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Heterogeneous–Homogeneous Effects during the Catalytic Oxidation of Butene

Although it is known that many gas phase free radical reactions are affected by the presence and the nature of a surface (*1–3*), a clear distinction is usually drawn between gas phase free radical reactions and heterogeneous catalyzed reactions, which do not usually involve gas phase free radicals. In at least two cases, however, there is clear evidence that closely linked heterogeneous and homogeneous reactions may be occurring in the same reactor (*4*, *5*). During a study of the oxidation of *n*-butene isomers to butadiene over tin–antimony oxide catalysts, further evidence of related heterogeneous–homogeneous reactions was obtained and this is the subject of the present note.

The oxidation of *n*-butene isomers over tin–antimony oxide has been shown to proceed via oxidative attack on the allylic hydrogen (*6*). The kinetics of the reaction have been measured (*6*) and the importance of mass transfer via surface diffusion at high temperatures has been established (*7*). Temperatures within and near to single pellets have been measured and the results have been compared with the predictions of a mathematical model (*8*). During these studies it was noted that the temperatures in the gas phase could sometimes exceed those within the catalyst and these results are reported and discussed below.

The equipment and technique used to measure temperatures in and around single pellets has been previously reported (*8*) together with methods of on-line gas chromatographic analysis (*6*, *8*). Thermocouples inserted in the pellet were calibrated between 450 and 550°C, to give an accuracy of temperature measurement of ±0.2°C. The pellet of catalyst contained 0.66 g of the oxides.

In order to check the importance of heterogeneous–homogeneous reactions, different experimental apparatus was used. In one set of experiments, mixtures of butene, oxygen, and nitrogen were fed to a tubular reactor containing catalyst, and the products of the reaction were taken immediately to a small jet-stirred reactor (*9*) which contained no catalyst. Gases leaving the catalytic reactor and the jet-stirred reactor could be analyzed. In a second set of experiments, mixtures of butene, butadiene, oxygen, nitrogen, and acetaldehyde were fed directly to the jet-stirred reactor.

During the course of the investigation of the temperature rise in single pellets (*8*), attempts were made to increase the flow rate of the gas in order to promote turbulence and to improve mass transfer to the pellet surface. Under these conditions, the temperature in the gas phase was found to increase dramatically in some cases (Fig. 1). These initial runs involved both varying flow rate and varying butene:oxygen ratios. Subsequent experiments showed that the large increase in temperature was more dependent on the butene:oxygen ratio than on flow rate

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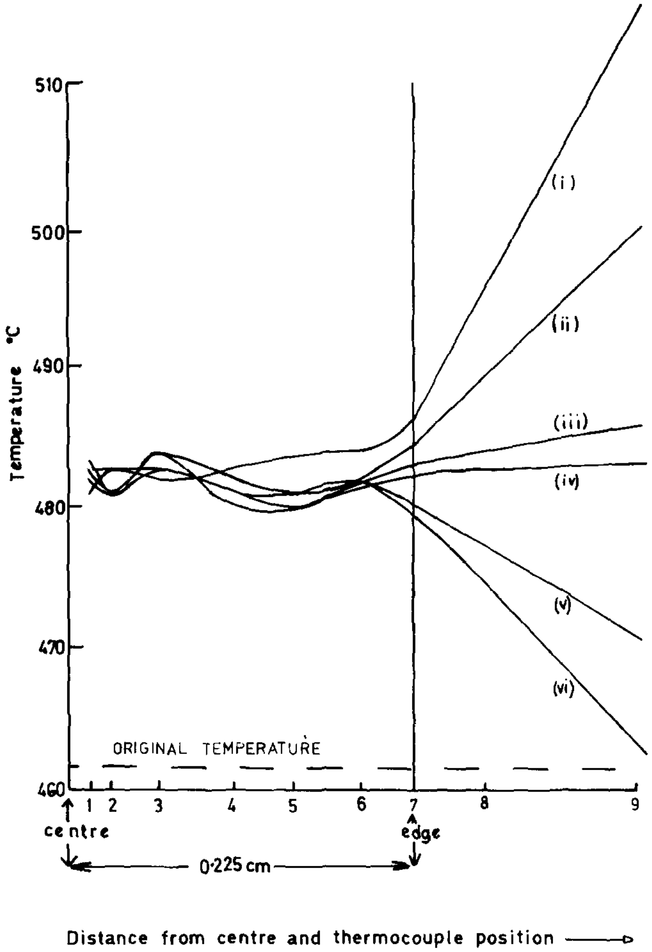

FIG. 1. Temperatures in and near a pellet. Starting temperature 462°C. Thermocouples (1–9) are placed at the positions shown.

	Oxygen: butene	Flow rate (ml min^{-1} at 25°C)
(i)	1.53	350
(ii)	1.27	290
(iii)	0.84	192
(iv)	0.67	150
(v)	0.35	80
(vi)	0.20	40

(Fig. 2). Replacement of the catalyst by a silica pellet of equal size gave minimal conversion of butene (<2%) and no significant temperature rise (<2°C).

These results would indicate that a gas phase reaction (which would otherwise not be significant) was being induced by the presence of the catalyst. The existence of such interactions has been suggested by several workers (*4*, *10–13*), and may originate from two possible causes. In the first the chemical reaction on the catalyst is

TABLE 1

Heterogeneous–Homogeneous Oxidation Reactions

Catalytic reactor			Gas phase reactor (molar fractions)										
Run	T_c[a] (°C)	Oxygen: butene	t[b] (sec)	T_g[c] (°C)	RCHO[d] In	C_4H_8		C_4H_6		CO		CO_2	
						In	Out	In	Out	In	Out	In	Out
1	460	0.63	0.6	450	0.0075	0.7	0.7	0.15	0.15	0.002	0.0021	0.005	0.005
2	460	0.63	2.2	450	0.013	0.46	0.46	0.32	0.33	0.0018	0.0017	0.01	0.011
3	460	3.15	2.2	450	0.031	0.12	0.12	0.58	0.58	0.0075	0.0073	0.031	0.031
4	460	2.8	0.71	475	0.006	0.053	0.053	0.093	0.094	0.0057	0.0057	0.066	0.067
5	460	2.7	2.7	475	0.007	0.024	0.024	0.118	0.118	0.0117	0.0131	0.133	0.134
6	460	2.8	1.66	545	0.006	0.0216	0.0219	0.118	0.114	0.0168	0.0178	0.129	0.131
7	460	2.8	2.66	545	0.006	0.0149	0.0150	0.111	0.112	0.0121	0.016	0.125	0.132
8	460	4.1	1.49	584	0.005	0.074	0.074	0.070	0.065	0.0048	0.01	0.082	0.085
9	460	4.1	2.28	585	0.006	0.0104	0.0092	0.108	0.087	0.113	0.223	0.170	0.178
10	—	—	2.0	450	0.01	0.4	0.4	0.3	0.3	0	0	0	0
11	—	—	2.0	475	0.01	0.4	0.39	0.3	0.3	0	0.01	0	0.005
12	—	—	2.0	500	0.01	0.4	0.37	0.3	0.28	0	0.052	0	0.03
13	—	—	2.0	525	0.01	0.4	*e*	0.3	*e*	*e*	*e*	*e*	*e*
14	—	—	2.0	475	0	0.4	0.4	0.3	0.3	0	0	0	0
15	—	—	2.0	500	0	0.4	0.38	0.3	0.3	0	0.004	0	0.001
16	—	—	2.0	525	0	0.4	0.36	0.3	0.28	0	0.045	0	0.03

[a] T_c = temperature of reactor containing catalyst.

[b] t is the residence time in the jet-stirred reactor, calculated as volume of reactor/inlet flow rate corrected to 27°C.

[c] T_g = temperature of jet-stirred reactor.

[d] Runs 1 to 9: aldehydes are a mixture of acetaldehyde, acrolein, methacrolein, and *n*-butyraldehyde produced by the catalytic reaction. Runs 10 to 16: acetaldehyde.

[e] Cool flame (*3*).

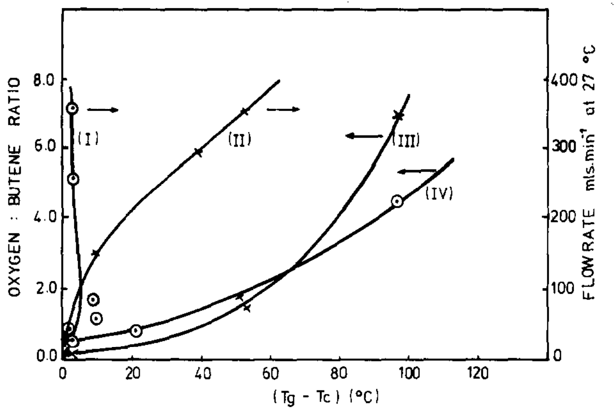

FIG. 2. The temperature difference between the gas phase and the catalyst as a function of oxygen:butene ratio and of flow rate. ($T_g - T_c$) = Temperature difference between the bulk gas phase (thermocouple 9) and the center of the catalyst (thermocouple 1). (I) oxygen:butene ratio = 0.25; (II) oxygen:butene ratio = 1.3; (III) flow rate = 350 ml min^{-1}; (IV) flow rate = 150 ml min^{-1}.

suggested to raise the solid temperature to the point where a gas phase reaction begins (*12*, *13*) while, in the second, the catalyst is suggested to produce intermediates (such as aldehyde or peroxides (*4*)) that can initiate gas phase reactions at low temperatures (*3*).

Inspection of the results in Fig. 1 show that the first explanation is unlikely. The temperature in the gas phase is seen to vary between 460 and 510°C, while the temperature of the catalyst remains effectively constant. As a result, the presence or absence of gas phase reaction cannot be ascribed to a rise in the catalyst temperature. The second explanation would seem more feasible, since aldehydes are produced in the system (Table 1) and have been shown to be produced by the catalytic oxidation (*6*). Peroxides could not be analyzed.

As a result of this observation, attempts were initiated to study the importance of the gas phase reaction in the absence and presence of aldehydes. Two types of experiment were carried out. In the first, a mixture of butene, oxygen, and nitrogen was passed over a bed of catalyst particles and the product gases were fed to an empty jet-stirred reactor (Table 1, runs 1–9). Gas phase oxidation was initiated at 475°C, and the products of the gas phase oxidation always contained more carbon monoxide than those from the catalytic oxidation.

In the second set of experiments a mixture of butene, butadiene, oxygen, and nitrogen with and without acetaldehyde was prepared and fed directly to the jet-stirred reactor (Table 1, runs 10 to 16). In the presence of acetaldehyde, gas phase oxidation was initiated at 475°C while, in the absence of aldehyde, the reaction began only at 500°C. Referring to the results summarized in Fig. 1, it is seen that the catalyst temperature (ca. 485°C) is sufficient to initiate gas phase oxidation if aldehydes are present, and is insufficient to initiate gas phase oxidation if aldehydes are absent.

It would appear, then, that intermediates produced by the catalyst (aldehydes and, possibly, peroxides) may initiate gas phase free radical reactions under conditions where they would otherwise not be expected.

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