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Heterogeneous Catalytic Oxidation of Aromatic Hydrocarbons in the Gas Phase

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A systematic account is given of experimental results. Kinetic data are considered from general principles based on the model of Mars and Van Krevelen supplemented by the concept of successive surface oxidation of the initial organic molecule. Certain general laws of the occurrence of reactions of this class are formulated. A list of 137 references is included.

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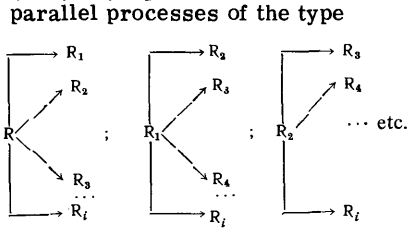
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I. INTRODUCTION

The heterogeneous catalytic oxidation of aromatic hydrocarbons in the gas phase includes a large number of reactions, many of practical interest. The most widely used at the present time are those yielding organic acid anhydrides (maleic, phthalic, naphthalic, trimellitic, and pyromellitic), as well as anthraquinone. The oxidation products often include other compounds of practical value—benzoquinone, naphthaquinone, aromatic aldehydes and acids, etc. In spite of the considerable variety of such reactions, their occurrence exhibits several common features, the elucidation of which should help to lay scientific foundations for the selection of catalysts.

The present Review will cover mainly work during recent years, since earlier research was the subject of a detailed discussion by Dixon and Longfield[1]. During the past fifteen years considerable improvements have been made in the experimental technique, which have permitted considerable broadening and deepening of our ideas on the kinetics and the mechanism of the oxidation of aromatic hydrocarbons. At the same time original concepts have been developed on the interrelationship between catalytic and physicochemical properties.

The oxidation of aromatic hydrocarbons usually proceeds by a consecutive-parallel mechanism. This means in general that, if a starting material R forms oxidation products R_1, R_2, ..., R_i (in order of increasing degree of oxidation), parallel processes of the type



occur, when each reaction takes place without the formation of gaseous intermediates, as well as the consecutive reactions

$$R \rightarrow R_1 \rightarrow R_2 \rightarrow R_3 \rightarrow \cdots \rightarrow R_i.$$

The complicated character of the processes creates certain difficulties in the analysis of their kinetics and mechanism, and compels recourse to various simplifications. In particular, pseudounimolecular equations are sometimes used for individual reactions in constructing a formal kinetic model, although the true kinetic relations are usually much more complex. Some authors select power formulae describing more or less satisfactorily the rates of accumulation of individual reaction products. This is in general a too crude approximation to the true kinetic equations, since the directly measurable rates of accumulation of products of mild oxidation depend on their rates of formation not only from the initial oxidisable substance but also from products of intermediate degrees of oxidation, as well as on the rate of conversion of the given reaction product into higher oxidation products. Hence such an approach is inconsistent with the consecutive-parallel character of mild oxidation established in many studies.

Definite advances in the rational interpretation of kinetic data on the basis of largely similar reaction schemes have been achieved in several recent publications. Before considering specific published information, therefore, a general discussion of such schemes and their consequences is advisable.

II. GENERALISED KINETIC MODEL OF THE CATALYTIC OXIDATION OF AROMATIC HYDROCARBONS

Mars and Van Krevelen[2,3] interpreted the kinetics of the oxidation of many substances in terms of a redox scheme involving two irreversible stages:

$$\text{Hydrocarbon R} + \text{Oxidised catalyst} \xrightarrow{r_R} \text{Oxidation products } R_1, R_2, \ldots + \text{Reduced catalyst} \quad (1)$$

$$\text{Reduced catalyst} + O_2 \xrightarrow{r_{O_2}} \text{Oxidised catalyst}\ . \quad (2)$$

Several workers have shown[4-8] that kinetic equations of the Langmuir-Hinshelwood type do not satisfy experimental results for the catalytic oxidation of aromatic hydrocarbons. For reactions (1) and (2) we can adopt the rate equations

$$r_R = k_R P_R \theta^a, \quad (3)$$

$$r_{O_2} = k_{O_2} P_{O_2} (1-\theta)^b, \quad (4)$$

where k_R and k_{O_2} are rate constants, θ is the coverage of the surface by oxygen, P_R and P_{O_2} are the partial pressures of the reactants, and a and b are the orders with respect to adsorbed oxygen and to oxygen vacancies on the catalyst surface respectively. In a steady state we should have

$$r_R = r_{O_2}/\nu, \tag{5}$$

where the stoichiometric coefficient ν, the number of oxygen molecules required to oxidise one R molecule to the products R_1, R_2, ..., R_i, is given by

$$\nu = \nu_1 S_1 + \nu_2 S_2 + \nu_3 S_3 + \ldots + \nu_i S_i, \tag{6}$$

in which S_i is the selectivity for R_i, and ν_i is the number of oxygen molecules involved in oxidising one R molecule to R_i. Substituting (3) and (4) in (5) yields

$$\frac{\theta^a}{(1-\theta)^b} = \frac{k_{O_2}}{k_R} \cdot \frac{1}{\nu} \cdot \frac{P_{O_2}}{P_R}, \tag{7}$$

from which it follows that the surface concentration of oxygen is a function of the ratio P_{O_2}/P_R.

For the simplest case $a = b = 1$, and from (3) and (7) we obtain for the surface coverage and the total rate of oxidation of R the formulae

$$\theta = \frac{1}{\nu} \cdot \frac{k_{O_2}}{k_R} \cdot \frac{P_{O_2}}{P_R} \Big/ \left(1 + \frac{1}{\nu} \frac{k_{O_2}}{k_R} \frac{P_{O_2}}{P_R}\right), \tag{8}$$

$$r_R = k_{O_2} k_R P_{O_2} P_R / (k_{O_2} P_{O_2} + \nu k_R P_R). \tag{9}$$

The coefficient ν is variable, but its relative variations are often small, and for convenience a mean value $\overline{\nu}$ is used. Equation (9) can be written in a different form. For example, if the process comprises the consecutive reactions

$$R \xrightarrow[(O)]{r_R} R_1 \xrightarrow[(O)]{r_1} R_2 \xrightarrow[(O)]{r_2} R_3 \xrightarrow[(O)]{r_3} \ldots \xrightarrow[(O)]{r_{i-1}} R_i,$$

and the kinetics of each is expressed by the equation $r_i = k_i P_i \theta$, it is readily found that the overall rate of conversion of the initial substance is given by

$$r_R = \frac{k_{O_2} k_R P_{O_2} P_R}{k_{O_2} P_{O_2} + \nu_1 k_R P_R + (\nu_3 - \nu_1) k_1 P_1 + (\nu_3 - \nu_2) k_2 P_2 + \ldots + (\nu_i - \nu_{i-1}) k_{i-1} P_{i-1}}. \tag{10}$$

Since

$$S_i = (k_{i-1} P_{i-1} - k_i P_i)/k_R P_R,$$

it can be shown from (6) that

$$\nu k_R P_R = \nu_1 k_R P_R + (\nu_2 - \nu_1) k_1 P_1 + (\nu_3 - \nu_2) k_2 P_2 + \ldots + (\nu_i - \nu_{i-1}) k_{i-1} P_{i-1},$$

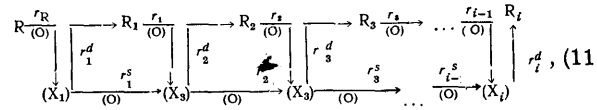
i.e. the kinetic equations (9) and (10) are equivalent.

In order to analyse the overall kinetics it is necessary to examine the detailed mechanism of the reduction stage (1). Two general schemes can be envisaged for such a mechanism. According to the first, all the observed reactions take place independently, via surface complexes specific to each reaction, e.g. on different types of active centres[9,10]. The second scheme, in contrast, is based on a close interrelationship between individual reactions. Oxidation on the surface takes place consecutively[11-16]:

$$R \xrightarrow{(O)} (X_1) \xrightarrow{(O)} (X_2) \xrightarrow{(O)} (X_3) \xrightarrow{(O)} \ldots \xrightarrow{(O)} (X_i)$$

(here and below parentheses denote the adsorbed state). The surface intermediates X_i yield on desorption the reaction products R_i, which may then partly undergo further oxidation. It is assumed that formation of a given product R_i involves the same final intermediate complex, independently of whether the complex has been formed from the initial compound R or by further oxidation of a product in an intermediate state of oxidation.

One variant of such a mechanism[15,16] can be represented as†



(11)

where the r with the various affixes are the rates of the individual stages. It is evident that this scheme corresponds to a consecutive-parallel (in the generally accepted sense) reaction mechanism: the consecutive reactions are denoted by the stages

$$R \xrightarrow{(O)} (X_1) \rightarrow R_1 \xrightarrow{(O)} (X_2) \rightarrow R_2 \ldots,$$

and the parallel reactions by

$$R \xrightarrow{(O)} (X_1) \rightarrow R_1, \; R \xrightarrow{(O)} (X_1) \xrightarrow{(O)} (X_2) \rightarrow R_2$$

etc. Adopting for the individual stages in scheme (11) the expressions

$$r_R = k_R P_R \theta, \; r_i = k_i P_i \theta, \; r_i^d = k_i^d \theta_i, \; r_i^s = k_i^s \theta_i \theta$$

(in which the θ_i are the concentrations of the intermediate compounds X_i), we obtain for the selectivity with respect to the individual reaction products the equations[16]

$$S_1 = \frac{1}{(1 + n_1\theta)(1 + k_1\theta\tau)}, \tag{12}$$

$$S_2 = \frac{1 - S_1}{(1 + n_2\theta)(1 + k_2\theta\tau)}, \tag{13}$$

$$S_3 = \frac{1 - S_1 - S_2}{(1 + n_3\theta)(1 + k_3\theta\tau)}, \tag{14}$$

$$S_4 = \frac{1 - S_1 - S_2 - S_3}{(1 + n_4\theta)(1 + k_4\theta\tau)} \tag{15}$$

etc., where the $n_i = k_i^s/k_i^d$ are the ratios of the oxidation rate constants for the surface compounds X_i to their desorption rate constants, and τ is proportional to the contact time. In the particular case in which further oxidation of the products can be neglected and the process has a parallel mechanism (e.g. at low degrees of conversion of R), Eqns. (1)–(15) simplify to[14,15]

$$S_1 = \frac{1}{1 + n_1\theta}, \tag{16}$$

$$S_2 = \frac{1 - S_1}{1 + n_2\theta}, \tag{17}$$

$$S_3 = \frac{1 - S_1 - S_2}{1 + n_3\theta}, \tag{18}$$

$$S_4 = \frac{1 - S_1 - S_2 - S_3}{1 + n_4\theta}. \tag{19}$$

The set of equations (8), (9), and (12)–(19) describes the kinetics of all partial reactions within the framework of the given kinetic model. We can formulate certain consequences of the above ideas for the mechanism, which will then be compared with experimental results.

(1) A close analogy should exist between the catalytic reaction under steady-state conditions and the surface

† Such a scheme is a kinetic model of a process in which the structure of intermediate complexes, their charges, etc. can be disregarded. Certain chemical aspects of the oxidation of aromatic hydrocarbons have been discussed in a review (in terms of the model of Mars and Van Krevelen)[17].

reduction of the catalyst by the initial hydrocarbon. As reduction proceeds, the surface concentration of oxygen decreases, while the selectivity for products of milder oxidation increases in conformity with Eqns. (12)–(19) with simultaneous decrease in the rate of reduction. At the same surface coverage during catalysis and reduction their rates and selectivities will also be closely similar.

(2) Selectivity during catalysis is determined by the ratio P_{O_2}/P_R of oxidant to reductant in the reaction mixture under otherwise similar conditions, since this ratio determines the surface coverage (formulae 7 and 8).

(3) Addition to the initial mixture of a product may inhibit the process, the more strongly the greater the reactivity of the compound (e.g. Eqn. 10). The Reviewer has already discussed this question in greater detail[18].

(4) In a series of catalysts of the same type a correlation should be observed between the activity and the oxygen–catalyst bonding energy q_S, analogous to that observed for complete oxidation, the mechanism of which also involves stages of alternating reduction and oxidation of the catalyst[19-21].

(5) If the variation in the rate constants of all stages in a series of catalysts is due mainly to the variation in q_S, a correlation will be observed between the selectivities S_i and q_S. Absence of such correlation may indicate that the progress of the reaction is influenced significantly by other physicochemical properties of catalysts and reactants (other than the energy of bonding of oxygen to the catalyst).

III. EXPERIMENTAL RESULTS ON THE OXIDATION OF INDIVIDUAL AROMATIC HYDROCARBONS AND THEIR OXYGEN-CONTAINING DERIVATIVES

1. Oxidation of Benzene

The catalytic oxidation of benzene to maleic anhydride (MA) is an industrial process. Low yields of phenol and *p*-benzoquinone (BQ) are also produced. The kinetics of the oxidation of benzene on the catalysts V_2O_5–K_2SO_4–SiO_2 [2,3,22] and V_2O_5–MoO_3 [23] are described by Eqn. (9).

The mechanism of the interaction of benzene with an oxide catalyst was represented[12] by the scheme

$$\begin{array}{ccccccc} \text{Benzene} & & \text{Phenol} & & \text{BQ} & \text{MA} & \text{CO}_2, \text{CO} \\ \downarrow\uparrow & & \uparrow\downarrow & & \downarrow\uparrow & \downarrow\uparrow & \downarrow\uparrow \\ (C_6H_6) & \rightarrow & (C_6H_5OH) & \rightarrow & (C_6H_4O_2) & \rightarrow (C_4H_2O_3) & \rightarrow (CO_2, CO) \end{array} . \qquad (20)$$

Such a scheme is consistent with experimental results showing that on separate oxidation phenol is converted into *p*-benzoquinone, maleic anhydride, and carbon dioxide[24], *p*-benzoquinone into maleic anhydride and carbon dioxide[25], and maleic anhydride into carbon dioxide[9,26]. Consecutive surface oxidation of the initial hydrocarbon forms the basis both of (20) and of scheme (11) discussed in Section II. However, the Reviewer prefers (11), since the reversible adsorption stages in (20) are inconsistent with the observed kinetics: equations like that of Mars and Van Krevelen[2,3,22,23] were deduced on the hypothesis of irreversible interaction between reactants and catalyst. The same equations, as will be shown below, agree with experimental results for other aromatic hydrocarbons and their oxygen-containing derivatives.

Several studies have been made on the effect of the chemical composition of a catalyst on its catalytic properties in the oxidation of benzene. Schaefer[27] used a microcatalytic pulse method to obtain information on the activities and selectivities of several vanadium oxides. On the assumption that unchanged activity of a specimen during an experiment indicates constancy of its chemical composition, he obtained the sequence of specific activities

$$VO_{1,99} > VO_{2,03} > VO_{2,17} > VO_{2,33} > VO_{2,50} .$$

Experiments on the interaction of benzene with vanadium oxides in the absence of molecular oxygen showed[27] that the rate of catalysis exceeded the rate of reduction by factors of 1.5–7, but the sequence of the catalysts with respect to their rate of reduction by benzene was identical with the above sequence of catalytic activity.

The initial specific activities of various oxides (for degrees of conversion of benzene approaching zero) decrease in the sequence[13]

$$Co_3O_4 > Mn_2O_3 > Cr_2O_3 > NiO > CuO > Fe_2O_3 > SnO_2, U_3O_8 > TiO_2 > V_2O_5 > ThO_2 > ZnO > Bi_2O_3 > Nb_2O_5 > WO_3 > ZrO_2 > MoO_3 > Ta_2O_5 > Sb_2O_4.$$

On plotting $\lg r_{sp}$[13] against q_S (for oxides for which values of the latter were known[20]), the Reviewer obtained a characteristic curve passing through a maximum (Fig. 1*a*), which indicates that the energy of bonding of oxygen to the catalyst has a significant influence on the relative variation in the activity of individual oxides[19-21].

Among the catalysts investigated[13] only three exhibit sufficiently high selectivity with respect to products of mild oxidation (among which maleic anhydride predominates), forming the sequence $V_2O_5 > MoO_3 > WO_3$. The mixed V_2O_5–MoO_3 systems used in industry are more active and more highly selective than is vanadium pentoxide. Maximum activity corresponds to specimens containing 25–30 mole % MoO_3.[12,28] The initial selectivity for maleic anhydride[12] also passes through a maximum, reaching 62% and 25 mole % MoO_3 (the corresponding selectivities on the individual vanadium and molybdenum oxides are respectively 35% and 10%).

In a series of V_2O_5–MoO_3 catalysts an antiparallel relation is observed[30] between the specific activity and the strength of bonding of oxygen to the catalyst estimated from the initial rate of reduction by hydrogen[29] and the equilibrium partial pressure of oxygen[30] by infrared spectroscopy[31]. The opposite result is obtained when the strength of bonding is estimated from the activation energy of isotopic exchange of oxygen: addition of molybdenum(VI) oxide to vanadium(V) oxide increases the strength of bonding of oxygen to the catalyst until the composition reaches ~ 25 mole % MoO_3.[32,33] The cause of this discrepancy is obscure and requires further investigation.

The mixed vanadium–molybdenum oxide catalyst surpasses in specific catalytic activity and selectivity other binary oxide systems containing molybdenum trioxide and oxides of tin, titanium, uranium, antimony, iron, and bismuth[34]. The selectivity of V_2O_5–MoO_3 catalysts is improved by additions of thallium(III), cadmium(II), silver(I),[35] and phosphorus(V)[36] oxides. This is evident from the patent literature, where V_2O_5–MoO_3–P_2O_5 catalysts are proposed alone[37-39] and with additions of bismuth(III),[40] silver(I),[41] nickel(II), and cobalt(II + III)[42] oxides.

Phosphorus pentoxide has been regarded[43] as a structure promoter, and has been reported[44] as increasing the life of a catalyst. It may also modify chemically the catalyst surface, increasing the acidity and thereby facilitating desorption of an acidic substance—maleic anhydride—in conformity with the views of Golodets[45] on the role of acid–base properties in catalytic oxidations.

2. Oxidation of Toluene

The kinetics of the oxidation of toluene on a V_2O_5–K_2SO_4–SiO_2 catalyst can be described[2,3,46] by Eqn. (9). At low degrees of conversion the oxidation products contain[46] 86% of benzaldehyde, 4% of benzoic acid, 7% of *p*-benzoquinone, and 3% of maleic anhydride, the yield of carbon dioxide being insignificant.

Trimm and Irshad[47] established a first order with respect to toluene and zero order with respect to molecular oxygen in the oxidation of toluene on a catalyst comprising molybdenum trioxide and pumice, which may be regarded as a particular case of Eqn. (9). The slow stage involves[47] interaction of toluene with surface O^{2-} ions. The main reaction product at low degrees of conversion of toluene is benzaldehyde, with conversion into carbon dioxide not exceeding 3%.

The rate of oxidation of toluene on copper(II) oxide with additions of molybdenum and tungsten oxides (on a Silit carrier) at 350–450°C is proportional to the concentration of molecular oxygen and independent of the concentration of toluene[48]. The reaction products are benzaldehyde (selectivity up to 85% with 0.6–6% conversion of toluene) and carbon dioxide.

The sequence of oxides with respect to initial specific catalytic activity in the oxidation of toluene is[49]

$$Co_3O_4>CuO>Mn_2O_3>Fe_2O_3>Cr_2O_3>U_3O_8>NiO>V_2O_5>TiO_2>ThO_2>WO_3>ZnO>SnO_2>\\ >MoO_3>Bi_2O_3>Ta_2O_5>Nb_2O_5>ZrO_2>Sb_2O_4.$$

The initial selectivity of these oxides for benzaldehyde decreases in the sequence[49]

$$V_2O_5>MoO_3>WO_3>U_3O_8>NiO>Sb_2O_4>Cr_2O_3>TiO_2>Fe_2O_3>Nb_2O_5>\\ >Mn_2O_3>CuO>Ta_2O_5>Co_3O_4>SnO_2,\ ZnO,\ ThO_2,\ ZrO_2,\ Bi_2O_3.$$

On vanadium, molybdenum, and tungsten oxides benzaldehyde is accompanied by benzoic acid. The first two of these oxides are more selective[50] than those of copper, manganese, cobalt, lead, and iron in the oxidation of toluene to benzaldehyde. The specific catalytic activity of the oxides correlates approximately with the energy of bonding of oxygen to the catalyst (Fig. 1*b*).

It was of interest to analyse the relation between the selectivity for benzaldehyde and the energy of bonding of oxygen to the catalyst surface. If the reaction mechanism is represented by scheme (II), where R denotes toluene, R_1 benzaldehyde, R_2 benzoic acid, etc., formula (16) can be used for the selectivity for benzaldehyde (initial selectivities correspond to conditions under which complete oxidation of the products can be neglected). Applying the Brønsted–Temkin relation to individual stages in (11) on the assumption that the variation in their activation energies is determined mainly by the bonding energy q_S, we obtain

$$\begin{aligned} E_R &= E_R^0 + m_R q_s, \\ E_{O_s} &= E_{O_s}^0 - m_{O_s} q_s, \\ E_i &= E_i^0 + m_i q_s, \\ E_i^s &= (E_i^s)^0 + m_i^s q_s, \\ E_i^d &= (E_i^d)^0 + m_i^d q_s, \end{aligned} \qquad (21)$$

where $m = \alpha\gamma$ (in which α is the transport coefficient and γ a coefficient proportional to the number of oxygen–catalyst bonds ruptured or formed in the given stage). The validity of formulae (21) for E_R and E_{O_2} is confirmed by the correlation found between specific activity and bonding energy.

Differentiation of S_1 (Eqn. 16) with respect to q_S yields the expression

$$\frac{dS_1}{dq_s} = \frac{1}{RT}\left[(m_1^s - m_1^d) + (m_R + m_{O_s})(1-\theta)\right]\frac{n_1\theta}{(1+n_1\theta)^2}. \qquad (22)$$

Il'chenko and Golodets[51,52] have shown that the formation of highly oxidised products involves cleavage of a larger number of oxygen–catalyst bonds than does the formation of products of mild oxidation, so that $m_1^s > m_1^d$. It then follows from Eqn. (22) that the dependence of S_1 on q_S should pass through a minimum. Fig. 2*a* indicates that such a relation holds approximately for oxides of transition metals. Most oxides of non-transition metals are non-selective and depart from the correlation. It will be shown below that this is observed also for the similar oxidation of *o*-xylene to *o*-tolualdehyde.

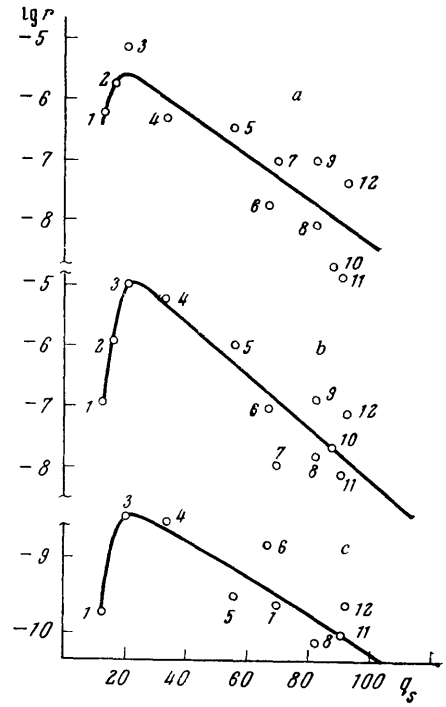


Figure 1. Dependence of $\lg r$ (where r is the reaction velocity, mole m^{-2} s^{-1}) on the oxygen–catalyst bond energy q_S (kcal g-atom^{-1} O)[20] in the oxidation of: *a*) benzene (400°C);[13] *b*) toluene (400°C);[49] *c*) *o*-xylene (300°C)[89] on the oxides: 1) NiO; 2) MnO_2 (or Mn_2O_3); 3) Co_3O_4; 4) CuO; 5) Fe_2O_3; 6) V_2O_5; 7) SnO_2; 8) ZnO; 9) U_3O_8; 10) WO_3; 11) MoO_3; 12) TiO_2.

As in the oxidation of benzene, a mixed V_2O_5–MoO_3 catalyst is more active and selective towards the oxidation of toluene than are the vanadium and molybdenum oxides separately[53]. The specific activity of binary oxide systems falls in the sequence[54]

$$V—Mo—O>Fe—Mo—O>Ti—Mo—O>Sb—Mo—O>U—Mo—O>Bi—Mo—O.$$

Among these the iron–molybdenum oxide catalyst is the most selective for benzaldehyde[54].

The poor selectivity of bismuth molybdate is explained by its great ability to accelerate not only the oxidation of methyl groups but also secondary dealkylation and degradative oxidation of toluene[55]. A selective catalyst for the oxidation of toluene to benzaldehyde is copper oxide to which

tungsten and molybdenum oxides have been added, in contrast to copper oxide alone[48]. Addition of phosphorus pentoxide to molybdenum trioxide increases the activity and the selectivity for benzaldehyde, as well as the stability of the catalyst[56]. The activity of this mixed catalyst is increased by promotion with oxides of vanadium, chromium, titanium, tin, aluminium, bismuth, nickel, cobalt, and iron, while the oxidation of benzaldehyde to benzoic acid is accelerated[56]. Highly selective oxidation of toluene to benzaldehyde is achieved on a molybdenum–tungsten–aluminium oxide catalyst[57], and on molybdenum(VI) oxide with additions of vanadium(V), zirconium(IV), and copper(II) oxides on ferrochrome[58].

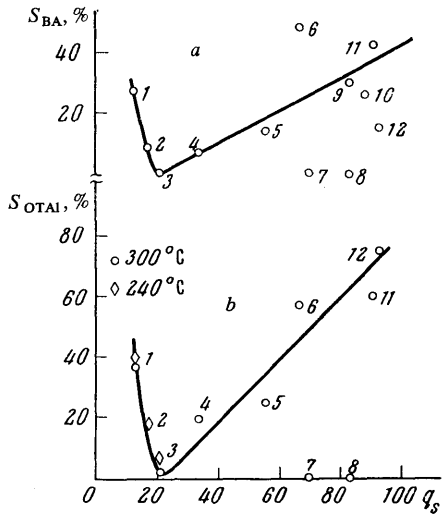


Figure 2. Dependence on q_S of the selectivity for: *a*) benzaldehyde in the oxidation of toluene (400°C)[49]; *o*) *o*-tolualdehyde in the oxidation of *o*-xylene[89]. Numbering as in Fig. 1.

The vanadium(V)–tin(IV) oxide system is evidently highly selective, in comparison with the other catalysts studied, for the oxidation of toluene to benzoic acid[59,60]. The same system exhibits high selectivity in the oxidation of benzaldehyde to benzoic acid[61]. Results of fundamental importance for an understanding of the nature of the selective action of catalysts were also obtained[61]. The relative catalytic activity a and the selectivity for benzoic acid S of manganese dioxide, vanadium pentoxide, and the mixed catalysts were compared[61] with their thermodynamic functions—the enthalpy and the free energy ΔH and ΔF (in kcal mole^{-1}) of removal of oxygen from the oxide—Table 1, in which x is the degree of reduction of the catalyst. The antiparallel relation between catalytic activity and free energy of removal of oxygen is attributed[61] to a redox mechanism. Such a mechanism is confirmed by the close parallel between catalytic oxidation and the reduction of catalysts by benzaldehyde: at a given temperature the two processes exhibit almost the same selectivity for benzoic acid.

The suggested[61] interpretation of selective oxidation was based on certain qualitative considerations. After the adsorbed organic radical has reacted with a surface oxygen atom of the catalyst, its subsequent fate depends on the probability of (i) desorption or (ii) further chemical interaction with a neighbouring oxygen atom. Decrease in the latter probability leads to increased selectivity. This explains the increase in selectivity with the steepness of the gradient $\partial\Delta H(x)/\partial x$, since subsequent removal of a second or a third oxygen atom from the same cell requires more energy than does removal of the first atom.

Table 1.

Catalyst	$\Delta F_{x=0,02}$	$\partial\Delta H(x)/\partial x$	a	S, %
MnO_2	10	8	$\geqslant 10$	0
V_2O_5–O_5–SnO_2	24	200	5	90–100
V_2O_5	38	80	1	70–80

The results obtained[61] by the kinetic method combined with infrared and electron spin resonance spectroscopy indicate for the formation of benzoic acid the detailed mechanism

$$C_6H_5CHO + (M{-}O) + (O) \rightarrow (C_6H_5COO{-}M) + (OH),$$

$$\left(C_6H_5C(=O)-O-M\right) \rightarrow \left(C_6H_5C\begin{matrix}O\\ O\end{matrix}M\right),$$

$$\left(C_6H_5C\begin{matrix}O\\ O\end{matrix}M\right) + (OH) \rightarrow C_6H_5COOH + (M).$$

The reduced surface centres formed (M) are oxidised by interaction with molecular oxygen to the original oxidised state (M–O). The suggested mechanism and the hypothesis to explain selectivity evidently agree in large measure with the general mechanism expressed by scheme (11). However, energetic non-uniformity is not the only factor determining selectivity. Indeed, a diminished probability of further oxidation of the adsorbed organic complex (which is equivalent to decrease in k_i^S and hence n_i in the selectivity equations 12–19) may result from increase in the oxygen–catalyst bond energy in a series of catalysts, even if their surface oxygen is energetically equivalent.

3. Oxidation of *p*- and *m*-Xylenes

The orientation of methyl groups in *p*- and *m*-xylenes, in contrast to that in the *ortho*-isomer, does not permit formation of the very stable phthalic anhydride, so that their oxidation is considerably less selective than that of *o*-xylene. At low degrees of conversion the main products of the catalytic oxidation of the *para*- and *meta*-isomers on vanadium catalysts are *p*- and *m*-tolualdehydes and carbon dioxide (small quantities of acids are also formed)[62,63]. The formation of aldehydes and carbon dioxide proceeds by a parallel scheme[64,65].

The kinetics of the oxidation of *p*-xylene on tin vanadate[62] and on vanadium pentoxide on silica gel[64,65] is described by Eqn. (9). Increasing the reactant concentrations in the oxidation of *m*-xylene on a V_2O_5–K_2SO_4–SiO_2 catalyst[63] results in a gradual slowing down in the growth of the reaction velocity, which tends to approach a constant value; this is a characteristic feature of Mars–Van Krevelen kinetics. The main oxidation products at high

degrees of conversion of *p*- and *m*-xylenes on vanadium catalysts[66] are maleic anhydride and carbon dioxide, with slight formation of aldehydes and acids.

At low degrees of conversion the oxidation of these isomers on a catalyst comprising molybdenum trioxide and pumice yields monoaldehydes and carbon dioxide[47]. The formal kinetic orders are 0.71 and 0.75 with respect to *m*- and *p*-xylenes, the corresponding values with respect to molecular oxygen being 0.40 and 0.49. The power relation is interpreted[47] as an approximation to a Langmuir–Hinshelwood type of equation.

4. Oxidation of *o*-Xylene

The oxidation of *o*-xylene to phthalic anhydride (PhA) is a promising industrial process, competing successfully with manufacture from naphthalene. This was responsible for the great interest taken by research workers in the reaction. Furthermore, many other oxidation products are obtained—*o*-tolualdehyde (oTAl), *o*-toluic acid (oTAc), phthalide (Ph), etc.—which makes the process an interesting model reaction.

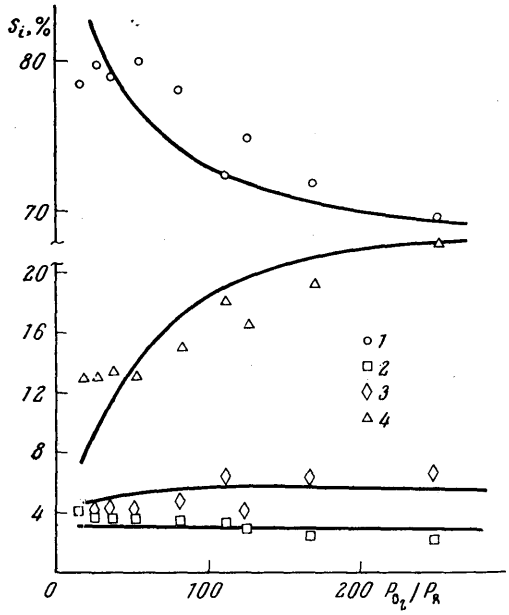


Figure 3. Dependence on the ratio P_{O_2}/P_R at 330°C of the selectivity for: 1) *o*-tolualdehyde; 2) *o*-toluic acid; 3) phthalide; 4) phthalic anhydride. The full curves have been calculated by means of Eqns. (8) and (16)–(19) with $n = 36$, $n_1 = 0.5$, $n_2 = 11$, and $n_3 = 4.5$.[15]

The mean composition of the oxidation products for low degrees of conversion (< 5 mole %) on a V_2O_5–K_2SO_4–SiO_2 catalyst at 290–310°C was 80% of *o*-tolualdehyde, 12% of *p*-benzoquinone, and 8% of carbon dioxide. The kinetics of the process was described satisfactorily by Eqn. (9), which held also for the oxidation of *o*-xylene at low degrees of conversion on fused vanadium pentoxide at 310–330°C.[6,15,67] The Mars–Van Krevelen model was used to interpret the kinetics of oxidation at high degrees of conversion on vanadium catalysts[5,68,69]. The use of other common kinetic models (the Rideal and Langmuir–Hinshelwood models) to analyse the experimental data gave negative results[4–6].

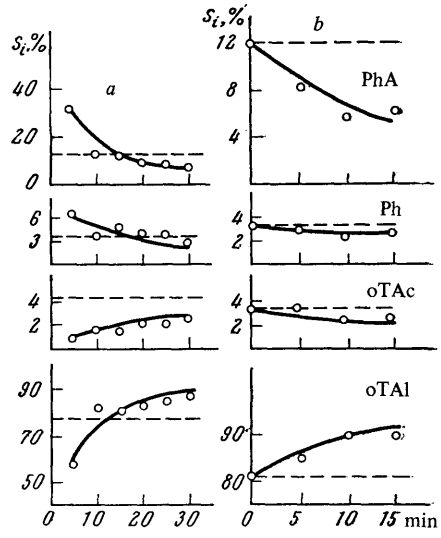


Figure 4. Dependence of selectivity on time of reduction of fused vanadium pentoxide by *o*-xylene at 330°C: *a*) catalyst specimen previously oxidised with oxygen; *o*) catalyst specimen after the catalytic oxidation of *o*-xylene under steady-state conditions[72].

Over a restricted range of conditions the kinetics of the oxidation of *o*-xylene can be described by empirical power equations[5,70,71], but such relations do not agree with experiment as well[5] as the theoretical relations based on the mechanism of Mars and Van Krevelen.

The Reviewer has used[14,15] scheme (11) to interpret the kinetics of partial reactions in the formation of individual products. In the present case this can be written

$$\begin{array}{l} \qquad\qquad\quad \text{oTAl} \quad \text{oTAc} \quad \text{Ph} \quad \text{PhA} \\ o\text{-Xylene} \xrightarrow[(O)]{} (X_1) \xrightarrow[(O)]{} (X_2) \xrightarrow[(O)]{} (X_3) \xrightarrow[(O)]{} (X_4) \end{array} , \qquad (23)$$

where separate experiments have demonstrated[6] that complete oxidation of the products can be neglected under the given range of conditions. Fig. 3 shows that experimental results for the selectivity with respect to all the products satisfy the theoretical relations expressed by formulae (8) and (16)–(19).

The above mechanism is supported by experimental results on the surface reduction of vanadium pentoxide by *o*-xylene[72], which takes place at about the same rate as does catalysis. The variation in selectivity on reduction agrees qualitatively with Eqns. (16)–(19) relating selectivities to surface coverage by oxygen (reduction is accompanied by decrease in θ). These results are plotted in Fig. 4 (the difference in the initial selectivities for an oxidised specimen and a specimen on which catalysis has taken place is due to a difference in the initial

surface coverage, which is higher for the oxidised specimen, on which the original selectivity for more highly oxidised products is greater, in conformity with Eqns. 16–19).

The kinetics of the oxidation of *o*-xylene has been investigated[9] on a high-temperature vanadium catalyst under gradient-free conditions. The principal reactions involved were conversion of *o*-xylene into *o*-tolualdehyde, phthalic anhydride, maleic anhydride, carbon monoxide, and carbon dioxide, and of *o*-tolualdehyde into phthalic anhydride. The rates of all these reactions are represented by formulae of the same type:

$$r_{ij}=\frac{k_{ij}c_{ij}}{1+b_ic_X+a_i(c_{oTAl}+c_{PhA}+c_{MA})},$$

where j denotes the oxidisable compound and i the type of active centre in the catalyst, k_i, a_i, and b_i are constants, the c are concentrations, and X denotes *o*-xylene. These equations were deduced from the postulates that each reaction takes place on a separate type of active centre differing in energy of bonding of oxygen with the catalyst; the mechanism, regarded as the same for all the reactions, involved reversible adsorption of the oxidisable compound on the oxidised surface, interaction of the adsorbed molecule with surface oxygen, and desorption of the product. Reaction is inhibited by all organic components of the gas phase owing to their reversible adsorption. Oxygen vacancies are rapidly filled by oxygen from the gas phase, so that zero order with respect to molecular oxygen is observed.

Although the rate equations in Ref. 9 describe the experimental results, the physical premises underlying them are open to doubt. Thus it is not clear how the oxygen–catalyst bond energy determines unambiguously the direction in which the oxidisable substance changes.

Experimental rates of oxidation of *o*-xylene under gradient-free conditions on a vanadium catalyst have been interpreted[5] by means of a scheme according to which the hydrocarbon is converted into *o*-tolualdehyde, phthalic anhydride, and carbon dioxide, *o*-tolualdehyde into phthalic anhydride and carbon dioxide, and phthalic anhydride into carbon dioxide. The kinetic equations

$$r_i=\frac{k_iP_jk_{O_2}P_{O_2}}{k_{O_2}P_{O_2}+(k_1+k_2+k_3)P_X+(k_4+k_5)P_{oTAl}+k_6P_{PhA}}$$

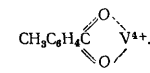
were suggested for each of these reactions, where i denotes the number of the reaction and j the oxidisable compound, k_1, k_2, and k_3 are oxidation rate constants for conversion of *o*-xylene into *o*-tolualdehyde, phthalic anhydride, and carbon dioxide respectively, k_4 and k_5 are rate constants for oxidation of *o*-tolualdehyde into phthalic anhydride and carbon dioxide, and k_6 is the rate constant of oxidation of phthalic anhydride to carbon dioxide. These equations were deduced on the hypothesis that each individual reaction occurs by irreversible interaction of the organic reactant with adsorbed oxygen at rates $k_iP_j\theta$, and that oxygen is adsorbed irreversibly at the rate $k_{O_2}P_{O_2}(1-\theta)$.

The agreement between the kinetic results and the above equations, together with the Arrhenius dependence of the resulting rate constants, indicates that the main features of the mechanism assumed in Ref. 5 are correct. Nevertheless, the view that individual reactions take place in isolation on the catalyst surface is in some degree artificial. A more reasonable mechanism is that represented by scheme (11), according to which the final intermediates leading to formation of a given product are the same independently of the oxidisable compound from which they had been formed. Furthermore, the above equations indicate that at low degrees of conversion the selectivity should not depend on reactant concentrations, which contradicts experiment (Fig. 3).

The close analogy between catalysis and reduction noted above suggests that the catalytic process involves surface oxygen ions O^{2-}, since it is difficult to expect other forms of oxygen, e.g. the radical-anions O^- and O_2^-, to be present on the surface during the reduction experiments. Moreover, these species are less reactive towards aromatic hydrocarbons than are other reductants (hydrogen, carbon monoxide, etc.).[73]

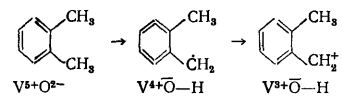
Interaction of *o*-xylene with the surface of vanadium pentoxide is accompanied by electron transfer from the hydrocarbon to the oxide[74]. Addition of small quantities of metallic palladium to the oxide accelerates significantly its reduction by *o*-xylene[75], probably because activation of carbon–hydrogen bonds is facilitated on the metal surface. The part played by additions of metals to oxides in the catalytic oxidation and reduction of the latter has been examined in detail in a review by Il'chenko[76].

With regard to the nature of the compounds X_i postulated in scheme (23) it may be suggested[72] that there is probably no significant difference in the mechanisms of formation of benzoic acid from toluene and of benzaldehyde and *o*-tolualdehyde from *o*-xylene. The structure of compound X_2 responsible for the formation of *o*-toluic acid can then be written[61]



Another acidic substance is phthalic anhydride, formed from X_4, which is most probably also saltlike in character. According to infrared-spectroscopic data[77] surface phthalates on vanadium pentoxide are readily decomposed, and can therefore be assumed to take part in the catalytic process.

We have not yet considered the mechanism of the formation of products of degradative oxidation—maleic anhydride and carbon dioxide—which may also be formed from the surface compound X_4, so that a single chain of consecutive surface reactions takes place. However, it is also possible that products of degradative oxidation are formed at least partly by a different path, when the primary attack on the hydrocarbon affects the aromatic ring. This view is held by Vanhove and Blanchard[78], who suggest that the initial interaction of *o*-xylene with a vanadium–titanium oxide catalyst in the formation of products of mild oxidation—*o*-tolualdehyde, phthalide, phthalic anhydride—follows the scheme



(reduction of the catalyst surface may involve[78] several metal ions because of the rapidity of electron transfer in the oxide lattice, so that V^{4+} ions will be formed preferentially, in agreement with experimental results). The resulting carbonium ion interacts with oxygen O^{2-} of the catalyst to give an adsorbed alkoxide ion. The latter does not undergo desorption: when a mixture of *o*-tolylmethanol and ^{14}C-labelled *o*-xylene is oxidised, the unchanged alcohol is non-radioactive. On the other hand, the alkoxide ion may serve as an intermediate species in the oxidation of *o*-xylene, since the oxidation products of *o*-tolylmethanol are also *o*-tolualdehyde, phthalide, and phthalic anhydride.

Repetition of the processes of detachment of hydrogen from the adsorbed species, electron transfer to the catalyst, and interaction with a surface oxygen ion may ultimately yield phthalic anhydride. Such is the suggested[78] mechanism of the formation of products of mild oxidation.

The degradative oxidation of *o*-xylene to maleic anhydride and oxides of carbon is attributed[78] to a competing reaction between an oxygen ion of the catalyst and the unsaturated portion of the aromatic molecule. This is consistent with results obtained by the same workers[79] on the oxidation of *o*-xylene in which a methyl group is labelled with carbon-14: the maleic anhydride detected among the reaction products is non-radioactive, so that the carboxy-groups have been formed from carbon atoms of the aromatic ring. A mechanism of formation of maleic anhydride was suggested[79] involving surface compounds of quinonoid type, which is supported by the detection of quinones among the oxidation products from *o*-xylene[4,71].

It is suggested[78] that the unsaturated part of the oxidisable molecule interacts with an oxygen ion after preliminary bonding to the catalyst as a π-complex. It is assumed also that oxidation on a series of catalysts will be more selective the weaker the bond between the π-complex and the catalyst surface.

Several studies have been made on the effect of the chemical nature of a catalyst on its activity and its selectivity in the oxidation of *o*-xylene. Investigation of the catalytic properties of individual oxides of vanadium by a pulse method showed[80] that their chemical composition changed significantly even during a short period in an atmosphere of the reaction mixture, although formation of new phases was not observed. The oxides V_2O_4, V_6O_{13}, and V_3O_7 had closely similar initial specific activities lower than that of V_2O_5 and even lower than that of V_2O_3. With increase in the number of pulses the activity and the selectivity change, abruptly with V_2O_5: after the catalytic properties of the pentoxide have been constant during the first ten pulses, the activity increases rapidly to a new constant value.

Investigation of the phase constitution of a vanadium oxide catalyst corresponding to steady-state oxidation showed[81] that, in air containing 1.1% of *o*-xylene, the catalyst comprised V_2O_5, $V_2O_{4.34}$, and V_2O_4 phases. Electron diffraction established that the $V_2O_{4.34}$ layer was located above the V_2O_4 layer. The appearance of the latter is explained in macrokinetic terms: conditions for reduction of the initial vanadium pentoxide are more severe inside the catalyst grains. With increase in the *o*-xylene concentration to 3.3 mole % the catalyst rapidly loses its activity, being converted almost completely into V_2O_4 (at the edge of the layer V_2O_3 is also detected).

The vanadium catalysts used according to the patent literature in the manufacture of phthalic anhydride from *o*-xylene can be divided into three main groups: vanadium pentoxide alone or with small quantities of additives is applied on relatively non-porous carriers (high-temperature catalysts); vanadium–potassium sulphate catalysts on carriers (silicon and titanium dioxides) resemble those employed for the oxidation of naphthalene (low-temperature catalysts); and mixed vanadium–titanium oxide catalysts (usually on an inert support) have recently found widespread application. High-temperature catalysts are not very selective, but the high temperatures permit large outputs because of the use of very short contact times[9,71,79]. The V_2O_5–K_2SO_4–SiO_2 catalysts possess enhanced selectivity, especially at low degrees of conversion, when the main product is *o*-tolualdehyde[4,63,69,71]. This applies also to vanadium–titanium oxide catalysts[82].

Investigation by Vanhove and Blanchard[82,83] of the effect of composition in the third group of catalysts indicated that specimens containing 12.5 and 89.5 mole % of titanium dioxide are initially the most selective for C_8 products. The latter specimen also possesses the maximum activity per unit mass of the catalyst. The initial selectivities correlate with the activation energies of the isotopic exchange of oxygen[83]. Increasing the degree of conversion of *o*-xylene even up to ~ 100% has little effect on the selectivity for products of degradative oxidation, mainly shifting the distribution of C_8 products towards formation of phthalic anhydride[82]. On the whole this applies also to other types of vanadium oxide catalysts[4,63,69,71,79].

Conversion of *o*-xylene into phthalic anhydride is relatively slight on tin, silver, and copper vanadates, as well as on molybdenum oxide catalysts[66]. Several studies have been made of the individual oxidation of products of the mild oxidation of *o*-xylene on vanadium catalysts[9,71,84-86]. Oxidation of *o*-tolualdehyde on the fused pentoxide[84] yields *o*-toluic acid, phthalide, phthalic anhydride, maleic anhydride, carbon monoxide, and carbon dioxide, with kinetics conforming to Eqn. (9). Power equations have been suggested[71] for the oxidation of *o*-tolualdehyde on a high-temperature vanadium catalyst and on a vanadium–potassium sulphate–silica gel catalyst. On the latter, as in the oxidation of *o*-xylene, methylbenzoquinone was formed. The oxidation of *o*-toluic acid on vanadium pentoxide at 450° C gives[85] phthalic anhydride in 85 mole % yield; the corresponding yield from *o*-xylene under analogous conditions was 67 mole %. The oxidation products from phthalide on a V_2O_5–K_2SO_4–SiO_2 catalyst are phthalic anhydride (92–95% selectivity) and carbon dioxide[71,86].

The properties of non-vanadium catalysts in the oxidation of *o*-xylene have not been adequately investigated. Popova and Kabakova[87] used copper(II) oxide with additions of molybdenum and tungsten oxides at 370–450° C. The rates of overall conversion of *o*-xylene and of formation of *o*-tolualdehyde (with ~ 15% selectivity at 380° C) and carbon dioxide are independent of the concentration of the hydrocarbon but proportional to that of molecular oxygen.

The Reviewer has obtained[88,89] initial specific activities and selectivities for the oxidation of *o*-xylene on titanium, vanadium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, tin, and chromium oxides, as well as on metallic platinum. An approximate correlation has been established between the specific activity of an oxide and the energy of bonding of oxygen (Fig. 1*c*). The specific activity of metallic platinum exceeded about thousandfold that of oxides with similar energy of bonding of oxygen, which results from the different natures of oxides and metals[19,20].

The initial selectivity for products of mild oxidation is quite high not only on typical catalysts for this process (vanadium pentoxide, molybdenum trioxide) but also on those which under normal conditions catalyse complete oxidation (Co_3O_4, MnO_2, NiO). On the cobalt oxide at 240° C, for example, the initial selectivity for phthalic anhydride is 64% (and for C_8 products 74%).

The reduction of catalysts by *o*-xylene (in experiments on cobalt and iron oxides) takes place at rates closely similar to the rate of catalysis. The gradual decrease in the rate of reduction with time is accompanied by an increase in selectivity for products of mild oxidation. Thu the rules of reduction are qualitatively the same as for vanadium pentoxide (Fig. 4).

If the oxidation of *o*-xylene takes place by mechanism (11), the dependence of the selectivity for *o*-tolualdehyde on the bonding energy for oxygen should obviously be ana-

logous to that already discussed for the selectivity for benzaldehyde in the oxidation of toluene (Eqn. 22). This is indeed the case: an approximate correlation is observed between S_{0TAl} and q_S for oxides of transition metals[88,89] (Fig. 2*b*). In contrast to this, no regular relation is found between the selectivity for phthalic anhydride and the bonding energy[88,89]. One reason may be that the intermediate yielding this product may be saltlike, with its heat of desorption (also the activation energy) depending not only on q_S but also on the acid–base properties of the surface[45].

Results for the properties of catalysts at low degrees of oxidation both of *o*-xylene[88,89] and also of toluene[50] indicate that no sharp boundary exists under these conditions between catalysts of "complete" oxidation (cobalt, manganese, and nickel oxides) and those of "mild" oxidation (vanadium and molybdenum oxides). Differences between them are apparent with increase in the degree of conversion of the initial hydrocarbon, when further oxidation of the reaction products begins to play an appreciable part. This is accompanied on catalysts of the former type by a sharp increase in the proportion of combustion products, whereas on vanadium pentoxide further oxidation leads to a redistribution of C_8 products (with predominant formation of phthalic anhydride) and in lesser degree to an increase in the yield of products of degradative oxidation[4,63,69,71,79,82]. The resistance of phthalic anhydride to further oxidation on vanadium oxide catalysts largely determines their effectiveness.

Another factor may be that the rate of further oxidation decreases with increase in the oxygen–catalyst bond energy. However, the question then arises why the rate of oxidation of the initial hydrocarbon undergoes a greater change than do the rates of conversion of products of mild oxidation. Indeed, on the assumption that a process takes place by a consecutive scheme

$$R \xrightarrow[O_2]{r_R} RO \xrightarrow{r_{RO}} RO_2$$

and that

$$r_R = k_R P_R \theta,\ r_{RO} = k_{RO} P_{RO} \theta,$$

it is easy to show that the selectivity for RO is

$$S_{RO} = \left(1 + \frac{k_{RO}}{k_R} \frac{x}{1-x}\right)^{-1},$$

where x is the degree of conversion of the initial hydrocarbon. With different catalysts at the same degree of conversion the selectivity is evidently governed by the ratio of the reactivities of R and RO, which are measured by the rate constants k_R and k_{RO}. If, for example, the ratio k_{RO}/k_R is independent of q_S, oxides having low bonding energies are more effective catalysts, since the reaction velocity on them will be higher for the same selectivity. However, experience shows that in most cases the selectivity for products of mild oxidation increases with q_S, including processes occurring predominantly by a consecutive scheme[90].

5. Oxidation of Acenaphthene, Pseudocumene, and Durene

As with *o*-xylene the structure of these hydrocarbons permits the formation of acid anhydrides by oxidation of methyl groups without degradation of the aromatic ring.

The oxidation of acenaphthene was investigated on vanadium pentoxide alone and with potassium sulphate, on the latter with iron and copper vanadates respectively, and on manganese dioxide (with pumice as carrier) over the range 320–450°C.[91] The chief products of mild oxidation on vanadium catalysts were acenaphthylene and naphthalic anhydride, but on manganese dioxide only acenaphthylene was formed. Increasing the ratio of air to acenaphthene tended to increase the yield of naphthalaldehyde relative to acenaphthylene (on manganese dioxide the proportion of combustion products increased). These results are qualitatively consistent with scheme (11). Oxidation of acenaphthene begins at lower temperatures on manganese dioxide than on vanadium catalysts, but the maximum yield of acenaphthylene—the product of mild oxidation—was lower on the dioxide. The yield of naphthalic anhydride reached 75–80% on the most effective of the catalysts studied[91] (iron vanadate with potassium sulphate). An active catalyst giving an 87% yield of naphthalic anhydride from acenaphthene at 355°C comprised 6% of vanadium pentoxide with 94% of titanium dioxide[92].

The oxidation of pseudocumene on vanadium pentoxide with added silver(I) and tungsten(VI) oxides at 410–420°C produces trimellitic (yield 40%), phthalic (28%), and maleic (11%) anhydrides[93]. A comparative examination of the oxidation of benzene, toluene, *o*-xylene, pseudocumene, and durene on a vanadium–molybdenum–phosphorus oxide catalyst with added sodium and nickel on synthetic corundum shows[93] that the rates of overall conversion of the alkylbenzenes are closely similar, and that the presence of isolated methyl groups in the acid anhydrides formed tends to increase the rate of production of carbon dioxide (the maximum yield of products of mild oxidation is observed with *o*-xylene). A molybdenum–tungsten oxide catalyst (1 : 9) on alundum can be used for the highly selective oxidation of pseudocumene to triformylbenzene[94].

The oxidation of durene was investigated[95–97] on fused vanadium pentoxide, the latter with additives on a carrier, V_2O_5–MoO_3–Al_2O_3, V_2O_5–SnO_2, V_2O_5–P_2O_5–kieselguhr, V_2O_5–K_2SO_4–SiO_2, V_2O_5–SnO_2–P_2O_5, V_2O_5–MnO_2–pumice, and vanadium–potassium catalysts. The best results were obtained on finely crystalline fused vanadium pentoxide: at 430–450°C with 100% conversion the yield of pyromellitic anhydride was 52–55 mole %. The fused pentoxide has been recommended also by other workers[98–100]. The yield of the anhydride is increased[101] by a considerable excess of molecular oxygen above the stoichiometric quantity. Investigation of the individual oxidation on fused vanadium pentoxide of certain products of the incomplete oxidation of durene—pyromellitic and maleic anhydrides, mono- and di-methylmaleic anhydrides, and 3-methyl-, 4-methyl-, and 4,5-dimethyl-phthalic anhydrides—showed[100,102] that the unsubstituted cyclic anhydrides were the most resistant to oxidation. The main reaction products other than oxides of carbon from the oxidation of duroquinone on fused vanadium pentoxide are dimethylmaleic anhydride and acetic acid[103]. Catalysts recommended in the patent literature for the oxidation of durene are V_2O_5–Cr_2O_3,[102] V_2O_5–MoO_3–P_2O_5 on SiC or Al_2O_3,[103] V_2O_5–WO_3–P_2O_5–Na_2O on Al_2O_3,[104] and V_2O_5–Cr_2O_3–Sb_2O_3–SnO_2 on Al_2O_3.[105] On the last catalyst the yield of pyromellitic anhydride at 360°C is 80 mole % (the temperature rises to 590°C during the process).

6. Oxidation of Naphthalene and Methylnaphthalenes

The oxidation of naphthalene on a vanadium oxide catalyst is the first industrial process for the gas-phase production of phthalic anhydride. Other products are

naphthaquinone (NQ), maleic anhydride, and oxides of carbon.

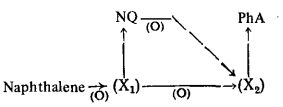
Equation (9) was suggested[2,3] to describe the kinetics of the oxidation of naphthalene on a fluidised bed of a V_2O_5–K_2SO_4–SiO_2 catalyst at 337° C. This was confirmed[106] for low degrees of conversion on the same catalyst at 300–335° C. The chief oxidation products were[106] naphtha-1,4-quinone and phthalic anhydride, with insignificant yields of maleic anhydride and carbon dioxide; naphtha-1,2-quinone was also formed (at most 5% on the content of the 1,4-quinone).

Roiter et al.[10] investigated the kinetics of the oxidation of naphthalene at 330–360° C on a V_2O_5–K_2SO_4–SiO_2 catalyst deposited on glass for degrees of conversion of naphthalene over the range 15–80% in a gradientfree reaction vessel. The equations

$$r_{PhA} = k_{PhA} P_N^0 P_{O_2},$$
$$r_{NQ} = k P_N P_{O_2} / P_{NQ}^{0,6} (1 + b P_N)$$

were suggested for the rates of formation of phthalic anhydride and naphthaquinone. The two reactions were assumed to take place in parallel, on different types of active centres[10].

The Reviewer[16] has attempted to interpret these results[10] by means of a redox model in which the reduction stage is represented by scheme (11). In the present case it can be written



(24)

The intermediate compound X_1 most probably has a quinonoid structure. The formation of such structures is indicated by electron spin resonance results obtained for the interaction of naphthalene with vanadium pentoxide[107]. The structure of X_2 can be regarded as a surface phthalate[77], as mentioned above for the mechanism of the oxidation of *o*-xylene.

The results in Ref. 10 are satisfactorily described by Eqn. (9) for the total rate of the process and by Eqn. (12) for the selectivity for naphthaquinone[16]. Closely similar rate constants and activation energies of oxygen adsorption are obtained for catalysts of the same chemical composition, independently of the initial oxidisable hydrocarbon (Table 2), which supports a mechanism based on a two-stage redox model[4].

The above ideas on the mechanism are confirmed by results obtained by Andreikov et al.[108] using a pulse method for the oxidation of naphthalene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 360–380° C. Under these conditions the reaction products were naphthaquinone and phthalic anhydride; irreversible adsorption of naphthalene and its oxidation products was not observed. The composition of the initial catalyst subjected to preliminary oxidation in a stream of air at 400° C (84% V^{5+} + 16% V^{4+}) differed considerably from the steady-state composition (6% V^{5+} + 94% V^{4+}). The latter composition was independent of its mode of attainment: it was the same for preoxidised and prereduced specimens. The high degree of reduction corresponds in terms of the redox model to low surface coverage θ and hence approximately zero order with respect to naphthalene and the first order with respect to molecular oxygen, which is indeed observed experimentally[108].

Comparison of the rates of catalytic oxidation and the reduction of the V_2O_5–K_2SO_4–SiO_2 catalyst by naphthalene, as well as the selectivities of both processes[108], confirms the redox mechanism (Table 3). With increasing reduction of an oxidised catalyst specimen by naphthalene the reaction velocity gradually diminished, with a simultaneous decrease in the selectivity for phthalic anhydride from 85% to 40%. These results are consistent with scheme (24).

Table 2. Rate constants and activation energies of the adsorption of oxygen (corresponding to Eqn. 9) in the oxidation of aromatic hydrocarbons on V_2O_5–K_2SO_4–SiO_2 catalysts.

t, °C	$10^8 k_{O_2}$, moles atm^{-1} m^{-2} s^{-1}	E_{O_2}, kcal mole^{-1}	Ref.
	benzene		
350	4.7	25[22]	22
375	9.6		
400	21.4		
	toluene		
300	0.96	29[46]	46
325	4.8		
350	13.6		
	o-xylene		
290	0.74	26[4]	4
300	1.08		
310	1.64		
	naphthalene		
312	1.56	28[106]	106
335	5.3		
330	2.45	32*	*
340	4.0		
350	5.05		
360	7.25		

* Calculated from data in Ref. 16.

A similar comparison of rates of catalysis and reduction on vanadium pentoxide alone and deposited on silica revealed[109] that catalysis was rather more rapid. This was attributed[109] to partial occurrence of the reaction by an associative mechanism. The difference between the rates of catalysis and reduction diminished with rise in temperature (for 18% of the pentoxide on silica at 400° C the rates were almost identical). A similar transition to a stepwise mechanism with rise in temperature was observed[110] for other oxidations, showing that the associative mechanism involves direct participation of surface O^{2-} ions in forming the reaction products, while desorption of the products is facilitated by the presence of O_2^- radical-anions on the surface (these are absent under the conditions of the reduction experiments).

Table 3.

t, C°	Catalysis $10^5 r$, mole g^{-1} min^{-1}	S_{PhA}, %	Reduction $10^5 r$, mole g^{-1} min^{-1}	S_{PhA}, %
380	1.68	56	1.62	53
370	0.97	49	0.92	45
360	0.49	42	0.42	41

Investigation of the kinetics of the oxidation of naphthalene on vanadium pentoxide alone is complicated by changes in the chemical composition and the phase constitution of the catalyst under the influence of the reaction conditions[111]

Power rate equations were obtained[112] over a narrow range of conditions for the kinetics of the oxidation of naphthalene to individual products. The same workers[113], having taken special measures to diminish the influence of composition changes in the catalyst on the kinetics, found that the rate of formation of phthalic anhydride on coarsely crystalline vanadium pentoxide below 385°C is independent of the naphthalene concentration and proportional to the molecular oxygen concentration, but above 390°C it is proportional to the naphthalene concentration (the dependence of the rate on the oxygen concentration above 390°C was not investigated).

Equation (9) applies to the kinetics of the oxidation of 1- and 2-methylnaphthalenes on several types of vanadium–potassium sulphate–silica gel catalysts[114,115]. The mutual inhibition of the oxidation of naphthalene and methylnaphthalenes in their mixtures was explained[114,115] in terms of a redox mechanism: in the simultaneous oxidation of hydrocarbons the steady-state surface concentration of oxygen is lower than when they are oxidised separately. The rate constants of catalyst oxidation k_{O_2} are the same for different oxidisable hydrocarbons. Decrease in the degree of conversion of methylnaphthalenes[115] is accompanied by increased selectivity for the naphthaldehydes, whose yield at degrees of conversion of 35% and below exceeds the aggregate yield of the remaining products. Such "mildness" of the action of V_2O_5–K_2SO_4–SiO_2 catalysts is evident also, as noted above, in the oxidation of *o*-xylene to *o*-tolualdehyde.

An attempt was made[116,117] to examine the catalytic properties of certain individual oxides of vanadium towards the oxidation of naphthalene under pulse and continuous régimes. The composition of the specimens changed significantly even during the initial pulses (except in the case of vanadium pentoxide, on which the first pulse had hardly any influence). The specific activity sequence obtained $V_2O_{4.34} > V_2O_3 > V_2O_4 > V_2O_5$ (380–415°C) therefore relates to partly modified catalyst compositions. The extreme members of the sequence differ ninefold in specific activity, and by a factor of 13.5 in rate of formation of phthalic anhydride. Below 370°C the oxides V_2O_4 and V_2O_3 change places in the sequence. The activity and the selectivity of the pentoxide remain unchanged for ~ 1 h, in spite of the appreciable change in chemical composition, after which sharp increases are observed in the activity and in the selectivity for phthalic anhydride. Those of the other oxides remained almost unchanged for several hours' operation.

The chemical composition of the catalyst changes initially probably in its surface layers. Thus grains of fused vanadium pentoxide that had functioned in industrial plants for $2\frac{1}{2}$ years were considerably reduced near the surface, whereas in the centre they remained almost unchanged[111]. The average chemical composition of separate fractions of a catalyst that had operated for a long time showed[118] a regular dependence on grain size: the content of V_2O_4 decreased from 90% to 30% between the 0.05-mm and the 0.5-mm fractions.

Vanadium–potassium sulphate systems and fused vanadium pentoxide are used in the manufacture of phthalic anhydride from naphthalene. The composite catalyst is more common though less efficient, since the selectivity for phthalic anhydride is greater thereon[119]. The properties of the mixed catalyst are improved by the continuous or periodic addition of sulphur compounds—sulphur dioxide[120–123], thionaphthen[123,124]—to the reaction mixture.

The role of potassium sulphate has not been adequately elucidated. The view has been expressed that this component diminishes the activity of vanadium pentoxide, while tending to enhance selectivity[119]. Investigation of the phase constitution and the chemical composition of vanadium–potassium sulphate systems indicates the formation of a number of chemical compounds between the pentoxide and potassium sulphate[125–127]. Study of the activity of vanadium–potassium catalysts as a function of the proportions of the components has established[128] the activity sequence

$$K_2O \cdot 4V_2O_5 > K_2O \cdot V_2O_4 \cdot 8V_2O_5 > K_2O \cdot 3V_2O_5 \gg 3K_2O \cdot 5V_2O_5 > KVO_3.$$

Tin vanadate is highly active towards the oxidation of naphthalene[129]. A correlation was found[130] in the series of catalysts V_2O_5, V_2O_5–TiO_2, and V_2O_5–SnO_2 between the rate of oxidation of naphthalene and the rate of reduction of the oxides by naphthalene.

7. Oxidation of Anthracene

Anthraquinone is the main product of the oxidation of anthracene on a vanadium catalyst; phthalic anhydride is also formed. The kinetic equation (9) is applicable to oxidation on vanadium(V) oxide–potassium sulphate with iron(III) oxide[131] and with silicon dioxide[7], and on cobalt molybdate on silica gel[8]. Rate equations based on the Langmuir–Hinshelwood model were inconsistent with experimental results[8].

During operation a vanadium–potassium sulphate catalyst undergoes abrupt deactivation[132]. At 370°C this ensues after 10 h, when the degree of conversion falls from 80% to 40%, and the selectivity for anthraquinone from 90% to 40%. The deactivation was attributed[132] to the highly reduced state of the catalyst due to the great reactivity of anthracene. Additions of iron and manganese oxides to the catalytic system improve the stability of the catalyst towards reduction[133].

The chief products of the oxidation of anthraquinone on a vanadium catalyst[134] at 330–410°C are phthalic and maleic anhydrides (proportion of the latter ~ 5%) with hardly any oxides of carbon. On the same catalyst at 350°C anthraquinone is oxidised more slowly than is anthracene by factors of 30–40 and than naphtha-1,4-quinone by factors of 10–15.[134] Since anthracene is far more reactive than naphthalene, it becomes clear why selectivity for anthraquinone can be maintained at a high level far more easily than in the oxidation of naphthalene to naphthaquinone.

8. Oxidation of Phenanthrene

Kinetic investigation of the oxidation of phenanthrene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 330–370°C gave empirical power equations[132,135] for the formation of phenanthra-9,10-quinone, 9-fluorene, the lactone of 2′-hydroxybiphenyl-2-carboxylic acid, 1,2-naphthalic, phthalic, and maleic anhydrides, and carbon dioxide. The rate of oxidation of phenanthrene is less than that of anthracene on the same catalyst; deactivation of the catalyst was not observed[132].

Addition to the reaction mixture of sulphur dioxide (0.04%) improves the yield of phenanthra-9,10-quinone from 3.5% to 25% (44.7% on the phenanthrene that has reacted) in the oxidation of phenanthrene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 383°C.[136]

The oxidation of phenanthrene on fused vanadium pentoxide is accompanied by significant activation of the catalyst after a few hours' operation[137].

IV. CONCLUSION

The published information surveyed, covering a large range of diverse reactions, reveals much in common in the oxidation of aromatic hydrocarbons. The consequences of the generalised kinetic model listed at the end of Section II have found confirmation in many studies. Thus the reactivity of different aromatic hydrocarbons on the same catalyst depends regularly on the energy characteristics of the oxidisable molecules (ionisation potentials[72,132], carbon–hydrogen bond energies[72]). As an example Fig. 5 illustrates the relation[72] between rate constants k_R found[4,22,46,106] by means of Eqn. (9) and the corresponding energy parameters.

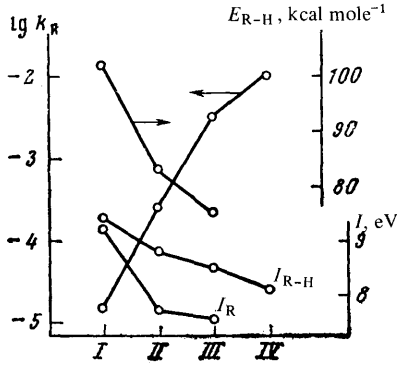


Figure 5. Variation of logarithm of rate constant k_R (with V_2O_5–K_2SO_4–SiO_2 catalyst[4,22,46,106]), R–H bond energy E_{R-H}, ionisation potential of initial molecule I_{R-H}, and ionisation potential of R· radical I_R. in a series of aromatic hydrocarbons: I) benzene; II) toluene; III) *o*-xylene; IV) naphthalene.

The above kinetic model obviously contains several simplifications. A more rigorous approach would take into account the non-uniformity of the catalyst surface. It is also possible that more than one oxygen atom is involved in individual primary stages (Eqns. (12)–(19) were deduced on the assumption that a single surface oxygen atom was involved in the oxidation stages). A further possibility is that, owing to an appreciable contribution by an associative mechanism[90,109,110], the view that the stages of reduction and oxidation of the catalyst take place independently may in individual cases (especially at low temperatures) be inadequate for interpreting the kinetic data.

Little experimental investigation has been undertaken on the reasons for the inhibiting effect sometimes exhibited by reaction products. A possible cause may be competition between oxidisable substances for available oxygen[18]. Inhibition may be due also to blocking of the surface by organic reactants. It is difficult to distinguish these two effects without detailed kinetic investigation. In many studies inhibition has been deduced from the dependence of the rates of formation of individual products on the concentration of the oxidisable substance, which is varied by changing the time of contact. Under these conditions the formal order with respect to the oxidisable substance is abnormally high, which is regarded as indicating inhibition. However, the latter may be apparent, since with increase in the period of contact not only the concentration of reaction products but also the probability of their further oxidation increases, so that the observed order may exceed the true value. In this connection it is noteworthy that, with the above experimental procedure, the formal reaction orders are always higher for products that are less oxidised and hence capable of further oxidation (independently of the nature of the initial oxidisable compound)[71,86,111,115,132].

Vanadium catalysts—the most widely used for the oxidation of aromatic hydrocarbons—are highly active towards their degradative oxidation. Many of the products detected under mild conditions therefore undergo further transformation. However, the chain of such conversions is terminated or strongly retarded if organic acid anhydrides are formed. High yields of the latter can always be obtained if the initial oxidisable molecule contains a chain of at least four carbon atoms that includes an unsaturated bond (aromatic hydrocarbons, butenes, pentenes, heterocycles, etc.).

Anthraquinone is also comparatively resistant to oxidation on vanadium catalysts, which is responsible for its high yield from the oxidation of anthracene. Naphthaquinone and especially benzoquinone are less stable. The decrease in the yield of quinones in the sequence—anthracene, naphthalene, benzene—is intensified also by the fall in reactivity of the initial hydrocarbon in the same sequence. Formation of quinonoid structures probably precedes oxidative degradation of the aromatic ring. In the case of alkylated hydrocarbons this process competes with oxidation of the alkyl groups. This may be why, in the oxidation of *o*-xylene on vanadium catalysts, a considerable yield of oxides of carbon is observed (as noted above, benzoquinone is unstable). Intermediate formation of quinonoid structures takes place also in the oxidation of naphthalene, but, in contrast to the oxidation of *o*-xylene, they may be precursors of phthalic anhydride, which is stable towards further oxidation; and smaller quantities of carbon dioxide are obtained from naphthalene than from *o*-xylene on the same catalysts[119].

Catalysts having the same chemical composition show largely similar behaviour in the oxidation of different aromatic compounds. Thus vanadium pentoxide undergoes partial reduction during the reaction, with the formation of lower vanadium oxides as separate phases. The resulting catalyst is more active and more selective than the initial system, independently of the nature of the oxidisable aromatic hydrocarbon (benzene[27], *o*-xylene[80], naphthalene[116,117], phenanthrene[137]). The great activity of vanadium pentoxide alone is often used to obtain a high output of a desired product of mild oxidation, despite a considerable loss of the initial hydrocarbon by combustion.

Vanadium–potassium sulphate systems are characterised by low outputs, but possess enhanced selectivity. The mildness of the action of such catalysts is especially clearly shown at not too high degrees of conversion of the oxidisable substance, when products of the mildest oxidation predominate—aldehydes from *o*-xylene[4] and methylnaphthalenes[114,115], quinones from naphthalene[10,106] and anthracene[132].

The Reviewer has enumerated certain general features of the selective catalytic oxidation of aromatic hydrocarbons in order to emphasise the interrelationship of mechanism, kinetics of various reactions, and selective action of various catalytic systems. This should facilitate future discussion of new experimental results concerning specific reactions.

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