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Mechanism of the Oxidation of o-Xylene to Phthalic Anhydride

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A mechanism is proposed for the selective oxidation of *o*-xylene to phthalic anhydride catalysed by V_2O_5/TiO_2. The chief catalytic species is identified as an oxohydroxy-vanadium group forming a monolayer on the TiO_2 (anatase) surface, and possible unit reactions involving this and related groups with *o*-xylene and with organic species formed from it are presented: these account for the formation of intermediate products (*o*-tolualdehyde, phthalide, etc.) as well as of phthalic anhydride itself. The five-membered ring products (phthalide, phthalic anhydride) may arise by dehydration of noncyclic precursors. The unique catalytic properties of the V_2O_5/TiO_2 system arise from the conjunction in the same active centre of a reducible V═O bond and an acidic hydroxyl group.

INTRODUCTION

The selective oxidation of *o*-xylene to phthalic anhydride catalysed by V_2O_5/TiO_2 is an important industrial process (*1*), the free-world production in 1986 being about 2.3 million tonnes. The reaction proceeds at near atmospheric pressure and at about 380–400°C to give almost complete conversion of *o*-xylene and selectivities to phthalic anhydride of 70–75% (*2*). Catalysts contain about 6% V_2O_5 supported on TiO_2 (anatase), the two in turn being carried on ceramic pellets or rings; small amounts of other oxides, acting as promoters, may also be present.

Work on this reaction performed before 1979 has been reviewed by Wainwright and Foster (*2*), although many of the earlier studies employed catalysts that were much less selective than those now used. There have been a number of more recent accounts of the reaction, some employing industrial catalysts (*3*) and others laboratory preparations (*4–7*). Its principal features are therefore well known. The major initial product is *o*-tolualdehyde (TAL), which is subsequently converted via *o*-phthalide (PL) to phthalic anhydride (PA): *o*-toluic acid is a minor intermediate, while maleic anhydride (MA) is a significant by-product resulting from the over oxidation of PA. The structures of these molecules are given below. Other minor by-products have also been reported, and carbon oxides are formed at all stages of the reaction.

It is a complicated reaction. To convert *o*-xylene to phthalic anhydride, 12 bonds have to be broken, and 12 formed; a number of other bond-breaking and bond-forming acts will doubtless also occur within the catalytically active species at the surface. In view of the considerable importance of the reaction it is strange that no greater degree of curiosity has been shown concerning its mechanism. Mechanistic discussions were originally confined to defining pathways by which the observable gas-phase components might be transformed (*5*). In an earlier paper (*6*), we outlined a "rake" mechanism to describe the course of the reaction, and suggested structures for possible adsorbed intermediates. More recently, FTIR studies of the interaction of toluene (*7, 8*) and of *o*-xylene (*8*), and of intermediate products, with V_2O_5/TiO_2 catalysts have led to more refined mechanistic speculations, but in both cases these appear to be based on unrealistic models for the catalytically active surface: a critique of these ideas will be developed below. An even less sophisticated discussion of the

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mechanism of these and related reactions has also recently appeared (*9*).

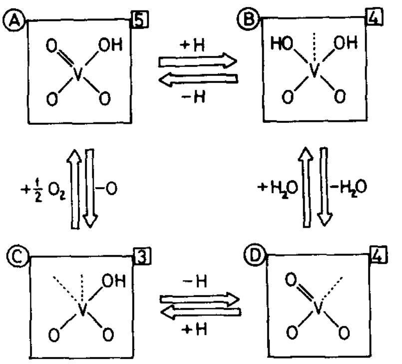
Equally strange is the lack of effort to understand how the nonselective reaction proceeds. There seems to be a blithe assumption that *o*-xylene and any product derived from it is capable of being deeply oxidized (*5*), but how and why this happens is rarely considered. It is not even known whether deep oxidation occurs at some specific type of site on the catalyst surface, or whether it necessitates some particular type of adsorbed intermediate. It has, however, been noted that at low temperatures and low conversion part of the *o*-xylene disappears as a strongly adsorbed carbonaceous deposit (*5, 6*), which acts as a catalyst poison and which under some circumstances vacates the surface to condense as an oily liquid downstream of the reactor (*6*). This phenomenon has been implicated in the formation of carbon oxides (*6*).

The purpose of this paper is to present a series of unit steps that can account for the formation of the selectively oxidized products. It is now possible to do this, since there is reasonable certainty as to the nature of the catalytically active species. The first step is therefore to review briefly what is known about this species, and to suggest how it may act to effect the observed reactions.

THE NATURE OF THE CATALYTICALLY ACTIVE SPECIES

The reason for the peculiar efficiency of the V_2O_5/TiO_2 combination for the selective oxidation of *o*-xylene has long been a matter for debate. The notion (*10*) that there exists a precise crystallographic fit between the surface of TiO_2 (anatase) and the layer structure of V_2O_5 has commanded much attention, but is open to criticism on a number of grounds. First, catalytic activity is now definitely attributable to a single VO_x monolayer in which the three-dimensional structure of V_2O_5 cannot exist (*5, 6, 11, 12*): this is not to say, however, that other phases approximating more closely to V_2O_5 that may exist at high V_2O_5 concentrations (*13, 14*), or even unsupported V_2O_5 (*15*), are necessarily inactive, but the evidence (*5, 12*) clearly suggests that such phases play only a minor role in the reaction. Second, the active surface is now well established to have both Lewis and Brønsted acidity, to extents depending on the amount of water and of "V_2O_5" present (*16*), for which the Véjux–Courtine model makes no provision. Third, direct examination by electron microscopy (*17, 18*) and the use of other methods of physical characterization (*7, 14, 19*) provide no support for their concept of the existence of a multilayer having the structure of V_2O_5 in register with the TiO_2 support.

We may therefore assume for the purposes of this paper that the catalytically active species reside in a monolayer of "V_2O_5" upon the TiO_2 surface and that they are capable of exhibiting both Brønsted and Lewis acidity, as well as electron-accepting character (*7*): they are easily reducible by H_2 to a V^{3+} species in a one-step process (*14*), and do not show the characteristic strong Raman band for the $V{=}O\cdots V$ vibration (*14, 16*). Bearing in mind EXAFS studies (*20*) and much other work (*21*), the principal surface species is formulated as a tetrahedral oxohydroxy vanadium complex (Structure A of Scheme 1), where both the lower oxygen atoms form part of the anatase surface. The surface of a monolayer catalyst is therefore quite different from that of V_2O_5 itself. Although Structure A is proposed as the chief species present under reaction conditions, when water from the partial combustion of the *o*-xylene is present, under anhydrous conditions there may occur an intermolecular dehydration, leading to linear chains of V–O–V bridged species. Evidence pointing in this direction (*16, 22*) does not therefore conflict with what is proposed here, since it has been obtained under anhydrous conditions. The hydration of Lewis acid centres



SCHEME 1. Proposed structures of catalytic species having single V atoms. The numbers are the oxidation states of the V atoms in the species shown, and the broken lines denote possible points of attachment of atoms connected to the substituent groups on the aromatic ring.

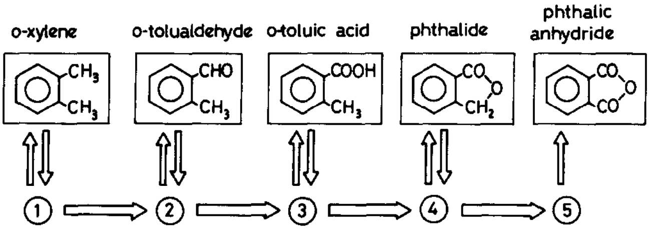
to Brønsted centres has been observed experimentally (*14*).

AN APPROACH TO REACTION MECHANISMS

Whereas both TiO_2 and V_2O_5 predominantly catalyse dehydration of isopropanol to propene, the surface complex gives about 25% dehydration and 75% dehydrogenation to acetone (*23*). While the former reaction is easily rationalized in terms of a proton-assisted elimination of water, the latter requires the addition of the isopropanol molecule at the OH bond across the V=O, with the formation of a V—O—C species. Internal electron movement then gives acetone and H_2. These reactions will be shown to be archetypal of those occurring during *o*-xylene oxidation. The conjunction of the acidic and oxidizing (i.e., H-accepting) functions in the V—OH and V=O bonds, respectively, accounts well for the unique catalytic properties of the V_2O_5/TiO_2 system.

In formulating a reaction mechanism, only four variants of the catalytic species are needed (Structures A–D in Scheme 1); these have vanadium oxidation states of 5, 4 and 3 as shown in the scheme, and three of the four are able to accommodate one or more bonds to atoms connected to the substituent groups on the aromatic ring, as shown by the broken lines. Hereafter the O atoms linking these species to the TiO_2 surface will be omitted for simplicity, as the breaking of V–O–Ti bonds is not envisaged. Only species A and D are assumed to be present at the outset; C is formed from A by reduction involving the organic reactants and is reoxidizable to A by molecular O_2. Ample amounts of O_2 and H_2O are present to allow the vertical transitions to take place freely: the mode of chemisorption of O_2 is not to be discussed in detail, but may involve species C. All the structures shown in Scheme 1 bear either an O atom or an OH group, or both, and are identified as those species which initiate unit reactions. We shall encounter additional species that are the products of such reactions and these may only have a bond linking the V atom directly or indirectly to the substituent C atom. It will usually be quite clear what has to be done to restore the initial structure of the active site. To describe the later stages of the reaction sequence, it will be necessary to invoke pairs of active sites having structures such as those shown in Scheme 1. No use is made of V–H bonds, and molecular H_2 is not suggested as a product.

Species A and B in Scheme 1 will show Brønsted acidity and Species D Lewis acidity. Both types of acid centre have been detected in calcined catalysts (*16, 21, 24, 25*), but under reaction conditions, where as noted above water is amply present, such V^{4+} species as are present (*24*) are expected to be predominantly in the hydrated form B. The presence of O_2 will ensure that the V^{4+} and V^{3+} concentrations remain low, so the net oxidation state of the V atoms will depend chiefly on the concentration of adsorbed radicals formed by reductive processes. Of the species depicted in Scheme 1, species A is considered to be the most abundant, and for these reasons, chemisorptive reactions of the *o*-xylene and of the intermediate products are represented



SCHEME 2. Simplified form of the "rake" mechanism based on five surface intermediates.

as involving the Brønsted acid centre A rather than either B or C.

A GENERAL OUTLINE OF THE TRANSFORMATION OF *o*-XYLENE TO PHTHALIC ANHYDRIDE

The sensible way to represent the reaction mechanism is as a "rake" comprising a series of adsorbed intermediates, each converted to the next by partial oxidation, and some if not all of which can desorb, if necessary by further chemical reaction, to give the observed gas-phase products. Scheme 2 illustrates the principle and resembles that given before (*6*), save that *o*-toluic acid is now included as an intermediate product. Routes to "polymer," carbon oxides, maleic anhydride, and other products are not included. It should be easily possible to evaluate the relative magnitudes of the unit rate constants that define a given pattern of product yields as a function of conversion, but this has apparently not been tried and will not be undertaken in this paper.

The chief purpose of the ensuing discussion is to try to identify probable structures for the adsorbed species involved and possible mechanisms for the various component reactions.

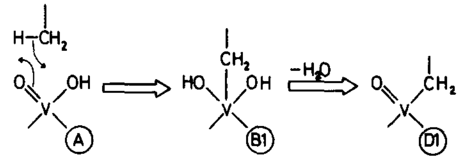
THE GROUND RULES

Every unit reaction is formulated as being radical rather than ionic in nature: although some of the bonds involved are undoubtedly highly polar, the radical representation is probably nearer the truth. All unit reactions of the organic molecules can then be classified into one of three types, viz., (i) H atom abstraction; (ii) O atom insertion (i.e., O═V—C≡ to V—O—C≡); and (iii) O atom rearrangement (i.e., V—O—C≡ to V—C═O). It soon becomes apparent that each unit step can be written in more than one way; those shown below have been selected as being the most likely, but may not be unique. The bases on which the selection has been made include (a) the use where possible of species A rather than D on the grounds that it is likely to be more abundant; (b) the use where possible of a single V species, rather than an adjacent pair; (c) inherent chemical probability; and (d) simplicity.

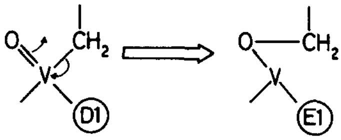
H ATOM ABSTRACTION

H atom abstraction occurs in one of three ways: (i) from a $-CH_3$ group in a molecule not already attached to the surface, as in the initial chemisorption of *o*-xylene; (ii) by breaking a C–H bond where the carbon atom is already attached to the surface; and (iii) from a $-CH_3$ group where the molecule is attached to the surface via the other substituent group.

The C–H bonds in the $-CH_3$ groups of *o*-xylene are weakened by the presence of the aromatic ring. The chemisorption of *o*-xylene is therefore most economically shown as in Scheme 3. In this and subsequent schemes, each structure is denoted by a letter identifying its form as shown in Scheme 1, and a number defining the nature of the bond(s) to the substituent C atom. Structure E has only the bond(s) to this C atom.



SCHEME 3



SCHEME 4

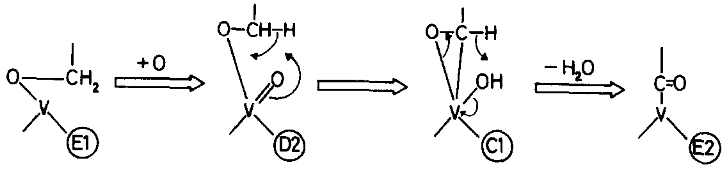
The same reaction will describe the chemisorption of the second $-CH_3$ group, where the other substituent group is attached to a neighbouring V atom (see below). A second method of H atom abstraction will also be considered later. Note that when the remainder of the organic molecule is not undergoing reaction, it is not shown in the reaction schemes.

There seems to be general agreement that the reaction is initiated by activation of the $-CH_3$ group, although both Miyata *et al.* (*7*) and van Hengstum *et al.* (*8*) prefer to depict this as a simultaneous reaction of two C–H bonds with V=O groups and the formation of a V—O—C bond with the aid of a third V=O group, involving the reduction of three V^{5+} species to V^{4+}. The likely separation between V=O groups on the surface is such as to render this mechanism improbable. Failure to recognise Structures B1 or D1 in FTIR may not be surprising: they may quickly undergo the next reaction step. There is the additional suggestion for the adsorption of toluene (*7*) that the aromatic ring may be π-bonded to a neighbouring Lewis acid centre (e.g., Structure D in Scheme 1). Even if this were to apply with *o*-xylene, it would have no effect on reactions at the substituents.

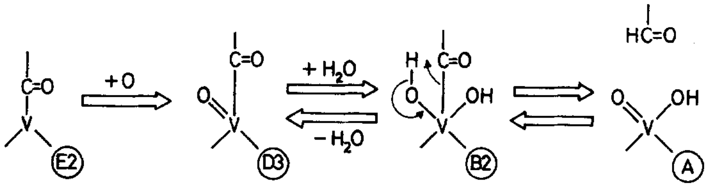
O ATOM INSERTION AND REARRANGEMENT

The next and very important step is to construct a C—O bond. This may occur by O atom insertion into the V—C bond of Structure D1 (Scheme 4). Rearranging this structure to make a $>C=O$ group necessitates the elimination of two H atoms; this might proceed by the sequence shown in Scheme 5. These reactions are regarded as essentially irreversible. The carbonyl species E2 then leads preferentially to *o*-tolualdehyde in the gas phase. Since it can apparently also readsorb readily and undergo further reaction, its desorption and readsorption must be formulated with due regard to microscopic reversibility (Scheme 6). *o*-Tolualdehyde therefore chemisorbs on what is taken to be the most abundant surface species. There is incidentally no evidence for the formation of the *o*-toluyl alcohol, from which we conclude that the V–O–CH_2– species E1 shown in Scheme 5 is not hydrolysed to V–OH + $HOCH_2$–: this is as expected for an ether-like bond.

The work of van Hengstum *et al.* (*8*) shows clearly that the adsorbed form of *o*-tolualdehyde does not possess a normal C–H bond, and so our representation of it as Structures B2 or D3 in Scheme 6 is consis-



SCHEME 5



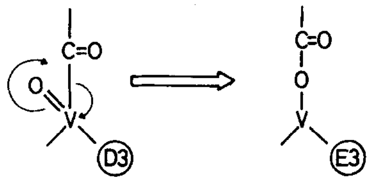
Scheme 6

tent with their observation. It has to be said that the significance of the partial bonds indicated by these authors by dashed or dotted lines is by no means clear. It seems preferable to employ normal, full covalent bond symbolism to represent any structures which may have some degree of stability.

The next step is to form a carboxy species and hence to provide a route to *o*-toluic acid in the gas phase. The carboxy species may be formed from the carbonyl species by a further O insertion step (Scheme 7). This then with low probability may form *o*-toluic acid in a manner analogous to that by which *o*-tolualdehyde is formed (Scheme 8). Structure E3 in these schemes is exactly as Structure D in the formulation of van Hengstum *et al.* (*8*), and it is accepted that it could equally be shown as a monodentate or bidentate ligand, as suggested by them, if this were more consonant with the infrared evidence. There is therefore no direct conflict between the proposals in this paper and the relevant experimental evidence available to date.

THE SEQUENCE OF EVENTS

This then completes the first phase of the reaction. There are very clear indications that one $-CH_3$ group must be fully oxidized to the $-COO\cdot$ stage (with the dot · representing bonding to the surface) before oxidation of the second $-CH_3$ starts. The dialdehyde is not observed as an intermediate product, and indeed it has been suggested (*6*) that premature oxidation of the second $-CH_3$ group (even just to the extent of the breaking of a C–H bond with consequent formation of a V–C bond) is likely to lead to deep oxidation. It appears that, once one $-CH_3$ group has achieved the $-COO\cdot$ stage, oxidation of the second may safely commence. It is doubtful whether progressive oxidation of the second $-CH_3$ group can occur at the same V atom as that to which the first fully oxidized substituent is already bonded: it is more likely that a second neighbouring atom is involved, and that the species participating at the start of the second phase is best represented as Structure A, E3 in Scheme 10. Reaction may then proceed on the second $-CH_3$ group as outlined above for the first.

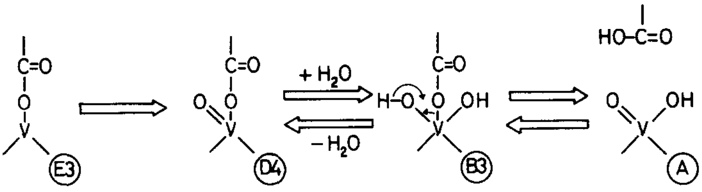


Scheme 7

THE FORMATION OF FIVE-MEMBERED RINGS

One of the strangest features of this reaction, and one that has been little commented on, is the ease with which the five-member ring products, viz., phthalide (PL) and PA, are formed. Ring closure by insertion of an O atom into a dicarbonyl species seems inherently improbable, and some alternative route to ring closure therefore needs to be found.

o-Phthalic acid readily undergoes ring closure by dehydration even at its melting point (210°C), and it is therefore possible that PA is formed after oxidation of both



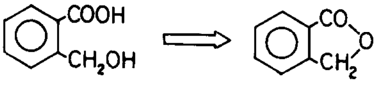
SCHEME 8

substituents to –COOH. Under reaction conditions, the dehydration would probably proceed so rapidly that the nonappearance of *o*-phthalic acid need not cause surprise. We will consider further below whether its actual formation is necessary or not. Arguing by analogy, PL could result from dehydration of another unobserved intermediate, 2-hydroxymethylbenzoic acid (Scheme 9). Ring closure by dehydration seems distinctly more plausible than invoking O atom insertion.

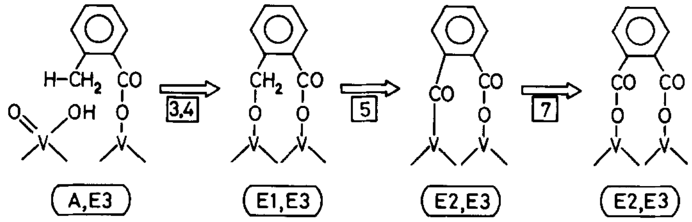
Returning to the reaction sequence, the reaction will continue as shown in Scheme 10: here the codes beneath each structure define the bonding about the V atoms, and the numerals by the arrows relate to the previous schemes, where details concerning the proposed reaction mechanisms may be sought. Now it is possible to envisage the structures E1, E3 and E3, E3 forming, respectively, PL and PA. This would, however, leave one of the V atoms in the 2+ oxidation state, a possibility ruled out by an admittedly arbitrary assumption. It is therefore worth exploring whether these structures might afford the cyclic products without the postulated noncyclic intermediates being completely desorbed from the surface. One possibility is illustrated in Scheme 11. The –OH groups attached to each V atoms are introduced to facilitate the elimination of H_2O and to maintain the oxidation state of the V atoms at a minimum of 3. These –OH groups could arise as shown in Scheme 12, *i* denoting any appopriate numeral. Cyclisation then proceeds through an adsorbed species tied to the surface at only one point (Scheme 11). The electron movements postulated closely resemble those that would describe ring closure in free *o*-phthalic acid, and exactly the same sequence applied to the structure E1, E3 above would account for the formation of PL. Two further remarks are in order. (i) An additional advantage of having a monoadsorbed species in the cyclisation step lies in its greater flexibility vis-à-vis its diadsorbed precursor; this may assist formation of the transition state. (ii) PL is an observed intermediate that can be converted to PA; reversal of the cyclisation, as depicted above for PA, to return it to the reaction sequence involves surface species (A and C) that are thought to be reasonably populous.

SOME FINAL CONSIDERATIONS

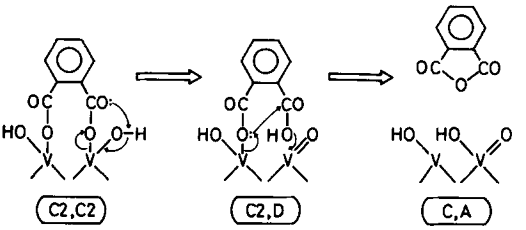
Maleic anhydride (MA) is a significant by-product at high conversion of *o*-xylene. It is usually thought to be formed from PA, but more probably it is formed from one of the last adsorbed intermediates in the reaction sequence. The critical step is likely to be the breaking of a C–H bond attached to the benzene ring, followed by ring opening of the latter. Once begun, the process goes to completion, that is, the four carbon atoms not involved in the anhydride ring or its precursor form carbon oxides: traces of citraconic anhydride (i.e., methyl-substituted MA) have, however, been reported.



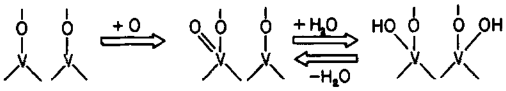
SCHEME 9



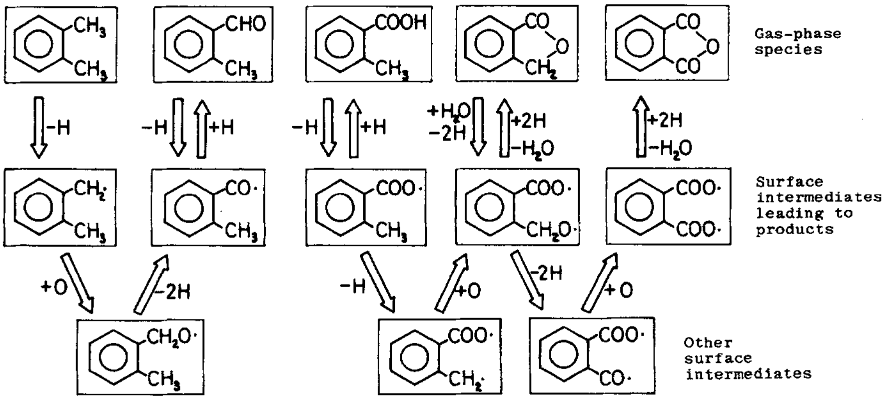
SCHEME 10



SCHEME 11



SCHEME 12



SCHEME 13. Reactions leading to observed C_8 products.

Comment was made earlier on the importance of understanding the mechanism of carbon oxide formation if positive steps are to be taken to suppress it. The reactant and each observable intermediate have at some time been implicated (*2*, *5*), and as just noted the overoxidation of PA to MA must afford further carbon oxides. Mention was made above of the suggestion (*6*) that chemisorption of *o*-xylene simultaneously through both $-CH_3$ groups might lead to a strongly adsorbed species that might ultimately (e.g., after polymerisation) suffer deep oxidation. A connection between the carbon imbalance and the formation of carbon oxides gave (*6*) some credence to this belief, but a quantitative analysis of the product concentrations as a function of conversion is needed to conform this idea. There are also strong indications that the nonselective process is associated, at least in part, with bare patches of TiO_2 surface (*4–7*, *12*).

In conclusion, the main outline of the proposed reaction scheme is shown in Scheme 13. However speculative the details of the various transformations may be, it seems inevitable that the reaction should follow a path similar to that shown. It is to be hoped that this theoretical analysis may stimulate further experimental work designed to unravel the course of this fascinating reaction.

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