings, one to introduce a thermocouple (used only in exploratory runs), and the other to replace the catalyst. To obtain an integral reactor, a second resin bed was added in the same reactor.

The reactor and the preheating section were in turn inmersed in a liquid Vaseline thermostatic bath electrically heated with an accuracy of 0.1°C.

A more detailed description of the equipment can be found elsewhere (*10*).

Sample Analysis

The samples were analyzed by a vapor phase chromatograph. The operating conditions for the different components were the following:

1. Acetone and mesityl oxide were ana-

lyzed with thermistor detector, a 2-m length column packed with Carbowax 400 over silanized Chromosorb W at 105°C, using hydrogen as carrier at a flow rate of 40 ml/min. Sample volumes of injection were 3–8 μl.

2. Diacetone alcohol was analyzed with an ionization flame detector, a 2-m length column packed with Carbowax 1500 over 3% Teflon, at 70°C, using nitrogen as carrier at a flow rate of 30 ml/min. Sample volumes of injection were 0.05–0.1 μl.

3. Water was analyzed with a thermistor detector, a 1-m length column packed with Porapak Q, at 120°C, using hydrogen as carrier at a flow rate of 40 ml/min. Sample volumes of injection were 0.5–2 μl.

Catalyst and Reagents

The catalyst was the macroporous ion exchange resin Amberlite IR-200 (from Rohm & Haas). As it is provided in its sodium form it was acidified in the conventional way and stored at constant moisture. It was screened and the fraction 0.149–0.177-mm diameter was used in the catalyst bed. Ion exchange capacity was measured to be 4.8 meq-g of H^+/g of dried resin. Every time the catalyst bed was replaced the water content of the new one was measured.

The reactants used were the following:

1. Diacetone alcohol ("Technical Grade" from Sintorgan), which was purified twice by vacuum rectification.
2. Acetone ("Pure" from Sintorgan).
3. Mesityl oxide (from Matheson, Coleman & Bell).
4. Distilled water.

Impurities were determined by chromatographic analysis. They were less than 1%.

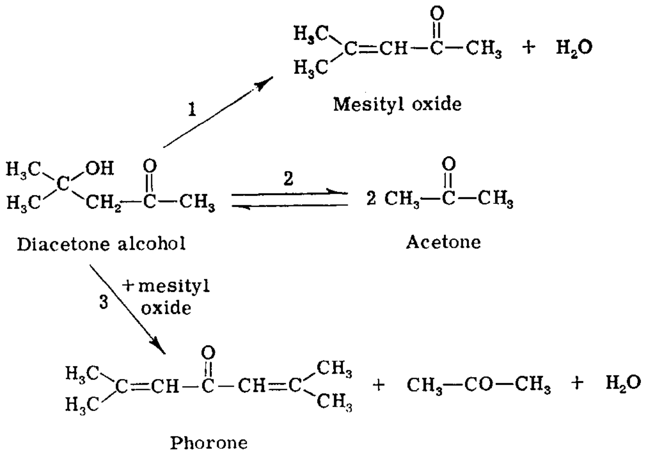
Exploratory Runs

Blank runs in the differential reactor without catalyst showed no conversion. On the other hand, runs of up to 0.10 conversion of mesityl oxide at 80°C with the diluted catalyst bed showed no temperature difference between reaction mixture in the catalyst bed and Vaseline in the thermostatic bath. It is to be observed that in the runs used for calculations, conversion was always lower.

Steady state was observed to be reached in a lapse which is three times the time necessary for the reaction mixture to flow from the reactor inlet to the sampling device with a minimum of 30 min.

When feeding diacetone alcohol, it was observed that the activity of the catalyst began to decrease after 2 weeks, showing at the same time a darkening. This can be due to phorone and other products of the further condensation of mesityl oxide, which would remain inside the resin giving a further polimerization. By extracting successively with ethyl ether, ethanol and water, the resin recovered practically its original capacity, but the darkening remained.

In a previous study (*11*) it was observed, that no acetone was formed from diacetone alcohol. On the contrary, we observed



acetone was obtained in the differential reactor when feeding diacetone alcohol but not when feeding mesityl oxide. This implies a modification in the scheme of reactions to be studied and led us to perform runs in an integral reactor in order to check the proposed scheme.

Reaction System and Variables Range

According to what was previously stated, let us propose the reaction system shown at the bottom of page 83; which can be schematically represented as follows:

$$\mathrm{D} = \mathrm{M} + \mathrm{W}, \qquad (1)$$

$$\mathrm{D} = 2\mathrm{A}, \qquad (2)$$

$$\mathrm{D} + \mathrm{M} = \mathrm{F} + \mathrm{A} + \mathrm{W}. \qquad (3)$$

We will discuss this scheme later on; however, let us mention for the moment that the first reaction is supported on the fact that conversion to mesityl oxide and water were always equal, within the experimental error. The second reaction was proposed because of the results of the exploratory runs. The third reaction had been observed already by Klein (*11*) and also by us in the exploratory runs. The production of heavier substances due to a further condensation of mesityl oxide are involved in the third reaction, which should then be regarded as an "overall reaction." The reversibility of the first reaction was considered by using the equilibrium constant reported in the literature (*11*).

The variables range is given in Table 1.

TABLE 1
Experimental Range of Variables

y_D	0.186–0.988
y_M	0.002–0.690
y_W	0.002–0.502
y_A	10^{-4}–0.801
T(°C)	30–50
m_c (g)	0.173–2.166
F (g-mole/hr)	0.120–4.603

The number of runs used in calculations was 193.

Calculations

The reaction rate of component i in the differential reactor can be calculated through,

$$r_i = \frac{\Delta n_i}{n_c \Delta t}, \qquad (4)$$

where Δn_i is the number of moles of component i which were obtained in the run and which were measured by the chromatographic analysis; n_c is the number of gram-equivalents of H^+ of the resin; and Δt is the time of sample recovery.

It is then observed that the main experimental error arises from chemical analysis (±5%) others being less than 0.5%. The error in the reaction rate calculation is then less than 10%.

The conversion of component i in the integral reactor was calculated as follows

$$x_i = \frac{\Delta n_i}{m_m} \frac{100}{M} \left(\frac{\text{g-mole of i}}{\text{total g-mole}} \right) \qquad (5)$$

where m_m is the sample mass and

$$M = \sum_{i=1}^{j} \left(P_{i_0}/(PM)_i \right) \qquad (6)$$

Conversion was calculated as a function of the "residence time" t_c. This relationship was represented by the polynomial

$$x_i = a_1 t_c^{0.5} + a_2 t_c^{0.2}, \qquad (7)$$

whose analytic differentiation led to the rate of formation of i, dx_i/dt_c. The error in this case may be higher than in the differential reactor; nevertheless, the $x_i(t_c)$ function was represented with an error less than 5%.

Gradients of composition in the external liquid boundary layer as well as inside the catalyst particle were determined to be negligible, in the latter case by using reaction rate expressions of the Langmuir-Hinshelwood type (*12, 13*).

Temperature gradients inside the resin bead were determined to be negligible too by applying Anderson's criterion (*14*).

On the other hand, the plug flow model was verified for conversions up to 0.40 (*15, 16*).

The equilibrium constant used for the first reaction was that reported by Klein (*11*):

$$K_1 = 1.70 \times 10^4 \exp(-3{,}247/T) \qquad (8)$$

Some of the results obtained are sum-

TABLE 2

Experimental Data

T (°C)	n_c (mg eq)	y_D	y_M	y_W	y_A	r_W (g-mole/hr g-eq)		r_A (g-mole/hr g-eq)	
						Expt	Calc	Expt	Calc
30	2.257	0.911	0.0067	0.080	0.0017	0.0340	0.0356	0.00584	0.00491
30	4.180	0.573	0.406	0.0190	0.0018	0.0204	0.0185	—	—
30	1.822	0.510	0.0075	0.0066	0.476	0.0526	0.0541	—	—
30	4.174	0.934	0.050	0.0117	0.0047	0.0431	0.0394	0.0156	0.0144
30	4.174	0.899	0.066	0.0288	0.0060	—	—	0.0101	0.0100
35	1.151	0.972	0.0142	0.0116	0.0027	0.123	0.116	0.0286	0.0298
35	1.822	0.439	0.0052	0.0049	0.551	0.0868	0.0869	—	—
35	2.257	0.908	0.0084	0.082	0.0018	0.0673	0.0682	0.00860	0.00632
35	4.174	0.883	0.073	0.0357	0.0080	0.0619	0.0600	0.0131	0.0141
35	4.019	0.564	0.411	0.0210	0.0042	—	—	0.0127	0.0119
40	0.939	0.980	0.0103	0.0077	0.0020	0.190	0.197	0.0506	0.0494
40	1.822	0.506	0.0095	0.0087	0.476	0.177	0.165	—	—
40	2.257	0.905	0.0096	0.083	0.0023	0.119	0.117	0.0210	0.0200
40	4.174	0.891	0.066	0.0339	0.0088	0.116	0.123	0.0338	0.0316
40	4.180	0.303	0.688	0.0066	0.0020	0.0376	0.0427	0.00940	0.0108
45	0.939	0.974	0.0129	0.0103	0.0029	0.315	0.310	0.0874	0.0849
45	1.830	0.374	0.0077	0.0071	0.611	0.212	0.220	—	—
45	2.257	0.495	0.0025	0.502	0.0002	0.0251	0.0223	0.00304	0.00264
45	4.180	0.299	0.690	0.0084	0.0030	0.0622	0.0669	0.0210	0.0250
45	4.174	0.871	0.078	0.0402	0.0111	0.173	0.169	0.0464	0.0438
50	1.822	0.501	0.0114	0.0105	0.477	0.387	0.367	—	—
50	0.833	0.977	0.0105	0.0092	0.0032	0.425	0.423	0.140	0.139
50	2.257	0.741	0.0150	0.239	0.0046	0.126	0.125	0.0214	0.0200
50	4.180	0.300	0.689	0.0078	0.0034	0.0788	0.0808	0.0352	0.0400
50	4.174	0.839	0.092	0.055	0.0145	0.248	0.255	0.0628	0.0631

marized in Table 2. The rest of them can be obtained elsewhere (*10*).

Analysis of Results

To establish a reaction scheme, it is necessary first to analyze the conversion–"residence time" curves for the products obtained from pure diacetone alcohol. These results must be obtained in an integral reactor. One of these results is shown in Fig. 2. We observe that the results for the formation of water and mesityl oxide differ very slightly, leading to the assumption that both products correspond to the same reaction (the first one for us). There is a minor tendency, however, for the results for mesityl oxide to give lower conversions than water. This should be interpreted in terms of a systematic error or even well in terms of another reaction, much slower than the first one, which should involve mesityl oxide but no water as a reactant. This possibility must be investigated.

On the other hand, acetone is also produced but at a rate very much slower than water and mesityl oxide. At these conditions, the only source for acetone production could be the diacetone alcohol decomposition (second reaction in our scheme).

To verify the possible existence of the other reaction (the third one) with mesityl oxide as one of its reactants, mixtures of diacetone alcohol and mesityl oxide of different compositions were fed to the differential reactor at different temperatures. Phorone was detected as one of the reaction products, leading us to propose reaction (3). However, phorone can polymerize. Hence, reaction (3) should be regarded as an overall reaction which includes the possibility of formation of higher polymers.

Rates of formation of water and acetone

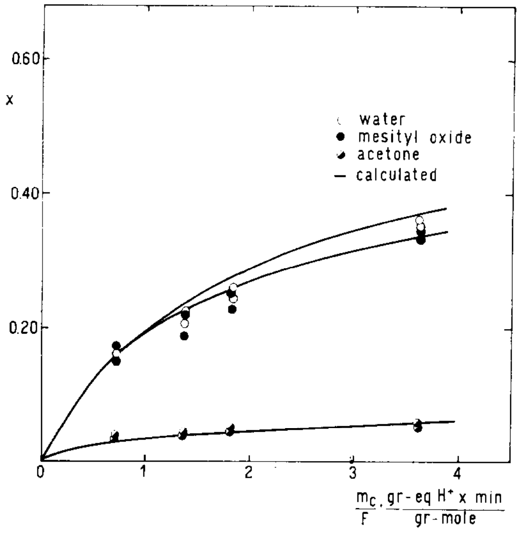


FIG. 2. Integral reactor data.

are strongly depressed by mesityl oxide, specially at low molar fractions of it, indicating mesityl oxide is adsorbed by the resin.

On the other hand, a similar inhibiting effect on rates of formation of acetone and mesityl oxide is observed by water when feeding the differential reactor with mixtures of diacetone alcohol and water at different compositions and temperatures. This inhibiting effect of water has been observed also in other vapor and liquid phase reactions catalyzed by ion exchange resins (*5*, *17–19*).

The influence of the remaining reaction component, acetone, on the rate of formation of water, when feeding the differential reactor with mixtures of diacetone alcohol and acetone at different compositions and temperatures, showed a slight depressing effect. This is explained as due to the lower polarity of acetone compared with the other reaction components.

All these runs were performed at five temperature levels: 30, 35, 40, 45, and 50°C.

So far, and on the evidence of integral reactor results, we have arrived at a hypothetical reaction scheme. In turn, differential reactor results gave us some picture on the mechanism of the proposed reactions.

Our next step should then be to obtain a quantitative interpretation of these differential reactor results by means of kinetic expressions based on some model of the reaction mechanism.

Provided these kinetic expressions were right they must predict the results observed in the integral reactor.

On the other hand the apparent activation energies for the first and second reactions were calculated from the rates of formation of water and acetone at 35, 40, 45, and 50°C, when feeding the differential reactor with pure diacetone alcohol. The values obtained were $E_1 = 17.3$ and $E_2 = 20.3$ kcal/g-mole. Furthermore, activation energies for the homogeneous reactions were reported to be $E_1 = 20.4$ kcal/g-mole for nitric and perchloric acids as catalysts (*20*), and $E_2 = 19.1$ kcal/g-mole (*21*) and $E_2 = 18.0$ (*22*) for sodium hydroxide as catalyst. This should show no diffusional falsification of activation energies in our results.

KINETIC INTERPRETATION OF RESULTS

The models of the reaction mechanisms, which were applied to interpret the reaction results were:

1. The Langmuir-Hinshelwood for the first and second reactions.
2. A phenomenological rate expression of the type of a potential law for the third reaction.

All the possible mechanisms for the first and second reactions were postulated. Firstly, a multiple linear regression was performed on the rates of formation of water and acetone. On the basis of these results, the most probable kinetic expressions were selected. Secondly, a nonlinear regression following the method proposed by Marquardt (*23*, *24*) was made on the most probable kinetic expressions arising from the linear regression. Computation were done in a digital computer IBM/360.

It is necessary to point out that, when proposing different Langmuir-Hinshelwood mechanisms, the reaction involving two active sites was included. In this mechanism, we have neglected the possibility of diffusion of intermediates between sites since distance between two adjacent sites appears to be of the order of 1.2 Å. This value comes from the assumption that all

TABLE 3

MECHANISMS SELECTED FROM LINEAR REGRESSION FOR FIRST REACTION (D = M + W)

Case	Controlling step	Kinetic expression
1	$Ds + s = Ms + Ws$	$r_1 = \dfrac{k_1K_D(y_D - y_My_W/K_1)}{(1 + K_Dy_D + K_My_M + K_Wy_W + K_Ay_A)^2}$
2	$(Ds + s = Ms + Ws)$ $Ms = M + s$	$r_1 = \dfrac{k_MK_1(y_D/y_W - y_M/K_1)}{1 + K_Dy_D + K_Wy_W + K_1K_My_D/y_W + K_Ay_A}$
3	$2(D/2)s = Ms + Ws$	$r_1 = \dfrac{k_1K_D(y_D - y_My_W/K_1)}{(1 + (K_Dy_D)^{0.5} + K_My_M + K_Wy_W + K_Ay_A)^2}$

the sites are accessible to reactants and uniformly distributed.

First and Third Reactions

The rate of formation of water is given by,

$$r_W = \frac{1}{n_c}\frac{dn_W}{dt} = r_1 + k_3y_Dy_M. \qquad (9)$$

For the first reaction, 26 mechanisms were formulated, from which 16 kinetic expressions arose (*10*). Two linear regressions were made in order to obtain the numerical value of the parameters of r_1 in the first one and of k_3 in the second one.

Those mechanisms which showed a high scattering in the final results (ratio between the sum of squares of errors of reaction rate and the square of the mean value of reaction rate) and/or a significative negative value in the parameters were neglected. Thus, three mechanisms were selected, as shown in Table 3. It is to be pointed out that the first results showed the adsorption constant of acetone was 10^4 times lower than the other adsorption constants, as could be foreseen from the influence of acetone on reaction rate as compared with the influence of the other reaction components. This fact, how-

TABLE 4

NONLINEAR REGRESSION RESULTS FOR FIRST REACTION (D = M + W)

T(°C)	k_1[a]	s	K_D	s	K_M	s	K_W	s	k_3[a]	s	S
					Case 1						
30	0.270	0.022	1.32	0.24	13.64	3.36	9.26	1.24	0.0645	0.0096	2.28×10^{-4}
35	0.699	0.112	0.467	0.121	8.51	2.70	7.28	1.25	0.0859	0.0296	1.89×10^{-3}
40	0.895	0.031	0.953	0.081	7.25	1.66	7.86	0.99	0.175	0.036	4.14×10^{-3}
45	1.54	0.08	0.733	0.070	7.97	1.40	7.28	0.63	0.290	0.038	4.10×10^{-3}
50	1.85	0.05	1.08	0.08	4.07	1.48	6.73	0.73	0.228	0.129	1.51×10^{-2}
					Case 2						
	k_M										
30	0.0486	0.0423			1.082	1.005			6.70×10^{-9}	0.037	3.84×10^{-3}
35	0.0248	0.0136			0.229	0.146			9.80×10^{-9}	0.081	1.35×10^{-2}
40	0.0234				0.109				1.59×10^{-8}		5.14×10^{-2}
45	0.0327				0.106				8.65×10^{-9}		1.05×10^{-1}
50	0.0870				0.217				1.30×10^{-7}		2.56×10^{-1}
					Case 3						
	k_1[a]		K_D								
30	0.417	0.134	6.25	4.72	32.60	6.85	18.92	3.83	0.0692	0.0105	3.05×10^{-4}
35	0.613	0.235	0.992	0.640	11.63	3.54	9.92	1.93	0.0858	0.0291	1.75×10^{-3}
40	1.14	0.13	6.86	2.20	13.40	3.56	14.59	2.45	0.174	0.039	4.91×10^{-3}
45	1.66	0.24	2.96	0.95	12.53	2.52	11.49	1.39	0.288	0.043	5.01×10^{-3}
50	2.69	0.27	11.70	4.30	6.50	4.18	14.06	2.55	0.132	0.232	2.14×10^{-2}

[a] Units of reaction rate constants are g-mole/min g-eq of H^+.

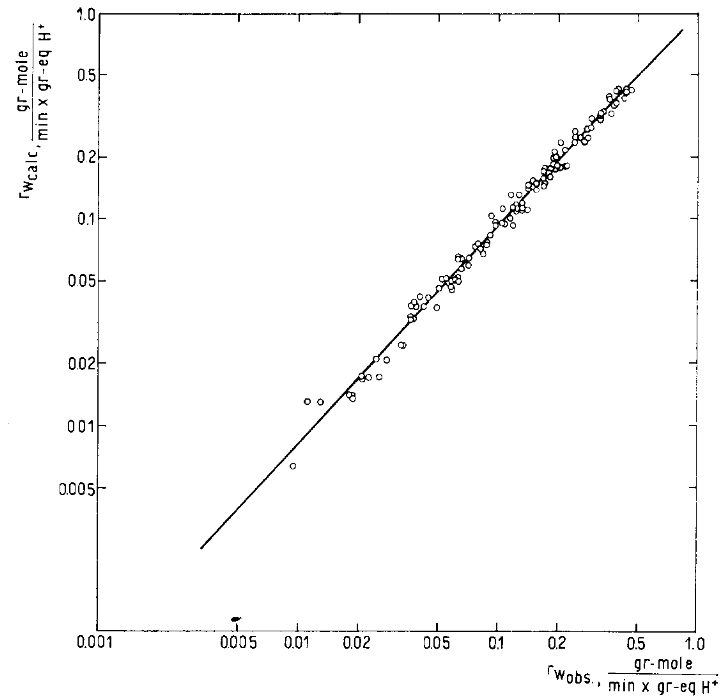


FIG. 3. Calculated vs observed reaction rate for first reaction (D = M + W).

ever, led to a nonconvergence of the nonlinear regression. Hence a value of $K_A = 0$ was taken (*25*).

The results from the nonlinear regression are shown in Table 4 from where it is possible to conclude the most probable mechanism is the first one

$$\frac{1}{n_c}\frac{dn_W}{dt} = \frac{k_1K_D(y_D - y_My_W/K_1)}{(1 + K_Dy_D + K_My_M + K_Wy_W)^2} + k_3y_Dy_M, \quad (10)$$

which corresponds to a surface reaction on a double active site.

In arriving at this conclusion, analysis of the sum of squares of errors, as well as relative error of every parameter in the nonlinear regression, were performed.

The calculated reaction rate is plotted as a function of the observed one in Fig. 3 for all the temperatures. As shown, the fitting of results is quite good.

Second Reaction

The rate of formation of acetone is given by,

$$r_A = \frac{1}{n_c}\frac{dn_A}{dt} = 2r_2 + k_3y_Dy_M. \quad (11)$$

TABLE 5

MECHANISMS SELECTED FROM LINEAR REGRESSION FOR SECOND REACTION (D = 2A)

Case	Controlling step	Kinetic expression
1	Ds = As + A	$r_2 = \frac{k_2K_Dy_D}{1 + K_Dy_D + K_My_M + K_Wy_W + K_Ay_A}$
2	(Ds = As + A) As = A + s	$r_2 = \frac{k_AK_2y_D/y_A}{1 + K_Dy_D + K_My_M + K_Wy_W + K_2K_Ay_D/y_A}$
3	Ds + s = 2As	$r_2 = \frac{k_2K_Dy_D}{(1 + K_Dy_D + K_My_M + K_Wy_W + K_Ay_A)^2}$
4	2(D/2)s = 2As	$r_2 = \frac{k_2K_Dy_D}{(1 + (K_Dy_D)^{0.5} + K_My_M + K_Wy_W + K_Ay_A)^2}$

TABLE 6

NONLINEAR REGRESSION RESULTS FOR SECOND REACTION (D = 2A)[a]

Case 1

T(°C)	k_2[b]	s	K_D	s	K_M	s	K_W	s	k_3[b]	s	S
30	0.0372		0.434		1.25		53.14		7.95×10^{-8}		2.92×10^{-5}
35	0.093	1.58	0.52	13.45	2.72	33.85	141.6	1270	6.45×10^{-3}	0.032	2.14×10^{-4}
40	0.624		0.0484		0.692		19.4		1.0×10^{-9}		7.26×10^{-4}
45	1.28		0.0437		0.350		24.4		8.12×10^{-8}		3.45×10^{-4}
50	1.23	9.71	0.078	0.671	9.42	7.82	22.0	14.9	0.146	0.034	1.58×10^{-3}

Case 2

	k_AK_2	s	K_D	s	K_M	s	K_W	s	K_AK_2	s	k_3[b]	s	
30	0.25	48.2	2.69×10^{-4}	14 200	41 600	7.88×10^{6}	233 300	4.42×10^{7}	21.53	4060	0.0199	0.0671	7.98×10^{-5}
35	0.14	17.1	7.89×10^{-4}	1570	10 200	1.26×10^{6}	89 400	1.10×10^{7}	6.45	792	0.0310	0.0365	3.02×10^{-4}
40	1.04	61.2	7.40×10^{-4}	7020	40 800	2.40×10^{6}	253 000	1.49×10^{7}	39.82	2340	0.0801	0.109	2.26×10^{-3}
45	2.19	111	6.26×10^{-3}	24 400	99 200	5.00×10^{6}	491 400	2.46×10^{7}	34.22	1710	0.139	0.153	2.87×10^{-3}
50	0.75	14.9	1.23×10^{-4}	1040	13 900	2.78×10^{5}	61 500	1.22×10^{6}	8.88	177	0.215	0.134	6.49×10^{-3}

Case 3

	k_2[b]	s	K_D	s	K_M	s	K_W	s	k_3[b]	s	
30	0.0408	0.510	0.783	78.5	1.11	90.5	21.62	1010	1.59×10^{-8}	0.0540	2.80×10^{-5}
35	0.146	3.25	0.243	9.02	0.483	10.7	24.01	181	2.43×10^{-4}	0.385	2.24×10^{-4}
40	0.115	0.925	0.743	40.1	1.28	52.5	13.25	352	1.0×10^{-9}	0.030	6.63×10^{-4}
45	1.22	58.6	0.049	2.62	4.54	14.3	7.64	21.7	0.111	0.020	4.36×10^{-4}
50	3.89	42.5	0.023	0.261	3.69	1.63	6.80	2.19	0.173	0.028	1.37×10^{-3}
						Case 4					
30	0.0650	1.24	16.64	1650	3.61	173	61.93	2490	7.95×10^{-8}	0.048	2.94×10^{-5}
35	0.115	2.50	0.778	3.27	25.60	252	31.47	307	0.0445	0.0121	2.39×10^{-4}
40	0.167	12.0	0.275	6.50	0.554	11.55	9.26	965	1.0×10^{-9}	0.028	6.64×10^{-4}
45	0.223		1.64		10.56		17.22		0.110		4.40×10^{-4}
50	0.814	15.80	0.018	0.399	4.12	6.20	7.56	10.55	0.173	0.028	1.37×10^{-3}

[a] In this table and in Table 4 blank spaces are due to the fact that the covariance matrix has a negative element in the principal diagonal at the point of convergence.

[b] Units of reaction rate constants are g-mole/min g-eq H^+.

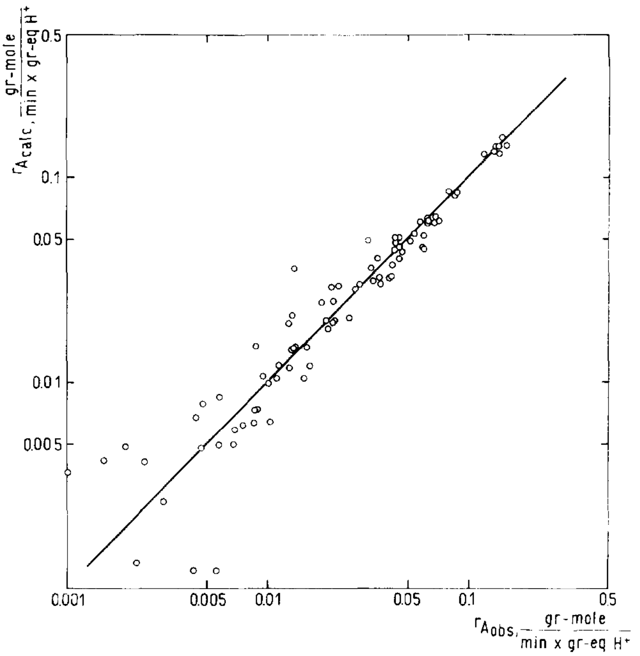


FIG. 4. Calculated vs observed reaction rate for second reaction (D = 2A).

The second reaction was analyzed in a similar way as the first one, but neglecting the influence of the reverse reaction. Eighteen different mechanisms were formulated, from which 14 kinetic expressions arose (*10*). The selection performed on the results from the linear regression left four mechanisms as the most probable (see Table 5). A value of $K_A = 0$ was also assumed here. Table 6 shows that the third mechanism seems to be the most probable:

$$\frac{1}{n_c}\frac{dn_A}{dt} = 2\frac{k_2K_Dy_D}{(1 + K_Dy_D + K_My_M + K_Wy_W)^2} + k_3y_Dy_M, \quad (12)$$

which corresponds to a surface reaction on a double active site.

The calculated reaction rate is plotted as a function of the observed one in Fig. 4. Although the fitting of the results is good, a greater scattering is observed at low reaction rates. However we must point out that, as the nonlinear regression minimizes the difference between calculated and observed reaction rate that difference is magnified for low values if the plot is log–log.

On the other hand, we found the errors of calculation of the parameters are relatively high. This can be due to two sources:

1. As reaction rate was very low experimental errors increased.
2. The lack of an experiment design led to a high covariance among parameters. Another disadvantage was the impossibility

TABLE 7

DATA USED TO PREDICT INTEGRAL REACTOR PERFORMANCE (50°C)

Reaction 1				
$k_1{}^a = 1.77$	$K_D = 1.08$	$K_M = 3.23$	$K_W = 6.41$	$K_1 = 0.745$
Reaction 2				
$k_2{}^a = 0.20$	$K_D = 0.50$	$K_M = 3.72$	$K_W = 6.85$	
Reaction 3				
$k_3{}^a = 0.050$				

[a] Units of reaction rate constants are g-mole/min g-eq H^+.

of measuring reaction rates for binary mixtures of acetone and diacetone alcohol (*26*, *27*).

Prediction of Integral Reactor Performance

The kinetic expressions for the three reactions were integrated numerically assuming plug flow to calculate conversion as a function of residence time for the values of the parameters given in Table 7.

The results are presented as the curves of Fig. 2 showing the agreement with the observed conversions is very good.

CONCLUSIONS

The liquid phase dehydration and decomposition of diacetone alcohol catalyzed by an acid ion exchange resin was studied at five temperature levels (30, 35, 40, 45, and 50°C).

The proposed reaction mechanism involves three reactions linearly independent:

1. Dehydration of diacetone alcohol to mesityl oxide.
2. Decomposition of diacetone alcohol to acetone.
3. Reaction between diacetone alcohol and mesityl oxide to give acetone, water, phorone, and higher products of the condensation of mesityl oxide.

Water and mesityl oxide strongly inhibited reaction rate due to adsorption effects. On the contrary, acetone did not.

Analysis of differential reactor data showed the first two reactions are controlled by a surface reaction on a double site. A potential law rate equation was in turn used for the third reaction.

The proposed reaction scheme was verified, checking calculated and experimental results in an integral reactor.

The macroreticular structure of the catalyst seems to be the reason for which we have observed the second reaction which was undetected in other studies (*11*) on microreticular resins.

On the other hand, the formation of mesityl oxide from acetone is very much slower than the three proposed reactions.

A reversible deactivation of the catalyst was observed after 2 weeks of feeding diacetone alcohol. The deactivation can be explained in terms of a progressive condensation of mesityl oxide inside the resin.

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