F. G. KLEIN[1] and J. T. BANCHERO

Department of Chemical and Metallurgical Engineering,
University of Michigan, Ann Arbor, Mich.

Condensation of Acetone to Mesityl Oxide

Sulfonated polystyrene-divinylbenzene resin as ion exchange resin catalyst . . .

- **Substantially reduces side reactions**
- **Improves yield and reaction efficiency**

IN RECENT years, there has been much interest in the possible application of ion exchange resins as catalysts for a large variety of organic reactions (*8*, *10*). Cation exchange resins of the sulfonated polystyrene-divinylbenzene type seem to be especially suited as catalysts because of their thermal stability and high concentration of mobile ions. The hydrogen form of such resins may contain up to 5.5 equivalents of hydrogen ions per liter and will behave as a strong acid.

Since a large group of reactions are catalyzed by acids under homogeneous conditions, it would be expected that the hydrogen form of the cation exchange resin would also act as a catalyst. However, when such a resin is used as a catalyst, the reactants and products must readily diffuse through the resin matrix and the reaction must be rapid enough to proceed below about 100° C., the recommended upper limit on the temperature of continuous operation of the resin (*3*). If these criteria are met, the use of a cation exchange resin as a catalyst may have important advantages. Since the resin is a substantially insoluble solid, no separation or neutralization step will be required and continuous fixed-bed operation may be achieved easily. The use of an ion exchange resin may also cause a substantial reduction of side reactions and thus improve product yield and reactant efficiency.

The reaction selected for investigation was the condensation of acetone to form mesityl oxide. A sulfonated polystyrene-divinylbenzene ion exchange resin (Dowex 50-X8) in the hydrogen form was used as the catalyst. This reaction is of interest because the use of the ion exchange resin catalyst provides a single-step operation for the manufacture of mesityl oxide from acetone. The major

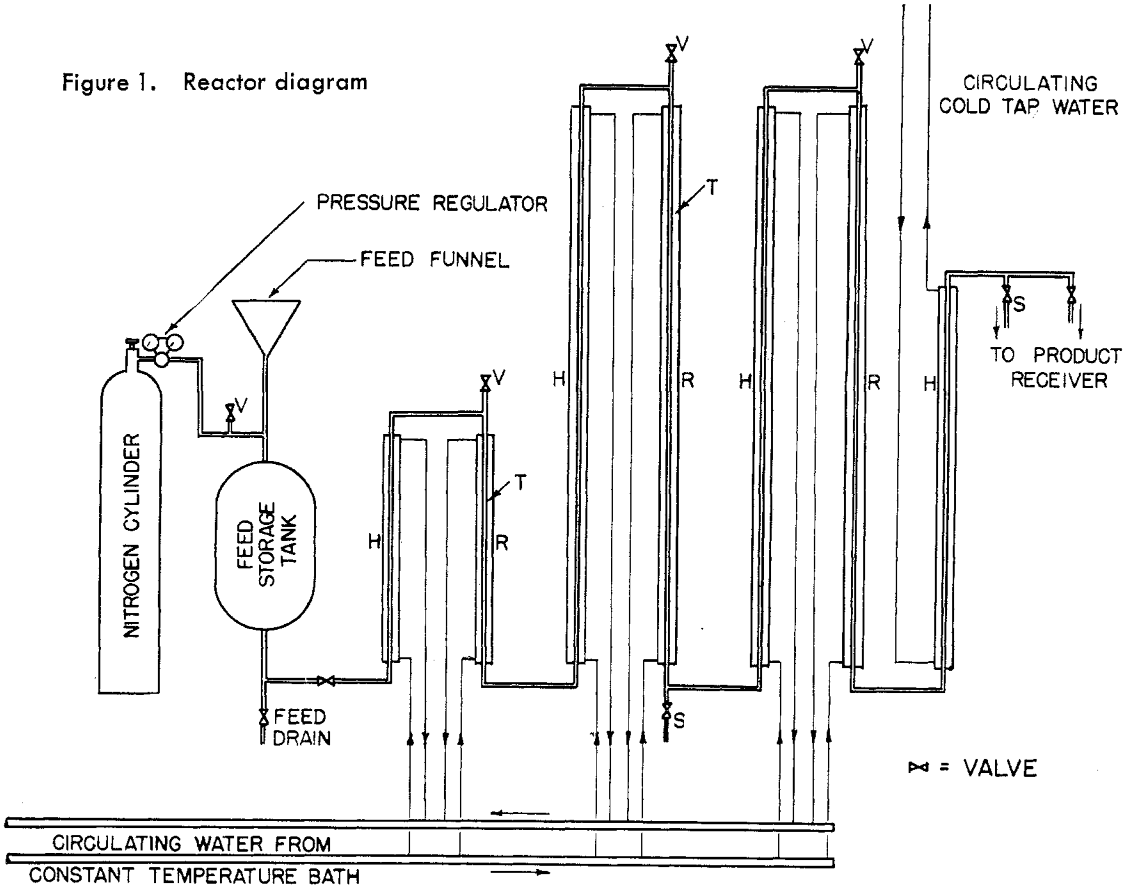

Figure 1. Reactor diagram

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[1] Present address, E. I. du Pont de Nemours & Co., Inc., Martinsville, Va.

by-product produced, diacetone alcohol is easily converted to mesityl oxide by the same catalyst.

Continuous Fixed-Bed Reactor

A continuous fixed-bed reactor, shown in Figure 1, was used. It consisted of a feed storage tank followed by a number of reactor sections and heat exchangers. Water from a constant temperature bath was circulated through the jackets of the various sections to provide isothermal conditions. A nitrogen cylinder was used to maintain a pressure of 120 pounds/square inch gage on the feed tank and provide flow of the reactant through the system.

The reactor was divided into separate sections in order to simplify catalyst changes and maintenance. A typical section is shown in Figure 2. The inside tube holding the catalyst was $^1/_2$-inch outside diameter, 16-gage, Type 316 stainless steel. Stainless steel was chosen for all parts in direct contact with the resin to avoid any possibility of corrosion. The reactor jacket was $^3/_4$-inch outside diameter, 16-gage carbon steel and was provided with $^1/_4$-inch tubing inlet and outlet connections for the circulating water. The catalyst charge was supported on a small wad of glass wool placed over a screen. The screen was held in place by a piece of stainless steel tubing welded into the base of the reactor section.

The heat exchanger sections of the reactor, which did not contain any catalyst, were of similar design as the previously described sections except that they were carbon steel and that the inside and shell tubes were $^1/_4$ and $^1/_2$ inch, respectively.

During ordinary operation three catalyst-filled reactor sections were used, one was about 1 foot long and the other two each about 5 feet long. A slurry of the catalyst spheres in methanol was then poured in, up to the desired level. A layer of glass wool was placed on the catalyst and a layer of 25- to 35-mesh steel shot, about 5 inches deep, was placed on the glass wool. Some cooling took place between the heat exchange and reactor sections and the steel shot was useful in increasing the flow rate and the heat transfer surface necessary to get the reactants back to the proper temperature before entering the catalyst bed.

Temperatures within the reactor were measured by copper-constantan thermocouples located just above the catalyst bed. Various tests indicated that there was a negligible temperature change of the liquid in flowing through the catalyst bed.

Samples were taken at two locations in the reactor. The first location corresponded to about half the total depth of bed, and the second location was at the outlet end of the reactor. Hypodermic needles were welded directly to the sample lines. Evacuated rubber-capped serum bottles were impaled on the needles and the samples injected directly into these bottles upon opening the valve in the sample line.

The acetone used was anhydrous grade material, containing less than 0.1 wt. % water, supplied by the Carbide and Carbon Chemicals Co. The infrared spectrum of this material was identical to that of reagent grade acetone except for the water peak, which indicated that the water content was lower than that of the reagent grade. Some water was absorbed by the acetone from air during its handling, so that the water content of the acetone feed to the reactor was greater than 0.1%. However, the water content rarely exceeded 0.20%.

The cation exchange resin used was a sulfonated polystyrene-divinylbenzene resin (Dowex 50-X8) which has been described by Bauman and others (*3*). Before use, it was completely converted to the hydrogen form by treating it continuously with a 6 to 10% solution of reagent grade hydrochloric acid. Conversion was considered complete when tests of the effluent samples with a flame spectrophotometer showed no increase in amount of sodium ion. The resin was washed with distilled water and dried for at least a week in an atmosphere maintained at 75° F. and 50% relative humidity. The dried resin was then screened five times and the fractions obtained were rolled down an inclined plane to remove nonspherical particles. The screened resin was thoroughly washed with methanol to remove moisture from the resin before it was charged to the reactor.

Reactor Operation

The reactor sections were charged with a known number of equivalents of hydrogen ion. Usually, the acetone feed had to pass through 197 meq. of hydrogen ion in the catalyst to reach the first sample tap and total of 360 meq. to reach the second sampling location.

During the course of an ordinary run the storage tank was first drained and flushed with nitrogen. Then acetone was charged and about 120-pound/square inch gage nitrogen pressure applied. After the desired pressure was reached, the circulating water was turned on and the acetone was allowed to enter the reactor. The flow rate of the reactants was regulated by means of

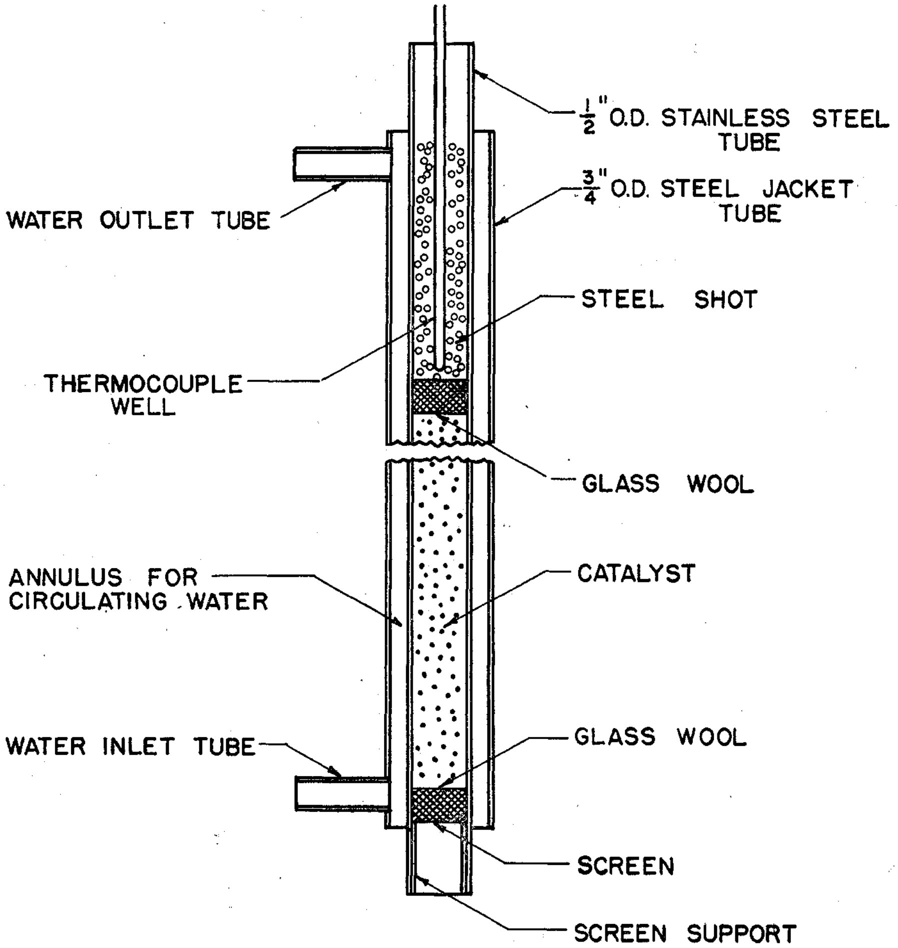


Figure 2. Reactor section

the needle valve on the downstream side of the reactor.

Table I. Experimental Data

Run No.	Temp., ° C.	Space Vel., Liter/(Min.) (Equiv.)	H_2O, Wt. % In acetone feed	H_2O, Wt. % In reactor product	Reactor Product, Wt. % MO	Reactor Product, Wt. % Diacetone Alcohol
20- to 25-Mesh Resin, 196.8 meq. of hydrogen ions						
109A[a]	30	0.0212	−0.015	0.209	1.14	3.2
110A	45	0.0160	0.056	0.677	3.69	2.4
111A	45	0.0565	0.058	0.244	1.33	2.8
113A	30	0.0411	0.077	0.048	0.26	2.0
114A	60	0.0121	0.077	1.248	6.80	2.3
115A	60	0.0780	0.044	0.537	2.93	0.6
117A	30	0.0668	0.079	0.023	0.13	1.3
119A	45	0.0755	0.074	0.178	0.97	1.7
120A	45	0.0451	0.074	0.288	1.57	0.9
121A[a]	30	0.0404	−0.055	0.110	0.60	1.6
122A[a]	60	0.0412	−0.055	0.691	3.77	1.8
123A	75	0.0732	0.112	0.712	3.89	2.4
124A	75	0.0416	0.112	1.069	5.10	2.9
125A	75	0.0190	0.020	1.647	8.98	2.6
20- to 25-Mesh Resin, 360.2 meq. of hydrogen ions						
109B[a]	30	0.0116	−0.015	0.289	1.58	2.6
110B	45	0.0088	0.056	0.752	4.10	4.5
111B	45	0.0309	0.058	0.359	1.96	4.0
113B	30	0.0225	0.077	0.254	1.39	1.8
114B	60	0.0066	0.077	1.337	7.29	5.0
115B	60	0.0426	0.044	0.855	4.66	0.8
117B	30	0.0365	0.079	0.188	1.03	1.5
118B	30	0.0240	0.079	0.333	1.82	0.9
119B	45	0.0412	0.074	0.366	1.99	1.8
120B	45	0.0248	0.074	0.476	2.60	1.3
121B[a]	30	0.0221	−0.055	0.334	1.82	2.2
122B[a]	60	0.0225	−0.055	1.025	5.59	2.2
123B	75	0.0400	0.112	1.183	6.45	3.0
124B	75	0.0227	0.112	1.482	8.09	4.1
125B	75	0.0104	0.020	1.955	10.67	3.2
30- to 35-Mesh Resin, 196.8 meq. of hydrogen ions						
86A	45	0.0680	0.035	0.340	1.85	1.4
87A	45	0.0134	0.035	0.805	4.38	1.7
88A	30	0.0320	0.042	0.244	1.33	1.9
92A	45	0.0350	0.048	0.386	2.10	1.1
93A	60	0.0751	0.048	0.436	2.38	1.5
95A[a]	75	0.0103	0.251	2.038	11.11	2.6
96A[a]	75	0.0711	0.251	1.025	5.58	3.0
97A	60	0.0390	0.042	0.734	4.00	1.2
98A	60	0.0142	0.042	1.274	6.94	0.8
99A	30	0.0561	0.031	0.207	1.13	0.6
100A	30	0.0156	0.031	0.373	2.03	0.8
101A	45	0.0372	0.035	0.390	2.12	1.5
102A	75	0.0375	0.035	1.415	7.72	0
103A	30	0.0375	0.021	0.200	1.09	1.8
104A	45	0.0159	0.021	0.581	3.17	1.2
105A	30	0.0147	0.075	0.316	1.72	. . .
106A	30	0.0576	0.075	0.160	0.87	0.5
107A	60	0.0760	0.103	0.491	2.68	1.6
108A	75	0.0367	0.103	1.175	6.41	1.6
30- to 35-Mesh Resin, 360.2 meq. of hydrogen ions						
86B	45	0.0372	0.035	0.593	3.23	0.9
87B	45	0.0073	0.035	0.911	4.96	2.1
88B	30	0.0175	0.042	0.327	1.78	3.2
89B	45	0.0241	0.042	0.596	3.25	1.1
92B	45	0.0192	0.048	0.621	3.39	1.2
93B	60	0.0414	0.048	0.807	4.40	1.6
95B[a]	75	0.0056	0.251	2.411	13.15	2.9
96B[a]	75	0.0388	0.251	1.401	7.63	2.6
97B	60	0.0215	0.042	1.078	5.88	0.9
98B	60	0.0078	0.042	1.508	8.22	1.2
99B	30	0.0307	0.031	0.267	1.46	2.0
100B	30	0.0085	0.031	0.506	2.76	. . .
101B	45	0.0203	0.035	0.643	3.50	1.2
102B	75	0.0205	0.035	1.741	9.50	1.5
103B	30	0.0205	0.021	0.263	1.43	4.2
104B	45	0.0087	0.021	0.651	3.55	2.1
105B	30	0.0080	0.075	0.457	2.49	. . .
106B	30	0.0315	0.075	0.331	1.81	0.6
107B	60	0.0415	0.103	0.748	4.08	2.5
108B	75	0.0202	0.103	1.601	8.73	3.0

Steady-state conditions were attained by passing at least three reactor volumes of acetone through the catalyst (about 900 ml.) and checking temperatures periodically. At the end of this period four analytical samples were obtained in tared serum bottles at each of the two sampling locations.

When the run was completed, the feed storage tank was drained and methanol was forced into the reactor system to displace all the acetone. When not in use the catalyst was kept wet with methanol to prevent shrinkage and cracking.

Analytical Methods

The reactor products were analyzed for water and diacetone alcohol. The amount of water in the reaction product is assumed to be stoichiometrically equal to the moles of mesityl oxide formed, since side reactions were found to be almost negligible. Repeated checks by distillation have proved this to be so. The water was analyzed by the method of Bryant and Smith (*4*). This method was chosen over the Karl Fischer procedure because of the large quantities of ketone present and because of the small samples (3 grams or less) used.

The analysis for diacetone alcohol proved impossible by chemical means because of the water present. A method employing infrared spectroscopy was evolved. A recording double-beam infrared spectrophotometer was used. The diacetone alcohol peak at 2.86 microns was employed. However, the water present in the reaction mixture interferes at this peak, consequently it was necessary to place equal concentrations of water in acetone in a reference cell to minimize interference. By using the base-line technique (*15*) it was possible to obtain a calibration which followed Beer's law for any given water content. The analytical method used for diacetone alcohol did not permit use of the data obtained for correlation purposes, but did indicate that there were appreciable quantities of diacetone alcohol present. Distillation of samples of reactor product verified this.

Experimental Data

To minimize the necessity of frequent catalyst changes, the various resin sizes were investigated consecutively for the complete range of variables. The resin sizes studied were: 20 to 25, 30 to 35, and 120 to 140 U. S. Standard mesh. At each one of those resin sizes conversions were obtained at four temperatures: 30°, 45°, 60°, and 75° C. For each run, samples were obtained at two catalyst bed locations: after the reactants had passed through 197 and 360 meq. of ion ex-

Table I. Experimental Data (*Continued*)

Run No.	Temp., ° C.	Space Vel., Liter/(Min.) (Equiv.)	H_2O, Wt. %		Reactor Product, Wt. % MO	Reactor Product, Wt. % Diacetone Alcohol
			In acetone feed	In reactor product		
		120- to 140-Mesh Resin, 196.8 meq. of hydrogen ions				
41A	30	0.0287	0.188	0.339	1.85	0.9
43A	30	0.0107	0.202	0.419	2.28	1.2
44A	45	0.0100	0.170	0.987	5.39	0.9
45A	45	0.0608	0.170	0.400	2.18	0.5
46A	30	0.0127	0.072	0.153	0.84	5.0
47A	30	0.0190	0.072	0.296	1.62	0.9
48A[a]	30	0.0597	0.394	0.146	0.80	2.4
49A[a]	30	0.0475	0.394	0.246	1.34	0.3
50A	30	0.0109	0.193	0.375	2.04	0.8
54A	30	0.0590	0.052	0.220	1.20	0.8
55A	45	0.0260	0.010	0.617	3.37	2.5
56A	45	0.0465	0.010	0.382	2.08	5.4
57A[a]	45	0.0561	−0.066	0.444	2.42	1.9
59A	60	0.0305	0.015	1.032	5.64	2.6
60A	60	0.0114	0.015	1.467	8.00	2.6
61A	60	0.0700	0.033	0.746	4.07	1.4
62A	75	0.0168	0.033	2.070	11.29	3.0
63A	75	0.0439	0.069	1.380	7.52	1.8
64A	75	0.0717	0.069	1.066	5.80	1.4
65A	60	0.0473	0.009	0.740	4.03	2.1
67A	45	0.0154	0.189	0.629	3.43	2.9
68A	45	0.0344	0.189	0.551	3.01	0.7
69A[a]	60	0.0724	0.277	0.633	3.45	0.7
70A	60	0.0868	0.075	0.477	2.60	2.1
71A	60	0.0575	0.075	0.654	3.56	1.3
72A	45	0.0356	0.024	0.452	2.46	2.8
74A	45	0.0293	0.146	0.591	3.22	4.0
75A	60	0.0714	0.146	0.824	4.49	1.8
76A	30	0.0162	0.0	0.526	2.87	1.0
77A	45	0.0139	0.0	0.585	3.19	1.2
79A[a]	45	0.0261	−0.022	0.533	2.91	3.0
80A[a]	45	0.0123	−0.022	0.859	4.68	0.8
82A	45	0.0170	0.127	0.625	3.41	0.7
83A	45	0.0563	0.118	0.378	2.06	2.1
		120- to 140-Mesh Resin, 360.2 meq. of hydrogen ions				
41B	30	0.0157	0.188	0.471	2.57	0.9
43B	30	0.0059	0.202	0.418	2.28	1.3
44B	45	0.0055	0.170	1.433	7.82	1.0
46B	30	0.0070	0.072	0.543	2.96	2.0
47B	30	0.0104	0.072	0.444	2.42	1.5
48B[a]	30	0.0323	0.394	0.212	1.16	2.0
49B[a]	30	0.0259	0.394	0.402	2.19	0.7
50B	30	0.0060	0.193	0.582	3.18	1.6
54B	50	0.0322	0.052	0.351	1.92	0.6
55B	45	0.0142	0.010	0.982	5.36	2.6
56B	45	0.0254	0.010	0.720	3.93	0.8
57B[a]	45	0.0307	−0.066	0.608	3.31	0.8
58B[a]	60	0.0331	−0.066	1.077	5.67	2.2
59B	60	0.0167	0.015	1.337	7.29	1.6
60B	60	0.0063	0.015	1.632	8.90	2.6
61B	60	0.0382	0.033	0.924	5.03	5.6
62B	75	0.0092	0.033	2.499	13.63	3.6
63B	75	0.0240	0.069	1.838	10.00	2.0
64B	75	0.0392	0.069	1.466	7.98	1.4
65B	60	0.0258	0.009	0.934	5.09	2.7
66B	60	0.0467	0.009	0.695	3.79	2.1
67B	45	0.0084	0.189	0.734	4.00	5.4
68B	45	0.0188	0.189	0.724	3.95	1.4
69B[a]	60	0.0395	0.277	0.877	4.78	0.7
70B	60	0.0474	0.075	0.798	4.35	1.9
71B	60	0.0314	0.075	1.024	5.58	1.2
72B	45	0.0194	0.024	0.572	3.12	4.5
73B	45	0.0090	0.024	0.751	4.13	0.7
76B	30	0.0088	0.0	0.664	3.62	0.9
77B	45	0.0076	0.0	0.799	4.36	1.8
79B[a]	45	0.0143	−0.022	0.744	4.05	2.4
80B[a]	45	0.0067	−0.022	0.921	5.03	1.8
82B	45	0.0093	0.127	0.718	3.91	1.5
83B	45	0.0307	0.118	0.522	2.85	1.0

[a] Poor blanks were obtained in the analysis, but runs were still considered usable for correlation purposes. These runs corresponded to either high or low apparent water content of acetone. Prior and subsequent water analyses on acetone from the same drum gave less than 0.20 wt. % water. Conversion data do not depend directly on the blank in the analysis.

change resin. The flow rates investigated ranged from 1.5 to 15 ml. of acetone feed per minute, which corresponds to space velocities from 0.00417 to 0.0761 liter per (minute) (equivalent). A minimum of three runs for each sampling location were obtained at each temperature covering the full range of flow rates. A total of 71 usable runs are listed in Table I.

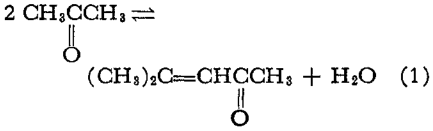
The units of space velocity, liters per (minute) (equivalent), were chosen primarily from the point of view of practical application. The liquid flow rate can be easily expressed in liters per minute. The catalyst can be expressed in terms of weight, volume, or equivalents of hydrogen ion. The latter was chosen because it eliminates ambiguity resulting from variations in weight or volume due to swelling of the resin.

The runs were carried out in completely random order. This was done to indicate whether there was any catalyst deactivation and also to check on the reproducibility of the runs.

Reaction and Resin-Phase Catalysis

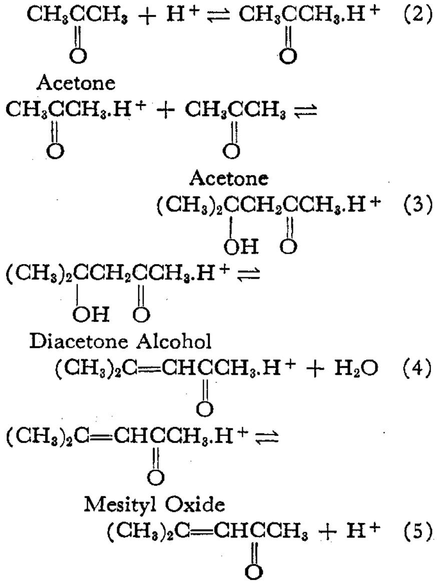
The major reaction under consideration may be represented by the following equation:

2 Acetone ⇌ Mesityl Oxide + Water



$$2\ CH_3\underset{\underset{O}{\|}}{C}CH_3 \rightleftharpoons (CH_3)_2C{=}CH\underset{\underset{O}{\|}}{C}CH_3 + H_2O \qquad (1)$$

Using mechanisms proposed by Ingold (7) and Alexander (1), a series of equations may be written indicating the possible sequence of reactions when acetone forms mesityl oxide:



$$\underset{\text{Acetone}}{CH_3\underset{\underset{O}{\|}}{C}CH_3} + H^+ \rightleftharpoons CH_3\underset{\underset{O}{\|}}{C}CH_3.H^+ \qquad (2)$$

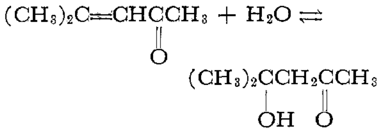
$$CH_3\underset{\underset{O}{\|}}{C}CH_3.H^+ + \underset{\text{Acetone}}{CH_3\underset{\underset{O}{\|}}{C}CH_3} \rightleftharpoons (CH_3)_2\underset{\underset{OH}{|}}{C}CH_2\underset{\underset{O}{\|}}{C}CH_3.H^+ \qquad (3)$$

$$\underset{\text{Diacetone Alcohol}}{(CH_3)_2\underset{\underset{OH}{|}}{C}CH_2\underset{\underset{O}{\|}}{C}CH_3.H^+} \rightleftharpoons (CH_3)_2C{=}CH\underset{\underset{O}{\|}}{C}CH_3.H^+ + H_2O \qquad (4)$$

$$\underset{\text{Mesityl Oxide}}{(CH_3)_2C{=}CH\underset{\underset{O}{\|}}{C}CH_3.H^+} \rightleftharpoons (CH_3)_2C{=}CH\underset{\underset{O}{\|}}{C}CH_3 + H^+ \qquad (5)$$

Formation of diacetone alcohol from acetone in the presence of an acid catalyst has not been reported in the literature. However, diacetone alcohol was a major by-product and probably was formed from mesityl oxide by the reversible acid-catalyzed reaction:

Mesityl Oxide + Water ⇌ Diacetone Alcohol


$$(CH_3)_2C{=}CHC({=}O)CH_3 + H_2O \rightleftharpoons (CH_3)_2C(OH)CH_2C({=}O)CH_3 \quad (6)$$

This possiblity seems to be supported by the results obtained in two runs made with diacetone alcohol as the feed, where only mesityl oxide and water, but no acetone, were obtained as products:

	Run 85	*Run 133*
Resin size, mesh	120–140	60–65
Space velocity, liter/(min.)(equiv.)	0.00267	0.01580
Temperature, ° C.	45	75
Diacetone alcohol in product, wt. %	41.8	23.3
Mesityl oxide in product, wt. %	50.2	64.2
Acetone in product, wt. %	0	0
Heavies in product, wt. %	Negligible	1.0

Consequently, the over-all reaction probably followed the sequence:

2 Acetone ⇌ Mesityl Oxide + Water ⇌ Diacetone Alcohol

A number of quantitative reaction rate studies have been carried out with cation exchange resins as catalysts. Levesque and Craig (*11*) studied the esterification of butanol with oleic acid. They found the reaction rate was directly proportional to the surface area of resin employed. Haskell and Hammett (*6*) carried out hydrolyses of aliphatic esters and found that the reaction rate was proportional to the mass of resin used.

This apparently anomalous situation may be explained by the other variables which enter into reactions catalyzed by ion exchange resins. Since the reaction takes place within the resin as well as on its surface, rates of diffusion of reactants and products in the resin, as well as mass transfer to and from the resin are important. If, for instance, the rates of diffusion in the catalyst are high compared to the reaction rate, it will appear that the rate of the reaction is proportional to mass or volume of catalyst used. But, if the rate of diffusion in the catalyst is very slow compared to reaction rate, then it will appear that the catalyst surface determines the rate of conversion of the reactants.

Saletan and White (*13*), who studied the formation of ethyl acetate in the presence of cation exchange resins, developed a rate equation which attempts to relate diffusion and resin-phase concentration of reactants with the reaction rate. Smith and Amundson (*14*) also derived a similar equation. Barker and White (*2*) used Saletan's method of correlation and applied it to the alcoholysis reaction between butyl acetate and ethanol.

Because of the insolubility of the resin in the surrounding reactants, it may be assumed that all of the reaction takes place in the resin phase. Applying this, Saletan and White (*13*) have related diffusional effects and reaction rates in a single catalyst sphere in differential equation form. By simplifying the nonlinear second-order differential equation obtained, the resulting integrated kinetic equation was found to be the originally postulated reaction rate equation modified by a factor ϕ, which was called the "resin efficiency factor." This factor, ϕ, was defined by the equation:

$$\phi = \frac{3\tau}{R}\left(\cot\frac{R}{\tau} - \frac{\tau}{R}\right) \qquad (7)$$

where R is the swollen resin radius, and τ is a function of the kinetics of the reaction and the diffusivities of the reactants.

In correlating the rate data obtained in the present investigation, it was found that none of the reaction mechanisms postulated would give a differential equation, relating diffusion and reaction kinetics, which could be reduced either to a linear form or to a nonlinear form that could be solved. However, the concept of a resin efficiency factor was employed in the empirical correlation finally obtained.

Correlation of Results

The following steps were used in correlating the data:

1. The integral conversions obtained from the experimental data were differentiated with respect to the reciprocal of the space velocity.
2. The rate equation was determined corresponding to a given reaction mechanism.
3. The method of least squares was used to determine the constants for the rate equation selected.
4. The rate equation was then integrated graphically and the curve of conversion versus reciprocal space velocity was compared with the experimental data.

Table II on differentiation of raw data illustrates the first step in the above procedure.

The difference data of this table were then plotted in the form of steps on a plot of rate of formation of mesityl oxide versus reciprocal space velocity (Figure 3). There are two series of overlapping steps, because one series is for the data obtained after the reactants had passed through 197 meq. of catalyst, and the other series for data after 360 meq. Since space velocity rather than flow rates were used for their computation, they should overlap provided the liquid-phase resistance to mass transfer is negligible. The area under the steps up to a given space-time is the integral conversion to mesityl oxide at that space-time.

The difference data were then smoothed by drawing the best curve through the tops of the steps so that the area of the curve above and below the steps was equal. Occasionally when data points were in close proximity to each other, their conversion and space velocity data were averaged rather than obtaining many small steps of greatly varying heights. In general, this gave a smoother series of steps and intoduced negligible error.

The next step in the correlation of the data was the selection of a rate equation. None of the rate equations derived from the postulated mechanism, Equations 2 to 5, fit the rate data properly (*9*). The best curves obtained from these rate equations generally gave low conversions at high space velocities and high conversions at low space velocities. An empirical approach was taken to correct for these deficiencies, and the following equation obtained:

Table II. Differentiation of Raw Data

Resin size: 20 to 25 mesh Temperature, 75° C.

Mesityl Oxide Concn. in Product, (MO) Mole/Liter	*Reciprocal Space Velocity (N/F_v), (Equiv.)(Min.)/Liter*	$\Delta(MO)$	$\Delta(N/F_v)$	*Rate of Formation of Mesityl Oxide,* $\frac{\Delta(MO)}{\Delta(N/F_v)} \times 10^3$
	For 360 meq. of hydrogen ion			
0.868	95.42			
		0.210	51.43	4.09
0.658	43.99			
		0.133	18.93	7.02
0.525	25.0			
		0.525	25.06	21.00
0	0			
	For 197 meq. of hydrogen ion			
0.731	52.13			
		0.256	28.09	9.11
0.475	24.04			
		0.159	10.35	15.33
0.316	13.69			
		0.316	13.69	23.10
0	0			

$$\frac{d(\mathrm{MO})}{d(N/F_v)} = \frac{k_1\phi[K_c(\mathrm{CH_3.CO.CH_3})^2 - (\mathrm{MO})(\mathrm{H_2O})]}{1 + k_2(\mathrm{MO})(\mathrm{H_2O})} \tag{8}$$

where MO is mesityl oxide.

The rate constants that best matched the data were calculated by the method of least squares. First, an approximation for $k_1\phi$ was obtained by dividing the reaction rate at zero conversion, by the kinetic driving force $[K_c(\mathrm{CH_3.CO.CH_3})^2 - (\mathrm{MO})(\mathrm{H_2O})]$ at that same conversion. Then substituting this value of $k_1\phi$ into Equation 8, a value of k_2 can be calculated by least squares.

The constants k_2 obtained in this manner are plotted on Figure 4. They fall on a straight line if log k_2 is plotted versus reciprocal absolute temperature. No parameters of resin size can be found since the points are scattered randomly. As a consequence, a single straight line can be drawn through these points.

The original value at $k_1\phi$ was an approximation dependent on how accurately the intercept of the rate versus space-time plot was obtained. Hence, new values of $k_1\phi$ were obtained on the basis of the k_2 for the best line of Figure 4. The rate constants $k_1\phi$ obtained by a least squares regression are plotted on Figure 5. In this plot, these composite rate constants are a function of resin size, and for each size they obey Arrhenius' law.

If the constants $k_1\phi$ and k_2, obtained in the manner described above and plotted in Figures 4 and 5, are used to calculate rates and integral conversions, then the conversions found would tend to be correct at high space velocities and somewhat high at low space velocities. This is due to the fact that the least squares method of correlation emphasizes adherence to the rate versus space velocity curve at high space velocities at the expense of the low space velocities.

Improvements were made on the integral conversion curves by adjusting k_2 and keeping $k_1\phi$ constant. Since $k_1\phi$ is more important at high space velocities, the curve remained essentially unchanged in that region. The constant k_2 is more important at low space velocities, thus by altering it, a better fit was obtained on this part of the conversion curve. The new series of k_2 data obtained is plotted on Figure 6. Again no parameters of resin size could be found, therefore the best straight line on semilogarithmic paper was drawn through them. These new corrected k_2 data are about 15% higher than the ones obtained by the method of least squares.

In Figure 5, $k_1\phi$ is dependent on resin size. Saletan (*13*), in his derivation of a rate equation for ion exchange resin catalysis, showed that ϕ is a function of τ and R, where τ in turn is a function of various concentration and diffusivity terms. He and Barker (*2*) found that τ remained essentially constant with changes in concentration of reactants. If it is assumed that this holds true for the acetone condensation also, then ϕ can be expressed in terms of τ and R. By matching the curves of $k_1\phi$ *vs.* $1/R$ (Figure 7) on a plot of the curve of ϕ *vs.* τ/R obtained from Equation 7, a value of τ was obtained which would fit all the data. Using τ equal to 0.0142 cm., the efficiencies obtained are summarized:

U. S. Standard Mesh	*As Screened, Av.[a] Radius, Cm.*	*Equiv.[a] Wt., G./Equiv.*	*Acetone-Swollen State* *Av. radius, cm.*	*Acetone-Swollen State* *H Ion concn. equiv./liter*	*Efficiency Factor,* ϕ
20–25	0.0374	267	0.0443	4.195	0.657
30–35	0.0271	270	0.0312	4.149	0.780
120–140	0.0057	251	0.00657	4.478	0.987

[a] In equilibrium with air at 75° F. and 50% relative humidity.

Using these efficiencies, a single rate constant k_1, plotted on Figure 8, was obtained for each temperature. Since both k_1 and k_2 are exponential functions of temperature only, the final form of the rate equation best expressing the conversion of acetone to mesityl oxide is:

$$\frac{d(\mathrm{MO})}{d(N/F_v)} = \frac{6.91 \times 10^4[\exp(-5330/T)]\phi[K_c(\mathrm{CH_3.CO.CH_3})^2 - (\mathrm{MO})(\mathrm{H_2O})]}{1 + 2.24 \times 10^{-8}[\exp(6720/T)](\mathrm{MO})(\mathrm{H_2O})} \tag{9}$$

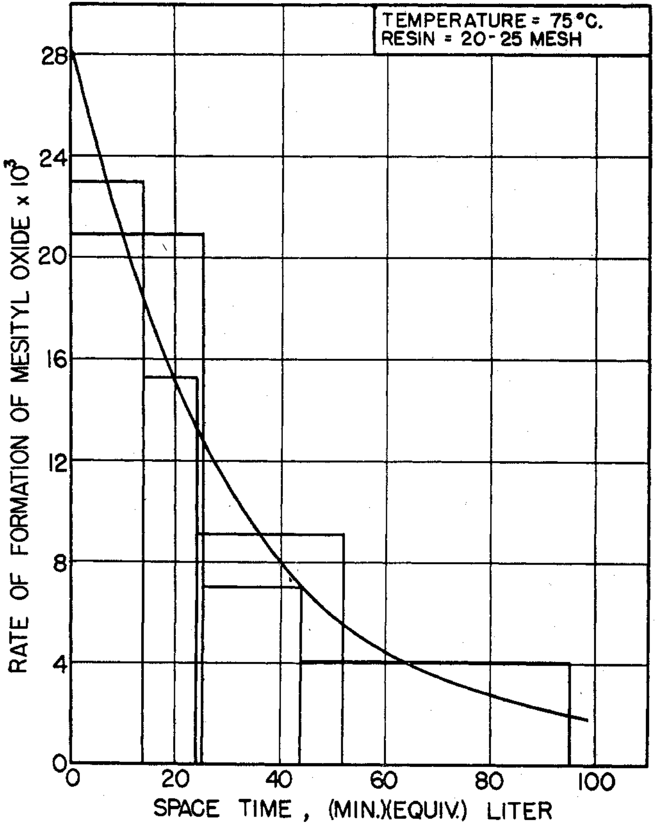


Figure 3. Differentiation of raw data

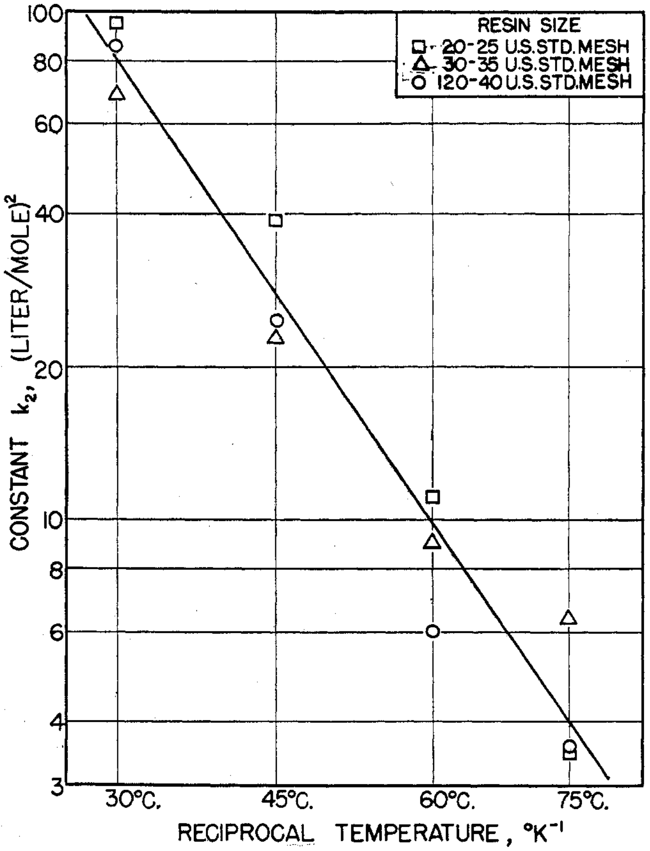


Figure 4. Effect Temperature on first approximation of k_2

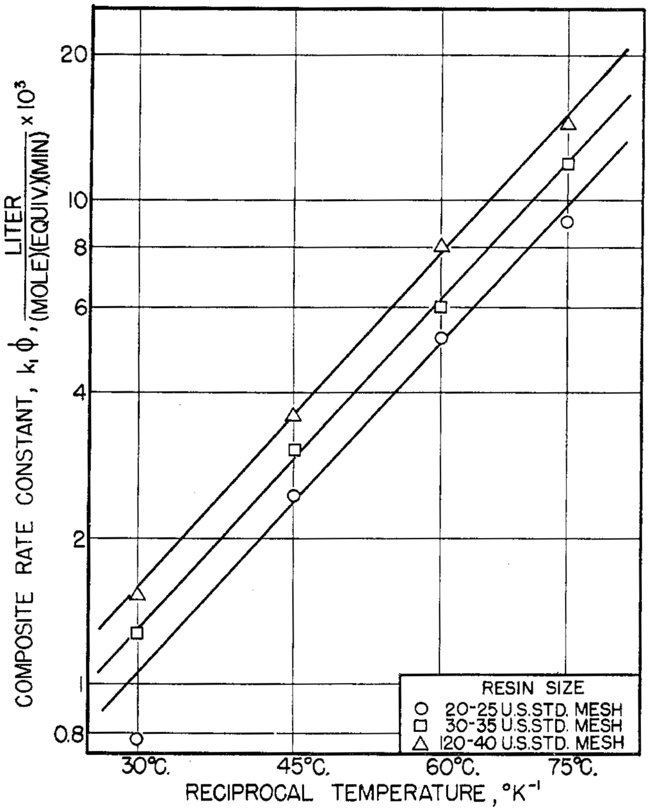


Figure 5. Effect of temperature on composite rate constant, $k_1\phi$

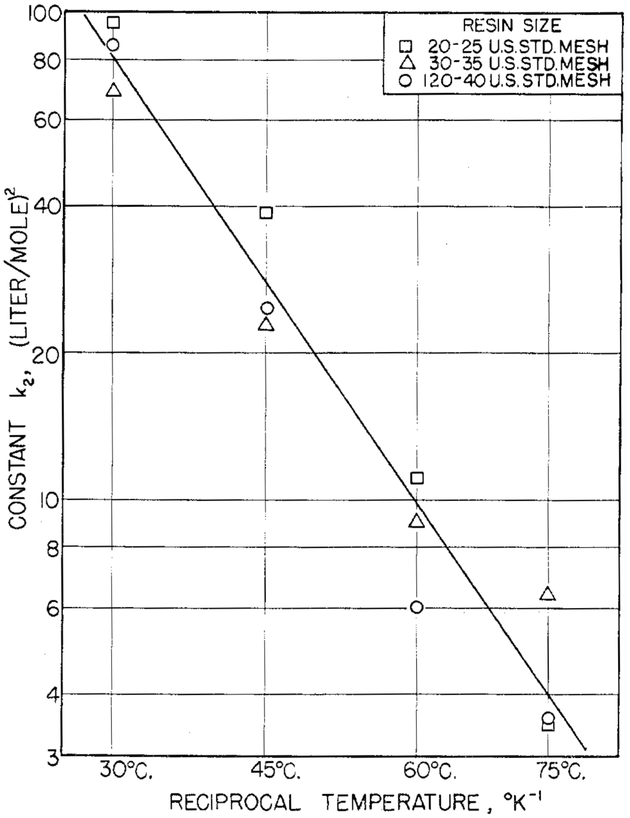


Figure 6. Effect of temperature of best constant k_2

where ϕ is defined as

$$\phi = \frac{0.0426}{R}\left(\text{Cot}\,\frac{R}{0.0142} - \frac{0.0142}{R}\right) \quad (10)$$

and K_c is defined as the equilibrium constant for the reaction from acetone to mesityl oxide, so that,

$$K_c = (\text{MO})(\text{H}_2\text{O})/(\text{CH}_3.\text{CO}.\text{CH}_3)^2 = 6.20 \times 10^{-3} \exp{(347/T)} \quad (11)$$

and where MO is mesityl oxide.

This equilibrium constant is the product of the equilibrium constant for the acetone-diacetone alcohol reaction obtained by Davis and Burrows (*5*) and another equilibrium constant for the diacetone alcohol–mesityl oxide–water system. The latter constant was calculated from data obtained in dilute aqueous solutions by Pressman, Brewer, and Lucas (*12*).

Figures 9, 10, and 11 show the curves calculated by use of Equations 9 and 10 and the corresponding experimental points. Fairly good agreement was obtained.

It was not possible to find a rate equation for the formation of diacetone alcohol. The data on diacetone alcohol conversion were not good enough to permit correlation. There seemed to be no trend with resin size, nor with temperature. In some cases also there seemed to be no trend with space velocity. It is probable that the poor accuracy of the diacetone

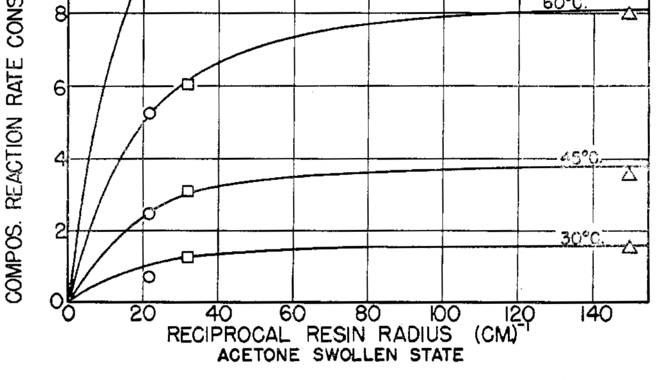


Figure 7. Variation of composite rate constant $k_1\phi$ with reciprocal resin radius

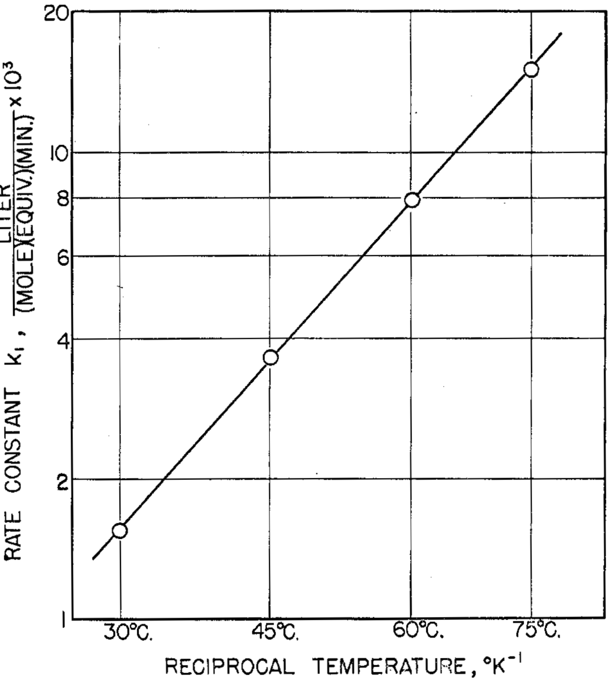


Figure 8. Effect of temperature on rate constant k_1

alcohol method of analysis is the reason for these difficulties.

Results

Equations 9 and 10 successfully correlate the rate data for the condensation of acetone to mesityl oxide when using the hydrogen form of Dowex 50-X8 as a catalyst for space velocities from 0.00417 to 0.0761 liter/(minute) (equivalent) over a temperature range from 30° to 75° C. for an acetone feed containing not more than 0.30 wt. % water. Two runs made with an acetone feed containing 1.85% water gave appreciably lower conversions than would be predicted by the correlation.

It is estimated that the experimental errors are:

Volumetric flow rates, %	±1
Temperature, ° C.	±0.2
Weight of water in 3 grams of product, mg.	±4
Weight per cent water in product, % abs.	±0.12
Weight per cent mesityl oxide, % abs.	±0.30
Weight per cent diacetone alcohol, % abs.	±2
Weight of resin, g.	±0.3

In the range of temperatures from 30° to 75° C., the logarithms of the constants k_1 and k_2 were linear functions of reciprocal temperature (Figures 6 and 8). The only notable deviation occurred at 30° C. for the 20- to 25-mesh resin.

The fact that both constants in Equation 8 fall on straight lines when plotted versus reciprocal temperature on semilog paper, tends to add credulity to the rate equation. The rate constant k_1 behaves in a manner usually expected of such constants, in that it increases very rapidly with temperature. The constant k_2 has an inverse variation with temperature. It may be an equilibrium constant, a product of several rate constants and equilibrium constants, or just a quotient of two rate constants. Any of these would explain the negative variation of k_2 with temperature.

The experimental results indicate a 50% change in composite rate constant $k_1\phi$ between 20- to 25- and 120- to 40-mesh resin size (Figure 5). Although the volume is essentially constant for a given number of equivalents of resin, the surface area is 6.7 times as great per unit volume for the smallest resin used, as for the largest. This indicates that the reaction rate is neither proportional to catalyst surface nor volume; it is somewhere in between, though closer to being proportional to volume. If the diffusivity in the catalyst would have been the important rate-determining step, then the reaction rate would have been proportional to catalyst surface area. Had diffusivity been unimportant in determining reaction rate, then the reaction rate would have been dependent on catalyst volume (or mass) only. Since the experimental results fall between these

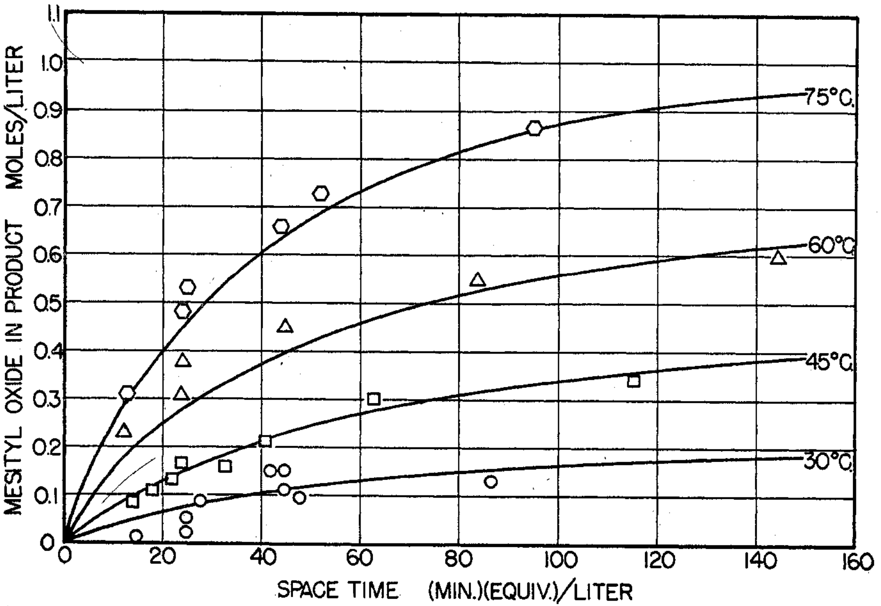


Figure 9. Integral conversion correlation, 20- to 25-U. S. Standard mesh resin

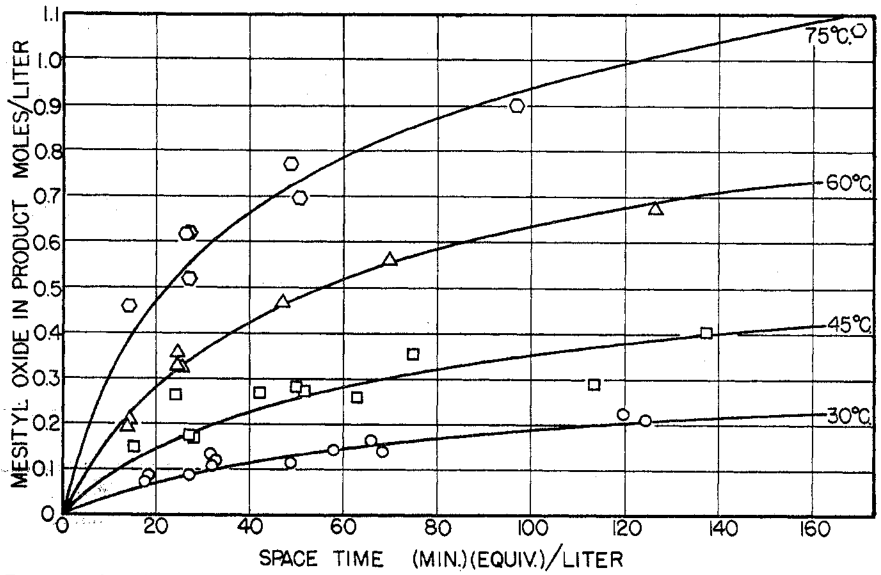


Figure 10. Integral conversion correlation, 30- to 35-U. S. Standard mesh resin

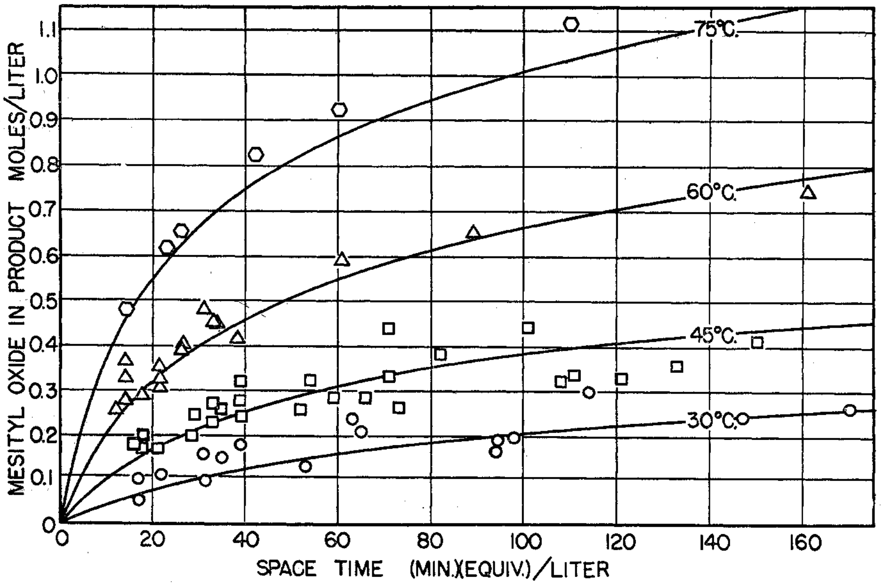


Figure 11. Integral conversion correlation, 120- to 140-U. S. Standard mesh resin

extremes, both the reaction rate and the diffusion into the catalyst are of importance, with the reaction rate being possibly the more important rate-determining step.

The resin efficiency factor ϕ was found to be independent of reactant concentrations and temperatures (Figures 5 and 7) and dependent only on catalyst radius. A single value of τ of 0.0142 was used to correlate all the data.

In correlating the data for mesityl oxide, the effect of the side reaction to diacetone alcohol has been neglected. At 75° C. the error introduced by the rate of formation of diacetone alcohol is very small, but at 30° C. it may be more appreciable since the amount of alcohol formed is similar in magnitude to the amount of mesityl oxide formed. Equation 8, therefore, cannot be used to determine the mechanism of the reaction. However, Equation 8 may be rearranged to the following form:

$$r_{MO} = k_1\phi[K_c(CH_3.CO.CH_3)^2 - (MO)(H_2O)]\left(1 + \frac{k_2}{k_1\phi} r_{MO}\right)$$

where

$$r_{MO} = \frac{d(MO)}{d(N/F_v)}$$

and MO is mesityl oxide.

The term $\left[1 + \frac{k_2}{k_1\phi}\right] r_{MO}$ is always larger than unity, so that the reverse reaction (mesityl oxide plus water yielding acetone) will always be more rapid than would be predicted by an ordinary second-order mechanism.

A possible explanation for this apparently high kinetic driving force for the reverse reaction could be found in the relatively high concentrations of mesityl oxide and water which might exist in the catalyst. The mesityl oxide has a relatively low diffusivity, therefore, it would be expected to build up in the resin phase before it would diffuse out. On the other hand, water which has a high resin phase distribution coefficient could also be present in appreciably high quantities. This seems plausible in view of the fact that the addition of about 2% water to the acetone feed tends to lower the conversion very appreciably, much more than might be indicated by the rate equation. A similar but lesser effect was noted with the addition of some mesityl oxide to the feed.

Behavior of Catalyst

During preliminary runs carried out in an agitated flask, it was noticed that as the reaction proceeded, the color of the catalyst changed from golden, to dark red, followed by brown, and finally black. During runs in the flow reactor the catalyst also turned completely black within a very short time. The black color was distributed throughout the resin sphere, not just on the surface. This leads one to believe that it is due to some reaction product which does not diffuse out of the catalyst. No way was found to remove the colored material, but the methanol used for flushing the reactor sometimes darkened appreciably. Attempts to extract this black color off the resin by refluxing methanol through it in a Soxhlet extractor did not succeed. The only conclusion reached is that it probably is a tarry product of the reaction.

A deposit such as the one found on the catalyst usually decreases the catalytic activity. Over the maximum time of use of any of the catalysts, about 150 hours, there was no evidence of any decrease in activity. Conversion data from runs with freshly charged catalyst checked very well with data obtained later.

Microscopic observations of the resin charged into the reactor and the catalyst taken from the reactor indicated that the spheres had appreciably increased in size, depending on how long they were in contact with the reactants. The 30- to 35-mesh resin used for about 50 hours showed a 19.6% increase in weight, and only 2% decrease in equivalents of hydrogen ions, based on the initial weight of the charge. Similarly, the 20- to 25-mesh resin used for about 40 hours showed a 11.1% weight gain, and only 2% equivalent loss based on initial weight. It should be pointed out that the used resin was difficult to titrate because it was not wet by water. Some methanol was added to improve the wetting qualities and may have brought about some error.

When charged into the reactor, the resin was composed entirely of perfect spheres. After use the resin charge was still essentially spherical, with less than 1% broken particles. During ordinary operation of the reactor, the resin underwent some severe swelling and shrinking in the confined space. The methanol used for flushing the reactor swells the resin much more than does the acetone. The expansion could not take place freely, which may have caused some breakage. The pressure drop across the resin bed was much greater for methanol than for acetone.

Special care was taken to prevent the reactor bed from drying completely at any time. The drying of the catalyst causes appreciable shrinkage. The subsequent wetting and sudden expansion in a very confined space breaks very many particles and increases the pressure drop appreciably.

Acknowledgment

The acetone and diacetone alcohol used in this investigation were donated by the Carbide and Carbon Chemicals Co. The cation exchange resin was contributed by the Dow Chemical Co.

Nomenclature

F_v = volumetric flow rate, liters/minute
k_1 = reaction rate constant, (liters)^2/(minute)(mole)(equivalent)
k_2 = constant in Equation 8 (liters/mole)^2
K_c = equilibrium constant for the liquid-phase reaction, acetone to mesityl oxide and water
N = equivalents of hydrogen ion in the resin
r_{MO} = reaction rate, (moles mesityl oxide)(minute)/(liter)(equivalent)
R = resin radius (acetone swollen), cm.
T = absolute temperature, ° K.
τ = penetration function determining resin efficiency
ϕ = volumetric efficiency of resin, defined by Equation 7
( ) = liquid-phase concentration, moles/liter

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