

High-Purity Alumina

III. Ion-Radical Cracking of Cumene on Alumina

SHAO E. TUNG AND EDWARD MCININCH

*From the Catalysis Research Laboratory, Central Research Division,
Continental Oil Company, Ponca City, Oklahoma*

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In cumene cracking, the ionic mode of cracking and the free radical mode are known to yield different types of reaction products. When cumene is cracked on high-purity alumina, characteristic products of both types are produced. The data can best be explained by assuming the occurrence of both modes of cracking on alumina surfaces.

In thermal-initiated free radical cracking, the primary free radical is generated essentially through the rupture of a carbon-carbon bond; but in the dehydrogenation-site-initiated free radical cracking, the initial step seems to be the breaking of a hydrogen-carbon bond.

There is more dehydrogenation-site-initiated free radical cracking than acid-site-initiated carbonium ion cracking on the alumina surface. At 450°C where the relative contribution of the ionic cracking is highest, the ratio between the ionic and free radical modes of cracking is roughly estimated to be (0.5-0.8):1. The lower contribution from an ionic mode of cracking suggests either that the activity of passive Bronsted acid sites on the alumina surface is modulated by the surface or that their population is not exceedingly large—less perhaps than the population of Bronsted acids on silica-alumina surfaces.

INTRODUCTION

In our previous report on hexene cracking over high-purity alumina (1) we have postulated that both the carbonium ion mode and the free radical mode of cracking occur on the alumina surfaces. In an effort to corroborate these postulations, in this work, we propose to examine the cracking reactions of cumene on high-purity alumina and compare these results with those obtained on a silica-alumina catalyst and on pure silica.

It is known that cumene cracking on silica-alumina occurs through a carbonium ion mechanism and yields benzene and propylene almost exclusively (2). On the other hand, free radical cracking of cumene generates an entirely different type of products with styrene (3), α -methylstyrene, and methane as the major components. Accordingly the data of cumene cracking should

be useful in demonstrating the relative contributions of each mode of cracking for a catalyst under investigation.

EXPERIMENTAL PROCEDURE

The catalysts used and the cracking procedure are essentially the same as what was previously reported (4). Three catalysts were studied. Alumina was prepared by hydrolyzing aluminum alcoholate with distilled water. The silica-alumina catalyst chosen was American Cyanamid's Aerocat, and the silica was prepared by hydrolyzing distillation-purified tetraethoxysilane.*

The same microreactor was employed. The catalyst sample was calcined for 4 hr at 650°C the day preceding the run and was stored in a vacuum desiccator overnight. The catalyst was weighed, and 0.800

* Detailed properties of these catalysts are given in ref. (4).

TABLE 1
 CUMENE CRACKING EFFLUENT GAS COMPOSITION

Gaseous effluent (mole %)	Aerocat						Alumina						Silica					
	200°C	250°C	300°C	350°C	450°C	550°C	600°C	350°C	400°C	450°C	500°C	550°C	600°C	500°C	550°C	575°C	600°C	650°C
Hydrogen	0	0	0	0	Trace	10.1	26.5	Trace	Trace	8.2	21.2	36.4	75.5	Trace	2.6	6.9	14.7	15.1
Hydrocarbons	100.0	100.0	100.0	100.0	99.99+	89.9	74.5	100.0	100.0	91.8	78.8	63.6	24.5	100.0	97.4	93.1	85.3	84.9
Composition of hydrocarbon effluent (mole % - on hydrogen-free basis)																		
Methane	0	0	0.01	0.02	0.19	1.46	5.36	0.72	1.86	4.40	12.82	19.42	42.35	0.25	1.48	5.17	11.09	25.04
Ethane	0	0	0	0	0.01	0.02	0.26	0	0	0.02	0.06	0.14	0.10	0	0.12	0.44	1.01	2.16
Ethylene	0	0	0.03	0.08	0.11	0.45	3.97	0.05	0.06	0.18	0.71	2.00	3.21	0.01	0.17	0.78	1.72	6.30
Propane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0.11	0.52
Propylene	5.58	26.83	35.13	44.20	47.39	45.01	35.95	1.24	2.61	5.97	10.86	7.22	2.65	0.30	0.86	1.75	2.37	2.45
Benzene	6.11	26.92	37.11	46.24	49.17	46.60	45.02	2.04	3.61	7.96	15.21	15.48	31.45	0.35	1.08	2.28	3.94	8.74
Toluene	0	0	0	0	0.03	0.22	1.03	0.08	0.17	0.37	1.92	3.50	5.59	0	0.03	0.15	0.34	1.01
Ethylbenzene	0	0.09	0.05	0.02	0.02	0.13	0.25	0.21	0.25	0.14	0.29	0.42	0.15	0	0.06	0.25	0.39	0.74
Cumene	87.00	44.82	26.80	8.26	1.16	0.26	0.15	91.60	82.12	69.48	22.23	4.97	1.08	96.96	89.12	72.60	53.04	7.30
<i>n</i> -Propylbenzene	0	0	0	0	0.14	0.11	0.11	0	0	0	0.63	0.33	0.20	0	0	0	0	0
I	0	0	0	0	0	0.05	0.03	0	0	0	0	0	0	0	0	0	0	0
Styrene	0	0	0	0.03	0.09	0.65	3.31	0.38	0.90	3.33	9.65	13.82	8.15	0.17	1.87	5.57	12.12	28.90
II	0.65	0.37	0.05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
α -Methyl Styrene	0.25	0.57	0.58	0.81	1.11	1.83	1.97	2.59	4.79	3.83	7.79	9.08	0.74	1.52	4.83	10.56	12.72	12.93
<i>cis</i> - β -Methyl Styrene	0.30	0.30	0.10	0.07	0.10	0.21	0.41	0.15	0.42	0.68	2.91	4.97	0.54	0	0	0	0.31	1.23
III	0.09	0.08	0.02	0.02	0	0.03	0.11	0	0	0	0	0	0	0	0	0	0	0
<i>trans</i> - β -Methyl Styrene	0	0	0.09	0.24	0.49	0.82	0.67	0.95	3.21	3.51	8.37	10.32	1.65	0	0.35	0.44	0.62	0.57
Indene	0	0	0	0	0	1.36	1.76	0	0	0	6.60	7.71	2.13	0	0	0	0.24	2.12
Σ Aromatics ^a	94.40	73.15	64.80	55.69	52.31	52.27	54.52	98.00	95.47	89.30	75.60	71.20	51.68	99.40	97.34	91.85	83.72	63.54
Σ Aromatics - Cumene ^b	7.40	28.33	38.00	47.43	51.15	52.01	54.37	6.40	13.35	19.82	53.37	66.23	50.60	2.44	8.22	19.25	30.68	56.24
% Cumene cracked ^a	8.84	38.73	58.64	85.17	97.78	99.50	99.72	6.53	13.98	22.19	70.60	93.02	97.91	2.45	8.45	20.96	36.65	88.51

^a Σ Aromatics = moles cumene feed per 100 moles hydrogen-free effluent gas, Σ Aromatics - cumene = moles cumene cracked per 100 moles hydrogen-free effluent gas, % Cumene cracked = $\{ (\Sigma \text{ Aromatics} - \text{Cumene}) / \Sigma \text{ Aromatics} \} \times 100$.

± 0.002 g was placed in the reactor and heated at 550°C for 1 hr under a nitrogen flow of 50–60 ml/min. At the end of this time, the reactor was cooled to the starting temperature and the reactant admitted. The cumene saturator was held in an ice bath, and the carrier gas flow (dry nitrogen) was maintained at 30 ml/min. The average concentration was determined as $7.2 \pm 0.4 \times 10^{-8}$ moles/ml. This value amounts to 2.16×10^{-6} moles/min of feed through the reactor.

Before the first gas sample for analysis was taken, the cracking was allowed to steady out for 3 hr (in the case of alumina, it was 6 hr) in an effort to get complete saturation of the catalyst. At the end of this saturation period, a 5-ml sample loop of the reactor tail gas was switched into the chromatograph and analyzed.

Analysis was performed on the gas sample by means of a 25-ft $\frac{1}{4}$ -inch OD, 30% Resoflex-on-firebrick column and a 3 ft, 100/200-mesh, silica gel column both at 115°C connected in series with a six-way valve in between. Using this arrangement, it was possible to analyze the aliphatic hydrocarbons, propylene and lower, on the silica gel and the aromatics on the Resoflex column. The sample was admitted to the column system and after the aliphatics had passed through both columns and the detector, the valve was turned. This turning of the valve changed the silica gel from following the Resoflex to preceding it and the aromatics were detected as they came through the Resoflex column.

Detection was accomplished by means of a hydrogen flame ionization detector. Concentration in the order of 5×10^{-11} moles in the 5-ml sample loop can be detected. One complete analysis took about 1 hr and 50 min. In several instances, the chromatograph was allowed to run for as long as 3 hr; but no further peak was observed. Concentration determinations for cumene reactant were made both preceding and following the run. The variation of the reactant concentration during a run is very small. The runs at different temperature levels were made immediately following each other.

Most of the components are identified through their characteristic retention times in the columns; however, α -methylstyrene, β -methylstyrenes, and indene were separated out by a gas chromatographic preparative unit and identified by NMR, IR, and mass spectrometer.

A separate tail gas sample (25 ml) was analyzed for hydrogen and methane using a thermal conductivity detector with nitrogen as the carrier gas and using a 15-ft 100/200-mesh silica gel column to perform the separation. From the methane contents in both analyses, the concentrations of hydrogen and the hydrocarbons can be correlated.

RESULTS

The cumene cracking results on the aforementioned three types of catalysts are summarized in Table 1. The relative yields of hydrogen and hydrocarbon are plotted in Fig. 1. As in hexene cracking

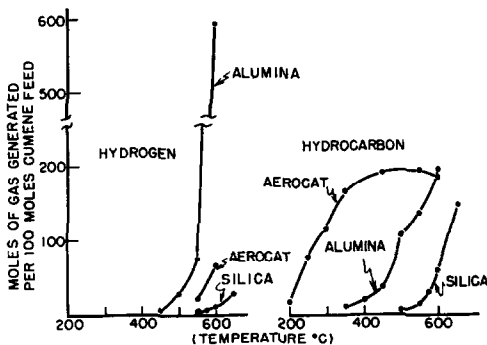


Fig. 1. Relative yield of hydrogen and hydrocarbon in cumene cracking.

(1), alumina generates more hydrogen than the others.

In the effluent gas, the summation of aromatics represents the total amount of cumene admitted from the feed gas,* and the difference between this and the remaining cumene represents the amount of cumene cracked. From these quantities, it is possible to calculate the composition of the product gas in terms of moles of component (methane, ethylene, propylene, benzene,

* It was experimentally confirmed that benzene does not crack beyond a negligible extent over alumina, Aerocat, and silica at 650°C .

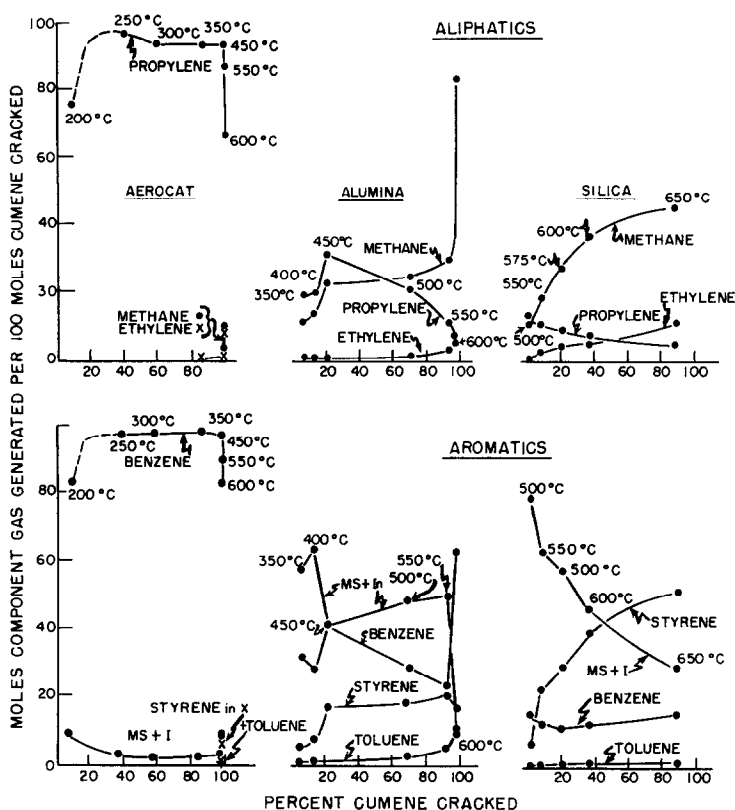


Fig. 2. Composition of cumene cracking product gas.

toluene, styrene, and MS + I*) generated per 100 moles of cumene cracked. These are plotted in Fig. 2 versus per cent decomposition. In making comparisons among catalysts, it should, however, be remembered that the same percentage of decomposition is realized at different temperature levels with different catalysts. The temperatures are indicated in the top curve of each plot.

As is clearly shown in Fig. 2, the cracking of cumene over silica-alumina yields essentially propylene and benzene between 250°C and 450°C. The propylene/benzene ratio in this temperature range varies from 0.95 to 1.0. Some deviation from this clean-cut rupture is observed either at higher or lower temperatures. In Table 1, it may be noticed that cracking on silica-alumina generates three minor components designated as I, II, and III not observed with other catalysts. They are not positively

identified, but from the matching of their retention times, they could be 1-methyl-2-ethylbenzene, *m*-diisopropylbenzene, and indene, respectively. If "II" is indeed diisopropylbenzene, then its variation with temperature as given in Table 1 suggests that some alkylation of cumene was taking place at low temperature levels such as 200°C in line with observations of Pansing *et al.* (5). The cumene was already substantially decomposed (85%) at 350°C. At 450°C, it had decomposed to the extent of 98%. Further heating to the higher temperatures generates more and more component gas other than benzene and propylene, as can be seen in Fig. 2. As will become clearer from the later discussions, this suggests most probably the participation of the dehydrogenation-initiated free radical mode of cracking at the high temperature levels.

Cracking of cumene on silica did not substantially start until 550°C. As Fig. 2

* Methylstyrene and indene.

indicates, its product contains only a moderate amount of benzene and propylene. The major cracking products are methane, styrene, and α -methylstyrene. These are typical products from the free radical mode of cracking.

Cracking of cumene on alumina generates a product gas richer in benzene than the corresponding product gas from silica, but alumina is far from being comparable with Aerocat in this respect. It also yields styrene, methylstyrenes, and toluene as major aromatic products. There is more of the methylstyrenes than styrene at all temperature levels. Between 350–450°C, the MS + I (α - or β -methylstyrenes + indene) and benzene curves both swing irregularly. The reasons for this swing cannot be easily assessed.* Between 450 and 550°C, both MS + I and styrene increase steadily at the expense of benzene. Above 550°C, a sudden change in composition occurs. The change seems to suggest decomposition of both styrene and methylstyrene to benzene, methane, etc.

Further comparison between the product gas from alumina and that from silica reveals their differences in two more aspects.

First, at low percentage of decomposition, more (MS + I) is present than styrene in the silica-cracking effluent. As cracking becomes more severe, the styrene concentration increases at the expense of (MS + I). The two curves eventually cross over, and at high decomposition levels, styrene is definitely in dominance. This rather unique concentration reversal is not observed in cracking over alumina. Secondly, the effluent from alumina yields more toluene than from silica.

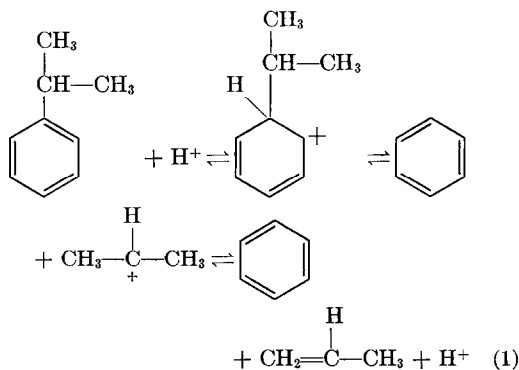
It is to be observed that, in the cases of alumina and Aerocat, the methylstyrene is distributed among its three isomeric forms. This can be ascribed to the isomerization capabilities of the surfaces of these catalysts. This isomerization is not shared by

* It is to be noted, however, that when the gas yields from alumina are plotted against temperature, the yield for MS + I levels off between 400° and 450°C and for benzene between 500° and 550°C. These "levelings" are likely the cause of irregular swing reported here.

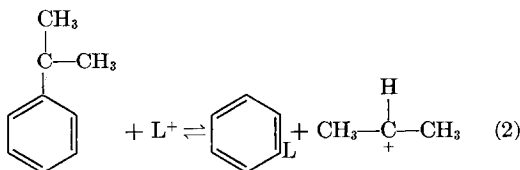
silica (below 600°C). In its product gases, α -methylstyrene exists in preference to its isomers. Indene was also found as a component in the alumina effluent.

DISCUSSION

Cumene cracking on silica-alumina is generally believed to proceed through carbonium ion intermediates. Two mechanisms have been proposed. Greensfelder, Voge, and Good (6) postulated that, in view of the great affinity of the benzene ring for protons, the dealkylation of cumene is simply an exchange between a propyl carbonium ion and a proton. Thomas (7) on the other hand, postulated the following:



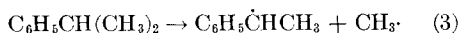
The mechanism of Thomas does point to the fact that, when cumene is cracked on a Lewis acid site denoted by L^+ , it will lead to the formation of a site-bound benzene.



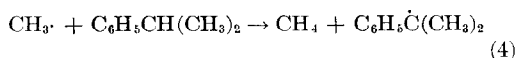
Thus, similar to hexene cracking (4), while the Lewis acids might contribute to the initial cracking, they could not by themselves sustain the cracking reaction on alumina, since the regeneration of Lewis acids for reuse from the site-bound species would depend on their interaction with protons.†

† The proton that might be generated through decomposition of the isopropyl carbonium ion tends to combine with a cation vacancy in alumina and thus becomes passive (4).

The free radical cracking of cumene has not been as exhaustively studied. Leigh and Szwarc (8) have investigated the pyrolysis of cumene by the toluene carrier technique and have proposed the primary step as being



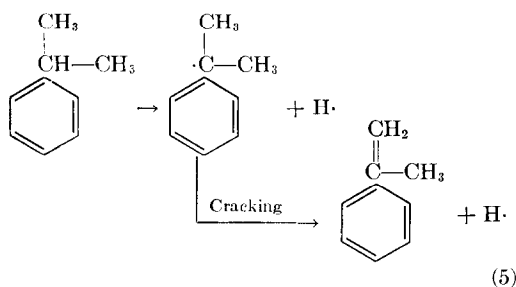
This is a plausible suggestion since carbon-carbon bonds are known to break more easily than carbon-hydrogen bonds. The methyl radical from Eq. (3) may further interact with cumene



Further decomposition of the tertiary radical so generated would lead to the formation of methylstyrene through β scission of a carbon-hydrogen bond. Since (3) is prerequisite to (4), one may logically expect a thermal-initiated free radical cracking to generate more styrene (from decomposition of $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_3$) than methylstyrene.

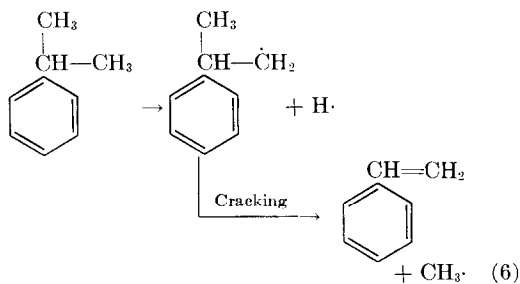
In the case of cracking over alumina, benzene, styrene, and methylstyrene, etc., all are found to be present in the product gas. This can best be explained by assuming the occurrence of both the ionic mode and the free radical mode of cracking on the alumina surfaces.

The free radical mode of cracking on the alumina surfaces is most probably site-initiated through dehydrogenation. In its primary step, a hydrogen atom is formed instead of a methyl radical



As the primary step in reaction (5) produces a more stable tertiary radical, that reaction would proceed faster than reaction (6); thus, in contrast to thermal-initiated

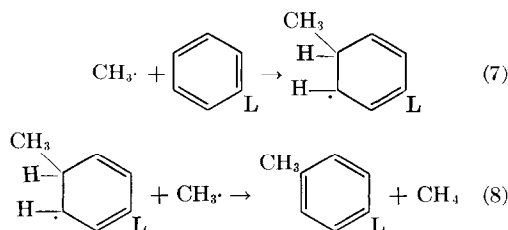
cracking, the dehydrogenation-site-initiated, free radical cracking may conceivably generate more α - and β -methylstyrene than styrene, as is actually observed in the

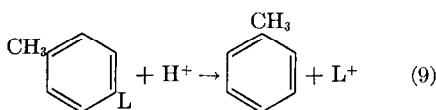


alumina cracking effluent. Indene in the product gas is probably coming from the dehydrocyclization of *cis*- β -methylstyrene.

In the case of cracking over silica, the concentration reversal of the styrene and (MS + I) can also be explained by assuming that, at the low-temperature end, the small percentage of cumene decomposition by the free radical mode is essentially dehydrogenation-site-initiated rather than thermal-initiated. The dehydrogenation capability of silica surfaces, although small, has nevertheless been demonstrated. Table 1 shows that a trace amount of hydrogen was indeed observed in the silica effluent at 500°C, and at 550°C, the hydrogen constitutes 2.6% of the issuing gas. As the temperature increases, thermal contribution increases, and at high temperature levels, it becomes dominant, leading to the styrene as the major component in the product gas.

Toluene found in the alumina effluent (not as much in the silica effluent) might be ascribed to the interaction of methyl radicals with the site-bound benzene which prevails over alumina surfaces (but not over silica surfaces).





The plausibility of reactions (7) and (8) has been discussed by Walling (9).*

To summarize, in the highly simplified cracking mechanism described here, the generation of BT (benzene and toluene) depends essentially upon the activity of the surface acid sites, while the generation of PTA (post-toluene aromatics including styrene, methylstyrene isomers, and indene)

over silica for a wide decomposition range permits us to roughly estimate the relative contribution of the ionic and the free radical modes of cracking over alumina. It is not certain how much of this 3.5% PTA in Aerocat effluent should be attributed to the ionic mode and how much to the free radical mode. In the extreme case, if all this 3.5% has ionic origin, then this value should be deducted from the PTA concentration in the alumina effluent so that the corrected PTA concentration may serve as an index to the extent of the free radical

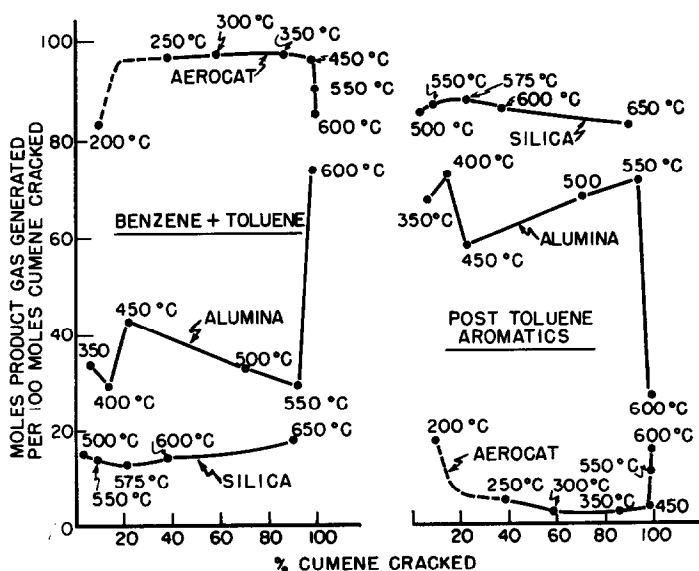


Fig. 3. BT and PTA in the cumene cracking product gas.

depends largely upon surface dehydrogenation sites. Both BT and PTA concentrations are plotted in Fig. 3. The plot shows that, for cumene cracking over Aerocat, there is a small amount of PTA (3.5% average) generated over a wide decomposition range. Similarly, some BT is generated over silica, and for a wide range of the extent of decomposition, this BT concentration remains relatively unchanged and averages 13.6%. This relative invariance both in the PTA concentration in the Aerocat effluent and the BT concentration

* An alternative acid-site reaction that might be proposed is: cumene \rightarrow *n*-propyl benzene \rightarrow 3-phenyl propyl radical \rightarrow toluene + ethylene.

cracking on alumina. On the other hand, if it has the free radical origin, then this correction is not necessary; thus the extent of the free radical cracking of cumene over alumina may be indicated by an index which varies in between the corrected and uncorrected PTA concentration in the alumina effluent. Similarly, the BT concentration in the alumina effluent, corrected or uncorrected for 13.6%, sets the limits within which lies the index for the extent of the ionic contribution. The maximum and the minimum ratio of the ionic contribution to the free radical contribution can next be computed from these limiting values. These ratios so computed for tem-

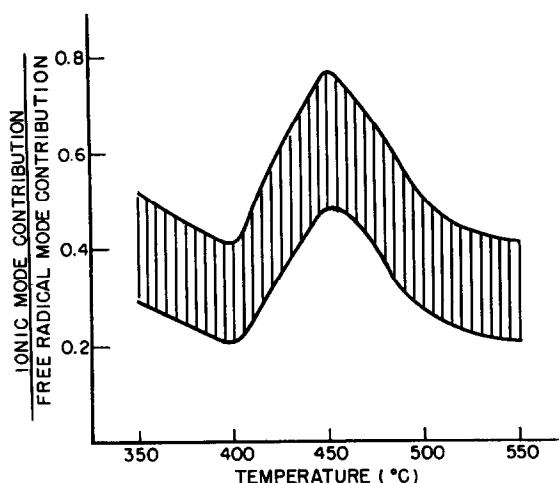


FIG. 4. Ratio of ionic mode contribution to the free radical mode contribution in cumene cracking on alumina.

peratures below 600°C* are plotted in Fig. 4 where the true value of the ratio would fall within the shaded area. This figure, imprecise as it may be, shows the relative ionic contribution peaks at 450°C, but at all temperature levels, the ionic mode of cracking contributes less than the free radical mode. This fact, together with the moderate magnitude of the amount of cracking, suggests either that the reactivity of passive Bronsted acids (which are assumed to be responsible for the ionic mode of cracking), even above 400°C, is modulated by the alumina surfaces or that their population on the surfaces is not exceedingly large—less, probably, than the population of Bronsted acids on the silica-alumina surfaces.

* Above 600°C, complication such as probable thermal cracking of methylstyrene sets in and this type of computation loses validity.

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