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The Oxidative Demethylation of Toluene, Using Bismuth Uranate as Oxidant

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When brought into contact with various bismuth uranates in a stream of an inert gas at 400–500°C, toluene is oxidized to benzene, CO_2 and H_2O. The best benzene yields are obtained using the compound Bi_2UO_6 with a high specific surface area. A fixed percentage of the oxygen atoms present in this compound gives rise to a rapid total combustion of the toluene. After the consumption of these atoms, toluene is converted into benzene with a selectivity up to 70%. During this process bismuth uranate can lose 60% of its oxygen atoms, corresponding to zero-valent bismuth and tetravalent uranium. The original activity is completely restored by oxidation with molecular oxygen. This opens the possibility of demethylating toluene by passing air and toluene alternately over bismuth uranate.

The kinetics of the reaction between toluene and bismuth uranate, investigated in micropulse and microflow systems and in a thermobalance, are complicated. The surface reaction appears to be first order in toluene with an energy of activation of 30 kcal $mole^{-1}$ at 480°, but the transport rate of oxygen from the bulk of the Bi_2UO_6 matrix to the surface also plays a role.

The selective reaction is likely to occur via a benzoate-like intermediate. The reoxidation of reduced bismuth uranate with air is very fast, and even proceeds at 100°.

INTRODUCTION

The oxidation of toluene has been the subject of numerous investigations during the last 80 years. This work has resulted in two industrial processes, namely, oxidation in the liquid phase, catalyzed by cobalt salts, to form benzoic acid, and oxidation in the gas phase over, e.g., vanadium pentoxide to form benzaldehyde or benzoic acid. It is much less known that toluene can be converted into benzene by oxidation. In 1890, Vincent (*1*) studied the reaction between toluene and lead oxide. Below 335°C benzene was the main reaction product, the oxide being reduced to metallic lead. Much later Norton and Moss (*2*) described a process in which toluene was oxidized by air over a cadmium oxide catalyst. However, in our laboratory, Heynen (*3*) found that this catalyst is unsuitable for continuous operation, since it is partly reduced to the metal. At the reaction temperature metallic cadmium has an appreciable vapor pressure, leading to a loss of catalyst during the process. Recently, Adams (*4*) mentioned the formation of benzene as a by-product in the oxidation of toluene over bismuth molybdate.

In a previous paper (*5*) we described the catalytic oxidation of toluene over bismuth uranate. The reaction took place in the gas phase at 400–500°C. Apart from CO_2 and H_2O, benzene was the only reaction product. In order to obtain a high selectivity, it proved necessary to carry out the reaction in the absence of gaseous oxygen, using bismuth uranate as the oxidant; the reduced uranate could easily be reoxidized by air at 400°C in a separate operation. In the first part of the present paper, we report on the preparation and properties of various bismuth uranates while in the second part we deal with kinetics of its reduction by toluene.

METHODS

Preparation of Bismuth Uranates

Literature on the mixed oxides of bismuth and uranium is rather limited. In 1889, Fischel (*6*) prepared a red compound by heating bismuth trichloride and uranyl hydroxide together. Later, Erfurth (*7*) examined the system bismuth oxide–uranium oxide in more detail. He found four different phases to be present: a hexagonal one between Bi_2UO_6 and $Bi_2UO_6 \cdot 0.8Bi_2O_3$, a cubic one between $Bi_2UO_6 \cdot Bi_2O_3$ and $Bi_2UO_6 \cdot 6Bi_2O_3$, a tetragonal one between $Bi_2UO_6 \cdot 7Bi_2O_3$ and $Bi_2UO_6 \cdot 18Bi_2O_3$, and finally, a compound $BiUO_4$ which is stable only in the absence of oxygen. His samples were prepared by mixing and prolonged heating of the oxides at 800–1000°C. In a similar manner, Hund (*8*) studied the system Bi_2O_3–UO_2 in an oxygen-free atmosphere, and showed the existence of a continuous range of phases with the fluorite structure between 0 and 100% bismuth oxide. Finally, a mineral uranosphaerite is known, with the formula $Bi_2O_3 \cdot 2UO_3 \cdot 3H_2O$. This decomposes upon heating (*9*).

In order to obtain bismuth uranate with a high surface area, we adopted the low-temperature method described by Batist *et al.* (*10*) for the preparation of bismuth molybdate. Bismuth nitrate or basic nitrate was dissolved in warm, dilute HNO_3. The solution was added to an excess of warm, concentrated ammonia. The white precipitate, consisting of $Bi_2O_3 \cdot xNO_3 \cdot yH_2O$ (*11*) was filtered off and thoroughly washed with water. Uranyl acetate or nitrate was dissolved in warm water and the solution was added to an excess of ammonia. The yellow precipitated $UO_3 \cdot xNH_3 \cdot yH_2O$ (*12*) was filtered off and washed with water. Both precipitates were kept under water to prevent the formation of clots. The two precipitates were transferred to a round-bottomed flask with water, and heated at 90–100°C under vigorous stirring. After a few hours, the original yellow color turned into orange and the gel properties disappeared. Apparently a reaction between the two compounds had taken place, either directly in the solid phase, or between dissolved uranic acid and solid bismuth hydroxide.

After 20 hr of stirring, the solid mass was filtered off, washed with water and dried for 20 hr at 135°C. Finally, the product was calcined in air at 500°C for 1 hr, to obtain almost quantitatively a brown, soft and amorphous material. Thermogravimetric analysis of the dried, uncalcined product revealed that no weight loss occurs above 500°, indicating that the dehydration is complete at that temperature. From simultaneous differential thermal analysis it appears that the process of calcination is exothermic. Since the dehydration should be endothermic, it follows that during the calcination another reaction between the two oxides takes place. No definite peaks due to phase transitions could be observed. Calcined samples, subjected to differential thermal analysis, did not exhibit endothermic or exothermic effects.

Properties of Bismuth Uranate

Fourteen samples with different Bi to U atomic ratios were prepared. Composition, color and surface area, determined according to the BET method, are given in Table 1. We also prepared samples of Bi_2UO_6 and $Bi_2UO_6 \cdot Bi_2O_3$ directly from the oxides at 800°C after the method of Erfurth (*7*). These samples will be referred to as the

TABLE 1

Bi/U atomic ratio	Color	Specific surface area (m² g⁻¹)
Pure Bi oxide	White-yellow	1.3
4/1	Ochre	11.4
3/1	Brown	25.3
2.33/1	Brown	30.0
2/1	Brown	22.4
1.86/1	Orange-brown	23.4
1.5/1	Orange-brown	41.5
1.22/1	Orange	15.3
1/1	Orange	48.2
1/1.22	Orange	27.8
1/1.5	Orange	30.4
1/1.86	Olive	23.9
1/2.33	Olive	26.4
Pure U oxide	Orange	25.0

high-temperature samples while those in Table 1 are described as the low-temperature samples.

X-Ray diffraction diagrams of the compounds were measured with a diffractometer, using Ni-filtered Cu radiation. The spectra of the low-temperature samples consisted of broad, diffuse lines which narrowed upon heating. No other lines appeared during this treatment. The crystallization process was followed in a Guinier camera with temperature programming, and proved to be complete at 700°C.[*] Therefore, we measured the X-ray diagrams after the samples had been heated at 700°C for 1 hr. The results, together with those of α-UO_3 and those of the high-temperature uranates, are given in Fig. 1. Table 2 gives the d-values of the high-temperature Bi_2UO_6. The X-ray pattern of the low-temperature sample with Bi/U = 2 heated at 700°C, and the high-temperature Bi_2UO_6 are identical, and agree with the diagram given by Erfurth (*7*). Therefore, our low-temperature sample consists of Bi_2UO_6 of low crystallinity. In the samples with Bi/U smaller than 2, α-UO_3 is present together with Bi_2UO_6. This is rather surprising, since pure α-UO_3 decomposes at 600°C to form U_3O_8 (*13*), while our samples had been heated at 700°C. Samples with a Bi/U atomic ratio between 2 and 4, show only lines of Bi_2UO_6. Very probably, a solid solution of Bi_2O_3 in Bi_2UO_6 is present. This is also in agreement with the results of Erfurth. At Bi/U = 4, a line pattern appears which is identical to that of our high-temperature $Bi_2UO_6 \cdot Bi_2O_3$. However, both diagrams differ from that given by Erfurth, indicating that the crystal structure of our sample is more complicated than the simple cubic structure of Erfurth. From our results, we conclude that apart from the degree of crystallinity, there is no difference between the samples prepared at low temperature from the hydroxides and those obtained by heating the oxides at high temperature.

TABLE 2

d-VALUES OF HIGH-TEMPERATURE Bi_2UO_6

4.847	1.632
3.264	1.616
3.232	1.464
2.820	1.410
2.364	1.393
2.001	1.300
1.986	1.292
1.939	1.286
1.703	1.266
1.693	1.256

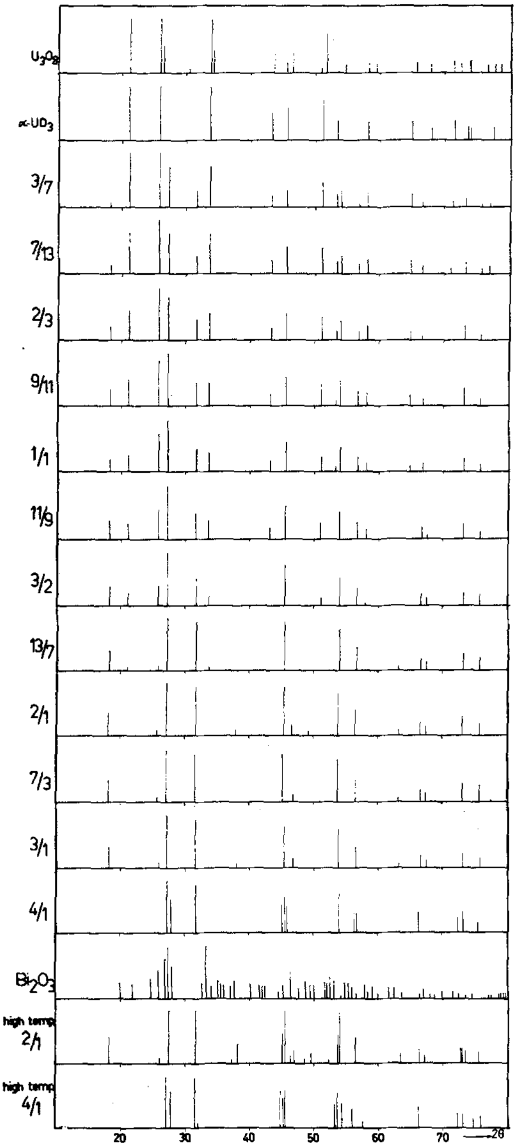

FIG. 1. X-Ray diagrams.

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[*] Guinier photographs were made at the Reactor Centrum Nederland under the supervision of Dr. E. H. P. Cordfunke.

We have tried to determine the melting points of our compounds under a microscope. A maximum temperature of 1500°C could be attained. Below this temperature, only Bi_2O_3 and the samples with Bi/U = 3 and 4 melted. Melting points were 830 and 1300°C, respectively. These measurements, however, were inaccurate, since thermogravimetric analysis revealed that all bismuth uranates lose oxygen at these temperatures.

The activities of the different samples in the reaction with toluene were compared using the pulse system described below. The reactor was filled with a quantity of bismuth uranate corresponding to 10 m^2. The reaction conditions were: temperature, 480°C; pulse volume, 0.534 cm^3; mole fraction of toluene in the feed gas, 0.023; gas flow, 25 cm^3 min^{-1}.

In Fig. 2 the maximum selectivities and productivities are plotted against the Bi/U atomic ratio. Experiments were also carried out at 450°C, but with every sample the selectivities were considerably lower than at 480°C. It is noted that the pure uranium oxide is not only an unselective, but also a very active oxidant. At 400°C the toluene was completely converted to CO_2 and H_2O.

As shown in Fig. 2, both the selectivity and the productivity have a sharp maximum at Bi/U = 2. Evidently, the active component is the compound Bi_2UO_6. Catalytic properties and crystal structure are often related. Therefore, we are studying the structure of Bi_2UO_6, already given by Erfurth, in more detail.

Since the samples on the U-rich side of the system consist of Bi_2UO_6 and α-UO_3, of which the first one is the selective, and the latter one the unselective component, it should be possible to improve the selectivities by removing the α-UO_3. For this purpose we used the carbonate leaching process described by Forward and Halpern (*14*). A few grams of bismuth uranate with Bi/U = 1/1.86 were added to a solution of 10 g sodium carbonate and 10 g of sodium bicarbonate in 100 ml of water, and boiled for 1 hr. The solution turned yellow. The solid was filtered off, washed with water and dried. In the X-ray diagram, no α-UO_3 lines could be detected. Upon adding NH_4OH to the filtrate, a yellow precipitate of sodium uranate was formed. The treated sample showed a higher maximum selectivity in the reaction with toluene than the original one; however, it was still inferior to the original compound with Bi/U = 2. The specific surface area of the treated uranate was 11 m^2 g^{-1}. The influence of the surface area on the maximum selectivity was studied by calcining a sample with Bi/U = 2 at 500, 600 and 700°C. Surface areas were determined and are given in Table 3 together with the selectivities.

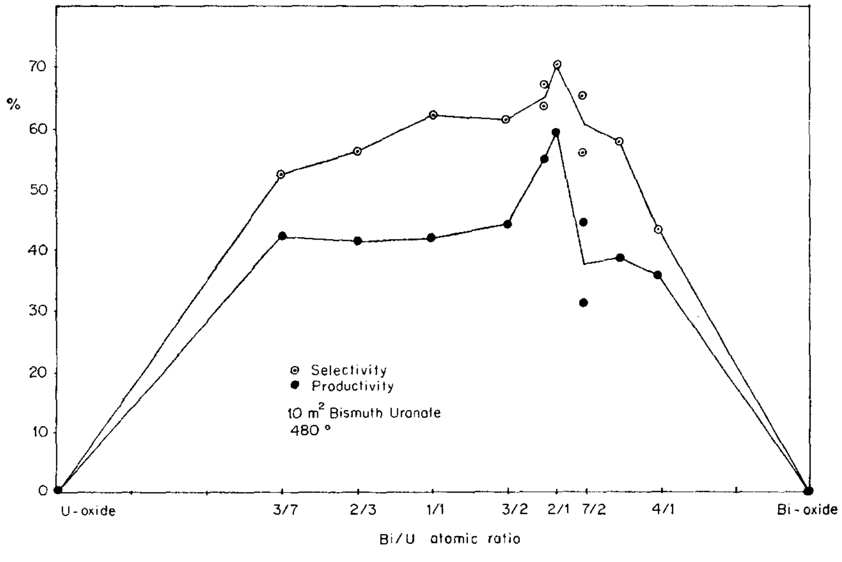

FIG. 2. Maximum selectivity and productivity as a function of catalyst composition.

TABLE 3

Calcination time (min)	Temp (°C)	Specific surface area ($m^2\ g^{-1}$)	Maximum selectivity %
15	500	31.6	72
30	500	28.0	72
60	500	27.0	70
120	500	21.4	69
30	600	16.2	66
60	600	13.4	65
30	700	4.9	55

In our kinetic experiments we used one batch of bismuth uranate with Bi/U = 2, calcined for 1 hr at 500°. This material had a surface area of 22.4 $m^2\ g^{-1}$. Titrations on the uranium content* gave the following results: total uranium content 32.47 wt %, U(IV) 0.55 wt %. The pore volume of the sieve fraction with particle size between 0.15 and 0.30 mm was determined by the mercury penetration method (*15*) using a Carlo Erba apparatus. The total pore volume was 0.315 $cm^3\ g^{-1}$. A value of 160 Å was found for the mean pore radius, leading to 36 $m^2\ g^{-1}$ for the calculated specific surface area. Since this value is considerably higher than that from the BET measurement, it is possible that the material crushed under the high pressure applied.

KINETICS OF THE TOLUENE OXIDATION

Preliminary experiments, already published (*5*), showed that bismuth uranate as such is a very active and unselective oxidant in toluene oxidation. However, as soon as it loses oxygen, the activity decreases and the selectivity increases. When approximately 2% of the oxygen atoms present in Bi_2UO_6 have been removed, a constant level of activity is reached. This level is maintained until the bismuth uranate has lost about 10% of its oxygen atoms. The oxidation of the reduced bismuth uranate is very rapid and exothermic, so that if oxygen is present in the feed gas, the uranate will keep its fully oxidized state. This means that Bi_2UO_6 is a selective oxidant but an unselective catalyst. It is also remarkable, that this compound can lose half of its oxygen atoms and subsequently be reoxidized to its original state as far as structure and oxidation properties are concerned.

We have studied these peculiar properties in three different ways:

a. The rapid decline in activity and rise in selectivity in the early stages of the reaction were studied in a micropulse system.

b. For experiments up to a high degree of reduction of the bismuth uranate, we used a microflow apparatus; this enabled a complete analysis of all reaction products to be made.

c. The oxygen depletion of bismuth uranate was also followed in a thermobalance, where we could measure the reduction rate from the decrease in weight of the bismuth uranate. In all these methods, a fixed bed of oxidant was used, implying that there is a gradient in reactant concentration over the reactor. This, in turn, could lead to a gradient in the degree of reduction of the bismuth uranate, making evaluation of the kinetic data very difficult. For that reason, we carried out our experiments at low conversion levels, so that the decrease in toluene concentration remained small in comparison to the mean toluene concentration.

Pulse apparatus

In the pulse experiments a constant flow of carrier gas passed through the reactor into a gas chromatograph; pulses of a nitrogen/toluene mixture were injected into this gas stream upstream of the reactor and subsequently analyzed. As carrier gas we used helium, freed of oxygen by passing it over a reduced BTS-catalyst. Helium pressure was 2.0 atm absolute and flow rate, 25 $cm^3\ min^{-1}$. Toluene/nitrogen mixtures were prepared in a vaporizer placed in a water bath. At constant intervals of usually 5 min, 0.534 cm^3 of this mixture was introduced into the carrier gas by means of a Becker gas sampling valve. The reactor consisted of a quartz tube, internal diameter 7.5 mm, heated by an electrical furnace. The bismuth

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* Titrations were carried out at the Reactor Centrum Nederland under the supervision of Dr. E. H. P. Cordfunke.

uranate (0.1 to 1.0 g with a particle size of 0.15–0.30 mm) was supported on a plug of quartz wool. In the experiments with 0.1 g of oxidant, a bed of quartz grains with the same particle size was used as support. The temperature was measured by a thermocouple in the middle of the fixed bed, and controlled to ±1° with a Eurotherm Thyristor controller. Products were analyzed by a Pye 104 gas chromatograph with a flame ionization detector. The column, 0.5 m in length, was filled with Porapak Q and kept at 185°C. Benzene and toluene peak areas were determined with a Kent electronic integrator. No other products could be detected with this system. Before and after each run, we measured some "blank" toluene peaks with an empty reactor. The amount of benzene formed and toluene converted during the reaction were calculated by comparing the peak areas with those of the blanks. No reaction took place in the empty reactor below 500°C.

Flow apparatus

In the flow apparatus, the feed gas passed over the oxidant in the microreactor as described above. Pressure in the reactor was atmospheric. Samples of the gaseous effluent were taken with a Becker gas sampling valve (sample vol, 0.50 ml) and analyzed by gas chromatography. Reaction products were condensed in an ice-cooled trap. Provisions were made to reoxidize the reduced bismuth uranate with air when required. Between reduction and reoxidation the system was flushed with nitrogen.

The analysis system for quantitative determination of O_2, N_2, CO, CO_2, H_2O, benzene and toluene is shown in Fig. 3. It consisted of three GLC columns and two double thermal conductivity detectors in series. On the first column (0.50 m Porapak at 185°C) benzene and toluene were separated from the other components. On the second column (2 m Porapak Q at 48°C) carbon dioxide and water were detected, while carbon monoxide, oxygen and nitrogen were determined on the third column (Molecular sieve 13X, 4 m, room temperature). Pressure build-up over these three columns was considerable; with a carrier gas pressure of 5 atm, the gas flow was 40 cm^3 min^{-1}. Total analysis time was 15 min. Since nitrogen is unaffected in the reaction, we used the nitrogen peak as an internal standard. The response of each of the components was calibrated by analyzing mixtures of known composition. Peak areas were determined with an electronic integrator.

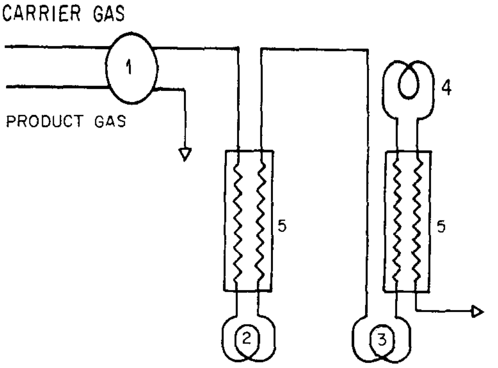

FIG. 3. Analysis system: (1) sampling valve; (2) column Porapak Q 0.5 m, 185°C; (3) column Porapak Q 2 m, 48°C; (4) column Molsieve 13X, 4m, 20°C; (5) thermal conductivity detector.

Thermobalance apparatus

The thermobalance apparatus consisted of a DuPont series 900/950 thermoanalysis system. The sample volume was at atmospheric pressure and could be flushed with a toluene/nitrogen mixture. Experiments were carried out under isothermal conditions, with temperature measured by a thermocouple placed just above the sample holder. The bismuth uranate, usually 22 mg, was spread on a 5 × 10 mm platinum foil.

Pulse experiments

Pulse experiments were carried out at 470–520°C, using 0.1 g of oxidant, and a toluene concentration corresponding to 0.15–0.25 μmoles of toluene/pulse. From the analytical data, the rate of conversion of toluene and the rate of formation of benzene were calculated. Assuming that the converted toluene, not transformed into benzene, is oxidized to CO_2 and H_2O (which assumption is to a great extent justified by the results of the flow experiments described below) we also calculated the amount of oxygen consumed, and the degree of reduc-

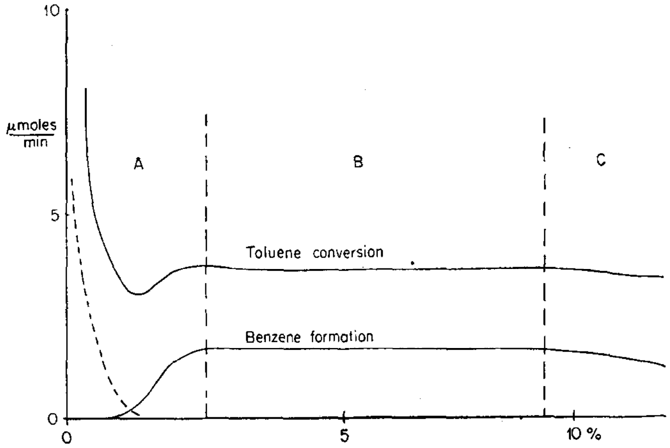

FIG. 4. Reaction rates as a function of the degree of reduction: 0.203 µmoles of toluene/pulse, 480°C, 0.1 g of Bi_2UO_6.

tion of the oxidant. The conversion rate and the rate of formation of benzene were plotted against the degree of reduction. The results of a typical experiment are given in Fig. 4.

Three definite regions can be clearly distinguished, to be called the A-, B-, and C-regions, respectively. In the A-region the conversion rate rapidly decreases and goes through a minimum; the benzene formation rate increases. Both rates have a constant value in region B, while they decline in region C. To account for the peculiar form of the curves in the A-region, it is supposed that the toluene conversion is actually the sum of two different processes, a fast and unselective one, declining with the degree of reduction, and a selective reaction which increases upon reduction. This can explain the minimum in the toluene conversion rate.

If a benzene/nitrogen mixture is used as the feed gas, a curve is obtained which is depicted in Fig. 4 as a broken line. Obviously, benzene is attacked in region A only, and is stable in region B. This suggests that on a fully oxidized bismuth uranate surface sites are present on which both benzene and toluene undergo total oxidation, while in the course of the reaction a second type of site is formed on which toluene is oxidized either to benzene or to CO_2 and H_2O, and by which benzene is not converted.

The nature of the first type of site is not yet fully understood. It is very unlikely that adsorbed molecular oxygen is responsible for the total oxidation. Before each experiment, the bismuth uranate was heated for approx 1 hr at the reaction temperature in an oxygen-free stream of helium. During this treatment, O_2 should be desorbed. Even heating the oxidant in helium for several hours at 550°C did not change the A-reaction rates. By heating a sample of fresh Bi_2UO_6 *in vacuo* at 600°C and measuring the amount of O_2 desorbed, we could calculate that on 1 g of Bi_2UO_6 only 4 µmoles of oxygen are present, corresponding to a degree of reduction of 0.001.* Another possibility is that the unselective sites are always present on the surface, but that they are poisoned by a slow adsorption of hydrocarbons during the process. However, these hydrocarbons would probably be desorbed in the time between the pulses. If the desorption were incomplete in that time interval, the length of this interval should affect the reaction rates. Should total desorption occur, no effect would be found. The latter proved to be the case, meaning that fast desorption takes place or that there is no adsorption at all.

Also in the B-region no influence of adsorption was found, for when we stopped pulsing in the B-region, heated the oxidant 100°C above the normal reaction temperature in helium during 1 hr, and thereafter continued the run under the original condi-

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* Experiment carried out by Dr. I. Matsuura.

tions, it appeared that the reaction rates after this heat treatment were unchanged.

The possibility of hydrocarbons poisoning the unselective sites could be ruled out even more definitely as a result of a series of experiments in which we determined the reaction rates on bismuth uranate samples with different specific surface areas. We used the samples described in Table 3 in an amount corresponding to a surface area of 10 m². It seems a reasonable assumption that for a certain number of sites to be poisoned, a given quantity of hydrocarbon must have passed through the bed. The reaction rates, plotted against the total quantity of hydrocarbon fed to the reactor, should then be identical for all samples. This assumption proved to be incorrect (Fig. 5). However, if the rates were plotted with the degree of reduction as abscissae, they coincided much better (Fig. 6).

Apparently, the rate of benzene formation always reaches its maximum at the same degree of bulk reduction. This does not mean that the degree of reduction at the surface is equal to that of the bulk. However, in pulse experiments it is unlikely that a gradient in oxygen content over the oxidant particle exists.

The results suggest that the unselective sites are present in fully oxidized bismuth uranate in a fixed percentage of the mass, and not as a fraction of the surface area of the solid. This could mean that a special kind of lattice oxygen exists, giving rise to a fast and unselective oxidation. The value of the maximum in rate of benzene formation depends on the surface area of the oxidant as well. This can also be seen from the maximum selectivities given in Table

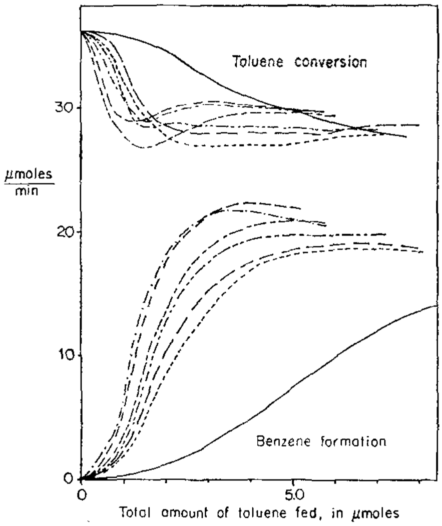


FIG. 5. Reaction rates as a function of the total toluene fed. 10 m² of Bi_2UO_6, 480°C, 0.7 μmoles of toluene/pulse.

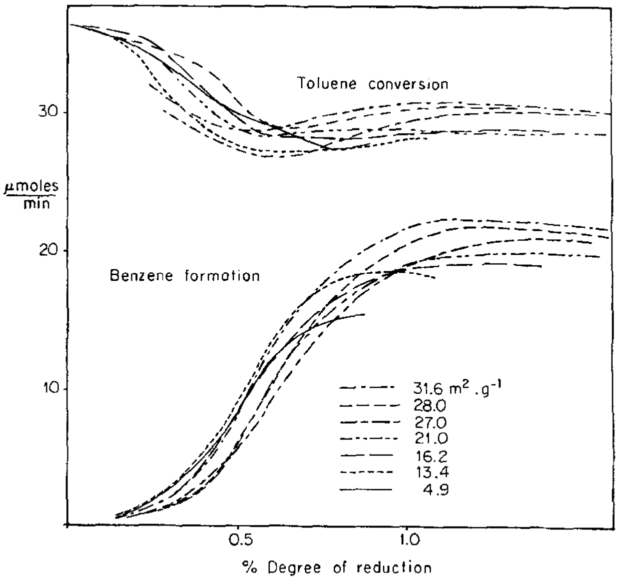


FIG. 6. Reaction rates as a function of the degree of reduction.

3. This effect is probably due to differences in the structure of the bismuth uranate surface.

In the B-region, the reaction rates are independent of the degree of reduction. Apparently, the number of active sites is constant. This enabled us to determine the influence of the toluene concentration and the reaction temperature on the reaction rate. The B-rates were a function of the conditions in region B only, and proved to be unaffected by the conditions in the A-region. We started every experimental run with fully oxidized Bi_2UO_6, and after passing the A-region took the average value of five pulses as the B-reaction rate.

In Fig. 7 the number of moles of toluene converted and benzene formed are given as a function of the inlet concentration. From the results it appears that both the rate of disappearance of toluene and the rate of formation of benzene are first order in toluene. The overall reaction can now be described by the following model

$$C_7H_8 \xrightarrow{k_2} C_6H_6 + CO_2 + H_2O,$$

$$C_7H_8 \xrightarrow{k_3} 7\ CO_2 + 4\ H_2O,$$

in which k_2 and k_3 represent first order rate constants; the rate constant of the total toluene conversion is $k_1 = k_2 + k_3$. Rate constants were determined as a function of temperature and for both reactions the activation energy is of the order of 25 kcal $mole^{-1}$ between 480 and 500°C.

In the Introduction we stated that the kinetics could not be measured accurately at high degrees of conversion, because a gradient in oxygen content over the fixed bed would occur. Since we know from Fig. 4 that the reaction rates are independent of the degree of reduction between 2 and 10%, we now can conclude that the B-reaction rates may also be determined at high conversions, provided that the first part of the oxidant is not reduced beyond 10%, while the last part must be reduced for at least 2%. Experiments carried out with 1.0 g of oxidant and a degree of conversion of approx 90% showed that the reaction rates were constant in a small range. We were therefore able to determine the B-reaction rates at high degrees of conversions as well, and with greater accuracy. The results of experiments with 1.0 g of Bi_2UO_6 are given in Fig. 8. The dependence of the contact time on the reaction rates was measured by varying the amount of oxidant in the reac-

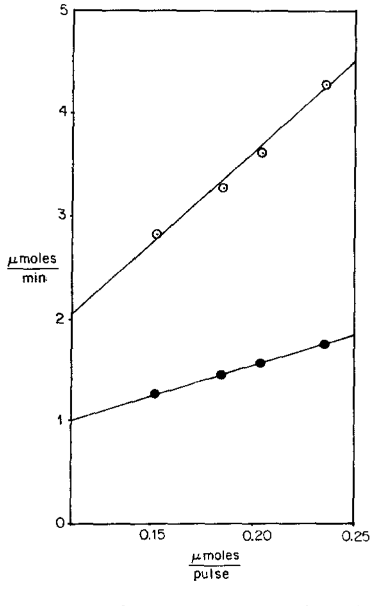


FIG. 7. Rate of benzene formation (●) and toluene conversion (⊙) as a function of the toluene inlet concentration; 0.1 g of Bi_2UO_6, 480°C.

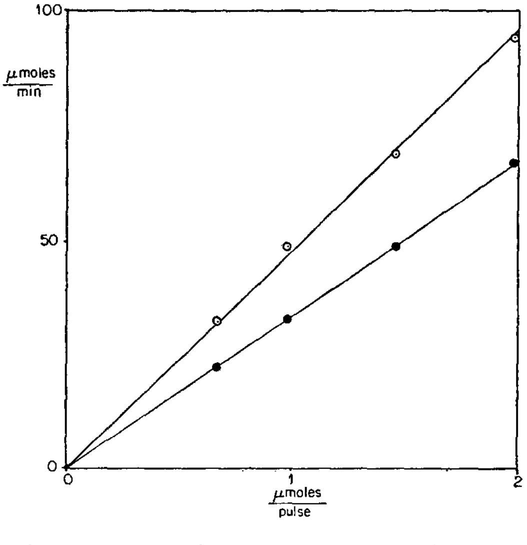


FIG. 8. Rate of benzene formation (●) and toluene conversion (⊙) as a function of the toluene inlet concentration; 1.0 g of Bi_2UO_6, 480°C.

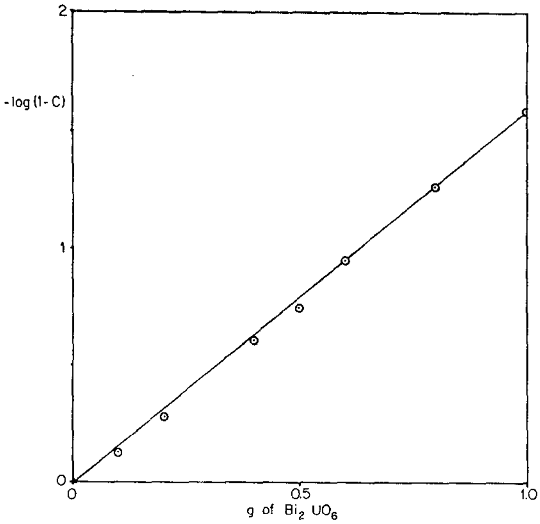


FIG. 9. $-$Log(1-conversion) as a function of the quantity of Bi_2UO_6 in the reactor. 0.67 μmoles of toluene per pulse; 480°C.

tor. Experimental results are given in Fig. 9. All these data, which, we emphasize, are valid only in the B-region, support the first order reaction model. We determined k_1, k_2 and k_3 for different temperatures and constructed an Arrhenius plot, given in Fig. 10.

The activation energy for k_1 is 30 kcal mole^{-1} and that for k_3 17 kcal mole^{-1} between 420 and 480°C, while that for k_2 declines from 55 at 420°C to 30 kcal mole^{-1} at 480°C. The curved form of the latter Arrhenius line could originate from diffusion limitations at the higher temperature. This is contradicted by the observation that varying the particle size of the oxidant did not affect the reaction rates at 480°C.

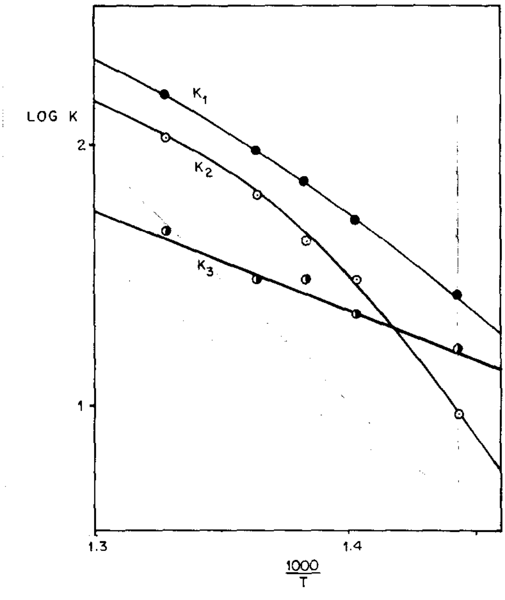


FIG. 10. Log rate constant as a function of the inverse temperature.

To check the occurrence of pore diffusion limitations, we calculated the effectiveness factor η, defined as the ratio of the actual reaction rate to the hypothetical one should the internal surface be fully effective. Methods to calculate η for catalytic reactions are given by, among others, Satterfield and Sherwood (*16*). His theory is also applicable to gas-solid reactions in which the physical properties of the solid remain unchanged in the process. For an experiment at 480°C with 1.0 g of oxidant, a toluene inlet mole fraction of 0.02 and a conversion degree of 90%, we found for the Thiele modulus Φ a value of 0.002. This means, that η is very near to 1, ruling out the occurrence of pore diffusion limitations.

We now think that at low temperatures the benzene formed remains adsorbed on the bismuth uranate surface. The apparent energy of activation is then actually composed of the energies of activation of the reaction and the desorption. The phenomenon of a reaction product retarding its own formation is not uncommon in catalytic oxidations. Batist, Prette and Schuit (*17*) observed, that in the oxidation of butene over bismuth molybdate the butadiene formed acts as a strong inhibitor, resulting in a curved Arrhenius line. The energy of activation of 30 kcal mole^{-1} that we find for our reaction is in good agreement with the values obtained by other authors for the catalytic oxidation of toluene (Table 4).

Finally, in the region C all reaction rates decline. Since the pulse experiments are inconvenient for attaining a high degree of reduction, we investigated the reaction in this region in the flow system and the thermobalance only.

Experiments in the flow system and the thermobalance

In the experiments carried out in the flow system, CO, CO_2, H_2O, benzene and toluene

TABLE 4

Author	Ref.	Catalyst	Energy of activation (kcal mole^{-1})
Downie, Shelstad and Graydon	(*19*)	V_2O_5	26.4
Kumar, Bhat and Kuloor	(*20*)	$SnO_2{\cdot}V_2O_5$	29.2
Reddy and Doraiswamy[a]	(*18*)	$MoO_3{\cdot}WO_3$	23
Trimm and Irshad	(*21*)	MoO_3	27.4

[a] Calculated from Reddy and Doraiswamy's experimental data.

could be determined quantitatively. CO proved to be absent; the other products accounted for approx 95% of the carbon and hydrogen atoms. In the condensed products, traces of benzaldehyde were found, identified by gas chromatography. In some experiments, small amounts of a white solid deposited in the colder part of the system. IR and PMR spectra were characteristic for diphenyl.

Experiments in these systems were usually continued until the reaction stopped. From the analysis results it was calculated that the degree of reduction of the bismuth uranate was then of the order of 30–60%, depending on the temperature. The reoxidation of the reduced material is very fast and exothermic. When air was passed over a reduced sample, starting at 100°C, the temperature rose to 400–500°C, and the oxygen was taken up quantitatively. If the reoxidation is carried out at the normal reaction temperature, the air has to be supplied very slowly in order to prevent overheating and sintering of the bismuth uranate. The properties of the reoxidized samples are identical to those of the original ones. We have performed up to 50 runs on the same bismuth uranate sample without being able to observe any decrease in activity. Such a peculiar behavior is reported for a few other compounds. Recently Swift, Bozik and Ondrey (*22*) and Massoth and Scarpiello (*23*) described a process for the oxidative dimerization of propene using bismuth oxide as the oxidant. They found that unsupported bismuth oxide can be reduced reversibly, provided that the degree of reduction does not exceed 60%. If the oxide is reduced beyond 60%, particles of bismuth metal are formed, which are not easily reoxidized. Supported Bi_2O_3, on the other hand, can be reduced completely to the metal and subsequently be reoxidized. The explanation lies in the fact that the metal atoms are separated by the support and cannot form clusters.

Batist *et al.* (*24*) found that bismuth molybdate can be reduced reversibly to a degree of reduction of 67%. He presumes that in the reduced material the bismuth is in the zero-valent and the molybdenum in the tetravalent state. We have tried to estimate the equilibrium composition of the system Bi_2UO_6–toluene by carrying out some thermodynamic calculations. Since no thermodynamic properties of Bi_2UO_6 are known, we first considered the reaction between toluene and each of the oxides separately. We calculated ΔG_f^{750} and ΔH_f^{750} for each of the components, taking the elements at 25°C and 1 atm as the standard state. Thereafter we calculated ΔG_r^{750} and ΔH_r^{750} for a number of reactions likely to occur (Table 5). It follows that bismuth oxide is easily reduced to the metal but that uranium will not be reduced beyond the tetravalent state. One must, however, keep in mind that the uranium oxides are not always well-defined compounds, but that they can form nonstoichiometric oxides, dependent on the conditions. Thermodynamic properties of these oxides are not well known.

To find ΔG_r^{750} and ΔH_r^{750} for the overall reaction between Bi_2UO_6 and toluene, the thermodynamic constants for the reactions,

$$Bi_2O_3 + UO_3 \longrightarrow Bi_2UO_6,$$

$$2\,Bi + UO_2 \longrightarrow Bi_2UO_2,$$

should be available. Since we know from the literature that ΔG for the reaction between metal oxides to form mixed oxides

TABLE 5

HEAT OF REACTION AND FREE ENERGY OF REACTION AT 1 atm AND 750 K, TAKING THE ELEMENTS AT 25°C AS STANDARD[a]

	($k$cal mole^{-1})	
	ΔG_r^{750}	ΔH_r^{750}
$6Bi_2O_3 + C_7H_8 \rightarrow 12Bi + 7CO_2 + 4H_2O$	−399	−29
$Bi_2O_3 + C_7H_8 \rightarrow 2Bi + C_6H_6 + CO_2 + H_2O$	−66	+3
$54UO_3 + C_7H_8 \rightarrow 18U_3O_8 + 7CO_2 + 4H_2O$	−1055	−724
$9UO_3 + C_7H_8 \rightarrow 3U_3O_8 + C_6H_6 + CO_2 + H_2O$	−176	−112
$9U_3O_8 + C_7H_8 \rightarrow 27UO_2 + 7CO_2 + 4H_2O$	−397	−92
$\frac{3}{2}U_3O_8 + C_7H_8 \rightarrow \frac{9}{2}UO_2 + C_6H_6 + CO_2 + H_2O$	−58	−7
$9UO_2 + C_7H_8 \rightarrow 9U + 7CO_2 + 4H_2O$	+1396	
$\frac{3}{2}UO_2 + C_7H_8 \rightarrow \frac{3}{2}U + C_6H_6 + CO_2 + H_2O$	+212	
$3UO_2 + O_2 \rightarrow U_3O_8$	−95	−87
$U_3O_8 + O_2 \rightarrow 3UO_3$	+7	−10
$2Bi + \frac{3}{2}O_2 \rightarrow Bi_2O_3$	−89	−141

[a] Calculated with data taken from (*25*) and (*26*).

is always well below 100 kcal mole^{-1}, and mostly in the order of 50 kcal mole^{-1}, we may safely state that the *difference* in ΔG and ΔH for the reactions (1) and (2) does not exceed 50 kcal. As a result, Bi_2UO_6 and Bi_2UO_2 may, in our reaction, be considered as a mixture of the oxides of bismuth and uranium with an error in the thermodynamic constants of ±25 kcal. Thus we find for the overall reactions:

$$\frac{9}{2}Bi_2UO_6 + C_7H_8 \rightarrow \frac{9}{2}\,Bi_2UO_2 + 7CO_2 + 4H_2O \qquad \begin{aligned}\Delta G_r^{750} &= -456 \pm 112\ \text{kcal},\\ \Delta H_r^{750} &= -94 \pm 112\ \text{kcal},\end{aligned}$$

$$\frac{3}{4}Bi_2UO_6 + C_7H_8 \rightarrow \frac{3}{4}Bi_2UO_2 + C_6H_6 + CO_2 + H_2O \qquad \begin{aligned}\Delta G_r^{750} &= -67 \pm 38\ \text{kcal},\\ \Delta H_r^{750} &= -7 \pm 38\ \text{kcal},\end{aligned}$$

$$Bi_2UO_2 + 2O_2 \rightarrow Bi_2UO_6 \qquad \begin{aligned}\Delta G_r^{750} &= -106 \pm 50\ \text{kcal},\\ \Delta H_r^{750} &= -173 \pm 50\ \text{kcal}.\end{aligned}$$

These results indicate that the reduction of Bi_2UO_6 by toluene is thermodynamically a very favored reaction. The end product is Bi_2UO_2, composed of zero-valent Bi and tetravalent U. The selective reaction is not as favored as the unselective one, and is also less exothermic.

To obtain an accurate analysis of the reaction products in the flow system, the toluene concentration must be considerably higher than in the pulse system. Under these conditions the kinetics of the reaction differ from that in the pulse apparatus. There is also a rapid and unselective reaction in the initial stages, followed by an increasing benzene production, but a strict division into three different regions is impossible now. The reaction is dependent on the degree of reduction over the whole range (Fig. 11).

In the thermobalance we were able to investigate the reaction kinetics at very low degrees of conversion as well. Here, $d[O]/dt$ curves could be obtained, congruent to the curves derived from the pulse experiments, but the reaction rates were lower. However, if the toluene concentration exceeds a certain value, the zero order in oxygen changes into a positive one (Fig. 12). We know from pulse experiments that the number of active sites does not change between certain limits of degree of reduction. This implies that, even at high toluene concentrations, the reaction rates should be constant between these limits. The observation that this is not the case if the toluene concentration exceeds a certain value can be explained by presuming that then the rate of oxygen transport from

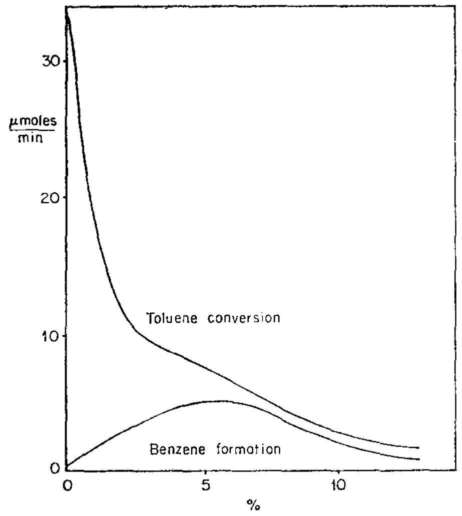


FIG. 11. Reaction rates as a function of the degree of reduction; 34 μmoles of toluene/min; mole fraction of toluene, 0.117; 470°C; 0.5 g Bi_2UO_6.

the bulk to the surface is beginning to play a role. In the pulse system, this rate is of little importance since less oxygen, namely, approx 10 μatoms, is consumed per pulse than is actually present on the bismuth uranate surface. [On the surface of 1 g of oxidant (22 m^2), about 10^3 μatoms of oxygen can be accommodated.] In the time between the pulses, the removed oxygen is replenished by diffusion from the bulk. At low toluene concentrations in the thermobalance, implying low reaction rates, the oxygen diffusion keeps up with the rate of oxygen removal from the surface. At higher toluene concentrations, the oxygen transport rate becomes a limiting factor.

We also observed that the form of the $d[O]/dt$ curve in the thermobalance experiments remains the same when the reaction rates are raised by increasing the temperature. If the explanation given above is correct, this can only happen when the oxygen transport rate through the lattice has about the same energy of activation as the chemical reaction. The energy of activation for oxygen diffusion in Bi_2UO_6 is unknown, but for the comparable $Bi_2O_3 \cdot 2MoO_3$ Batist *et al.* (*24*) found a value of 29 kcal $mole^{-1}$, while for UO_2 a value of 30 kcal $mole^{-1}$ is reported (*30*). The model we have just described gives a rough view of what happens if toluene reacts with bismuth uranate, but a more quantitative approach still has to be developed.

REACTION MECHANISM

For the mechanism of the oxidative demethylation reaction, two alternative routes may be suggested:

a. Oxidation of toluene to benzaldehyde, followed by dissociation into benzene and CO.

b. Oxidation to benzoic acid, followed by dissociation into benzene and CO_2.

Each step of these routes is a plausible reaction. The oxidation of toluene to benzaldehyde or benzoic acid, both with the aid of an oxidant and catalytically, is well known. Dissociation of benzaldehyde and

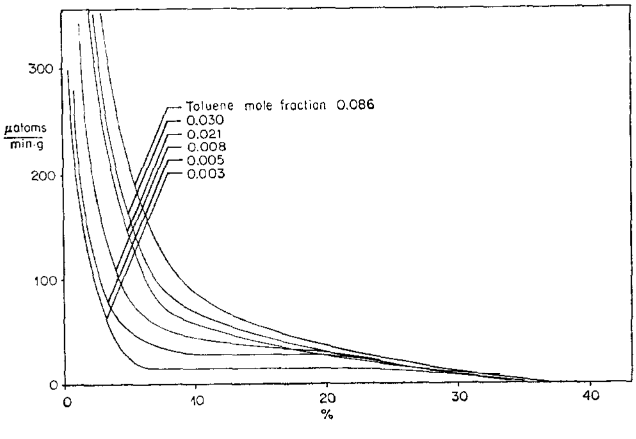
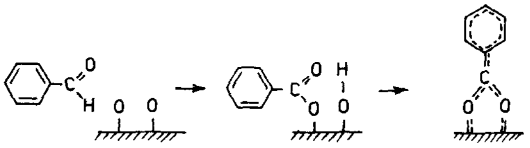


FIG. 12. Rate of oxygen depletion as a function of the degree of reduction; 455°C.

benzoic acid can occur both thermally and catalytically. The thermal process is a free radical reaction, in which many by-products like biphenyl are formed. Since we find only traces of the latter substance, the thermal decomposition is not likely to occur. The catalytic decarboxylation of benzoic acid was already investigated in 1914 by Sabatier and Mailhe (*27*). He found that CdO, ZnO and TiO_2 gave the best benzene yields. It is striking that CdO and ZnO are mentioned by Norton and Moss as very suitable catalysts for the oxidative demethylation of toluene and other alkyl-aromatics (*2*).

As to the catalytic decarbonylation of benzaldehyde, not much is known. The benzene formed as a by-product in the catalytic oxidation of toluene to benzaldehyde over bismuth molybdate probably originates from this reaction. CO should be formed, but is absent in our reaction products. This can be explained by the observation that CO is very rapidly oxidized to CO_2 by bismuth uranate. When benzaldehyde is passed over bismuth uranate, it reacts almost completely; part of it undergoes total combustion, part is converted into benzene. Traces of benzaldehyde could be identified among our reaction products.

These results indicate that the demethylation reaction might occur via one of the paths described above. Which route is actually followed is difficult to decide. It is not certain that benzaldehyde or benzoic acid are produced as free molecules, a direct dissociation of the molecule in the adsorbed form also being possible. Furthermore, benzaldehyde will probably be adsorbed on an oxide surface in the following form:



as was demonstrated by Sachtler *et al.* (*28*) for stannic vanadate; such an adsorbed molecule can hardly be discerned from adsorbed benzoic acid. Similar results were obtained by Galwey (*29*), who studied the desorption of hydrocarbons from a nickel oxide surface. He showed that benzaldehyde, benzoic acid, phenyl benzoate and nickel benzoate all formed benzene with the same energy of activation, and suggested that a common intermediate exists.

We now think that the selective demethylation reaction occurs via such an benzoate-like intermediate. This intermediate dissociates and forms a phenyl radical, which picks up an adsorbed hydrogen atom to form benzene. A small part of the phenyl radicals recombine to produce biphenyl. As mentioned before, we ascribe the nonselective oxidation in the initial stages of the reaction to a special kind of lattice oxygen.

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