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# The Oxidative Demethylation of Toluene

## II. Kinetics of the Reduction of Bismuth Uranate by Toluene*

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The kinetics of the reduction of bismuth uranate by toluene have been studied in micro-pulse and micro-flow reactors and in a thermobalance, at toluene mole fractions between 0.003 and 0.122 and temperatures between 455 and 527°C. During the reduction the $Bi_2UO_6$ is converted into metallic bismuth and $UO_2$. In the overall reaction rate both the chemical reaction rate at the surface and the rate of oxygen diffusion through the lattice of the solid play a role. A kinetic model comprising these two steps is derived.

It appears that $Bi_2UO_6$ contains two types of lattice oxygen, viz, approximately 2% of a nonselective oxygen with $D = 3 \times 10^{-22}$ m$^2$ sec$^{-1}$ and a diffusion energy of activation $E = 26$ kcal mole$^{-1}$, and a more selective oxygen with $D = 3 \times 10^{-20}$ m$^2$ sec$^{-1}$ and $E = 63$ kcal mole$^{-1}$ (at 470°C). Some evidence is found for bismuth uranate having a shear structure, the small amount of nonselective oxygen occupying positions in the shear planes.

## INTRODUCTION

In a previous paper (*1*), we described how toluene can be demethylated oxidatively, using bismuth uranate as oxidant. From kinetic data obtained in micro-pulse and micro-flow reactors and in a thermobalance we concluded that in the pulse system the reaction rates are determined by the chemical reaction at the surface of the bismuth uranate, while under continuous flow conditions the rate of oxygen diffusion through the lattice also plays an important part. In the present paper we offer further evidence for this conclusion, on the basis of a detailed analysis of the kinetics of the reduction of bismuth uranate by toluene. First, we shall discuss a number of kinetic models that might hold for the reduction of a solid oxide by a gas. In the second part we shall consider to what extent the information obtained is applicable to the reduction of bismuth uranate.

## THEORY OF THE REDUCTION OF OXIDES

In the literature (*1, 2*) the rate of reduction of an oxide by a gas is usually described by the so-called shrinking-core relation, which is based on the assumption that reaction takes place at the surface of a gradually shrinking core of unreacted material, and that the chemical reaction is the rate-determining step. Sometimes, the diffusion of gas through the layer of product formed around the unreacted core is supposed to be rate-determining (*3, 4*). However, for the reduction of bismuth uranate by toluene these models appeared to be inadequate. Instead, we suppose that the reaction proceeds via a chemical reaction at the surface, leading to a reduction of the surface layer, followed by diffusion of

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oxygen ions from the interior to the surface of the particle. In such a process, both the rate of chemical reaction and diffusion play a role. Assuming that the chemical reaction is first order in reducing agent concentration $(T)$, and independent of the concentration of oxygen atoms of the surface (O) if (O) is high, we obtain:

$$-\frac{d(\mathrm{O})}{dt} = k(T) \text{ or: } \alpha = k(T)t. \quad (1)$$

The case that (O) is high will occur if the diffusion coefficient for the oxygen diffusion through the lattice has such a value that only a small gradient in the oxygen concentration is required to maintain an oxygen diffusion rate of the same order of magnitude as the chemical reaction rate.

For the case that an appreciable oxygen concentration gradient is required, a model has been derived by Batist *et al.* (*5*) for the reduction of bismuth molybdate by *l*-butene. The authors make the following assumptions:

1. The physical properties of the solid (surface area, particle size, diffusion coefficients) do not change during the reaction.
2. The solid is semi-infinite with one boundary plane at which the reaction takes place.
3. The diffusion occurs in one direction only, perpendicular to the boundary plane.
4. The rate of the chemical reaction at the surface is equal to that of the diffusion from the bulk to the surface.

They found the following expression:

$$f = \frac{S\rho D}{k\lambda}\left\{e.\mathrm{erfc}\left(\frac{k\lambda t^{1/2}}{D^{1/2}}\right) - 1 + \frac{2k\lambda t^{1/2}}{\pi^{1/2}D^{1/2}}\right\}, \quad (2)$$

in which $f$ is the degree of conversion of the solid, $S$ the specific surface area (cm$^2$ g$^{-1}$), $\rho$ the density (g cm$^{-3}$), $k$ a rate constant (sec$^{-1}$), $\lambda$ a so-called jump distance (cm), of the order of the lattice constant, $D$ the diffusion coefficient of oxygen in the lattice (cm$^2$ sec$^{-1}$), and $t$ the reaction time (sec). Furthermore, $e\cdot\mathrm{erfc}\ x$ is equal to $e^{x^2}\ (1 - \mathrm{erf}\ x)$.

Equation (2) can be solved numerically. Between certain limits of $t$, it can be written in the approximate form:

$$f = -A + Bt^{1/2}, \quad (3)$$

in which $A = \frac{S\rho D}{k\lambda}$ and $B = \frac{2S\rho D^{1/2}}{\pi^{1/2}}$.

With these expressions the authors calculated $k$ and $D$ for the reduction of bismuth molybdate.

In the following we shall derive a somewhat more general version of Eq. (2). For this we will replace the assumptions 2, 3 and 4 respectively, by:

2a. The solid consists of spherical particles.

3a. The diffusion occurs radially from the bulk of the solid to the surface.

4a. The reaction takes place in a thin surface layer, over which the oxygen gradient is negligible.

This last replacement means that we no longer require the rates of diffusion and chemical reaction to be equal. Consequently we will consider a spherical particle with radius $a$ and surface layer thickness $d$, $d$ being small compared to $a$. The concentration of removable oxygen in the sphere is a function of the distance to the centre $r$ and the time $t$, and will be named $c$ or $c(r,t)$. Oxygen atoms are removed from the surface layer by chemical reaction and replenished by diffusion from the bulk. The number of oxygen atoms $M_1$ removed per unit of time $\Delta t$ from the surface layer is given by:

$$M_1 = 4\pi a^2 dk' c_0 c\Delta t, \quad (4)$$

in which $c_0$ is the concentration of reducing agent, kept constant during the process, and $k'$ a rate constant. The number of atoms $M_2$ transferred from the sphere to the layer is equal to:

$$M_2 = -4\pi a^2 D\left(\frac{\delta c}{\delta r}\right)_{r=a}\Delta t, \quad (5)$$

in which $D$ is the diffusion coefficient. For the net oxygen transport we obtain:

$$\left(\frac{\delta M}{\delta t}\right)_{r=a} = 4\pi a^2 d\left(\frac{\delta c}{\delta t}\right)_{r=a}$$

$$= -4\pi a^2 D\left(\frac{\delta c}{\delta r}\right)_{r=a} - 4\pi a^2 dkc,$$

with $k = k'c_0$.

The boundary conditions now become

$$\frac{\delta c}{\delta t} = -\frac{D}{d}\left(\frac{\delta c}{\delta r}\right) - kc \quad \text{at } r = a \text{ and } t \geqslant 0. \tag{6}$$

For a spherical particle:

$$\frac{\delta c}{\delta r} = 0 \text{ at } r = 0 \text{ and } t \geqslant 0. \tag{7}$$

We assume $c(r,0)$ to be equal to 1 and solve Fick's second law for a spherically symmetrical system:

$$\frac{\delta c}{\delta t} = D\left(\frac{\delta^2 c}{\delta r^2} + \frac{2\delta c}{r\delta r}\right) \quad 0 < r < a, \tag{8}$$

with boundary conditions (6) and (7) and initial condition $c(r,0) = 1$ by the Laplace transform method. Introducing the notation:

$$\tilde{c}(r,p) = \int_0^\infty e^{-pt}c(r,t)\,dt, \tag{9}$$

Eq. (8) becomes:

$$p\tilde{c} - 1 = D\left(\tilde{c}'' + \frac{2}{r}\tilde{c}'\right) \quad 0 < r < a, \tag{10}$$

where $c'$ and $c''$ are the first and second derivatives to $r$ of $c(r,t)$, respectively. Equation (6) becomes:

$$-\frac{D}{d}\tilde{c}' = p\tilde{c} - 1 + k\tilde{c} \quad r = a. \tag{11}$$

Substituting $\tilde{c} = u/r$ in Eq. (10) we obtain:

$$pu - r = Du''. \tag{12}$$

The solution of (12) with $q = (p/D)^{1/2}$ is:

$$u = Ae^{-qr} + \frac{r}{p} + Be^{+qr}$$

since for $r = 0$, $u = 0$ it follows that $A + B = 0$ and:

$$u = Ae^{qr} - Ae^{-qr} + \frac{r}{p} = Q\sinh qr + \frac{r}{p},$$

hence:

$$\tilde{c} = Q\frac{\sinh qr}{r} + \frac{1}{p}. \tag{13}$$

By substitution of (13) in (11) for $r = a$ it follows that:

$$-\frac{D}{d}\left(Qq\frac{\cosh qa}{a} - Q\frac{\sinh qa}{a^2}\right) = pQ\frac{\sinh qa}{a} + kQ\frac{\sinh qa}{a} + \frac{k}{p} \text{ or:}$$

$$Q\left\{-\frac{D}{d}\left(q\frac{\cosh qa}{a} - \frac{\sinh qa}{a^2}\right) - p\frac{\sinh qa}{a} - k\frac{\sinh qa}{a}\right\} = \frac{k}{p}$$

With $p = Dq^2$ one obtains:

$$Q = \frac{ka}{p\{[(D/da) - Dq^2 - k]\sinh qa - (Dq/d)\cosh qa\}}.$$

$Q$ substituted in (13) gives for $r = a$:

$$\tilde{c}(a,p) = \frac{k\sinh qa}{p\{[(D/da) - Dq^2 - k]\sinh qa - (Dq/d)\cosh qa\}} + \frac{1}{p}. \tag{14}$$

Equation (14) represents the Laplace transform of the concentration $c$ at the surface of the sphere. By inversion of the Laplace transform it follows that:

$$c(a,t) = 2c(r,0)\sum_{n=1}^{\infty}\frac{(kad/D)e^{-D\beta_n^2 t}}{a^2d^2\beta_n^4 + a^2\beta_n^2[1 + (3d/a) - (2kd^2/D)] - (kad/D)[1 - (kad/D)]}, \tag{15}$$

in which $\beta_n$ are the roots of:

$$\tan a\beta = \frac{a\beta}{1 - (kad/D) + ad\beta^2}. \tag{16}$$

Equation (15) gives the concentration of removable oxygen at the surface of the particle, $t \geqslant 0$. The amount of oxygen $\phi(t)$ present in the sphere at $t \geqslant 0$ is given by:

$$\phi(t) = \int_0^a 4\pi r^2 c(r,t)\, dr.$$

With Fick's second law it follows that:

$$\phi'(t) = 4\pi \int_0^a D \frac{\delta}{\delta r}\left(r^2 \frac{\delta c}{\delta r}\right) dr$$
$$= 4\pi D a^2 \left(\frac{\delta c}{\delta r}\right)_{r=a}, \quad (17)$$

and with boundary condition (6):

$$\phi'(t) = -4\pi a^2 d \left(\frac{\delta c}{\delta t}\right)_{a,t} - 4\pi a^2 dkc(a,t). \quad (18)$$

By integration of Eq. (18) we obtain:

$$\phi(t) = 8\pi a^2 dc(r,0) \sum_{n=1}^{\infty} \frac{kad/D}{a^2d^2\beta_n{}^4 + a^2\beta_n{}^2[1 + 3(d/a) - 2(kd^2/D)] - (kad/D)[1 - (kad/D)]} \left(\frac{k}{D\beta_n{}^2} - 1\right) e^{-D\beta_n{}^2 t} + A,$$

in which $A$ is a constant. Since at $t = \infty$, $\phi(t) = 0$, it follows that $A = 0$. At $t = 0$, $\phi(0) = 4/3\pi a^3 c(r,0)$.

The degree of conversion $f$ is defined as:

$$f = \frac{\phi(0) - \phi(t)}{\phi(0)},$$

and therefore:

$$f = 1 - \frac{6d}{a} \sum_{n=1}^{\infty} \left[\frac{k}{D\beta_n{}^2} - 1\right] \frac{kad/D}{a^2d^2\beta_n{}^4 + a^2\beta_n{}^2[1 + 3(d/a) - 2(kd^2/D)] - (kad/D)[1 - (kad/D)]} e^{-D\beta_n{}^2 t}. \quad (19)$$

Relation (19) represents the degree of conversion of the solid as a function of time. It can be solved numerically, provided that the values of $k$, $a$, $d$ and $D$ are available. The values of the roots $\beta_n$ of Eq. (16) can be found using the computer procedure known as REGULA FALSI.

In a similar way the degree of reduction at the *surface* can be found:

$$f_s = 1 - \frac{c(a,t)}{c(a,0)}. \quad (20)$$

These relations are applicable to gas–solid reactions involving a chemical reaction step followed by internal diffusion of a reacting species through the lattice of the solid. Examples are the reduction of oxides by various gases, the reduction of chlorides by hydrogen, but also the isotopic exchange of oxides. For the latter process a relation, similar to ours, was derived by Klier and Kučera (*6*), valid for the case that oxygen in an oxide is exchanged with a given quantity of labeled gaseous oxygen. Our model would describe such exchange experiments if the concentration of the labeled oxygen in the gas phase was kept constant.

## EXPERIMENTAL PART

The apparatus, the experimental procedures, and details on the preparation and properties of bismuth uranate have already been given in our previous paper.

## RESULTS

### a. *Phases Present in Reduced $Bi_2UO_6$*

Bismuth uranate was reduced in the pulse and in the flow systems. Partly reduced samples were removed from the reactor under $N_2$ and examined by X-ray diffraction. The only phases detectable were bismuth metal and $Bi_2UO_6$. A sample, completely reduced by $H_2$ at 800°C for several hours consisted of bismuth metal and $UO_2$. The changes in *d*-values of $Bi_2UO_6$ with increasing degree of reduction $\alpha$ were within experimental error. Bi metal was present in all samples, even in those with a degree of reduction of a mere 4%. The intensities of the bismuth lines increased with $\alpha$. It was established that some bismuth metal particles has a diameter as large as 10 to 50 $\mu$m. The conclusion was drawn that during reduction bismuth uranate disintegrates; metallic bismuth is separated and forms large conglomerates, while the remaining uranium oxide phase remains dispersed in the bismuth uranate lattice.

### b. *Reduction Kinetics in the Pulse System*

When bismuth uranate is reduced in a pulse system, and the reaction rates are plotted against the degree of reduction, curves are obtained of which Fig. 1 is a typical example. Three regions can be clearly distinguished. We already demonstrated (*1*) that the fast and nonselective oxidation in the A-region is due to the presence of a small percentage (2%) of a special kind of lattice oxygen that we called A-oxygen. In region B the reaction rates are independent of $\alpha$ (zero order in oxygen) and first order in toluene. The activation energy for the rate of reduction is 30 kcal mole$^{-1}$.

### c. *Reduction Kinetics in the Flow System*

The results of a typical experiment are given in Fig. 2. A division into three definite regions is now impossible. There is a continuing decrease in toluene conversion rate, while the rate of benzene formation has a maximum at higher degree of reduction of the bulk than during pulse experiments. Regions with constant activity are absent. Furthermore, the reaction rates are considerably lower. The reproducibility of the flow experiments is not too good. This may be due to incomplete reoxidation of the bismuth uranate between the experimental runs. When bismuth uranate is strongly reduced, the bismuth metal formed fuses to large conglomerates which are difficult to reoxidize. As a result, the regenerated sample may still contain free bismuth metal or bismuth oxide, resulting in an error in the calculated degree of reduction. Furthermore, incomplete reoxidation of Bi metal implies that the Bi/U ratio in the bismuth uranate has become smaller than 2, which affects the selectivity, as shown in (*1*). This effect is absent in the experiments carried out with the pulse system or the thermobalance, since in these systems we performed every run with a new sample of the same batch of bismuth uranate.

A systematic decrease in activity or selectivity with the number of reaction cycles

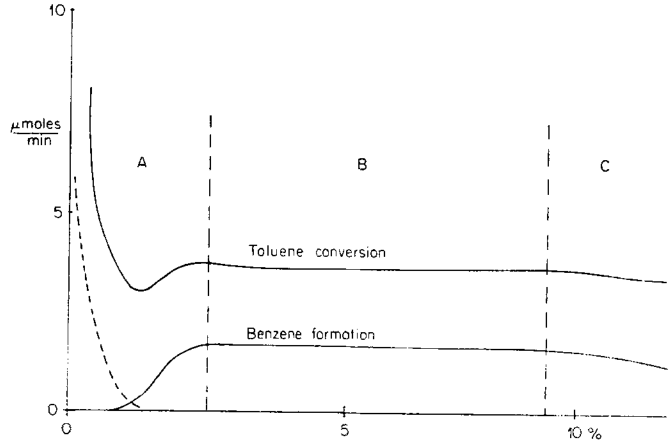

FIG. 1. Reaction rates as a function of the degree of reduction.

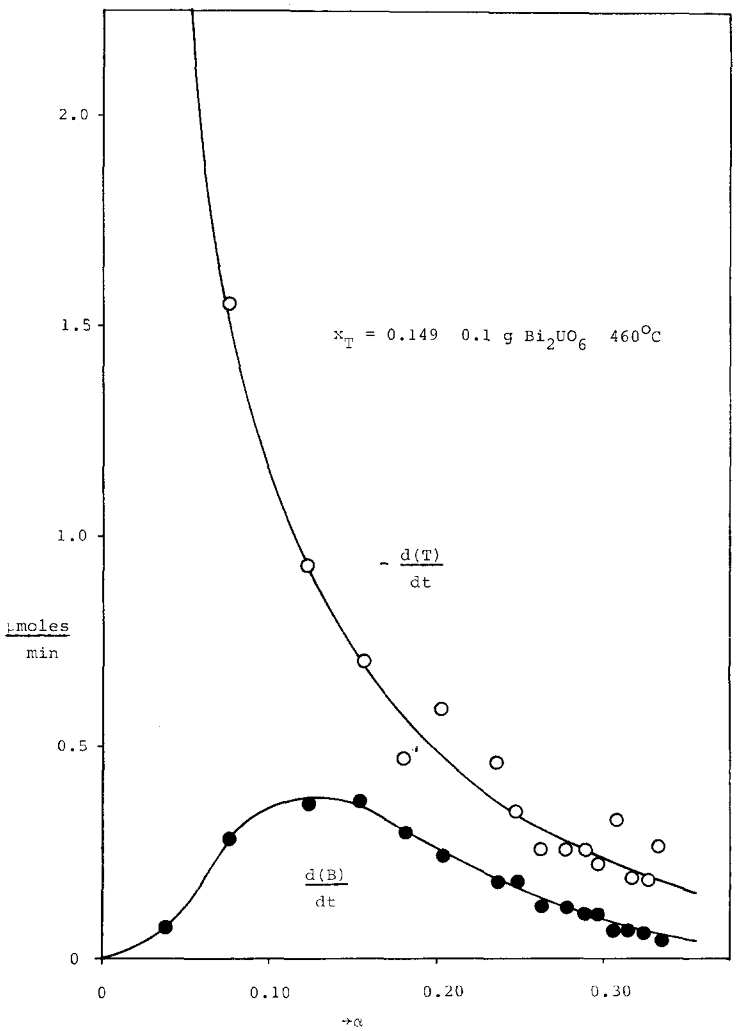

FIG. 2. Reaction rates as a function of the degree of reduction of $Bi_2UO_6$ in the flow reactor.

could not be observed. Although the form of the curves of which Fig. 2 gives an example is not straightforward, it appears that if the degree of reduction of the oxidant is plotted against the square root of the reaction time, a straight line is obtained (Fig. 3).

All kinetic data to be discussed in the following were obtained at gas flows higher than 40 $cm^3$ $min^{-1}$, where the influence of the gas flow on the reaction rates is negligible. Within the experimental error, no influence on the reaction rates was observed when the particle size was reduced tenfold.

Figure 4 shows the influence of the toluene concentration on the conversion rate of toluene. It is seen that the conversion rate becomes zero order in toluene at a mole fraction $x_T > 0.07$. Figure 5 gives the rate of formation of benzene. The selectivities are represented in Fig. 6. In Fig. 7 the degree of reduction $\alpha$ has been plotted against the square root of the time for various toluene mole fractions. Straight lines passing through the origin are obtained. Thus it appears that Eq. (3) is obeyed, indicating that under these conditions the chemical-reaction-plus-diffusion model holds.

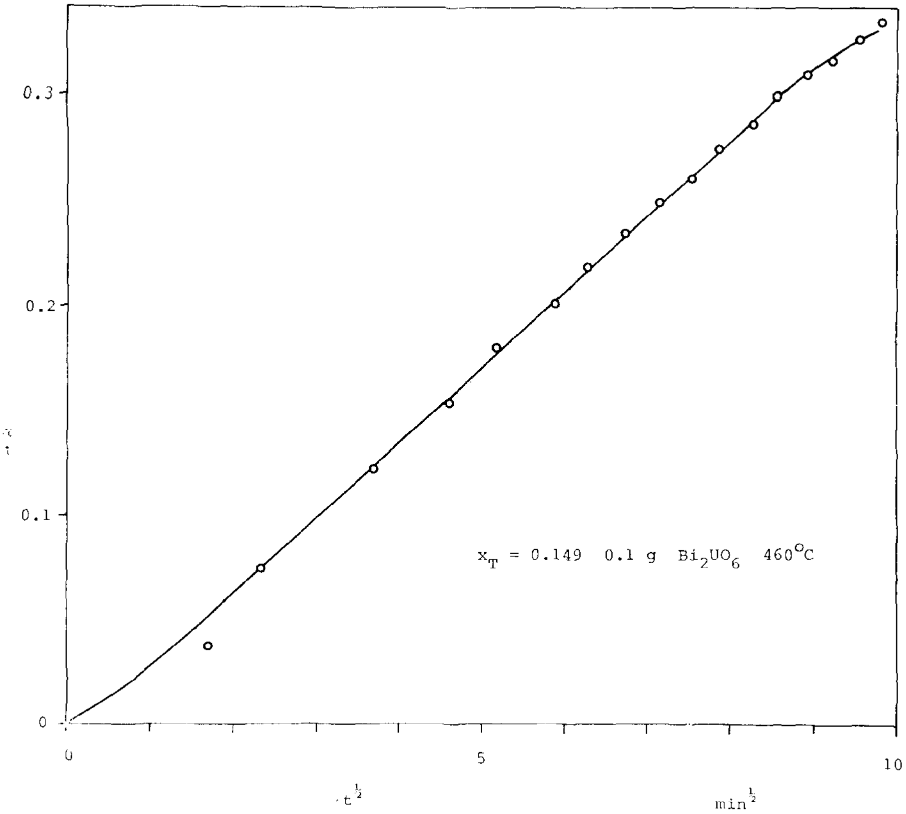

FIG. 3. Degree of reduction of bismuth uranate as a function of the square root of time; flow reactor.

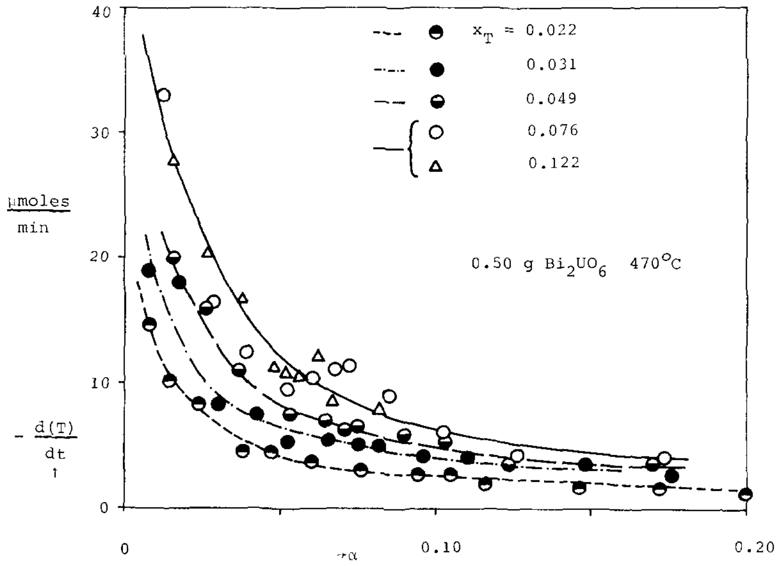

FIG. 4. Rate of toluene conversion as a function of the degree of reduction; flow reactor.

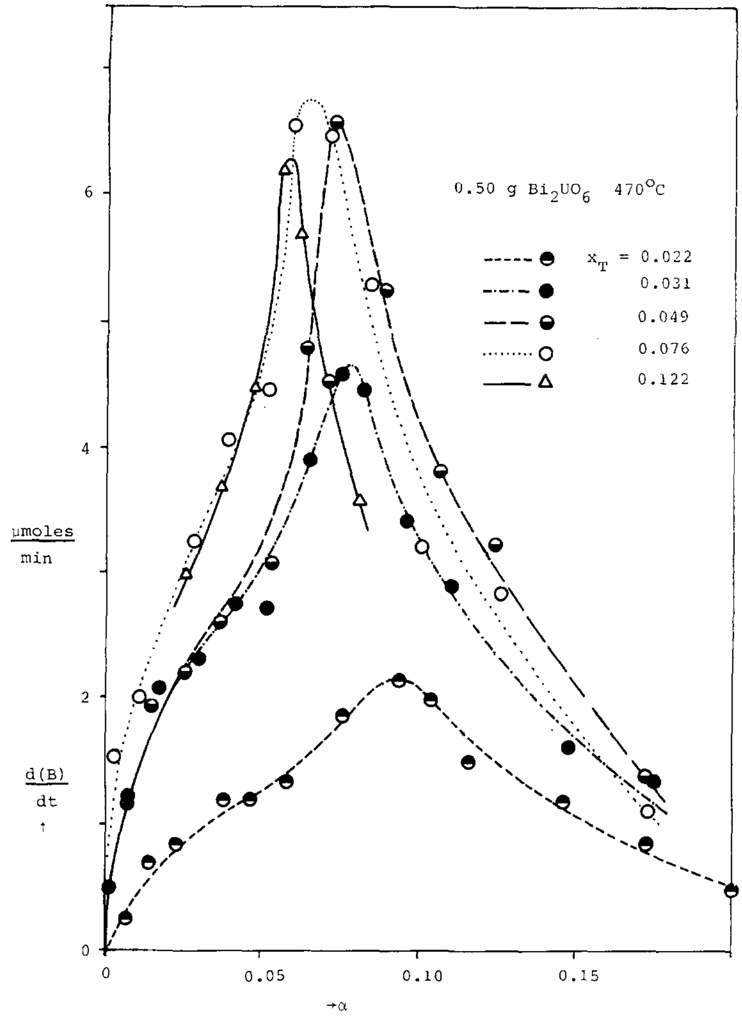

FIG. 5. Rate of benzene formation as a function of the degree of reduction; flow reactor.

Within the experimental conditions the effect of the temperature on the selectivity is small. There is a slight tendency towards a higher selectivity at higher temperatures. The effect of the temperature is investigated in more detail in the thermobalance experiments.

### d. *Reduction Kinetics in the Thermobalance*

Since the relations for $-d(O)/dt$ are much less ambiguous than those for $-d(T)/dt$ or $d(B)/dt$, we devoted particular attention to the former reaction rate. To investigate $-d(O)/dt$, the thermobalance is more suited than the flow reactor system. The degree and the rate of reduction of $Bi_2UO_6$ can be measured accurately and continuously, both at the high toluene concentration required in the flow apparatus and at the lower concentrations used during pulse experiments. Under the conditions used, no physical limitations occur, while also the adsorption of hydrocarbons or the formation of "coke" appeared to be negligible.

The effect of the toluene concentration is shown in Fig. 8. At toluene mole fractions of 0.0030 and 0.0055 three regions are dis-

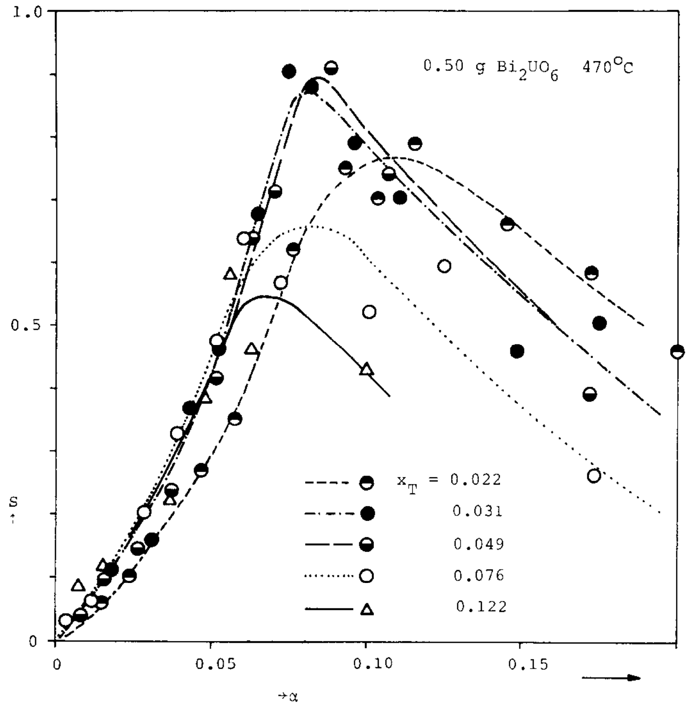

FIG. 6. Selectivity as a function of the degree of reduction of bismuth uranate; flow reactor.

tinguished just as during pulse experiments: a rapid decline in reduction rate at low $\alpha$ resembling region A of the pulse experiment, followed by a region in which the rate remains constant, and a final region in which the rate declines once again. At $x_T > 0.02$ the rate of oxygen depletion declines continuously, the curve with $x_T = 0.0084$ being an intermediate case.

The curves of $\alpha$ plotted versus $t^{1/2}$ are depicted in Fig. 9. Evidently the relation $\alpha = k\ t^{1/2}$ is obeyed up to $\alpha \simeq 0.30$ at higher toluene concentration, but at lower toluene mole fraction the expression holds good only to $\alpha \simeq 0.10$.

The effect of the reaction temperature was studied at toluene mole fractions of 0.0030 and 0.030. In Fig. 10 the rates are given as a function of $T$ for the lower toluene concentration. The three regions are clearly distinguished, and the region of constant activity appears to extend to a higher degree of reduction at the higher reaction temperature. At all temperature levels shown in Fig. 10 Eq. (3) holds for the lower toluene concentration up to $\alpha \simeq 0.10$ and for the higher concentration up to $\alpha \simeq 0.30$.

The effect of the specific surface area of the solid was studied at $x_T = 0.0030$ only. Results are represented in Fig. 11. It is clear that the reaction rates in the constant activity region expressed per square meter of bismuth uranate surface area are approximately equal. However, this region extends to $\alpha \simeq 0.40$ with the samples having a high specific surface area, while it ends at about 0.12 with the sample having a low area.

The results obtained for the reduction of

TABLE 1
REDUCTION OF BISMUTH URANATE BY TOLUENE UNDER FLOW CONDITIONS

| Mole fraction | Degree of reduction | Kinetic model |
|---|---|---|
| <0.005 | $\alpha < 0.10$ | $\alpha = kt^{1/2}$ |
| | $\alpha > 0.10$ | $\alpha = kt$ |
| >0.02 | $\alpha < 0.30$ | $\alpha = kt^{1/2}$ |

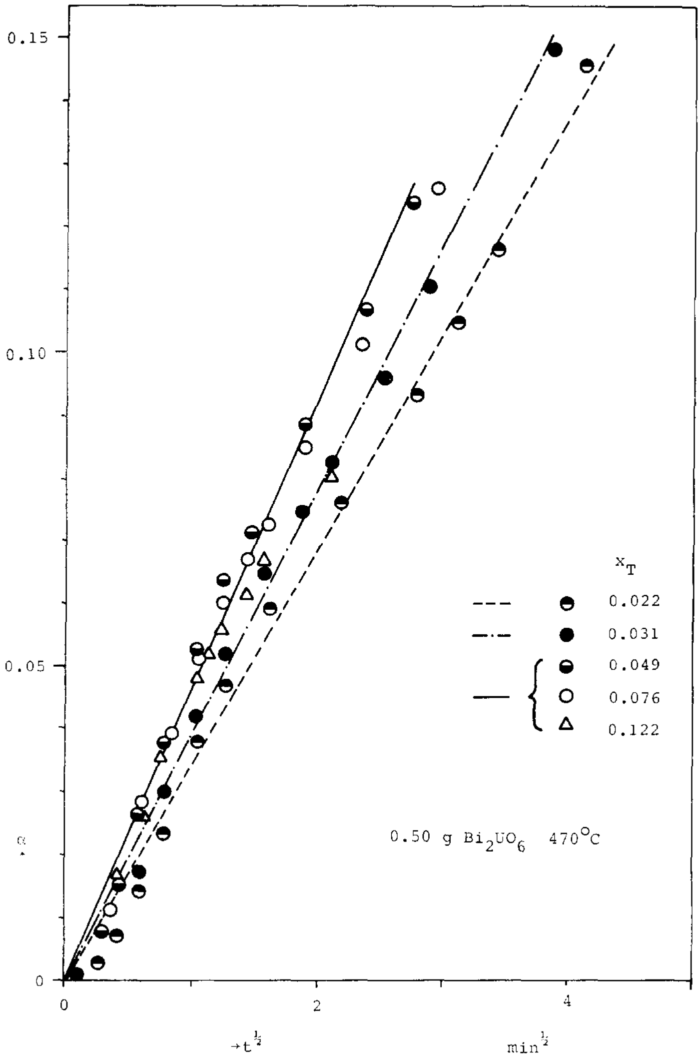

FIG. 7. Degree of reduction of bismuth uranate as a function of the square root of time; flow reactor.

bismuth uranate by toluene have been summarized in Table 1.

e. *Oxidation of Benzene*

The oxidation of benzene was studied to investigate the consecutive oxidation of benzene formed from toluene. Under pulse conditions the oxidation of benzene is negligible at $\alpha > 2\%$. However, in the flow system the bismuth uranate behaves differently, and some benzene is oxidized at a higher degree of reduction as well. Since the only reaction products are $CO_2$ and $H_2O$ the benzene reaction rate is always proportional to the rate of reduction of bismuth uranate. Therefore it is sufficient to investigate the latter reaction rate in the thermobalance.

Figure 12 gives the degree of reduction as a function of $t^{1/2}$ for a number of temperatures. Equation (3) is obeyed up to $\alpha = 0.05$. After that the reduction rate declines and at $\alpha > 0.10$ a region follows in which $\alpha = k\,t^{1/2} + C$.

Our toluene oxidation experiments were carried out under differential conditions. Therefore, the consecutive oxidation of benzene may be neglected. However, the results

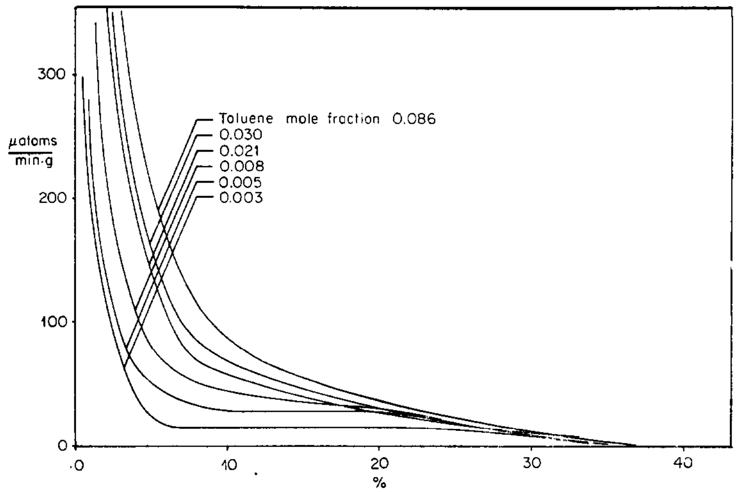

FIG. 8. Reduction rates as a function of the degree of reduction; thermobalance.

obtained for the oxidation of benzene indicate that the consecutive reactions must be taken into account when large conversions are used.

## DISCUSSION

If we review our experimental data in the light of the models derived, the reduction of bismuth uranate by toluene can be visualized in the following way:

a. **Under pulse conditions** the small quantity of oxygen removed during a pulse can be replenished in the time interval between the pulses. The oxygen diffusion does not play a role in the reaction kinetics, and the concentration of oxygen at the surface

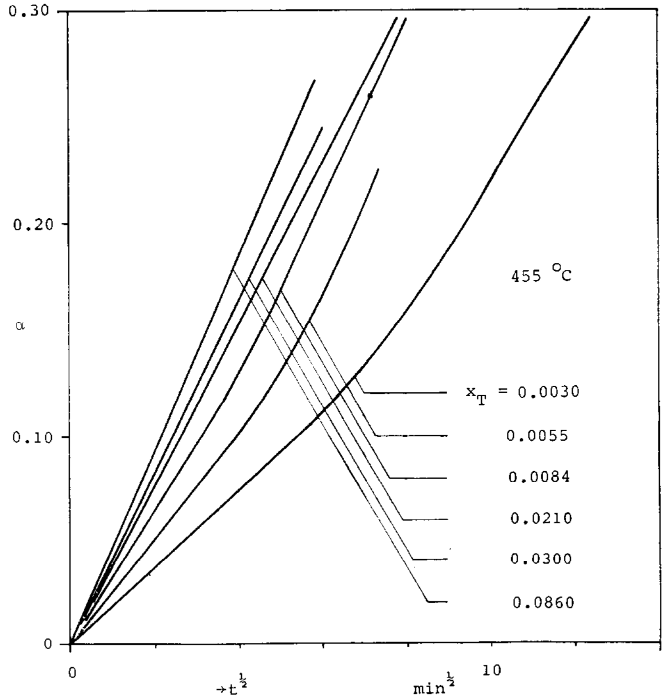

FIG. 9. Degree of reduction as a function of the square root of time; thermobalance.

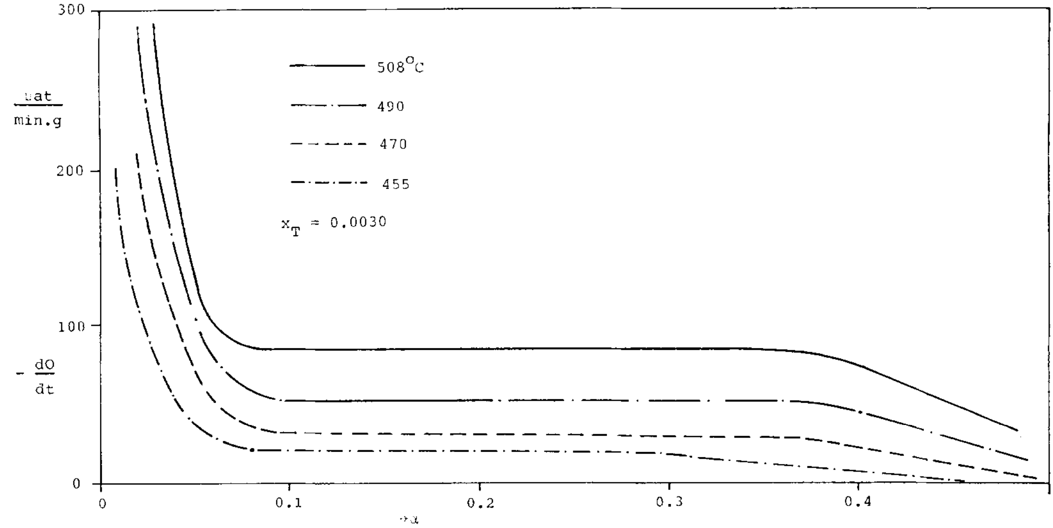

FIG. 10. Reduction rates as a function of the degree of reduction; thermobalance.

is equal to or only slightly lower than in the bulk. First, the nonselective A-oxygen is rapidly consumed. Then the B-oxygen, participating in the more selective reaction, is removed, and Eq. (1) is operative. A region of constant activity (region B) is observed, under conditions where in the flow system and the thermobalance a continuous decrease in activity is observed, with much lower reaction rates than in the pulse system. Thus the kinetics in this region B of the pulse experiments are those of the chemical reaction at the surface and are unaffected by the diffusion. When the surface oxygen concentration has decreased too much, Eq. (1) loses its applicability and the reaction rates decline (region C).

**b. Under continuous flow conditions at low toluene concentration,** the rate of diffusion is of the same order of magnitude as the chemical reaction rate. After removal of the A-oxygen, which follows Eq. (3), the activity is constant [Eq. (1)]. Eventually, the oxygen concentration becomes too low, and the observed rate of reaction declines. When the temperature is increased, the oxygen diffusion is accelerated more rapidly than the chemical reaction, which explains why the region of constant activity extends further at the higher temperature.

**c. Under flow conditions at high toluene concentration** the chemical reaction is enhanced, and now the diffusion rate enters the picture. Equation (1) holds no longer, and the chemical-reaction-plus-diffusion model becomes operative [Eq. (3)]. The concentration of oxygen at the surface is considerably lowered, and the reaction rate declines continuously. If we assume that the diffusion of the A-oxygen through the lattice is slower than that of the B-oxygen, although the former reacts more rapidly, we can also understand why at high toluene concentration, i.e., in the diffusion controlled regime, a definite A-region cannot be observed. Then the A-oxygen is consumed more slowly than the B-oxygen, and the regions A and B overlap. On the other hand, at low toluene concentration the rate of reduction of these A-oxygen atoms also follow the chemical-reaction-plus-diffusion model [Eq. (3)]. When the particle size of the crystallites is reduced by using a bismuth uranate having a higher specific surface area, the region of constant activity extends up to a higher value of $\alpha$, which is not surprising since now the oxygen atoms have to move a shorter distance to the surface, and the diffusion plays a minor role in the process.

With the above results, it should be possible to calculate the value of $D$ for the two types of oxygen. The most accurate value is obtained by using Eq. (19). To fit

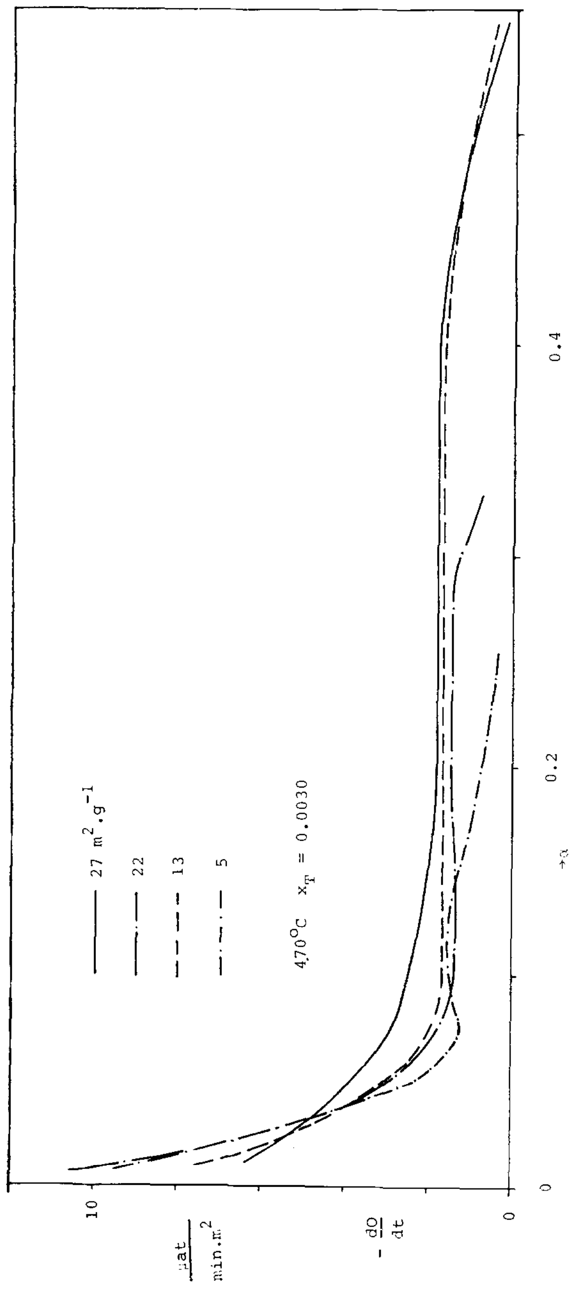

FIG. 11. Rate of reduction of bismuth uranates with different surface areas; thermobalance.

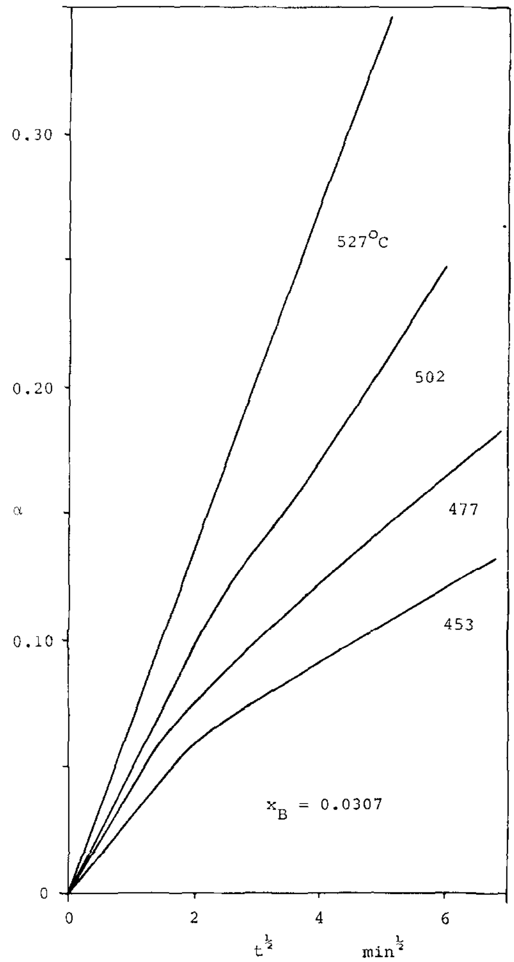

FIG. 12. Degree of reduction of bismuth uranate as a function of the square root of time; thermobalance.

this equation to the experimental data, four variables must be known, viz, the chemical reaction rate constant $k$, the particle radius $a$, the diffusion coefficient $D$ and the thickness of the surface layer $d$. It is evident that with four variables a great number of experimental curves can be simulated. Therefore it is essential to estimate the parameters beforehand, preferably from other sources. Since under flow conditions at toluene mole fractions higher than 0.02 the reduction of bismuth uranate follows relation (*3*) (Figs. 3, 7, and 9) we used the procedure described by Batist *et al.* (*5*) in order to find provisional values of $k$ and $D$ for the B-oxygen. In our case the constant $A$ proved to be too small to determine $k$ accurately.

The diffusion coefficient which follows from $B$ in Eq. (3) is $0.5 \times 10^{-20}$ $m^2$ $sec^{-1}$ at 473°C. The energy of activation for the diffusion coefficient as determined from Eq. (3) follows from Fig. 3 (circles) and has a value of 63 kcal $mole^{-1}$. The average crystallite radius is 150 Å. For the layer thickness $d$ we chose a value of 5 Å, this being the smallest cell parameter of $Bi_2UO_6$.

With these values for $a$, $d$ and $D$ we calculated the degree of conversion $f$ as a function of the time $t$ for various values of $k$ with Eq. (19). The final values of $k$, $a$, $d$ and $D$ were obtained by an iterative method. In Fig. 14 some experimental curves are given together with the calculated points. Agreement is excellent. It can be seen that at low $f$ the simulated curve hardly deviates from the relation $f = kt^{1/2}$. The energy of activation for $D$ as obtained from the best fit is 63 kcal $mole^{-1}$ (Fig. 13, dots).

The particle radius $a$ and the surface layer thickness $d$ that we used in our simulations are not known exactly. For that reason we also tried to fit the experimental curve with other values of $a$ and $d$. It appeared that when $d$ is increased at constant $a$ and $D$, the rate constant $k$ has to be reduced. The particle radius $a$ and the diffusion coefficient $D$ are related similarly. The model is much more sensitive to changes in $a$ or $D$ than in $k$ or $d$. However, with $a = 200$ Å we again obtained for $D$ an energy of activation of 63 kcal $mole^{-1}$. The fact that at higher toluene concentrations $c_0$, changes in this concentration have little effect on the overall reaction rate (as follows from Figs. 7 and 10) is in agreement with the observation that changes in $k$, which is proportional to $c_0$, hardly influences the simulated curve.

It must be noted that the reduction of $Bi_2UO_6$ follows Eqs. (3) and (19) in spite of the fact that the process is actually the sum of a nonselective and a selective reaction, while the ratio between these reactions varies with time. For the reduction rate it appears to be unimportant whether an oxygen atom reacts selectively or not,

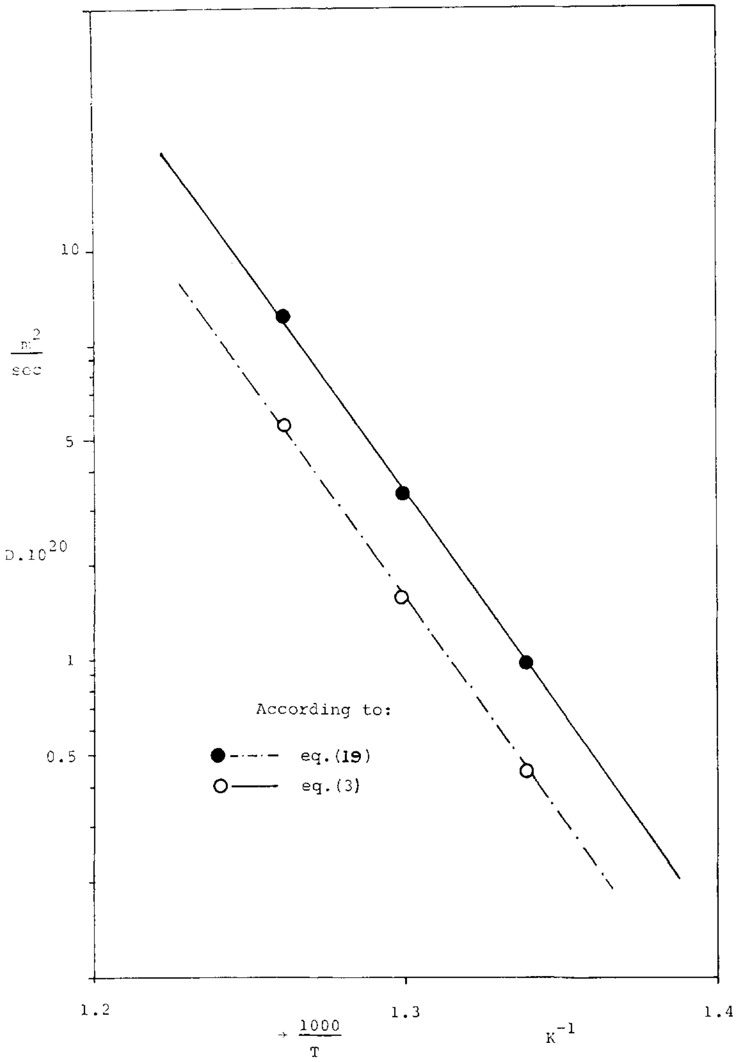

FIG. 13. Arrhenius plot for the diffusion coefficient of oxygen in bismuth uranate.

although in the latter case far less toluene will be converted per atom of oxygen. Let us now compare the results as obtained with Eqs. (2), (3) and (19). Except for very low values of $f$, Eq. (2) yields the same curve as Eq. (3). In Fig. 15 one of the experimental curves (solid line) is plotted against $t^{1/2}$, together with the data simulated according to Eq. (2) with $D = 3.4 \times 10^{-20}$ m$^2$ sec$^{-1}$ (dots), to Eq. (19) with $D = 3.4 \times 10^{-20}$ (circles) and to Eq. (2) with $D = 1.6 \times 10^{-20}$ (triangles). Apart from the fact that the use of Eq. (2) results in a lower value of $D$ than Eq. (19), as was already noted, the agreement between the two models is reasonably good as long as the degree of conversion remains low. Furthermore, the same energy of activation for $D$ is found.

With these relations we also determined the diffusion coefficient of the A-site oxygen: (a) from toluene oxidation experiments; toluene mole fraction 0.0030; (b) from benzene oxidation experiments at $\alpha < 5\%$; benzene mole fraction 0.0307. At 470°C, $D$ is $3 \times 10^{-22}$ m$^2$ sec$^{-1}$. The activation energy is 26 kcal mole$^{-1}$ in both cases. When the activation energy of $D$ was determined from benzene oxidation runs at high $\alpha$, 63 kcal mole$^{-1}$ was found, just as in

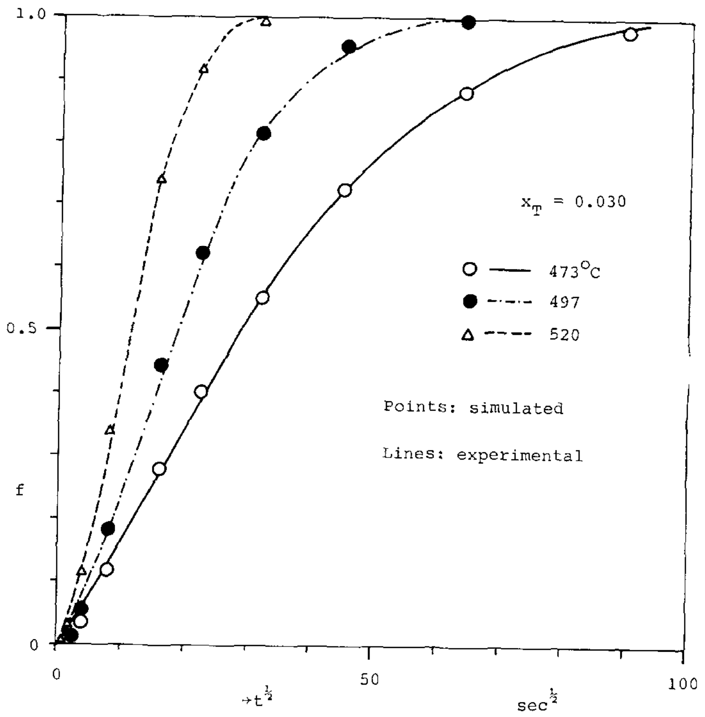

FIG. 14. Reduction of bismuth uranate; comparison between simulated and experimental data.

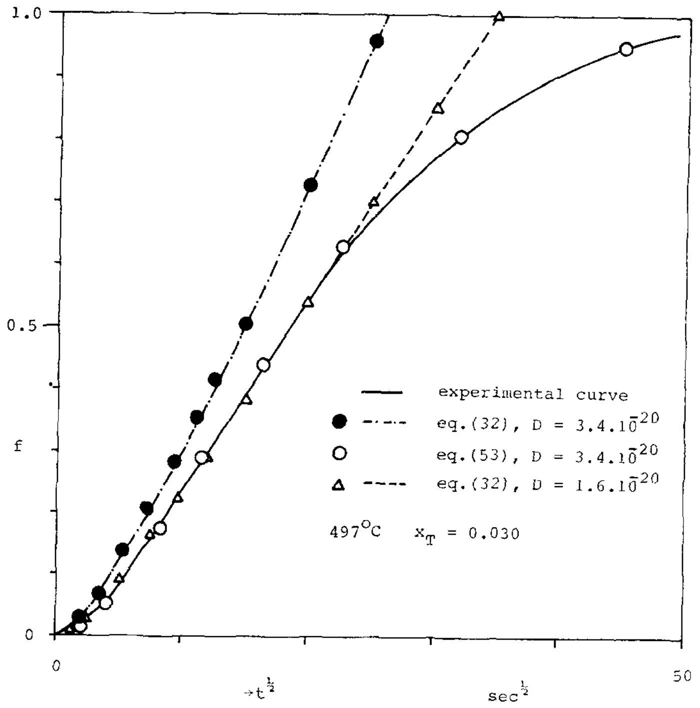

FIG. 15. Reduction of bismuth uranate; comparison between experimental and simulated data.

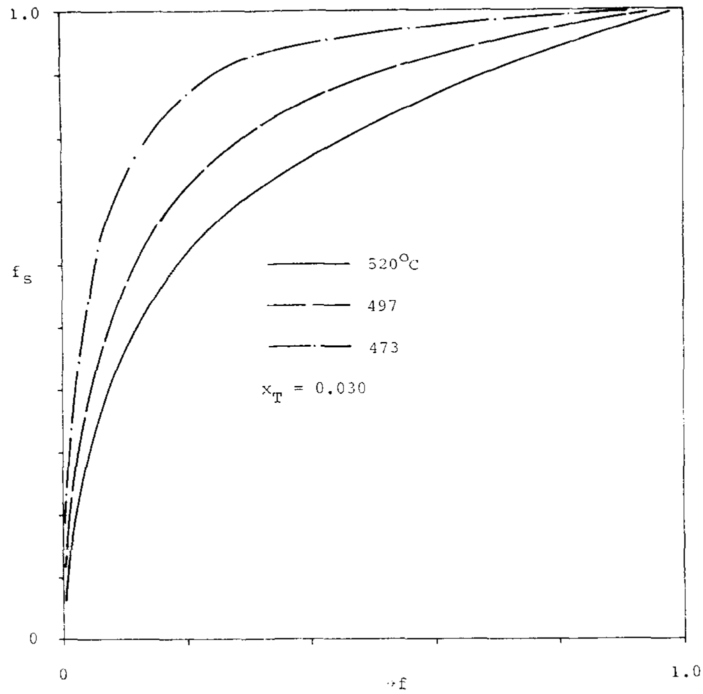

FIG. 16. Calculated degree of surface conversion as a function of the degree of bulk conversion.

the toluene oxidation experiments. This illustrates that indeed two kinds of lattice oxygen exist, the reactive A-type with low $D$, and the less reactive but more selective B-type with high $D$ and a high energy of activation for $D$.

The concept of two types of oxygen has also been brought forward by Grasselli and Suresh (*7*) for the antimony/uranium oxide catalyst, and by Boreskov, Ven'yaminov and Pankrat'ev (*8*) for the iron/antimony oxide catalyst. During reduction in a pulse system the latter catalyst behaves similarly to bismuth uranate. Boreskov, Ven'yaminov and Pankrat'ev attribute this to the presence of a surface layer of nonselective oxygen. Grasselli and Suresh found that their catalyst contains 0.65% of selective oxygen, further reduction leading to total combustion of the reductant. He states that one of the four types of oxygen of the unit cell is responsible for the selective oxidation; however, this cannot be brought into agreement with the unit cell he proposes.

Our experiments clearly indicate that the A-oxygen in bismuth uranate is a special kind of lattice oxygen. As with Grasselli and Suresh, the quantity is too small to correspond to a special position in the unit cell. A possibility is that bismuth and antimony uranates have so-called shear structures (*9*). This means that the lattice is built up from blocks consisting of a small number of unit cells, regularly divided by shear planes. The oxygen atoms in these planes have a coordination different from that in the blocks and therefore may exhibit different oxidation properties and diffusion coefficients. Since it seemed very interesting to compare the reduction kinetics of bismuth uranate and antimony uranate, we briefly studied the latter catalyst as well. It was found that when Sb/U is reduced under the same conditions as described above, first about 0.5% of the available oxygen is removed. This process proceeds very rapidly, and is followed by a much slower reduction obeying Eq. (1). Apparently the ratio of chemical reaction rate to oxygen diffusion rate is high for the A-oxygen, and low for the remaining B-oxygen. Thus we were unable to determine the diffusion coefficient for the two types of oxygen.

It was shown in Figs. 1 and 6 that the selectivity, i.e., the number of moles of benzene formed per mole of toluene converted, is a function of $\alpha$. In pulse experiments there is a rapid and unselective oxidation at $\alpha < 0.02$, attributed to A-oxygen, followed by a region in which the selectivity is about 70% up to $\alpha = 0.10$. Thereafter the selectivity again declines. Under pulse conditions $\alpha_{\text{bulk}} = \alpha_{\text{surface}}$, so that evidently the selectivity has a maximum between 2 and 10% of surface reduction. No pulse experiments were carried out at $\alpha > 12\%$. In the flow system the selectivity at the very beginning of the process is higher than that in the pulse system, but it rises more slowly, and attains its maximum only at $\alpha = 0.10$ (Fig. 6). If we now realize that in the flow reactor the degree of reduction of the bismuth uranate surface is greater than the overall degree of reduction, we see that the maximum selectivity under flow conditions corresponds to a much higher surface $\alpha$ than in the pulse system. The degree of surface conversion as a function of the degree of bulk conversion was calculated according to Eq. (20), and the results are shown in Fig. 16. It follows that $f_{\text{surface}}$ differs considerably from $f$. At high toluene concentrations $f_{\text{surface}}$ already has a value of at least 12%, while $f$ is a mere 1%. This proves that the selective region found under pulse conditions occurs at such very low levels of bulk reduction in the flow system that it will not be found in flow experiments. Instead, the degree of reduction at which the maximum selectivity was found in the flow system corresponds to 28% of surface reduction. Apparently the selectivity has another maximum at this value of $f_{\text{surface}}$. The high degree of surface reduction under flow conditions also explains why the reaction rates in this system are substantially lower than in the pulse system under identical conditions.

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