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Catalytic Oxidation of Propylene, Isobutene, and Benzene over Lead Monoxide

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The catalytic oxidation of propylene, isobutene, and benzene has been studied over a lead monoxide catalyst in the general temperature range 230–310°C. The catalyst was prepared by evaporation to give a thin layer upon which electrical conductance measurements were also made, and the electrical conductance was used to give information about the nature of the adsorbed species and of the nonstoichiometry of the oxide. It is concluded that propylene adsorption was accompanied by electron donation to the catalyst and that under catalytic conditions the oxide was *p*-type. In all cases the reaction proceeded entirely to give carbon dioxide and water vapor, and the reaction was shown to be first order in oxygen pressure and zero order in hydrocarbon pressure, with activation energies of 26, 28, and 30 kcal mole^{-1} for propylene, isobutene, and benzene, respectively. It is concluded from the pressure dependence data that reaction involves only physically adsorbed molecular oxygen. Using radiation in the near-UV and visible regions, a search was made for photoadsorption and photocatalysis, but no such effects could be detected.

INTRODUCTION

It was first demonstrated unequivocally by Heijne (*1*) that lead monoxide is an amphoteric semiconductor, and more recent work by Anderson and Tare (*2*) has confirmed this conclusion. Because of this, we believe that lead monoxide is of interest as a model substance with which to explore possible relations between nonstoichiometry and catalytic activity. With this in mind, the present work was undertaken to study the behavior of lead monoxide as a catalyst for the oxidation of benzene and of some typical olefins.

EXPERIMENTAL

Reactions were studied in a static system. The reaction vessel was a spherical vessel, volume 280 ml, at the center of which was situated a basket of 0.5-mm diameter platinum wire from which lead oxide was evaporated onto the inside wall of the reaction vessel. The technique for the preparation of orthorhombic lead monoxide films followed the technique and conditions used by Heijne (*1*) and later by Anderson and Tare (*2*). In particular, the oxide was evaporated in a pressure of about 1 mtorr of oxygen with the reaction vessel at about 110–120°C. The lead oxide evaporated in about 20 to 30 sec and the film was then heated in 1 mtorr oxygen at 300°C for 1 hr, cooled to room temperature, pumped, and was then ready for the introduction of the reaction mixture.

Heijne (*1*) and Anderson and Tare (*2*) made electrical resistance measurements on evaporated films of lead oxide using a technique in which the lead oxide layer was sandwiched between a conducting substrate and a thin layer of evaporated silver. In this method, access of gas to the lead oxide must occur through the silver layer, and while this appeared to be satisfactory for oxygen, particularly at elevated temperatures, it seemed likely to us that the transport of

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hydrocarbon molecules would be very seriously impeded. For this reason, in the present work electrical resistance measurements were made using an apparatus based upon the technique of Dickens (*3*). It consisted of a flat silica disc onto which was evaporated a film of gold. Before deposition of the gold layer, a piece of 0.1-mm diameter wire was stretched tightly across the face of the disc, so that after deposition, the removal of this wire left a narrow gap in the gold layer. The lead oxide was evaporated over the gap and measurement was therefore made on an oxide specimen 20 mm long, about 2000 Å thick and of the order of 0.1 mm wide. The silica disc was joined into the measuring cell by a silica-to-Pyrex graded seal. The silica disc formed the closed end of a cylindrical well and this well was used to contain a heater or refrigerant for temperature control of the oxide specimen which had been deposited onto the electrode assembly. Electrical connections to the gold electrodes were made by pressing thin platinum foil contacts against the gold surface by means of the spring-loaded silica plates. Resistance measurements were made using a Keithley Model 610A electrometer with about 45 V across the specimen. The resistance of the cell in the absence of the oxide layer was greater than about 10^{13} ohm.

Pressure measurements in the range 10^{-2} to 10^{-6} torr were carried out with a thermistor gauge, calibrated against a McLeod gauge.

The progress of the reaction was monitored continuously by means of an AEI MS10 mass spectrometer which was connected to the reaction vessel via a glass capillary leak. In the same way as was noted by Kemball and Patterson (*4*), we found that the absolute sensitivity of the mass spectrometer decreased throughout the course of an experiment by as much as 40%. Following the suggestion of Kemball and Patterson (*4*), this was overcome by referring all peaks to an internal argon standard that was introduced into the mass spectrometer via a separate leak. Relative to argon, the calibrations for reaction mixture components remained constant to within 5% over a 12-month period.

Propylene was prepared by the dehydration of *n*-propanol with concentrated sulfuric acid and aluminum sulfate, all AR grade. The gas was scrubbed successively with 20% caustic soda solution, 10% caustic soda solution, distilled water twice, and finally dried over anhydrous magnesium perchlorate. It was then further purified on the vacuum line by two successive distillations, retaining in each case the middle third. No impurity was detected mass spectrometrically. Isobutene was prepared in a similar manner from tert-butanol.

Benzene of AR grade was used and was outgassed on the vacuum line before use.

Oxygen was prepared by heating AR potassium permanganate and the gas was purified by passage over soda-lime and through a liquid air trap.

Argon was used directly from spectrographically pure material supplied by the British Oxygen Company.

Xenon was high-purity grade and was used directly as supplied by the Linde Company.

Carbon dioxide used for calibration was commercial grade purified by two distillations on the vacuum line, retaining each time the middle third.

"Specpure" plumbous oxide from Johnson and Matthey was used, with the following impurities in parts per million: silicon, 5; calcium, 3; iron, 2; magnesium, aluminum, bismuth, copper, and silver, 1 each. For convenience, the material to be placed in the evaporation basket was pelletized.

Because lead monoxide is known to exhibit photoconductive properties, some catalytic and adsorption measurements were made under illumination. The lamp used was a Philips type 7023 tungsten-iodine globe with a quartz envelope. Radiation incident upon the specimen was limited to the visible and near UV by an air-cooled heat filter of absorbing glass. The light was collimated to some extent and reflected towards the reaction vessel by a semicylindrical reflector, and the lamp was arranged to illuminate the reaction vessel through an aperture in the wall of the oven that surrounded the reaction vessel. In order to ensure that the gas/solid interface was illuminated, a "window" was retained in the oxide film adjacent to the lamp. This was done by means of a magnetically operated glass flap situated within the reaction vessel which intercepted the oxide during evaporation.

RESULTS AND DISCUSSION

Adsorption and Resistance Measurements

a. Oxygen. Since the effect of oxygen on the electrical resistance of lead monoxide was previously studied (*1*, *2*) using a sandwich cell, some measurements with oxygen were made with the present apparatus for comparison. The effect of oxygen uptake on the oxide resistance was determined after varying pretreatments. In experiment A, oxygen was added at 24°C to an oxide specimen prepared in the standard way. The resistance increased from 3.75×10^{12} to 5×10^{12} ohm in less than a minute: the total oxygen uptake was 3.2×10^{16} O_2 molecules and the final pressure 10 mtorr. In experiment B, the oxide after standard preparation was heated at 200°C in 2 mtorr oxygen for 60 min. The film was then cooled to room temperature and the oxygen pumped away. The addition of a dose of oxygen at 24°C caused the resistance to rise from 8.3×10^{12} to 17×10^{12} ohm in less than 3 min and this was accompanied by the uptake of 3.1×10^{16} O_2 molecules, the final pressure being 17 mtorr. In experiment C, the oxide after standard preparation was heated at 200°C in 16 mtorr oxygen for 60 min. The film was then cooled to room temperature and the oxygen pumped away. The addition of a dose of oxygen at 51°C caused a rise in resistance from 0.3×10^{12} to 4.5×10^{12} ohm in less than a minute, and this was accompanied by the uptake of 1.1×10^{15} O_2 molecules, the final pressure being 13 mtorr. Pumping the specimen to 10^{-6} torr at 51°C caused the resistance to rise by a factor of about 2, and the addition of a dose of propylene, to the evacuated specimen then caused a further resistance rise by a factor of about 2.

Now we may conclude from previous work (*1*, *2*) that lead monoxide is made *p*-type, at least in its surface layer, by treatment in oxygen pressures above about 2×10^{-2} torr. It thus seems likely that the oxide specimens in experiments A, B, and C above were all *n*-type, but of decreasing majority carrier concentration in that order. This agrees with the observed increase in resistance on oxygen adsorption, and with the observation that in experiment C a much smaller amount of adsorbed oxygen was required to effect the resistance change than was needed for A or B.

b. Propylene. The variation of lead monoxide resistance with propylene uptake was determined for a range of oxygen pretreatments. In this case the pretreatment consisted of heating the specimen, after preparation in the standard manner, in 10 mtorr oxygen at 200°C for varying times. After cooling to room temperature, the oxygen was pumped away, the resistance (R_1) was measured and was remeasured (R_2) after the addition of a dose of about 2.5×10^{16} propylene molecules. The results are contained in Table 1. These resistance changes occurred immediately and were reversible on pumping away the propylene. The adsorption was thus reversible and did not, at least at this temperature, involve fragmentation of the molecule.

TABLE 1

DEPENDENCE OF RESISTANCE CHANGE DUE TO PROPYLENE ADSORPTION ON PRETREATMENT OF OXIDE

Oxide heated in 10 mtorr O_2 at 200°C for (hours)	Difference between oxide resistance before (R_1) and after (R_2) propylene adsorption ($R_2 - R_1$, ohms)
0	-3.6×10^{12}
122	-3.1×10^{12}
146	-0.5×10^{12}
176	$+1.5 \times 10^{12}$

Since a specimen with no pretreatment is certainly expected to be *n*-type, the resistance decrease accompanying propylene adsorption shows that in the adsorption process, propylene is acting as an electron donor and for this it is reasonable to propose electron donation from the π orbitals of the olefin. On *n*-type specimens, the equilibrium propylene uptake amounted to about 0.7×10^{16} molecules. For comparison, with a film surface area of 210 cm^2, the surface could accommodate up to 7×10^{16} molecules if each occupied an area of 30 Å^2.

Increasing times of oxygen pretreatment resulted in smaller resistance decreases, until eventually the resistance decrease was replaced by a resistance increase on propylene adsorption. This is attributed to a transition to *p*-type behavior at extended oxidation times with the result that donor adsorption of propylene results in a decrease in hole concentration.

c. Mixture of propylene and oxygen. The resistance was measured during the addition of a mixture of standard reaction composition to a standard oxide specimen at 300°C. Three specimens were examined in this way: the behavior was the same in each case and typical results were as follows: resistance of standard film in vacuum at 300°C, 4.9×10^9 ohm; on the addition of a standard reaction mixture the resistance rose within 1 min to $>10^{13}$ ohm, after which it fell to a value of 1.5×10^9 ohm, i.e., below the initial value.

By comparison with previous data (*1*, *2*) and with data given in a previous section, we conclude that oxygen adsorption on the initial *n*-type film caused the initial rapid resistance increase, but the subsequent decrease was due to conversion to *p*-type behavior due to further reaction with oxygen and that a film under catalytic conditions is *p*-type.

d. Experiments under illumination. Experiments were carried out to see if illumination of the specimen during oxygen adsorption resulted in any modification of the uptake kinetics. A series of experiments was undertaken in the temperature range 24° to 190°C and with oxygen pressures in the range 10–30 mtorr. In no case was any effect of illumination observed. This result remained true for an oxide film prepared and maintained in total darkness up to the time of illumination during oxygen uptake. Illumination experiments were also carried out during propylene adsorption and no significant influence on the extent of uptake could be detected.

Catalytic Experiments

The surface areas of some lead monoxide films were measured by the BET method using the adsorption of xenon at 90°K, assuming an effective area per adsorbed xenon atom of 20 Å^2. Film areas either before or after catalytic experiments were within 10% of the geometric film area (210 cm^2) and the latter figure has been adopted in order to evaluate rates per unit area. The standard film weight was 50 mg of lead monoxide.

Films of lead monoxide were active for the oxidation of propylene, isobutene, and benzene. Unless otherwise specified, reactions were carried out with mixtures of standard composition in which pressures of each component in the reaction vessel at 0°C was 8.5 torr, corresponding to 1.07×10^{20} molecules.

In no case were products other than carbon dioxide and water detected. The overall reactions may thus be written

$$C_3H_6 + \tfrac{9}{2}\,O_2 \rightarrow 3\,CO_2 + 3\,H_2O \qquad (1)$$

$$C_4H_8 + 6\,O_2 \rightarrow 4\,CO_2 + 4\,H_2O \qquad (2)$$

$$C_6H_6 + \tfrac{15}{2}\,O_2 \rightarrow 6\,CO_2 + 3\,H_2O \qquad (3)$$

The most sensitive and reproducible measure of the reaction was provided by the carbon dioxide peak in the mass spectrometer. Kinetic expressions were thus derived in terms of p_{CO_2}.

If the rate of the reaction $(-dp_{HC}/dt)$ is given by either of the following expressions

$$\text{rate} = k(p_{HC})^0(p_{O_2})^1 \qquad (4a)$$

$$\text{rate} = k(p_{HC})^1(p_{O_2})^0 \qquad (4b)$$

the following rate expression is obtained for mixtures of stoichiometric composition which follow reactions (1), (2), or (3),

$$\ln\,[1 - x(p_{CO_2}/p^\circ_{O_2})] = -kt \qquad (5)$$

where $p^\circ_{O_2}$ is the initial pressure of oxygen, and where x takes the values $\frac{3}{2}$, $\frac{3}{2}$, and $\frac{5}{4}$ for reactions (1), (2), and (3) respectively. In obtaining Eq. (5) under these conditions, use has been made of relations such as

$$-(dp_{O_2}/dt) = -\tfrac{9}{2}(dp_{C_3H_6}/dt), \text{ etc.}$$

and

$$p^\circ_{C_2} = \tfrac{9}{2}p^\circ_{C_3H_6}, \text{ etc.}$$

Figure 1 shows typical data plotted according to the appropriate form of Eq. (5).

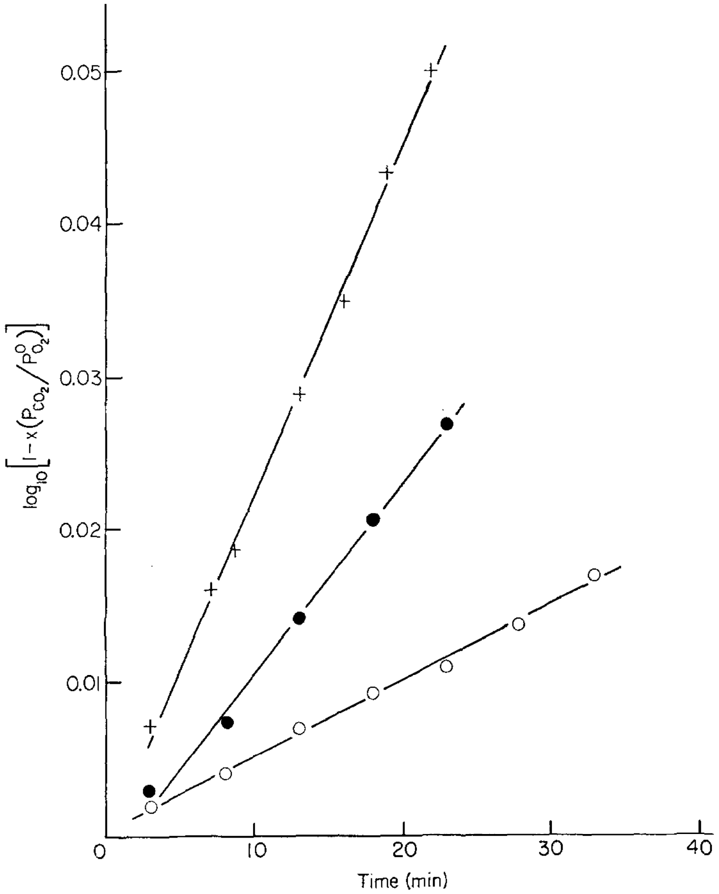

FIG. 1. Plot of kinetic data according to Eq. (5): ●, reaction of propylene at 286°C; +, reaction of isobutene at 296°C; ○, reaction of benzene at 269°C. Reaction mixtures of standard composition: $x = \frac{3}{2}$ for propylene and isobutene; $x = \frac{5}{4}$ for benzene.

Because of the ambiguity of the pressure dependences of Eqs. (4a) and (4b) in relation to Eq. (5), it was necessary to determine at least one of the pressure-dependence exponents independently. This was done by the method of initial rates with reactions of propylene and benzene. Experiments were carried out with mixtures of standard oxygen pressure but differing hydrocarbon pressures. The results are shown in Fig. 2, from which it is concluded that over a wide range of conditions the rates are independent of hydrocarbon pressure. Hence, the fit obtained using Eq. (5) also implies that the rate is dependent on $p^1_{O_2}$, i.e., Eq. (4a). We assume *mutatis mutandi* that this is also true for isobutene. The data in Fig. 2 for benzene at 270°C indicate a negative exponent for the benzene pressure at <2.5 torr.

The dependence of the rate constant k on temperature is shown in Fig. 3 for the three systems and the activation energies and frequency factors are recorded in Table 2.

TABLE 2
ACTIVATION ENERGIES AND FREQUENCY FACTORS

	Temperature range (°C)	Activation energy (kcal mole^{-1})	$\log_{10}$ (frequency factor) (hydrocarbon molecules sec^{-1} cm^{-2})
C_3H_6/O_2	230–310°	26	8.2
C_4H_8/O_2	262–315°	28	8.3
C_6H_6/O_2	250–310°	30	8.6

The uncertainty in the activation energy and frequency factor are estimated at ±2 kcal mole^{-1} and ±0.3 in the logarithm, respectively.

The near equality of measured and geo-

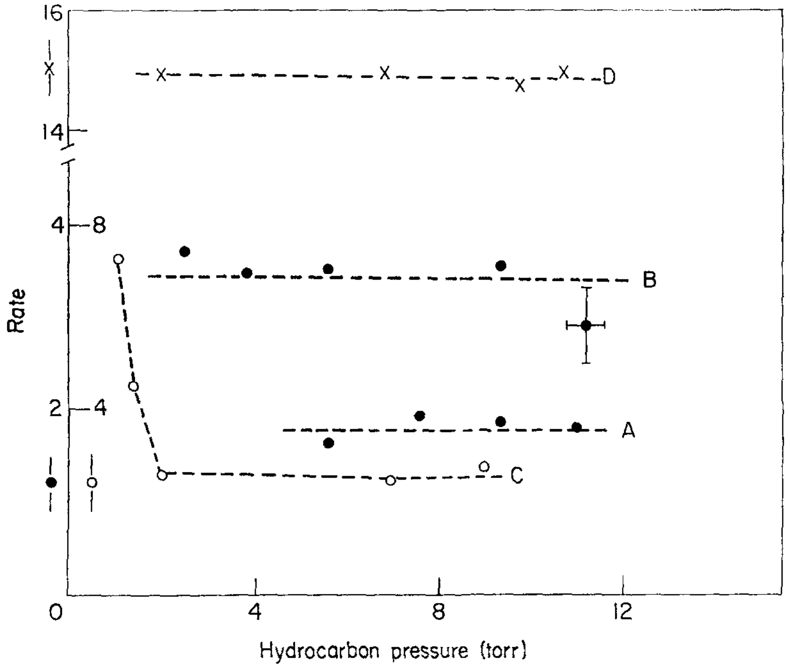

FIG. 2. Influence of hydrocarbon pressure on rate of oxidation over PbO film catalyst. A, Propylene at 260°C, initial oxygen pressure 8.7 torr. B, Propylene at 283°C, initial oxygen pressure 8.7 torr. C, Benzene at 270°C, initial oxygen pressure 21.0 torr. D, Benzene at 294°C, initial oxygen pressure 21.0 torr. Propylene rates in units of 10^{13} C_3H_6 molecules cm^{-2} min^{-1}; benzene rates in units of 10^{14} C_6H_6 molecules cm^{-2} min^{-1}.

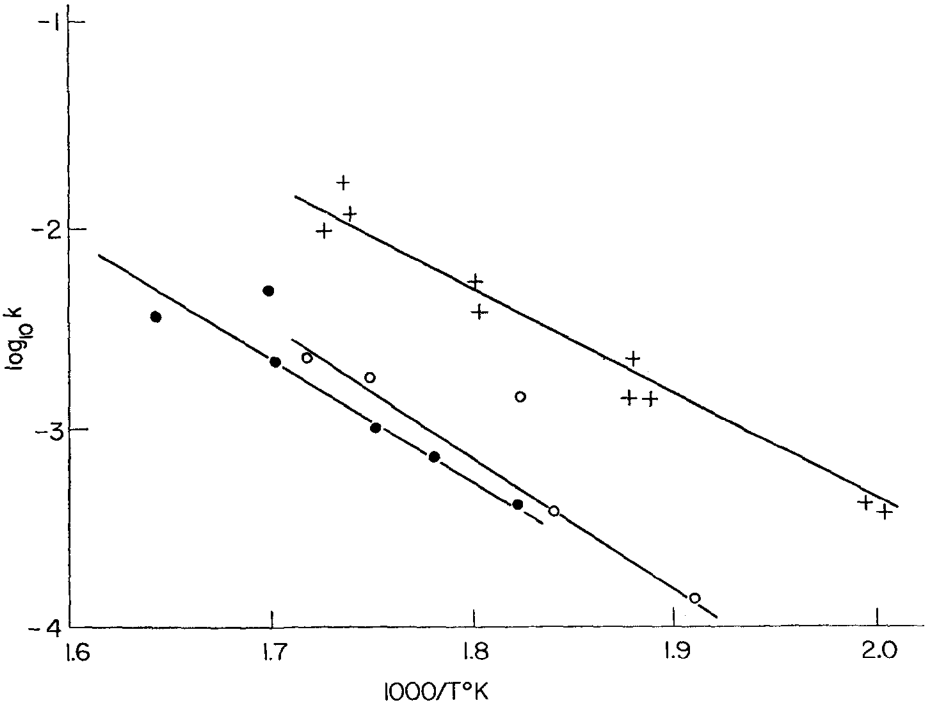

FIG. 3. Variation of reaction rate constant (k, min^{-1}) with temperature; +, propylene; ●, isobutene; ○, benzene.

metric film areas implies that reaction rates should be independent of film weight. This was checked using standard propylene/oxygen mixtures with films of varying weights, reaction being at 282°C. In four experiments with film weights ranging from 52.0 to 13.4 mg, the reaction rate was constant at $8.7 \pm 0.8 \times 10^{11}$ propylene molecules $\sec^{-1}$ cm^{-2}.

A blank experiment showed that there was negligible oxidation of isobutene up to 320°C on a clean glass surface in the absence of the lead monoxide film.

No influence of illumination on the rate of catalytic oxidation could be detected for any of the materials studied.

Since most reactions were zero order in hydrocarbon and first order in oxygen, we conclude that hydrocarbon was relatively strongly adsorbed, and oxygen relatively weakly adsorbed. On the other hand, acceptor adsorption (such as by oxygen) on a *p*-type oxide is expected to be strong, and donor adsorption (such as by olefin) weak. Thus the oxygen that takes part in the catalytic reaction in the steady state can most reasonably be identified as van der Waals adsorbed molecular oxygen, the surface coverage of which is low enough to be directly proportional to the oxygen pressure. Undoubtedly, under catalytic conditions, some strong oxygen adsorption occurs, together with some lattice incorporation; both processes leading to the creation of positive holes. This strongly bound oxygen cannot take part in the steady state reaction. The positive holes so generated are, when free at the surface, available to act as centers for donor hydrocarbon adsorption. Although it was found in the adsorption experiments that this hydrocarbon adsorption could be reversed on pumping to a high vacuum, the zero order pressure dependence shows that it must yet be sufficiently strong for the surface concentration of adsorbed hydrocarbon to be unaffected by modest changes in pressure under catalytic conditions.

There was found a distinct increase in activation energy in the sequence, propylene, isobutene, benzene. This is probably due to stabilization of isobutene and benzene with respect to propylene; isobutene by hyperconjugation; and benzene due to resonance.

Anderson and Sterns (*5*) showed that at 300°C and in oxygen pressures in the range 20–600 torr, lead monoxide could be slowly oxidized at least as far as PbO_n with $n = 1.5$. However, this was probably a two-phase system for $n > 1.04$, comprising a defect PbO phase and a pseudo-cubic phase. It is thus possible, but not certain, that under catalytic conditions, the catalyst would consist of *p*-type PbO, plus some pseudo-cubic phase.

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