Partial Oxidation of o-Xylene in Melts Containing Vanadium Pentoxide

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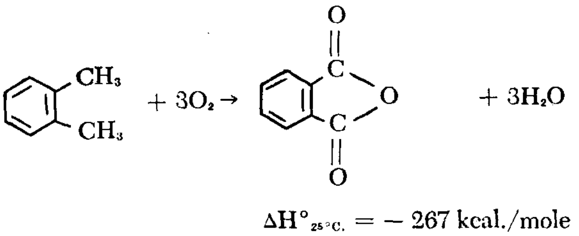
o-Xylene vapor in nitrogen was partially oxidized by bubbling it through a melt of the 39 wt. % vanadium pentoxide-potassium sulfate eutectic at temperatures from 528° to 598°C. The principal product was o-tolualdehyde; some benzene and traces of phthalide were formed but no organic acids. These products are similar to those found in o-xylene oxidation over a solid vanadium oxide catalyst, except for the absence of acid products but are far different from the product distribution found from homogeneous oxidation with air. The rate of reaction per unit of gas-melt interface was approximately equal to that reported for oxidation of o-xylene in air on an unsupported fused vanadium oxide catalyst. With o-xylene-air mixtures bubbled through either a vanadium pentoxide-potassium sulfate eutectic melt or vanadium pentoxide-potassium pyrosulfate melt, homogeneous reaction obscured any contribution from heterogeneous processes.

In present chemical technology, catalyzed gas-phase reactions are usually carried out in either fixed- or fluidized-bed reactors. With highly exothermic or endothermic reactions, isothermal operation is difficult to achieve in a fixed-bed reactor because of the poor radial heat transfer. In a fluidized bed essentially isothermal operation can be achieved, but the flow patterns and residence times of solids and gas are understood poorly. The purpose of this work was to explore a different contacting method, that of passing the reactant gas in the form of bubbles up through a vessel containing a melt which would act as an oxidizing agent or as a catalyst. In addition to providing a more nearly isothermal operation than the fixed-bed reactor, a melt reactor system may permit new methods of carrying out a catalytic reaction. For example, in a catalytic oxidation it may be possible to achieve more selective reaction and minimize overoxidation by not allowing the reactant to come in contact with the primary oxidant. By proper choice of a suitable melt, the reactants may be oxidized by the melt in one reactor, and the reduced melt reoxidized by a second gas stream, such as air in a second reactor, and then be recirculated to the first. The high catalytic activity of many metal oxides has been attributed to the ease with which they may alternate between two oxidation states. That of a solid vanadium pentoxide catalyst in *o*-xylene oxidation, for example, has been ascribed to a V_2O_5-V_6O_{13} oxidation-reduction system (*18*).

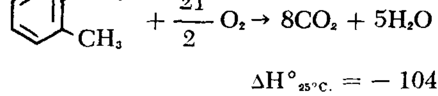
Many investigations have been reported in which a reacting gas was passed through a molten mass. In some cases the molten mass appeared to have been essentially noncatalytic and to have functioned merely as a heat transfer medium, for example, in the decomposition of propane in a molten lead bath (*6*). In other studies the molten mass was utilized as a reagent, for example in the chlorination of methane in potassium chloride–cupric chloride–cuprous chloride (*7*), in which no chlorine was fed to the reactor. Several studies have been reported in which the melt was used as a catalyst, for example, condensation of acetylene to form aromatics or of acetylene plus ammonia to form acetonitrile in a sodium chloride–potassium chloride–zinc chloride melt (*8*, *9*) and reaction of 1,1 dichloroethane and acetylene to form vinyl chloride in a zinc chloride-potassium chloride melt containing 5 wt. % mercuric chloride (*19*). The only report of a study with the higher melting point oxide types of melts is that by Topsoe and Nielsen (*20*), in which a mixture of sulfur dioxide was oxidized to sulfur trioxide in oxygen or in air in a vanadium pentoxide–potassium pyrosulfate melt. The reaction was carried out in a column packed with Raschig rings with a gas lift used for melt recirculation. The rate of reaction was reported to be comparable to that obtained in the usual fixed-bed process.

The choice of the oxidation of *o*-xylene in a vanadium pentoxide melt was based on the following considerations. Commercially, *o*-xylene competes with naphthalene as the feed stock for production of phthalic anhydride. The theoretical yield is 1.4 lb. of phthalic anhydride/lb. of *o*-xylene, but the best yields reported are only 0.9 to 0.95 lb./lb. (*4*), whereas napthalene is converted in almost quantitative yields. *o*-Xylene oxidation is well suited for an evaluation of melt-oxidation reactions, since the reactions involved



(1)

$$\Delta H^\circ_{25^\circ C.} = -267 \text{ kcal./mole}$$



(2)

$$\Delta H^\circ_{25^\circ C.} = -1046 \text{ kcal./mole}$$

are highly exothermic, a high temperature is required for reaction, yields are fairly low by present technology, and temperature control is required to prevent overoxidation. The commercial fixed-bed process for *o*-xylene conversion to phthalic anhydride uses a contact time of about 0.1 to 0.15 sec. (*16*) at 480° to 620°C. over a vanadium pentoxide-based catalyst.

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The melt systems selected for study here were the vanadium pentoxide–potassium sulfate eutectic mixture containing 39 wt. % vanadium pentoxide, which has a melting point of 430°C. and 14 wt. % vanadium pentoxide in potassium pyrosulfate. The latter was used by Topsoe and Nielsen in their study of the oxidation of sulfur dioxide to sulfur trioxide (*20*) at temperatures of about 490°C. These two compositions apparently bracket those used commercially for fixed- and fluidized-bed operation (silicon dioxide free basis) in the partial oxidation of naphthalene. No information was given on the composition of the vanadium pentoxide catalysts used commercially for *o*-xylene oxidation. However a recent patent (*14*) describes the use of a mixture of vanadium pentoxide and an alkali pyrosulfate which is liquid under reaction conditions, the preferred temperature of reaction being 270° to 350°C. A sulfur compound or sulfur dioxide is added to the feed stream to maintain the catalyst composition so it remains in the form of a liquid. The selectivity is also improved by adding a trace of bromine to the feed stream and incorporating a metal oxide in the catalyst to oxidize hydrogen bromide to bromine. The only other vanadium pentoxide melt known to us which has a melting point below 500°C. and which is not overly expensive is the 21% vanadium pentoxide–79% potassium metavanadate mixture with a melting point of 389°C. However, preliminary studies showed this system to be inoperable in our apparatus because of extreme foaming.

The fusion diagram for the vanadium pentoxide–potassium sulfate system is shown in Figure 1 (*3*). No diagram is available for the vanadium pentoxide–potassium pyrosulfate system, since a glassy substance rather than a crystalline phase is formed on cooling. The following are the sources of the chemicals used:

o-xylene	Phillips Petroleum Co.	99.89% min. purity
Vanadium pentoxide	Union Carbide Nuclear Co.	99.68% min. purity
Potassium sulfate	Baker Co.	reagent grade
Potassium pyrosulfate	Mallinckrodt Chemical Works	reagent grade

EXPERIMENTAL

A flow diagram of the apparatus is shown in Figure 2 and a sketch of the melt reactor in Figure 3. Metered air, free of carbon dioxide and water vapor, or metered nitrogen entered a 300 cc. spherical Pyrex vaporizer-mixer through a tangential connection. Liquid *o*-xylene was also fed into the mixer at a constant rate by a positive displacement syringe feed mechanism. The gaseous mixture was dispersed into the melt in the reactor by a Pyrex gas dispersion tube equipped with a fritted disk with a 170 to 220 μ nominal maximum pore diameter (Dow Corning Co. No. 20EC), located at the base of the reactor. Attempts to use a finer fritted disk disperser (No. 20C, 40 to 60 μ nominal maximum pore size) were unsuccessful; no gas could be forced through under the available pressure drop of about 1 atm. The effluent was cooled in an electrostatic precipitator-condenser, in which the fog of condensed products was forced to migrate to the wall by an electrostatic field. The coolant was solid carbon dioxide in carbon tetrachloride. The liquid drained countercurrent to the gas flow and was collected in a 10-ml. burette. The effluent gas from the electrostatic precipitator-condenser was bubbled through a laboratory wash bottle and then flowed through a wet test meter to exhaust.

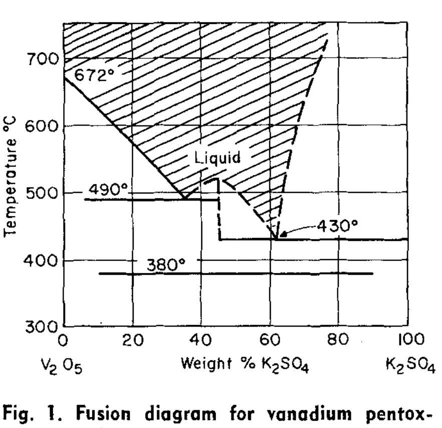

Fig. 1. Fusion diagram for vanadium pentoxide-potassium sulfate system.

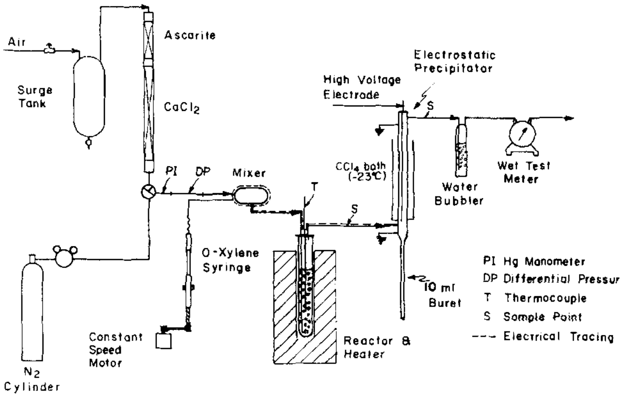

Fig. 2. Flow diagram of melt reactor system.

The reactor consisted of a 50 mm. O.D. Pyrex test tube 28 cm. long onto which a 2 in. I.D. Pyrex pipe 6 cm. long was glassblown. The 28 cm. length was inserted into a specially designed furnace whose core consisted of 2 in. schedule 40 carbon steel pipe. This was surrounded with heating coils controlled by a constant voltage transformer and Variacs and then with insulation. The pipe was provided with two sets of four vertical slots (¼ in. wide × 2 in. long) placed diametrically so that the expanded melt height could be measured and the appearance of the top of the melt examined directly. Insulation was cut out in front of the slots.

Six thin plate radiation shields were placed in the top 6 cm. of the reactor to reduce heat losses from the top of the melt. The reactor top was sealed with an aluminum flange with Swagelock fittings and a Teflon ferrule. Glass wool was packed around the top for insulation. Once the reactor was charged with the melt components the furnace was maintained continuously above their melting point, and voltage adjustments to alter the temperature were made at least 12 hr. before experimental data were taken. Thermocouple profiles in the absence of bubbling gas showed the axial temperature to be constant within ±1°C., except for a 2°C. drop at the bottom of the tube and a sharp temperature drop just below the top melt surface. Further details are given by Loftus (*12*). A corrosion problem may exist in sustained studies with these melts, since a sample of the potassium sulfate-vanadium pentoxide eutectic maintained at 600°C. for a period of two months with no gas bubbling through it dissolved a hole in the wall of a 50 mm. O.D. Pyrex test tube having a wall thickness of approximately 1 mm.

The following studies were made.

1. In run series FD, nitrogen alone was bubbled through the vanadium pentoxide-potassium sulfate eutectic melt at 509° to 570°C. and atmospheric pressure to determine the average bubble velocity as a function of temperature and to serve as a basis for estimating the total gas-liquid interfacial area. The viscosity of this melt system was determined in a falling ball viscometer; the results are reported elsewhere (*21*).
2. 1.1 mole percent *o*-xylene in air was bubbled through the vanadium pentoxide-potassium sulfate eutectic mixture at 500°C. and atmospheric pressure.

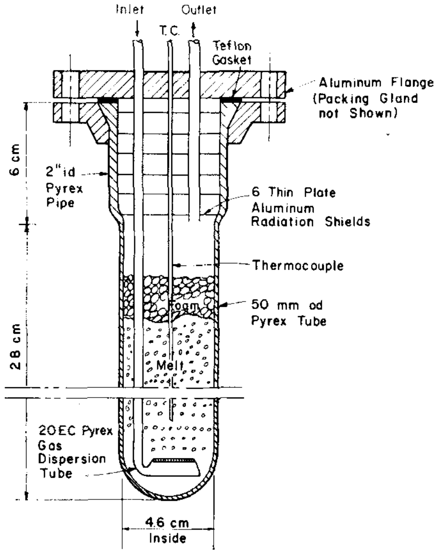

Fig. 3. Melt reactor.

3. In run series U, 0.3 to 1.8 mole percent *o*-xylene in nitrogen was bubbled through the same melt composition at 474° to 598°C. and atmospheric pressure to determine the extent of heterogeneous reaction in the absence of gaseous oxygen and to identify the stable products formed.
4. 0.4 to 1.2 mole percent *o*-xylene in air or in nitrogen was bubbled through the vanadium pentoxide-potassium pyrosulfate mixture at 423° to 510°C. and atmospheric pressure (14 wt. % vanadium pentoxide, 60 wt. % potassium sulfate, 26 wt. % sulfur trioxide).

Analytical Procedures

In the studies in which a substantial degree of oxidation of *o*-xylene occurred, the amount of o-xylene in the reactor effluent was determined by concentrating *o*-xylene on an adsorbing agent—the commercial detergent Tide—and subsequently by measuring the amount of *o*-xylene desorbed from the adsorbent with gas chromatography procedures. In the runs in which *o*-xylene in nitrogen was bubbled through the vanadium pentoxide-potassium sulfate eutectic, a similar procedure was used to determine the amount of benzene, toluene, *o*-xylene, carbon monoxide, and carbon dioxide in the exit vapors from the electrostatic precipitator-condenser. In these runs, the liquid products collected in the electrostatic precipitator-condenser were analyzed by gas chromatography methods with 20 wt. % Dow-Corning vacuum grease on 30-60 mesh Chromosorb-P firebrick as the partitioning agent. Details of the analytical procedures have been published elsewhere (*13*, *17*). With the vanadium pentoxide-potassium pyrosulfate system, sulfur trioxide was continuously evolved, so the sulfur trioxide content of the melt was determined periodically by removing a sample and by titrating with standard base with a *p*H meter.

In each group of studies several runs were made with the same melt charge. The normal procedure was to charge the reactor, melt the mixture, and then bubble nitrogen or reactants through the melt continuously for several days, changing the temperature from time to time and analyzing a sample of the reaction products after the new conditions were well established. When studying *o*-xylene in nitrogen, (run series U, Table 1 and Figure 4), benzene, *o*-tolualdehyde, phthalide, carbon dioxide, and a carbonaceous material were the only products detectable, with *o*-tolualdehyde constituting the major product. Conversion was low, so the liquid product consisted essentially of a dilute solution of *o*-tolualdehyde in *o*-xylene. Positive identification of the *o*-tolualdehyde was obtained by comparing infrared spectra of the unknown with those for pure *o*-xylene and for dilute solutions of *o*-tolualdehyde in *o*-xylene. Details are given by Loftus (*12*). The small amounts of phthalide and of benzene present in the product liquid were detected by infrared analysis and were also identified by their retention time in a gas chromatography column using 20% silicone grease on Chromosorb.

RESULTS

Fluid Dynamics

The expanded height due to bubbling in the bath containing the vanadium pentoxide–potassium sulfate eutectic was measured visually through slots in the furnace with a

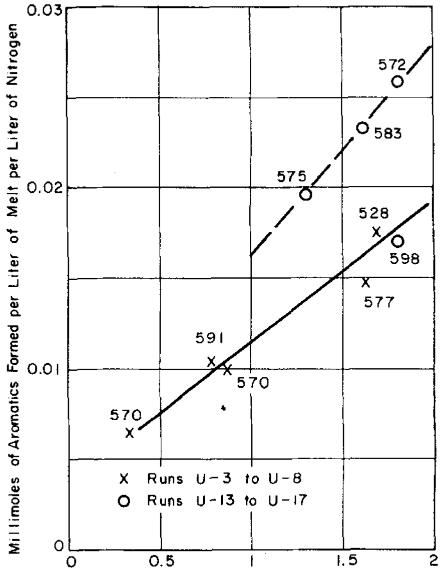

Fig. 4. Oxidation of o-xylene in potassium sulfate-vanadium pentoxide eutectic melt.

TABLE 1. OXIDATION OF *o*-XYLENE IN NITROGEN BY VANADIUM PENTOXIDE-POTASSIUM SULFATE EUTECTIC

Run	U-3	U-4	U-5	U-6	U-8
o-Xylene feed rate, cc./hr.	0.98	0.98	0.38	2.00	2.00
Melt temperature, °C.	570	591	570	577	528
Percent conversion to:					
Benzene	0.6	0.6	1.7	0.4	0.7
o-Tolualdehyde	1.6	1.9	2.2	1.4	1.2
Phthalide	0.005	Neg.	0.03	Neg.	0.05
Oxygen consumed, mmoles oxygen/hr.	0.237	0.257	0.177	0.377	0.456
Rate of formation of aromatics, mmoles/(sq. cm.)(hr.)	0.27×10^{-3}	0.28×10^{-3}	0.09×10^{-3}	0.43×10^{-3}	0.30×10^{-3}

cathetometer at each of several different gas volumetric flow rates and at each of several temperatures (run series FD). The mean bubble velocity was defined as expanded bed height divided by the gas residence time. Thus

$$\bar{u} = \frac{H}{(H-h)\,(\pi R^2/Q)} \qquad (3)$$

The value of $\bar{u}$ was found to be essentially independent of gas volumetric flow rate over a substantial range. Hence Equation (3) may be differentiated to give

$$\bar{u} = \frac{-1}{h\pi R^2} \times \frac{dQ}{d(1/H)} \qquad (4)$$

The average bubble velocity $\bar{u}$ was calculated from the slope of the straight line obtained by least-squares fitting of data on a plot of the reciprocal of expanded melt height $1/H$ vs. gas volumetric flow rate Q at constant melt temperature. Data were obtained from five runs at temperatures of from 509° to 570°C. and volumetric flow rates up to 40 cc. of nitrogen/sec. The average bubble velocity varied from 9.0 cm./sec. at 509°C. to 17.8 cm./sec. at 570°C. and was found to be inversely proportional to the melt viscosity. From the bubble velocity and melt viscosity at 500°, 540°, and 580°C., the product of mean bubble velocity and melt viscosity ($\bar{u}\,\mu$) had an average value of 3.87 g./sec.^{2} with an average deviation of 0.27 g./sec.^{2}

A clean gas-liquid interface is not at rest as in the case of a solid sphere surrounded by liquid. Levich (*11*) presented the complete solution, originally performed by Hadamard, for the linearized Navier-Stokes equation whose boundary conditions include a mobile interface. For a gas bubble whose density and viscosity are negligible compared to those of the melt, the Hadamard solution at low Reynolds number reduces to

$$\bar{u} = -\frac{g\,\rho\,D^2}{12\mu} \qquad (5)$$

which predicts a velocity 1.5 times that predicted by Stokes' law. Many investigators have reported that the velocities of gas bubbles in common liquids, such as water, aniline, etc., obey Stokes' law rather than the Hadamard relationship, which Levich attributed to the accumulation of surface-active agents that immobilize the interface. In the present studies foaming occurred when either nitrogen alone or nitrogen plus *o*-xylene was bubbled through the melt but there is no experimental evidence as to whether or not the gas-melt interface was immobilized. The average bubble diameter D in our studies was calculated from Equation (5) to be 0.15 cm. when $\bar{u}\,\mu$ = 3.87 g./sec.^{2} and a melt density = 2.25 g./cc. However, we were dealing with a range of sizes of bubbles present as a cloud; so the degree of applicability of this equation is uncertain. The melt density was found to vary by less than 2% over the temperature range of 500° to 580°C.

Reaction of o-Xylene–Air Mixtures

When the *o*-xylene–air mixture was bubbled through the vanadium pentoxide–potassium sulfate eutectic, the walls of the reactor adjacent to the slots became darkened, the melt foamed substantially, and upsets were frequent due to plugging of the outlet tube from the reactor. Two runs at 500°C. resulted in 35 to 42% conversion of the *o*-xylene but a poor material balance was obtained. The principal product was *o*-tolualdehyde, the acid yield (calculated as phthalic anhydride but not specifically identified) was less than 5% of the *o*-xylene disappearance. The residence time was estimated to be about 2 sec. in the bubbles and about 15 sec. in the foam and void volume above the melt. From corollary studies on the rate of homogeneous oxidation of *o*-xylene by air (in the absence of catalyst) (*17*), one may estimate that the rate of homogeneous oxidation would be sufficient to account for essentially all of the *o*-xylene disappearance, that is, under these circumstances the extent of catalytic reaction is completely obscured by homogeneous reaction.

Five runs were also made with a vanadium pentoxide–potassium pyrosulfate melt, the first three with 0.4 to 1.2 mole percent *o*-xylene in air at melt temperatures of 423° to 455°C. and the last two with 1.0 mole percent *o*-xylene in nitrogen, using one melt charge. The results scattered substantially, due in considerable measure to uncertainties in the analytical procedure. The amount of *o*-xylene reacted varied up to 50%, the principal products being *o*-tolualdehyde and carbon dioxide. The concentration of sulfur trioxide in the gas phase caused by dissociation of the pyrosulfate was estimated to be about 1%. Two runs to measure the rate of homogeneous oxidation of *o*-xylene by sulfur trioxide in nitrogen indicated that homogeneous reaction could account for a large portion if not all of the *o*-xylene that disappeared in these runs with the pyrosulfate melt.

Reaction of o-Xylene-Nitrogen Mixtures

Four series of runs (each series being made with a different melt charge) were performed in which *o*-xylene vapor in pure nitrogen was passed through the vanadium pentoxide–potassium sulfate eutectic melt. The radiation shields shown in Figure 3 were not used in these studies. The first was exploratory only, and experimental difficulties were encountered in the third.

The results of the second series (U-3 through U-8) is shown in Table 1. The melt weighed 763 g. and occupied a volume of 290 cc. and a height of 18.3 cm. In this series the gas flow rate varied from 16.5 to 18.7 cc./sec. (calculated at melt temperature), the gas superficial velocity was calculated to be 1.0 to 1.2 cm./sec., the void fraction in the melt 0.057 to 0.083, and the mean bubble residence time 1.0 to 1.7 sec. The bubble interfacial area in the total melt charge varied from 680 to 1,100 sq. cm. Nitrogen was bubbled through the melt continuously for 93 hr. and *o*-xylene was fed to the nitrogen for a total of 28 hr. Only traces of carbon dioxide and no carbon monoxide was found in the effluent gas. In run U-7 air alone was bubbled through the melt. A fourth series comprising four runs (U-13 to U-17) gave results similar to those of the second series, U-3 through U-8. The total nitrogen bubbling time was 140 hr. and that for nitrogen plus *o*-xylene was 18 hr. In all these runs the conversion of *o*-xylene was low, from 1.0 to 3.2%. However, the oxidizing agent was clearly the vanadium pentoxide–potassium sulfate melt, as shown by the very small amounts of reaction (about 0.01% *o*-xylene converted) that occurred when runs were performed in the same apparatus using the same nitrogen, but without the melt. The extent of this reaction in the absence of melt was within the manufacturer's specified maximum concentration of oxygen in the "prepurified nitrogen." The change in composition of the melt by loss of oxygen to reaction products was negligible. Calculations showed that after 28 hr. of operation (four runs of 7 hr. each) the vanadium oxide would change in composition from V_2O_5 to only $V_2O_{4.999}$.

In these melt studies the principal product was *o*-tolualdehyde, plus small amounts of benzene, phthalide, and carbonaceous deposits. No acid products were found, as shown by infrared spectra. No *o*-xylene oxide, the principal initial product in homogeneous oxidation, was detected nor was any 2-2′ dimethyl dibenzyl, which is also formed in the initial stages of the homogeneous reaction (*13*). Some carbonaceous material accumulated in the melt, amounting, for example, to 0.03 to 0.04 wt. % carbon at the end of run series U-3 through U-8. This is equivalent to 0.8% of the *o*-xylene fed to the reactor. The analytical procedure was checked against blanks.

o-Tolualdehyde was found to be the chief by-product, particularly at low conversion, of *o*-xylene oxidation to phthalic anhydride over solid vanadium pentoxide catalysts (*2, 5, 10, 15*), whereas *o*-xylene oxide and dimethyl dibenzyl were not. So it is evident that the characteristics of the reaction of *o*-xylene vapor with the vanadium pentoxide-potassium sulfate melt are similar to those with the solid vanadium pentoxide catalyst, except for the absence of acid products, and are very different than the homogeneous oxidation reaction with molecular oxygen.

Rate of Reaction

Figure 4 shows the quantity of aromatics (*o*-tolualdehyde, benzene and phthalide) formed as a function of the concentration of *o*-xylene in the nitrogen. The differences between the two groups of runs are caused probably by a different amount of interfacial area. A different disperser was used for the two sets of runs and there may also have been some variation in the degree of foaming. However, for either set the rate was approximately proportional to the *o*-xylene concentration. Calculations (*12*) showed clearly that the rate of mass transfer of *o*-xylene from the gas phase inside the bubbles to the gas-melt interface was so much more rapid than the observed rate of reaction that this mass transfer process could not be the rate-limiting step. The rate of mass transfer of some oxygenated species in the melt to the gas-melt interface could not be estimated in absence of knowledge as to what it might be. However, if this were rate-controlling the observed rate of reaction would be independent of *o*-xylene concentration, contrary to the facts. If the rate of reaction is assumed to be proportional to the total bubble area and to the *o*-xylene partial pressure in the gas space, the following expression is obtained:

$$\frac{N}{\pi R^2 H Q} = \frac{6}{\pi R^2 D}\,\frac{k_s}{\bar{u}}\,p \qquad (6)$$

This is consistent with the proportionality shown in Figure 4. The runs shown in Figure 4 were obtained over the temperature range of 528° to 598°C. (the temperature of each run is shown beside the datum point) but no effect of temperature on reaction rate is seen. The fluid mechanics study showed that the average bubble velocity was inversely proportional to the melt viscosity. If both u and k_s followed relationships of the Arrhenius type with respect to temperature and if the activation energy for surface chemical reaction were equal to that for viscosity (about 12 kcal.), the rate of reaction N would be independent of temperature.

In runs U-3 to U-8 and U-13 to U-17, the total gas interface in the melt was estimated to be 2.3 to 3.8 sq. cm./cc. of expanded melt volume. The specific surface reaction rate varied from about 10 to 70 × 10^{-5} mmoles of *o*-xylene converted to *o*-tolualdehyde, phthalide, and benzene/(hr.)(sq. cm.) of gas-melt interface. Bhattacharyya and Gulati (*1*) studied the activity for *o*-xylene oxidation of fourteen vanadium oxide-based catalysts and reported surface areas of five of them. These varied from 0.46 to 23 sq. m./g. The authors reported that no correlation existed between surface area and catalytic activity but the most selective catalyst, which also showed a relatively high space-time yield of phthalic anhydride, had the smallest specific surface area (sq. cm./g. of catalyst). This catalyst was unsupported, fused vanadium pentoxide and had a surface area of 4,600 sq. cm./g. The yield of phthalic anhydride was 85.6 g./(hr.)(liter) (of reactor volume) or 580 mmoles/(hr.)(liter). It is probable that severe diffusion limitations occurred in the higher area catalysts, which could at least in part account for the lower selectivity. Assuming that the rate on this lowest area catalyst reflected true intrinsic kinetics, and that 1 g. of catalyst occupies approximately 1 cc. of reactor volume, one then can say that the average specific reaction rate in their studies was about 10 × 10^{-5} mmoles of *o*-xylene converted to phthalic anhydride/(hr.)(sq. cm.) of catalyst surface.

Table 2. Comparison of Reaction Rates in Melt and over Solid Catalyst

	Melt	Solid catalyst
o-Xylene concentration in air, mole %	0.8	0.4
Contact time, sec.	0.9	0.3
Temperature, °C.	528 to 598	490
Conversion to:		
Phthalic anhydride	0	61.7
Maleic anhydride	0	9.6
o-Tolualdehyde	3.0	Not analyzed
Rate, $\frac{\text{mmoles } o\text{-xylene reacted}}{\text{sq. cm. of surface/hr.}}$	10 to 70 × 10^{-5}	10 × 10^{-5}

Although the conditions for the two experiments are somewhat different, as shown in Table 2, it appears that the bubble interface in our studies was approximately as reactive as the solid surface of the solid-fused vanadium pentoxide catalysts but that the bubble surface was not capable of producing phthalic anhydride. One can speculate that the much higher rates of oxidation observed upon passing a sulfur dioxide–air mixture through a vanadium pentoxide melt (*20*) over those observed here with *o*-xylene–air may be associated with the sulfur dioxide oxidation occurring primarily by solution of one or both reactants followed by liquid-phase oxidation within the bulk of the melt, whereas in the hydrocarbon oxidation the hydrocarbon is confined to the interfacial area and reaction occurs only there.

ACKNOWLEDGMENT

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NOTATION

D = diameter of bubble, cm.
g = local acceleration of gravity, 980 cm./sec.^{2}
H = effective (expanded) melt height, cm.
h = melt bed height at zero gas flow rate, cm.
k_s = reaction rate constant based on bubble interfacial area, moles/(sec.) (sq. cm.) (atm.)
N = g.-mole of *o*-xylene reacted per sec.
p = partial pressure of *o*-xylene, atm.
Q = volumetric gas flow rate at melt temperature and pressure, cc./sec.
R = reactor radius, cm.
$\bar{u}$ = average velocity of bubbles, cm./sec.
μ = melt viscosity, g./(cm.)(sec.)
ρ = melt density, g./cc.

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The Determination of Eddy Mass Diffusivities for the Air-Water System in a Wetted-Wall Column

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Eddy mass diffusivities as a function of radial position for different Reynolds numbers have been determined for air flowing countercurrently to water in a wetted-wall column. The ratios of the eddy mass diffusivity to the eddy viscosity also were determined. The wetted-wall column was constructed from Pyrex glass with an I.D. of 2.75 in. and a wetted section 39 in. in length. An approach section was constructed from the same material and of adequate length to insure full development of the velocity profile. The gas phase Reynolds numbers varied from 3,200 to 54,300. The liquid phase flow was laminar. The concentration and velocity profiles of the air stream were measured experimentally and bulk temperatures of all streams were obtained. A probe was developed to measure the concentration profiles. The probe consisted of platinum wires wrapped in a helix around a glass capillary tube on which a thin layer of lithium chloride in polyvinyl alcohol had been deposited. The resistance of the probe was a reliable indication of the water vapor concentration in the air stream. The probe was calibrated and used for all concentration measurements. Eddy mass diffusivities were evaluated from a solution of the steady state mass diffusion equation by means of a digital computer with experimental velocity and concentration profiles. Qualitatively, the eddy diffusivity profiles are similar to those which have been obtained for heat and momentum transfer. When these profiles are used with the diffusion expression, they are capable of accurate evaluation of the concentration profile. The ratio of the eddy mass diffusivity to the eddy viscosity was determined and was found to be less than 1.0 over most of the cross section, but the ratio increased to values greater than 1.0 near the center and near the walls of the column.

Boussinesq (*1*) has suggested that the eddy diffusivity be defined in a manner analogous to the molecular diffusivity; that is

$$\frac{N_a}{A} = -E\frac{dc_a}{dx} \qquad (1)$$

A combination of the molecular and eddy effects leads to the general expression for the total mass transferred

$$\frac{N_a}{A} = -(D_v + E)\frac{dc_a}{dx} \qquad (2)$$

Various investigators have found (*2* to *4*) that the eddy diffusivity varies with position; that is

$$E = E(x) \qquad (3)$$

Tao and Strunk (*5*) recently determined eddy thermal diffusivities for air flowing in circular conduits at various

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