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Catalytic Oxidations with Sulfur Dioxide

II. Alkylaromatics

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The catalytic oxidation of ethylbenzene with sulfur dioxide gives styrene in high yields (90% selectivity at 95% ethylbenzene conversion) over a number of catalysts. Catalyst activity declines due to coke formation but activity can be restored by air regeneration. The reaction rate increases almost linearly with pressure, with a similar increase in coke formation. Water retards the rate. Both ethyl groups in the diethylbenzenes can be converted to vinyl groups but the *ortho*-divinylbenzene is very rapidly cyclized to naphthalene. Alpha-methylstyrene is produced from isopropylbenzene in only 60–70% selectivity due to side reactions. Toluene is converted to a solid product containing both sulfur and oxygen. 1,5-Cyclooctadiene, 1,5,9-cyclododecatriene, and 1,2,4-trivinylcyclohexane are not converted to vinylic benzenes in high selectivity, due to competing reactions.

INTRODUCTION

The catalytic oxidation of certain olefins with molecular oxygen proceeds with good selectivity and is fairly well understood (*1*), but the corresponding oxidation of alkylaromatics, which should be similar according to the reactivities of the C–H bonds, is not particularly selective, due to dealkylation and complete combustion (*2*). The use of sulfur dioxide instead of oxygen as a milder oxidant has been shown to give much higher yields in certain systems (*3*), and the oxidative dehydrogenation of alkylaromatics using sulfur dioxide proceeds with remarkably high yields (*4*). This report summarizes some further investigations of the oxidation of alkylaromatics with sulfur dioxide.

The overall reaction for the dehydrogenation of ethylbenzene to styrene with sulfur dioxide can be written as

$$3C_6H_5C_2H_5 + SO_2 \rightleftarrows 3C_6H_5C_2H_3 + H_2S + 2H_2O.$$

As the following thermodynamic data indicate, the equilibrium constant, *Kp*, of this reaction becomes increasingly favorable to ethylbenzene formation with increasing temperature:

ETHYLBENZENE DEHYDROGENATION THERMODYNAMICS (*9*)

Temp (°C)	316	427	482	538	599	649
ΔH (kcal/mole Etϕ)	21.92	21.99	21.98	21.95	21.91	21.84
$\log_{10}Kp$	2.496	4.661	5.493	6.216	6.861	7.413

The heat of reaction, ΔH, shows that the reaction is appreciably endothermic but practically constant with temperature. It is less endothermic than the similar sulfur dioxide dehydrogenation of alkanes to form olefins, which for butane dehydrogenation to butylene is approximately 25 kcal/mole at 400°C.

EXPERIMENTAL METHODS

The exploratory studies reported here were carried out using equipment and techniques described earlier (*3*). A fixed bed of catalyst was used in a small quartz reactor at atmospheric pressure with a flow system. A more detailed study of ethylbenzene oxidation was made using a larger stainless steel reactor described below. The vapor effluent from the reactors was monitored and analyzed using a mass spectrometer. GHSV refers to the total feed gas hourly space velocity (volumes of feed, calculated at STP, per bulk volume of catalyst per hour).

The more detailed studies of ethylbenzene oxidation were made with a calcium-nickel phosphate catalyst which was prepared as follows: 413.4 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 72.7 g of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in about 2 liters of water. An ammonium phosphate solution was then prepared by dissolving 264.2 g of $(NH_4)_2HPO_4$ in about 2 liters of water and the calcium-nickel nitrate solution was added slowly with stirring while also adding ammonium hydroxide (1 conc $NH_4OH:1H_2O$) to maintain the pH at about 8. The pale green precipitate was filtered and washed with water, then dried at 115°C. The light ivory-colored dry material was crushed and screened to 10–20 mesh size, and finally calcined for 2 hr at 500°C.

Ethylbenzene, sulfur dioxide, and argon were metered separately and fed through heated lines to a fixed bed reactor containing 20 cm^3 (4.60 g) of catalyst in a 12-in. bed. All gases and liquids were fed to rotameters at 100 psig and flow rates were controlled following the rotameter. The large reactor was of $^{11}\!/_{16}$-in. i.d. stainless steel, 33-in. long. Into this was inserted an aluminum liner $^5\!/_8$-in. o.d. × 0.058-in. wall thickness flared at one end to make a flange at the bottom to seal between the steel tube and the take-off fittings. This aluminum liner extended the whole length of the reactor tube. The catalyst was loaded from the reactor bottom around a $^3\!/_8$-in. o.d. aluminum thermowell sleeve and held in place with Pyrex glass wool and aluminum spacers above and below the bed. This use of aluminum liners ensured that the reactant gases in normal flow through the reactor did not contact steel except by slow diffusion. Bed temperatures were measured by four thermocouples spaced at intervals down the bed in a stainless steel thermowell running up the center of the reactor from the bottom inside the aluminum thermowell sleeving. The reactor was heated by a four-section furnace controlled by four thermocouples taped to the outside wall of the reactor. The hot effluent vapors were sampled continuously at about 200°C in a mass spectrometer. All data in this report are based on the analyses of these hot vapors before cooling below about 200°C. On cooling to room temperature further reaction occurs, for example, between product hydrogen sulfide and excess sulfur dioxide to form sulfur. The main product stream after passing through the condenser and liquid–gas separator was put through a water spray chamber. Product gases, finely divided (aerosol) solids, and wash water were then released to drain and vent through a Grove back-pressure regulator. This wash chamber was found to be necessary to remove finely divided sulfur, formed on cooling the product gases, which passed as a smoke through the various trapping stages and deposited in the Grove regulator, frequently causing the regulator to malfunction. Water for the spray stage was pressured to 100 psig. Pressures were measured using brass or stainless steel Bourdon tube-type gages. Pressures given are those measured at the top of the catalyst bed. During operation at "atmospheric" pressure in this unit, a pressure drop of about 0.5 atm existed across the reactor. Since the outlet pressure was atmospheric these runs were made at an effective pressure of about 1.25 atm.

"Coke" deposited on the catalyst during these reactions unfortunately was not measured in most cases. In a few runs with ethylbenzene where the coke make was measured it averaged 3–5% of the ethylbenzene converted.

In the data which follow, conversion was calculated as:

$$\frac{100\ (\text{total C atoms in all products})}{\text{total C atoms in all products} + \text{C atoms in unreacted feed}},$$

for the hydrocarbon feed materials, and similarly based on S atoms for sulfur dioxide conversion. Selectivity was calculated as:

$$\frac{100\ (\text{C atoms in given product})}{\text{total C atoms in all products}}.$$

RESULTS

Ethylbenzene

The oxidative dehydrogenation of ethylbenzene to styrene with sulfur dioxide over selected catalysts proceeds extremely well. The only by-product of significance, other than a small amount of combustion, is benzothiophene, which is formed by a subsequent reaction of the styrene. Single-pass yields (conversion × selectivity) of styrene well over 80% can be obtained. Results with calcium–nickel phosphate are given in Table 1. Best results are obtained at about 550°C since operation at lower temperatures results in more benzothiophene at the same conversion. Conversion-selectivity data at 550°C are shown in Figure 1. Selectivity to styrene is well above 90% until very high conversions are reached, where benzothiophene starts to be formed. These data do not include coke formation and so are probably 3–5% higher than when coke is included. The catalyst gradually loses

TABLE 1

OXIDATION OF ETHYLBENZENE WITH SULFUR DIOXIDE OVER CALCIUM–NICKEL PHOSPHATE

Coke not included; silica reactor.

Time (min)	Press (atm)		GHSV	Temp (°C)	Conv (%)		Selectivity (%)			
	C_8H_{10}	SO_2			SO_2	C_8H_{10}	C_8H_8	C_8H_6S	$C_7H_8 + C_7H_6O + C_6H_6$	$CS_2 + COS + CO_2 + CO$
10	0.12	0.29	500	450	5	4	68	1	4	24
25	0.12	0.29	500	450	13	36	88	5	1	5
40	0.12	0.29	500	450	15	58	80	14	1	4
55	0.12	0.29	500	450	14	61	79	13	1	5
70	0.12	0.29	500	450	16	54	83	10	1	4
100	0.12	0.29	500	450	14	45	82	9	1	5
145	0.12	0.29	500	450	12	38	85	6	2	4
205	0.12	0.29	500	450	10	32	88	5	0	4
10	0.09	0.45	600	500	27	99	70	24	0	5
25	0.09	0.45	2000	500	24	76	91	4	0	3
22	0.14	0.14	2100	500	24	47	96	3	0	0
52	0.14	0.14	2100	500	15	30	97	1	0	1
82	0.14	0.14	2100	500	13	24	93	1	0	1
97	0.14	0.14	2100	500	11	21	94	1	0	1
25	0.12	0.29	930	550	23	94	87	10	0	2
55	0.12	0.29	930	550	18	92	91	5	1	2
145	0.12	0.29	930	550	19	92	91	4	2	2
295	0.12	0.29	930	550	19	86	91	2	2	2
340	0.12	0.29	930	550	21	81	90	3	3	2
10	0.09	0.45	6600	550	21	64	93	3	0	2
25	0.09	0.45	6600	550	19	47	92	1	0	3
40	0.09	0.45	6600	550	19	38	92	0	0	4
55	0.09	0.45	3300	550	20	68	92	2	0	3
70	0.09	0.45	3300	550	19	64	91	2	0	4
10	0.14	0.14	17000	550	12	22	97	1	0	0
25	0.14	0.14	17000	550	7	12	96	0	0	1
40	0.14	0.14	17000	550	5	8	91	0	1	1

TABLE 2

OXIDATION OF ETHYLBENZENE WITH SULFUR DIOXIDE

Coke not included, silica reactor; $P_{C_8H_{10}} = 0.09$ atm; $P_{SO_2} = 0.45$ atm.

Time (min)	GHSV	Temp (°C)	Conv (%)		Selectivity (%)			
			SO_2	C_8H_{10}	C_8H_8	C_8H_6S	$C_7H_8 + C_7H_6O + C_6H_6$	$CS_2 + COS + CO_2 + CO$
				Calcium phosphate				
10	3400	450	8	57	87	2	6	5
40	6700	500	10	53	90	2	5	2
87	5000	550	15	77	85	6	5	4
				Vanadium phosphate				
57	700	500	6	27	82	2	9	7
85	300	550	17	85	74	13	5	8
120	700	600	16	93	73	17	5	4
150	1000	600	10	71	80	9	7	5
				Indium phosphate				
7	1700	450	6	22	60	30	3	7
45	700	500	9	70	84	9	3	4
60	700	550	9	86	82	11	3	4
90	1400	600	10	80	87	7	3	3
				Bismuth phosphate				
7	1700	450	7	32	79	12	6	4
25	1700	500	7	48	89	6	3	3
32	1700	550	8	64	90	5	2	3
47	1700	600	11	93	85	11	2	2
				Chromium phosphate				
20	300	450	5	19	76	3	8	14
35	300	500	7	54	83	7	5	5
50	700	550	7	64	86	7	2	4
65	1000	600	9	66	88	5	4	3
				Cobalt phosphate				
7	1700	450	10	50	73	22	2	3
25	1700	500	11	79	91	4	2	3
40	3400	550	10	70	93	3	1	1
55	5100	600	13	79	93	2	2	2
70	3400	600	15	97	87	8	2	4
				Bismuth–iron phosphate				
20	700	450	7	64	88	6	2	4
50	1000	500	9	76	93	3	2	3
65	1700	550	12	92	92	4	1	2
85	3400	600	16	98	86	8	2	5

activity with time, due to coking, but the activity is restored by air regeneration. Figure 2 shows catalyst activity with time at two temperatures. At 450°C there appears to be an induction period, followed by a fairly rapid decline. However, at 550°C the induction period is apparently absent or quite short and activity declines only slowly for a period of over 4 hr. Several other phosphate catalysts were examined and the results are given in Table 2. All of these catalysts are quite good for

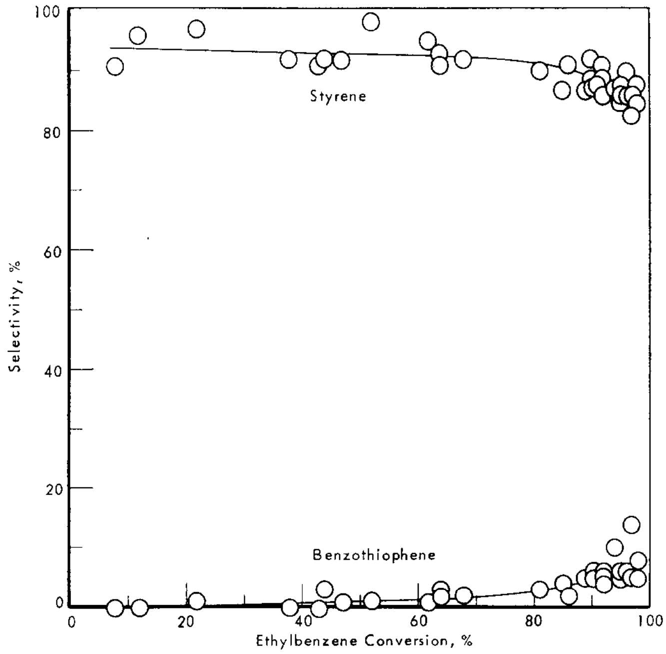

FIG. 1. Oxidation of ethylbenzene with sulfur dioxide over calcium-nickel phosphate at 550°C; coke not included.

this reaction. Calcium-nickel phosphate, bismuth-iron phosphate and cobalt phosphate are particularly outstanding.

Catalyst deactivation and regeneration. Since the catalyst loses activity during operation, it was necessary to determine how reproducible was the activity variation with standard atmospheric pressure operation, and how complete was regeneration, before other operating variables could be investigated in the larger reactor. Figure 3 shows the good reproducibility ob-

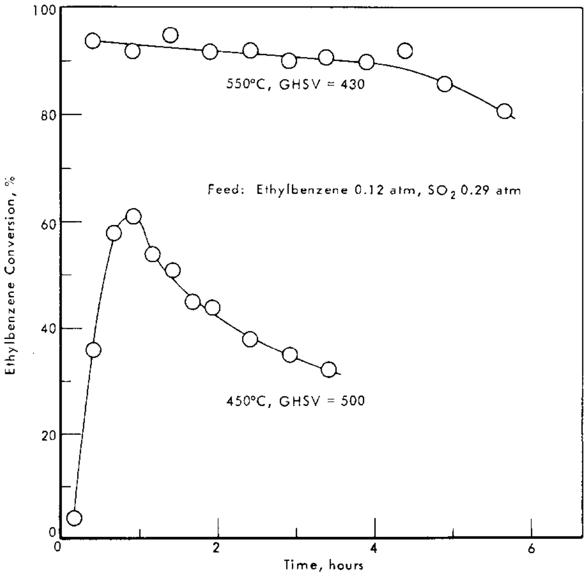

FIG. 2. Activity change with time for calcium-nickel phosphate catalyst; coke not included.

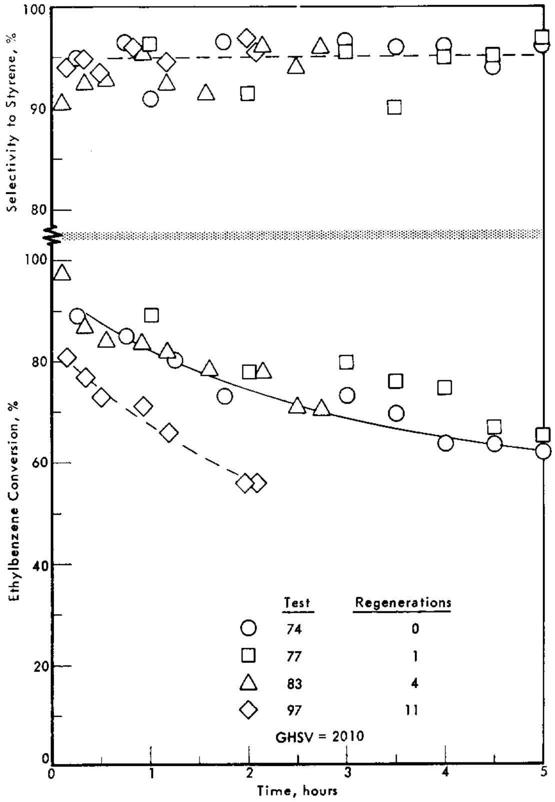

Fig. 3. Catalyst activity variation after regeneration; 555°C, atmospheric pressure; coke not included.

tained for the variation of ethylbenzene conversion with operating time for a feed of 70 ml/min of ethylbenzene, 330 ml/min of sulfur dioxide, and 270 ml/min of argon at about 555°C over 20 cm^3 of calcium-nickel phosphate. Run 74 was made on the fresh catalyst, 77 was made after regeneration in a stream of "air" (Ar/O_2 200 ml/min) at 420–450°C, 83 was made after 4 dehydrogenation-regeneration cycles, while 97 was made after 11 such cycles.

In a study of the influence of coke deposition on the activity of heterogeneous hydroisomerization catalysts, Van Zoonen (*5*) found that, under constant operating conditions, as the catalyst became coked the conversion of olefin decreased according to the square root of the process time following catalyst regeneration. In Fig. 4 some of the atmospheric pressure data obtained here are plotted in this form at constant pressure and temperature and appear to fit the relationship fairly well. The numbers alongside each curve indicate the number of test-regeneration cycles to which the catalyst had previously been subjected. The data of both Figs. 3 and 4 indicate that the activity of the catalyst was slowly decreasing with each test-regeneration cycle, but such activity loss could probably be slowed by carrying out the catalyst regeneration more frequently and at low temperature to cause less local hot spotting.

Surface area determination by nitrogen gas adsorption after outgassing at 500°C showed that the surface area of the catalyst had decreased from the 109 m^2/g of the fresh catalyst to 39 m^2/g after 12 dehydrogenation-regeneration cycles (i.e., immediately after regeneration following run 97). The data of Fig. 3 are re-plotted in Fig. 5 as the variation of the selectivity to styrene with ethylbenzene conversion level and shows that the selectivity to styrene holds up well to high ethylbenzene conversions. It also confirms that the selectivity

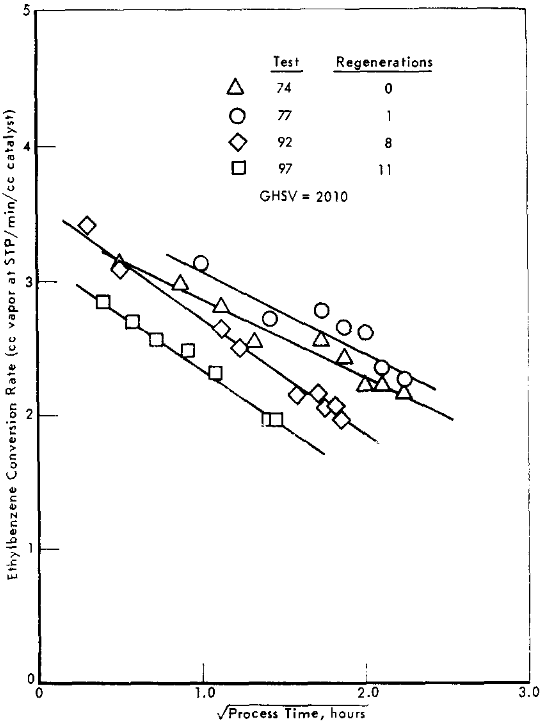

FIG. 4. Catalyst aging during testing for dehydrogenation of ethylbenzene to styrene, 555°C.

to styrene does not fall as the conversion of ethylbenzene decreases due to catalyst "coking."

Following each dehydrogenation run the catalyst was cooled to about 450°C and regenerated in a stream of 80% Ar–20% O_2 at 200 ml/min for about 4 hr. The progress of the regeneration was followed by

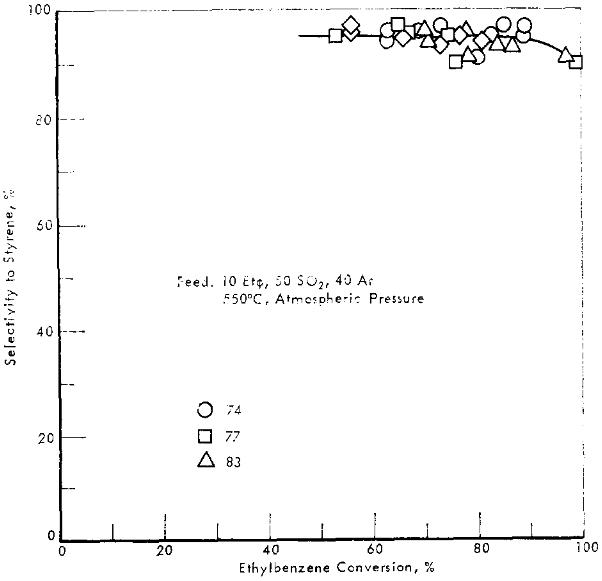

FIG. 5. Selectivity variation with conversion of ethylbenzene; coke not included.

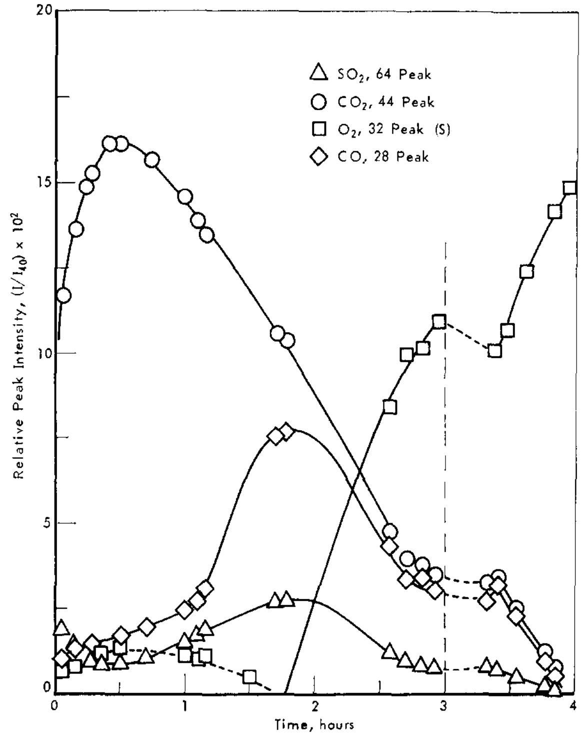

FIG. 6. Catalyst regeneration in argon–oxygen at 500°C following run 90.

continuously analyzing the gases leaving the reactor with the mass spectrometer using $Ar\text{–}O_2$ instead of air so that analysis for CO ($m/q = 28$) was possible. A typical regeneration is shown in Fig. 6 as the variation of peak intensities of the mass spectrometric analyses corresponding to the various oxidized products relative to the mass 40 peak intensity of argon. Instrument sensitivity per mole relative to the argon mass 40 peak was: SO_2, mass 64, 0.515; CO_2, mass 44, 0.572; O_2, mass 32,

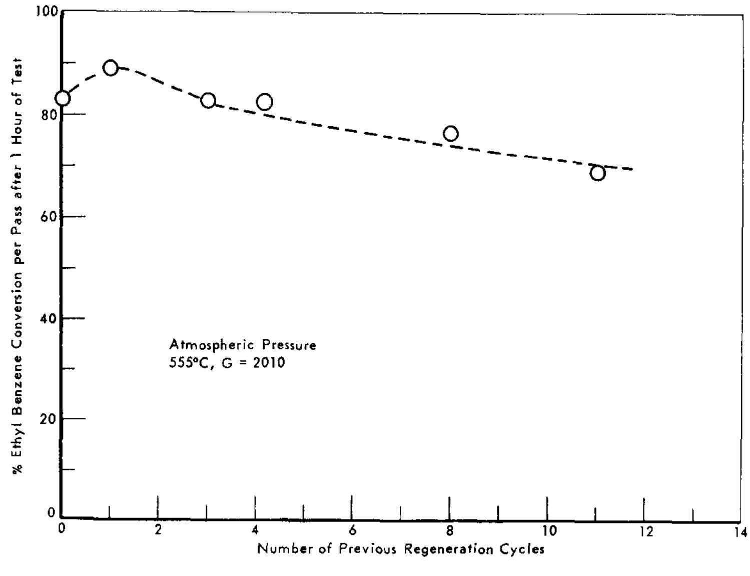

FIG. 7. Variation of catalyst activity with the number of regeneration-process cycles; coke not included.

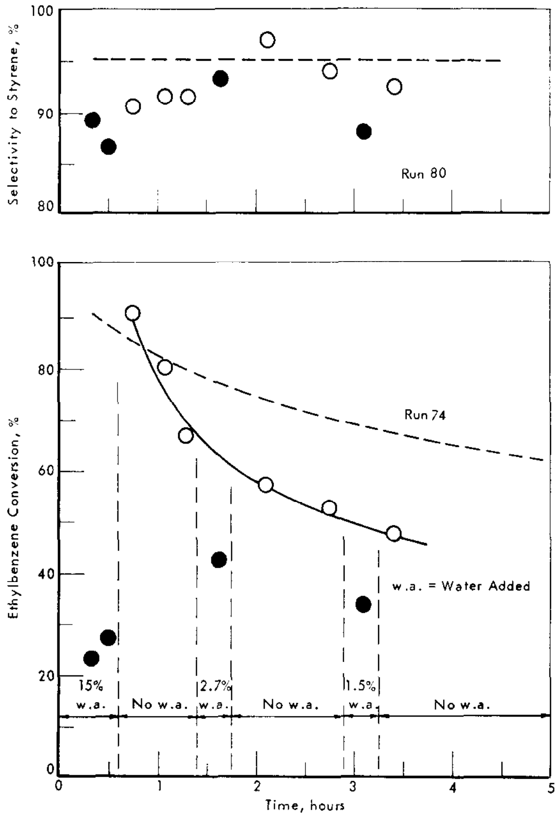

FIG. 8. Effect of added water in feed gases on dehydrogenation of ethylbenzene; 555°C, coke not included.

0.647; CO, mass 28, 0.844. Hence relative concentration is given by (relative peak intensity)/(relative molar sensitivity). During regeneration much heat was evolved and "hot spot" temperatures about 50°C above that of the rest of the catalyst bed developed and passed down through the catalyst bed. The peak at mass 32 observed during the initial stages of the regeneration is probably due to sulfur in the effluent gases, not to oxygen, since it passed through a maximum. The 32 peak due to oxygen began to rise rapidly coincident with the "hot spot" zone reaching the bottom of the catalyst bed. In Fig. 6, the discontinuity in the curves at 3-hr regeneration time represents an overnight shutdown, with oxygen flow off and the catalyst maintained at 500°C overnight in a static argon atmosphere; regeneration was continued the following morning. In the brief study of process variables which follows, a standard regeneration procedure was adopted of maintaining the hot spot temperature in the bed at about 500°C with 200 ml/min of 80% Ar–20% O_2 flowing over the catalyst, and continuing the regeneration until the carbon dioxide 44 peak was about 1% of the argon 40 peak.

Slight variation in the regeneration temperature and oxygen flow rate suggested that the time required for complete regeneration of the catalyst could probably be shortened by increasing the oxygen flowing over the catalyst if the heat evolved could be dissipated sufficiently rapidly to maintain the hot zone temperatures at about 500°C. The hot zone temperature in the apparatus used here could readily be controlled by varying in combination the furnace temperature and the oxygen supply rate. In the regeneration shown in Fig. 6, 3.7 g of carbon was removed as carbon oxides from the 20 cm^3 of catalyst.

The ultimate life of the calcium-nickel phosphate catalyst under these conditions

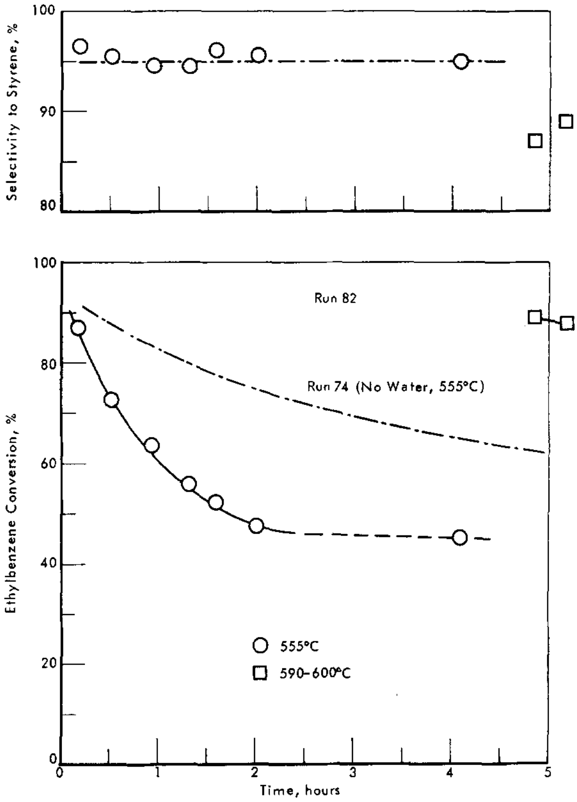

FIG. 9. Effect of 1% water vapor on dehydrogenation of ethylbenzene; 555°C, coke not included.

was not established. Figure 7 shows the loss in activity of the catalyst, measured by its activity under the standard atmospheric pressure operation conditions at the end of 1 hr of operation following regeneration, as a function of the number of regeneration-process cycles to which it had been subjected. Such lifetime data is extremely limited, but appears to resemble that found for the similar commercial catalyst used for butylene dehydrogenation in the presence of steam in the Dow process (*6*). In that process, a similar catalyst has a life of about 6 months, enduring operation and regeneration with air and steam at 650°C in continual 30-min process–30-min regeneration cycling.

Effect of water vapor on the dehydrogenation. No special precautions were taken to dry the cylinder argon and sulfur dioxide used in the standard atmospheric pressure operation of the reaction, yet addition of only 1% water to the feed gases significantly inhibited the oxidation reaction. This sensitivity to the presence of water added to the feed gases is shown in Fig. 8, which includes the best line through the data of run 74 of Fig. 3 for comparison. Water was added to the feed by saturating the argon diluent stream with water at a controlled temperature. In run 80, the feed gases of the standard composition of 10% ethylbenzene and 50% sulfur dioxide at the standard total gas hourly space velocity (GHSV) of 2010 contained 15% added water during the first 35 min of operation as indicated along the time axis. On removing water from the feed the catalyst recovered most of its activity almost immediately, but then lost activity with time much faster than when the catalyst had not been exposed to added water vapor. Even low water concentrations inhibited the reaction (Fig. 8), but water had only a slight effect on the selectivity to styrene. Figure 9 shows the inhibiting effect of 1%

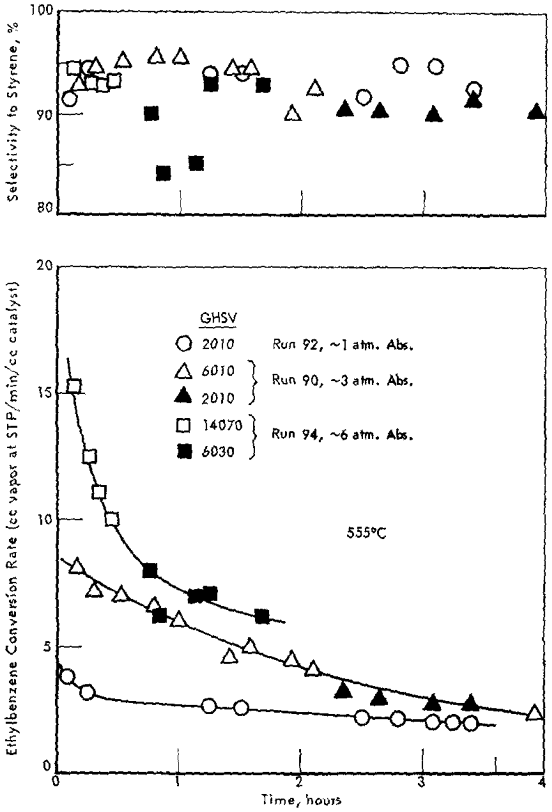

FIG. 10. Effect of operating pressure on dehydrogenation of ethylbenzene; coke formation not included.

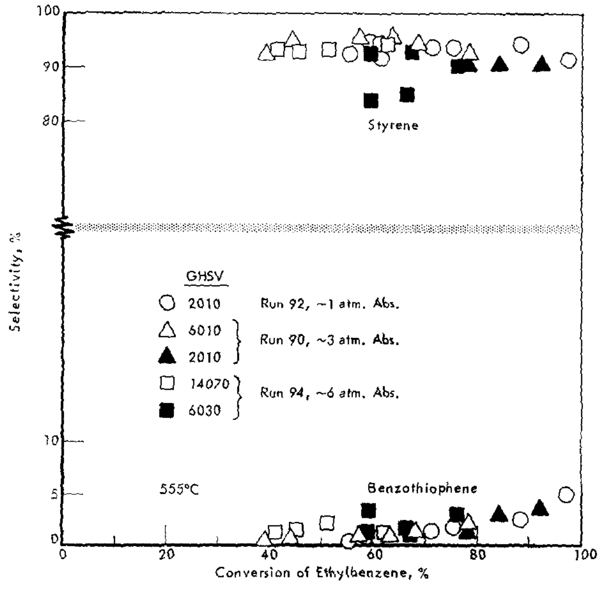

FIG. 11. Variation of selectivity with ethylbenzene conversion at different operating pressures; coke formation not included.

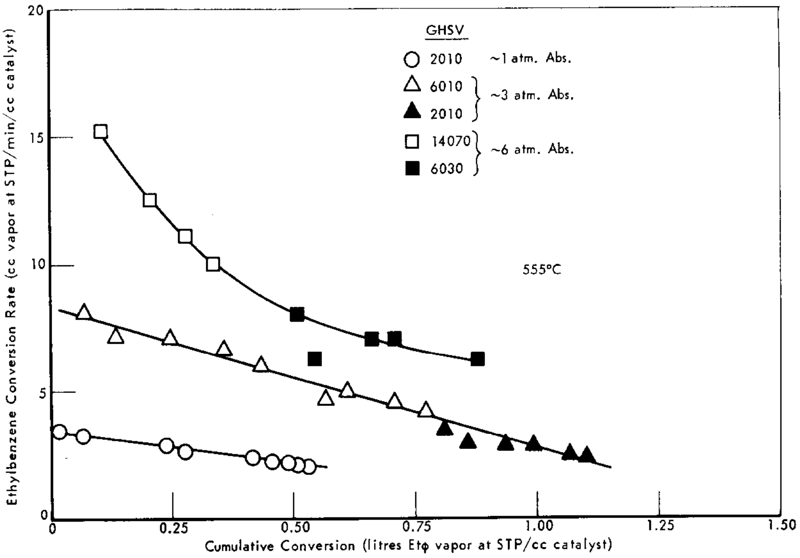

FIG. 12. Effect of operating pressure on dehydrogenation of ethylbenzene as function of amount converted after catalyst regeneration.

water added continuously to the feed gases during run 82. Raising the temperature from 555 to 590°C more than compensated for the inhibiting effect of 1% water, however.

Effect of operating pressure. The effect of varying the operating pressure on the dehydrogenation of ethylbenzene at about 555°C with a constant feed composition of 10% ethylbenzene, 50% sulfur dioxide, and 40% argon at different space velocities is shown in Fig. 10. The rate of dehydrogenation increases almost proportionally with the increase in total pressure, but the catalyst loses activity more rapidly at the higher pressures. Increasing the operating pressure has very little effect on the product composition as the variation of selectivities to styrene and benzothiophene with ethylbenzene conversion level in Fig. 11 shows. The selectivity values in the figures do not include losses to coke formation, which averaged about 4% selectivity to coke.

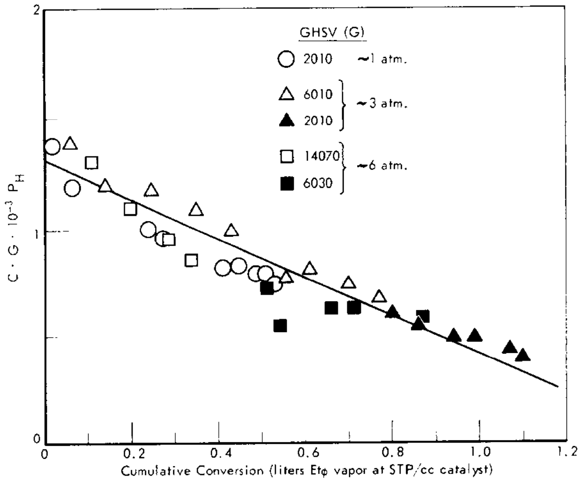

FIG. 13. Effect of cumulative conversion on rate of reaction at different pressures and space velocities.

The two lower selectivity values obtained at 6.3 atm pressure were obtained shortly after decreasing the gas space velocity (see Fig. 10) and may be spurious results. The effect of pressure on the rate of the reaction is presented somewhat more meaningfully in Fig. 12 as the variation of the absolute ethylbenzene conversion per pass relative to the total amount of ethylbenzene converted since regeneration of the catalyst. At atmospheric pressure and 3 atm pressure operation, the rate of dehydrogenation is almost directly proportional to the absolute pressure and the catalyst activity loss is directly proportional to the total amount of ethylbenzene which has been dehydrogenated over the catalyst since regeneration. These relationships are shown more clearly in Fig. 13 where C is the fractional conversion of ethylbenzene, G is the total gas hourly space velocity and P_{H} is the operating pressure at the head of the reactor (before the catalyst). In most cases at 3 and 6.3 atm a 5–10 psig pressure drop existed across the catalyst bed. Plotting the data in this manner assumes that the absolute rate of conversion of ethylbenzene is independent of the space velocity and directly proportional to the total pressure for a constant feed composition. The close agreement between the data at different pressures supports this assumption, although small systematic deviations do occur.

Loss to coke formation was only a small fraction of the ethylbenzene converted as the data of Table 3 indicate. The amount of coke deposited on the catalyst was determined from the area under the curves of the mass peaks due to CO_2 and CO relative to the argon 40 mass peak as in Fig. 6, knowing the argon flow rate over the catalyst. This amount of carbon was then related to the total amount of ethylbenzene converted as determined by mass spectroscopic analysis, using again a graphical method of integration. The operating pressure appears to have little effect on the selectivity to coke deposition.

The data of Table 4 give typical values for the formation of styrene from ethylbenzene and have been corrected for coke formation assuming that the selectivity to coke was independent of the ethylbenzene conversion level. The hydrogen sulfide observed in the exit streams, expressed as the fraction of that expected from the equation

$$3C_6H_5C_2H_5 + SO_2 \rightarrow 3C_6H_5C_2H_3 + H_2S + 2H_2O, \quad (1)$$

(with similar equations for the by-products) gives some idea of S lost in sulfiding the catalyst or as sulfur before analysis by the mass spectrometer. The summed selectivities to C_7 and C_8 in Table 4 consisted mainly of toluene and benzaldehyde, very little benzene being formed.

Summation. The oxidative dehydrogenation of ethylbenzene with sulfur dioxide gives high selectivity (~90%) at high ethylbenzene conversions (90%) at operating pressures from atmospheric to about 6 atm, and the rate of conversion of ethylbenzene is proportional to the operating pressure. However, the catalyst gradually becomes coked, and the loss in activity of the catalyst for dehydrogenation due to coke formation appears to be directly related to the amount of ethylbenzene converted. As a result, the catalyst requires regeneration more frequently when operated at higher pressure, but throughput is greater at the higher pressures.

TABLE 3
EFFECT OF PRESSURE ON SELECTIVITY TO STYRENE AND COKE FORMATIONS

Operating pressure (psig)	Duration of test (hr)	Moles Et-benzene flowed	Av Et-benzene Conv (%)	Selectivity (%)	
				Styrene	Coke
0–5	5.5	1.03	74	92	5
30	3.1	1.83	51	92	3
80	2.0	1.54	60	90	4

TABLE 4

OXIDATION OF ETHYLBENZENE WITH SULFUR DIOXIDE

Temp, 550°C; Feed: 1 C_8H_{10}; 4.7 SO_2; 3.9 Ar.

Run	Total press (atm abs)	GHSV	Operating time (hr[b])	Conv (%[a])		Selectivity (%[a])				
				C_8H_{10}	SO_2	C_8H_8	C_8H_6S	C_7H_8 + C_7H_6O + C_6H_6	CS_2 + COS + CO_2 + CO	H_2S (% of theory)
74–1	1.5	2010	0.25	89	7.3	90	3	1	1	96
–2	1.5	2010	0.75	85	8.4	92	2	0.5	1	67
–3	1.5	2010	1.25	80	6.3	86	3	4	2	100
–4	1.5	2010	3.0	73	7.5	92	1	1.5	1	50
90–1	3.4	6030	0.15	78	6.1	90	2	4	1	52
–2	3.4	6030	0.3	68	5.7	92	1.5	3	1	88
–3	3.4	6030	0.53	67	6.2	92	1.5	2	1	98
94–1	6.6	14070	0.12	62	8.5	90	2	2.5	1	66
–2	6.6	14070	0.25	51	6.3	89	2	3	1	109
–4	6.6	14070	0.43	41	4.7	89	1.5	4	1	110

[a] Coke included as in Table 3.

[b] Time "on stream" since latest regeneration.

Diethylbenzenes

The dialkylbenzenes were examined to see to what extent an additional alkyl group would be oxidized after another alkyl group had reacted. A mixture (approx. 50% of each) of *meta-* and *para-*diethylbenzenes was oxidized over calcium phosphate at 500°C. GLC analyses indicated that the two isomers reacted at the same rates. Results are given in Tables 5 and 6 and in Fig. 14. No reaction occurs in the absence of the sulfur dioxide oxidant

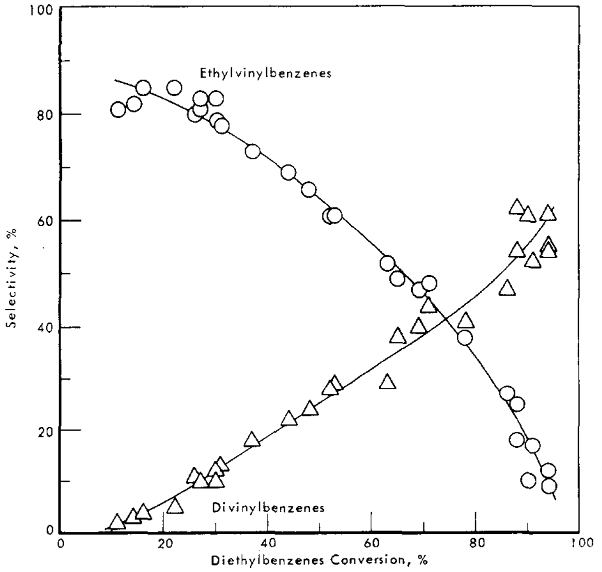

FIG. 14. Oxidation of *meta-para* mixture of diethylbenzenes with sulfur dioxide over calcium phosphate at 500°C.

TABLE 5

OXIDATION OF META–PARA MIXTURE OF DIETHYLBENZENES WITH SULFUR DIOXIDE

Calcium phosphate, 500°C; $P_{C_{10}H_{14}} = 0.15$; $P_{SO_2} = 0.42$. Coke formation not measured and neglected in calculations.

			Selectivity (%)				
Run	GHSV	$C_{10}H_{14}$ conv (%)	Ethylvinylbenzenes	Divinylbenzenes	Vinylbenzothiophene	Naphthalene + styrene + benzene	$CS_2 + COS + CO_2 + CO$
87–2	5300	52	61	28	2	6	3
–3	3500	30	83	10	1	2	4
–4	3500	71	48	44	0	5	4
88–2	3500	88	18	62	1	11	8
–3	3500	69	47	40	4	5	3
–4	3500	48	66	24	4	3	3
–5	3500	27	83	10	3	2	3
–6	3500	22	85	5	2	2	5
–7	3500	16	85	4	1	4	6
–8	3500	14	82	3	1	5	8
–9	3500	11	81	2	2	6	9

TABLE 6

OXIDATION OF META–PARA MIXTURE OF DIETHYLBENZENES WITH SULFUR DIOXIDE

Calcium phosphate, 500°C, $P_{C_{10}H_{14}} = 0.04$; $P_{SO_2} = 0.48$; coke formation not measured and neglected in calculations.

			Selectivity (%)				
Run	GHSV	$C_{10}H_{14}$ conv (%)	Ethylvinylbenzenes	Divinylbenzenes	Vinylbenzothiophene	Naphthalene + styrene + benzene	$CS_2 + COS + CO_2 + CO$
			Catalyst Regenerated				
88–11	3100	90	10	61	2	15	13
–12	3100	94	9	55	9	13	15
–13	3100	94	12	54	8	12	14
–14	3100	91	17	52	7	11	13
–15	3100	86	27	47	5	10	11
–16	3100	78	38	41	3	8	11
–17	3100	63	52	29	2	5	11
99–2	3100	94	9	61	6	14	10
–3	3100	88	25	54	4	9	8
–4	4700	65	49	38	3	5	5
–5	4700	53	61	29	1	4	5
–6	4700	44	69	22	1	3	5
–7	4700	37	73	18	1	2	6
–8	4700	31	78	13	0	2	7
–9[a]	4900	6	89	3	1	7	0
–10	4700	30	79	12	0	2	7
–11	4700	26	80	11	0	2	8
–12	4700	27	81	10	0	2	8

[a] No SO_2 fed.

(see run 99-9 of Table 6), indicating that the reaction is a true oxidation and not simply dehydrogenation. The ethyl groups are easily converted to vinyl groups and the second ethyl group reacts about as fast as the first, so that high yields of ethylvinylbenzenes cannot be obtained. Selectivity to divinylbenzenes is about 60% at diethylbenzene conversions of 90% or more. By-products, including benzothiophene types, are low. Coke formation was not measured here and hence the selectivity values given here represent upper limits. Catalyst activity declines quite rapidly with time (Fig. 15) indicating that coke formation is greater than with ethylbenzene. Activity decline is greater with increasing hydrocarbon partial pressure.

Ortho-diethylbenzene was oxidized over calcium phosphate and the results are given in Table 7. Figure 16 shows conversion selectivity plots for the principal products formed. Ethylvinylbenzene is formed rapidly and quite selectively, but it reacts further, so that high yields are not obtained. *Ortho*-divinylbenzene is formed but it is very rapidly converted to naphthalene. The steady-state selectivity to divinylbenzene is only about 9% over a wide range of conversion. Selectivity to naphthalene of almost 80% is obtained at about 95% conversion, but catalyst activity again declines very rapidly with time (Fig. 17).

Isopropylbenzene

The oxidative dehydrogenation of isopropylbenzene to α-methylstyrene was not as selective as that of ethylbenzene. Table 8 gives results with a calcium phosphate catalyst at various temperatures. α-Methylstyrene is the major product but selectivity is only 60–70%, primarily due to losses to acetone and phenol. No thiophenol is formed. The cause of these side reactions may be due to cracking of cumene to phenyl and isopropyl radicals which then abstract oxygen atoms from sulfur dioxide. It is doubtful that these results are caused by peroxide impurity in the feed since the cumene was fed by saturating a helium stream bubbled through the thermostated liquid. Appreciable quantities of peroxide would not be expected to be volatized.

TABLE 7

OXIDATION OF ORTHO-DIETHYLBENZENE WITH SULFUR DIOXIDE

Calcium phosphate; coke formation not measured and neglected in calculations.

	Press (atm)					Selectivity (%)[a]				
Run	$C_{10}H_{14}$	SO_2	GHSV	Temp (°C)	$C_{10}H_{14}$ Conv (%)	Ethylvinylbenzene	Divinylbenzene	Naphthalene	Styrene + benzene	CS_2 + COS + CO_2 + CO
101-2	0.04	0.48	3100	510	94	2	3	78	5	12
-3	0.04	0.48	6200	510	75	26	9	59	2	4
-4	0.04	0.48	6200	510	60	39	8	47	1	3
102-2	0.04	0.48	6200	510	85	20	9	66	2	4
-3	0.04	0.48	6200	510	63	38	9	39	1	3
-4	0.04	0.48	6200	510	44	56	9	31	1	3
-5	0.04	0.48	6200	510	35	64	8	23	1	4
-6	0.04	0.48	6200	510	29	68	8	18	1	5
103-2	0.05	0.32	10400	570	68	32	6	60	0	2
-4	0.05	0.32	10400	555	26	72	8	18	0	2
-5	0.05	0.32	10400	555	21	76	7	14	0	3
-6	0.05	0.32	10400	555	18	79	7	11	0	3

[a] No vinylbenzothiophene detected.

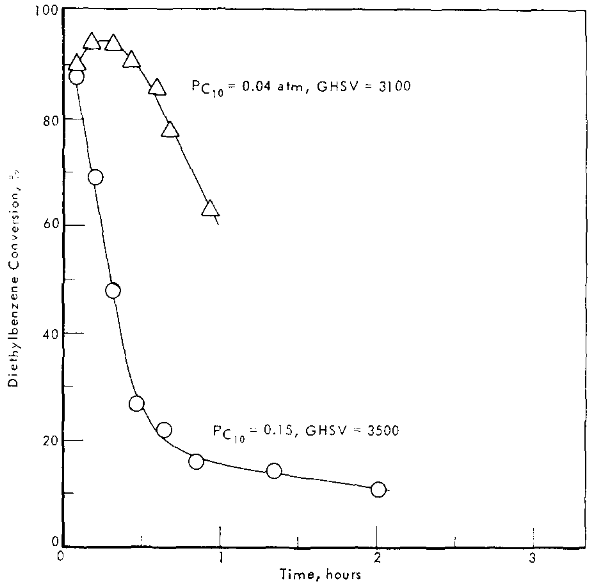

FIG. 15. Time dependence of calcium phosphate catalyst activity in sulfur dioxide oxidation of (*meta* + *para*) diethylbenzenes at 500°C.

sec-Butylbenzene

This compound was oxidized with sulfur dioxide over molybdenum sulfide at 450 and 500°C in an attempt to form 3-vinylbenzothiophene. Although calibration data were not available for accurate analyses, large amounts of phenylbutene and a compound of molecular weight 160 (vinylbenzothiophene or phenylthiophene) were formed. NMR analysis of the solid product indicated that this last material was phenylthiophene and not vinylbenzothiophene. Thus the thiophene ring is formed easier from a linear C_4 chain than from fusion of a C_2 chain with a phenyl ring. This is suported by the fact that butadiene

TABLE 8

OXIDATION OF ISOPROPYLBENZENE WITH SULFUR DIOXIDE

Calcium phosphate; $P_{C_9H_{12}} = 0.15$; $P_{SO_2} = 0.42$; coke not measured and neglected in calculations.

Run	GHSV	Temp (°C)	Conv (%)	Selectivity (%)						
				C_9H_{10}	C_9H_8S	C_8H_6S	C_6H_6O	C_3H_6O	C_7H_6O + C_6H_8 + C_6H_6	CS_2 + COS + CO_2 + CO
84-1	7000	250	7	18	0	0	25	40	9	7
-2	7000	500	40	72	1	0	5	16	1	4
-3	2800	500	63	72	1	0	5	16	3	5
-4	2800	550	68	65	3	0	6	16	3	7
-5	1400	550	67	68	1	0	7	18	1	4
-6	1400	600	68	69	1	0	7	17	3	4
-7	350	600	82	63	2	0	5	17	7	7
-8	350	600	81	60	10	2	5	16	3	5
-9	350	600	76	59	3	0	5	24	3	5
-10	350	600	56	62	6	0	6	16	4	5
-11	350	600	59	61	0	0	7	21	4	5

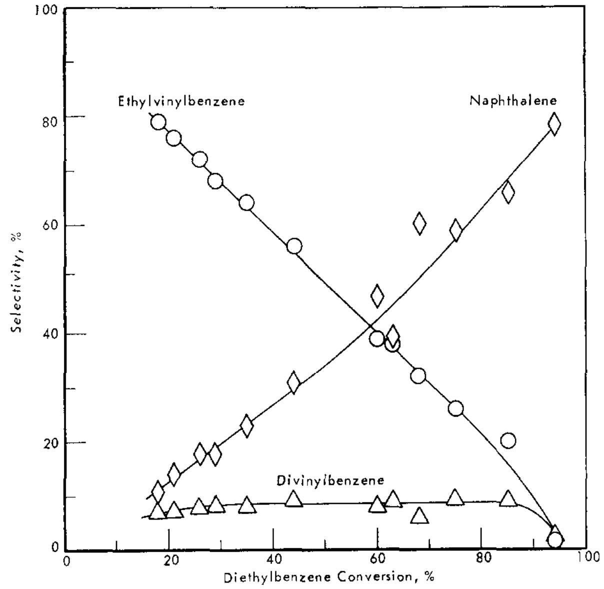

FIG. 16. Oxidation of *ortho*-diethylbenzene with sulfur dioxide over calcium phosphate.

formed from butane goes rapidly to thiophene (*3*), while styrene formed from ethylbenzene may accumulate to very high levels before benzothiophene starts to form to any appreciable extent.

Toluene

The sulfur dioxide oxidation of toluene over vanadium oxide has been reported by Strickland and Bell (*7*). Below 330°C, benzaldehyde was formed in very low yields, while at higher temperatures, benzoic acid was formed quite well. We examined the sulfur dioxide oxidation of toluene over calcium-nickel phosphate, but practically no products volatile at 200°C were found. At 475°C and 45% toluene conversion the only gaseous product de-

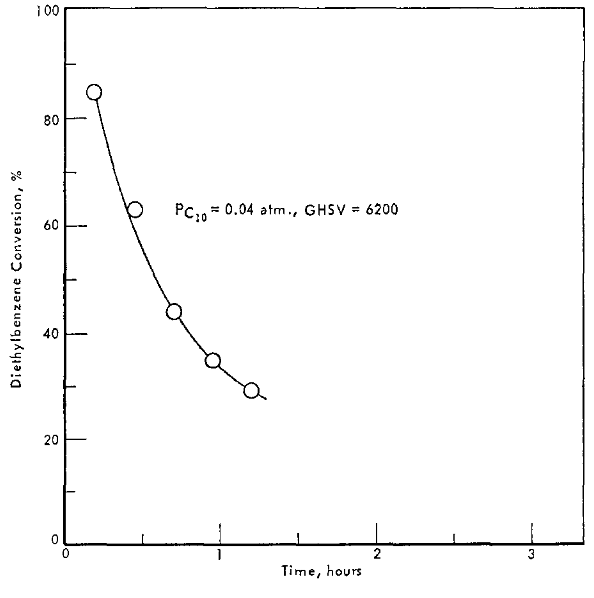

FIG. 17. Time dependence of calcium phosphate catalyst activity in sulfur dioxide oxidation of *ortho*-diethylbenzene at 510°C.

tected was water. No trace of benzoic acid was observed, although its volatility would have been sufficient to be detected. Some solid material was scraped from the product lines and found to be partially soluble in acetone. The acetone-insoluble portion was completely soluble in carbon disulfide and its melting point indicated it was sulfur. The yellow, recrystallized, acetone-soluble portion had a melting point of about 122°C and elemental analysis indicated $(C_7H_7O)_4S_3$ (oxygen by difference). It is not certain to what extent this material represents the bulk of the condensed products from the toluene reaction. At any rate, no clean reaction to any volatile product, like benzaldehyde, benzoic acid, or dibenzyl, is produced. Adding ammonia to the feed stream, to alter the reaction or to divert any intermediate, gave 62% toluene conversion at 475°C with selectivities of 23% to benzonitrile, 3% to thiophenol, 3% to combustion products and 71% to nonvolatile material.

1,5-Cyclooctadiene

It is known that 1,5-cyclooctadiene rearranges thermally to vinylcyclohexene. Oxidation of cyclooctadiene with sulfur dioxide over calcium–nickel phosphate was carried out at 500–550°C to see if styrene could be made in high selectivity. Styrene was the major product but the reaction was not clean. At 550°C, GHSV = 690, and 100% cyclooctadiene conversion, the selectivity to styrene was 40%; benzothiophene, 3%; ethylbenzene, 7%; thiophene, 4%; benzene, 5% butadiene, 24%; combustion products, 3%; and coke, 15%. Other conditions, including lower conversion, resulted in lower yields of styrene. The biggest sources of selectivity losses were butadiene and coke, both of which probably result from "thermal" reactions of the rather unstable cyclooctadiene.

1,5,9-Cyclododecatriene

This compound thermally isomerizes at 460°C to 1,2,4-trivinylcyclohexane. Catalytic oxidation of the cyclododecatriene over calcium–nickel phosphate at 400–500°C was carried out to see if trivinylbenzene could be made. The main gaseous carbon product was vinylnaphthalene, formed by ring closure of the *ortho*-divinyl segment (see Diethylbenzenes above). The maximum yields of this compound was less than 10%, the majority of the feed going to nonvolatile material. Small amounts of the intermediate dehydrogenation products were formed. No sulfur-containing products or butadiene were formed.

1,2,4-Trivinylcyclohexane

The sulfur dioxide oxidation of 1,2,4-trivinylcyclohexane was also examined with calcium–nickel phosphate at 450–550°C. Very severe losses to nonvolatile material occurred, with only small (about 5% yield) amounts of trivinylbenzene and vinylnaphthalene formed. It is possible that the desired reactions occurred but that the trivinylbenzene product is just too reactive at these temperatures.

DISCUSSION

Although no detailed study of the kinetics of these reactions was made, it is apparent from the data for ethylbenzene that the mechanism is complex. The variation of the rate of ethylbenzene conversion with pressure (Fig. 12) suggests an overall first-order relationship, but the effect of added water (Fig. 8) suggests inhibition by products must also occur. The data of Fig. 12 suggest that these dependences are not simply related to reactant concentration and conversion level, however, for large variation in space velocity (and hence also in conversion level) have little effect on the absolute rate of hydrocarbon conversion within experimental error. This suggests that the rate of reaction is not dependent on the hydrocarbon concentration and that a balance exists between conversion and inhibition. Possibly the rate of reaction is proportional to the concentration of some S species generated by the reaction and inhibited by water, which is a product of reaction. In a recent report (*8*) on the oxidative dehydrogenation of similar hydrocarbons with hydrogen sulfide and oxygen or sulfur oxides, several highly reactive sulfur species were considered to be the intermediates responsible for the dehydrogenation. The reactive sulfur species, such as S, S_2, or SH, would be formed *in situ* by Klaus-type reactions,

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S,$$

and react with the hydrocarbons to regenerate hydrogen sulfide:

$$S + RCH_2CH_3 \rightarrow RCH{=}CH_2 + H_2S.$$

Perhaps similar reactions occur when sulfur dioxide alone is fed with a hydrocarbon. In the early stages of reaction over a fresh oxide catalyst (Table 9), appreciable combustion to carbon oxides occurs which decreases with operating time as the catalyst surface is reduced. The amount of H_2S found in the product gases increases as the catalyst surface becomes reduced, but the H_2S/styrene molar ratio never reached the theoretical value of 0.33, due to side reactions to high sulfur content "combustion" products such as carbon disulfide. It is probable that sulfur dioxide reacts with the reduced surface to form reactive sulfur species on the catalyst similar to those mentioned above (and possibly also SO), which "sulfide" the surface and react with the hydrocarbon to generate hydrogen sulfide. Hydrogen sulfide generated in this manner could then react further with sulfur oxide species at the catalyst surface to regenerate the reactive intermediates. Similar reactions may also be occurring in the gas phase, but probably at a slower rate.

The addition of molecular oxygen to this hydrocarbon–sulfur dioxide feed appears to serve no useful purpose other than as a means to attain a thermal balance. As the data of Table 9 show, oxygen added to the feed reacted rapidly to completion but actually inhibited the overall hydrocarbon conversion even though the reaction temperature was higher, due to combustion heat. This inhibition is probably due to the extra water formed by the combustion reaction. Some benzaldehyde was formed but carbon oxides with corresponding water formation account for practically all of the oxygen, most of it going to carbon dioxide with about 20% going to carbon monoxide. Comparison of the H_2S/styrene ratios with and without added oxygen suggest that some oxygen also reacted with H_2S. The results reported by Vadekar and

TABLE 9

VARIATION OF PRODUCT DISTRIBUTION WITH TIME AND EFFECT OF OXYGEN ADDITION

Bismuth iron phosphate catalyst (2Bi:Fe:3P); reactant flow: 30He, 6 ethylbenzene, $30SO_2$.

		Conv (%)[a]	Selectivity to (%)[a]				
Time (min)	Temp (°C)	Ethylbenzene	Styrene	Benzaldehyde	C_8H_6S	$CO + CO_2$	H_2S/ styrene
5	545	97	71	2.2	7	5	.085
14	540	96	90	0.2	8	0.1	.074
25	540	96	92	0.4	6	0.1	.104
40	540	96	93	0.4	6	0	.156
55	540	95	93	0.4	6	0	.198
70	540	96	92	0.5	6	0	.229
95	540	97	91	0.6	7	0	.243
		$6O_2$ Added to feed gases—completely converted					
11	556	89	79	0.2	9	9	.088
19	556	85	82	1.3	6	9	.107
32	556	79	81	1.0	4	10	.134
47	556	78	82	1.5	4	9	.149
62	556	76	82	1.2	3	10	.159
77	556	74	81	1.0	3	11	.166
95	556	74	80	2.0	3	11	.171

[a] Losses to "coke" not included.

Pasternak (*8*), however, suggest that at high H_2S concentrations, added oxygen reacts preferentially with the H_2S rather than with the hydrocarbon as long as the oxygen/hydrocarbon and oxygen/H_2S ratios were held below or about unity. They report hydrocarbon combustion occurs for oxygen/H_2S ratios much above 1.5:1. Our data of Table 9 fit a scheme in which the added oxygen reacted rapidly to completion in the early part of the reactor to form mostly carbon oxides and water, with the SO_2 dehydrogenation reaction occurring slower and later in the reactor. Water formed in the combustion reaction probably inhibited the sulfur dioxide dehydrogenation reaction, so accounting for the lower overall ethylbenzene conversion and the correspondingly lower benzothiophene selectivity.

The strong inhibition observed, when small amounts of water vapor are added to the reactant gases (Figs. 8 and 9), is difficult to explain since considerably larger amounts of water are produced by the dehydrogenation reaction. Since the inhibiting effect is not rapidly reversible, some adsorbed species must be involved which probably is not water only, since the rate of catalyst deactivation with time is accelerated when small amounts of water are added to the feed (Fig. 8). This suggests that water accelerates the formation of "coke" or polymer material which slowly accumulates to poison the catalyst surface.

In deriving an equation to describe the kinetics of coke deposition on the catalyst, Van Zoonen (*5*) assumed a first-order dependence for both the reaction rate and coke deposition, and also that poisoning was due to the reactants having to diffuse through an increasing thickness of coke on the surface. Our data fit such an analysis quite well, as is shown by plotting ethylbenzene conversion versus the square root of the process time (Fig. 4) or versus the cumulative amount of ethylbenzene converted over the catalyst (Fig. 13). Such an analysis, however, does not differentiate between a side reaction of ethylbenzene or further reaction of a product as the source of coke deposition. In several instances when the amount of coke was determined by careful burn-off during regeneration in a dilute oxygen stream, calculation indicated that sufficient coke had been deposited to fill the pores of the catalyst to completely cover its surface, yet the catalyst still showed good activity for ethylbenzene dehydrogenation. This suggests either high mobility through the coke layer or that the coke itself had appreciable catalytic activity.

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REFERENCES

1. Voge, H. H., and Adams, C. R., *Advan. Catal.* **17,** 151 (1967).
2. Adams, C. R., *J. Catal.* **10,** 355 (1968).
3. Adams, C. R., *J. Catal.* **11,** 96 (1968).
4. Adams, C. R., *U. S. Pat.* No. 3,299,155 (1967).
5. Van Zoonen, D., *Proc. Int. Congr. Catal., 3rd, 1964,* Vol. 2, p. 1319. North-Holland, Amsterdam, 1965.
6. Noddings, C. R., Heath, S. B., and Carey, J. W., *Ind. Eng. Chem.* **47,** 1373 (1955).
7. Strickland, T. H., and Bell, A., *Ind. Eng. Chem.* **53,** 7 (1961).
8. Vadekar, M., and Pasternak, I. S., *U. S. Pat.* 3,403,192 (1968).
9. "Physical and Thermodynamic Properties of Elements and Compounds." Girdler Co., 1954. Louisville, Kentucky.