Reactions Involving Electron Transfer at Semiconductor Surfaces

Part 12.—Nature and Origins of Photoactivity on Oxides of 3d Transition Metals for Elimination Reactions of Secondary Alcohols

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Activity for conversions of the vapours of propan-2-ol and butan-2-ol into products corresponding formally to elimination of H_2, H_2O or a $(C_\alpha-C_\beta)$ bond from the parent alcohol were compared for oxides of the 3d transition metals under thermal- and photo-activation. Use of a gas-chromatographic, continuous reactant-flow technique with f.i.d. detection favoured the detection of products corresponding to a large turnover per surface site (t.a.p.s.). Under these conditions photoenhancement of the $(-H_2)$ and $(C_\alpha-C_\beta)$ products at significant levels was detected only over ZnO and TiO_2 and in the presence of gaseous oxygen. Such photocatalytic activity, and the contrasting absence of photoactivity continuing to high turnover over oxides featuring cations with partially filled 3d levels, is attributed to predominance and persistence of an O^--type character and reactivity only for holes photogenerated in the diamagnetic ZnO and TiO_2 samples. Photoassisted reaction of alcohol with several oxides at t.a.p.s. $\simeq 1$, *i.e.* with the first monolayer of those oxides, could be observed using a more sensitive mass-spectrometric technique. This also revealed incorporation of oxygen-18 into acetone produced from propan-2-ol under these conditions, and the origins of this exchange at low t.a.p.s. are considered. Poisoning experiments employing a gas-chromatographic pulsed reactant technique at low t.a.p.s. provide evidence that photoassisted activity on ZnO invo ves photoinitiated one-electron transfer processes.

The differing types and degrees of activation attainable, respectively, by photoactivation and by thermal activation upon surfaces of powdered samples of high-purity ($\geqslant 99.99\%$) oxides of the iron-group transition metals are compared in this study using as probe molecules the secondary alcohols propan-2-ol and butan-2-ol admixed with O_2. The study is part of a programme of work on metal-oxide-catalysed elimination reactions of alcohols[1-3] which includes amongst its objectives the critical evaluation of possibilities that photoactivation may enable elimination reactions to be effected at lower temperatures and with greater selectivities than under conventional thermal activation. Realization of selective photocatalytic pathways based on such possibilities would have two requirements: (i) photoactivation of sites on the metal oxide should selectively activate them for one particular elimination reaction, as might for example occur if photoactivation were to drive dehydrogenation $(-H_2)$ along a pathway involving radical intermediates formed by photoinitiated one-electron transfer[4,5] at the metal-oxide surface, whereas dehydration $(-H_2O)$ was thermally activated and proceeded solely by classical Lewis acid–base electron-pair interactions;[6,7] (ii) in addition, conversion of alcohol to photoproducts on any photoactivated sites should be rapidly followed by removal of products from the sites, as might for example result at low temperatures *via* photodesorption of photoassisted products,[8] thereby making sites available for further conversions. This could allow high values of turnover accomplished per photoactivated site (t.a.p.s*.) even at low temperatures. With

respect to the latter point, our recent results on photoassisted oxygen-isotope exchange on zinc oxides at room temperature led to recognition of the possibility that one single-photon activation of a site involving photoinitiated localization of an electron thereon, could in favourable circumstances allow it to turn over many reaction events (*i.e.* t.a.p.s*. $\gg$ 1) before further photoactivation.[9] Possibilities for satisfying the favourable conditions necessary for attaining such multiplier effects upon t.a.p.s*. appear lower for alcohol–metal-oxide interfaces than for ($^{16}O_2 + {}^{18}O_2$) ZnO interfaces. Activation of adsorbed alcohol at interfaces between u.v.-illuminated ZnO or TiO_2 and electrolyte solutions has been reported to involve an initial localization of a photogenerated hole to yield a radical, followed by a secondary one-electron transfer process.[10] The overall effect of such processes, which lead to a doubling of the photocurrent upon addition of alcohol, has been dubbed 'current doubling'. Detection of the latter at illuminated alcohol–metal-oxide interfaces has been taken to indicate occurrence of photoinitiated one-hole-transfer events. Alcohol conversions emanating from such localization of photogenerated holes would be limited to t.a.p.s*. $\leqslant$ 2 per single-photon activation of a surface site. Unless products were desorbed from the active site and allowed it to be reactivated repeatedly, such processes would not satisfy a criterion suggested by Childs *et al.*[11] for true photocatalytic activity, *viz.* continuation unchanged up to t.a.p.s*. $\geqslant$ 10.

EXPERIMENTAL

It has been widely reported[1, 3, 11] (*a*) that activity of TiO_2 and ZnO for selective oxidation of alcohol vapours can readily be measured using gas-chromatographic procedures (with flame ionization detection) on the basis of the steady-state level of conversion to ($-H_2O$) or ($-H_2$) or (C_α–C_β) product in the exit gases from a continuous-flow microcatalytic reactor; and (*b*) that the presence of molecular oxygen is essential in the gas phase if a continuing photocatalytic conversion to ($-H_2$) *etc.* is to be achieved. We therefore adopted such procedures for initial comparisons of the extent to which the metal oxides listed in table 1 can activate alcohols to undergo elimination reactions under thermal- or photo-stimulation. The high-purity metal oxides ($\geqslant$ 99.99% purity w.r.t. metal) and operation of the gas-chromatography system in both the continuous flow and pulsed reactant modes were described previously in full.[3] In the present study, gaseous oxygen at $p(O_2) \approx$ 380 Torr† was premixed with the alcohol-vapour reactant, and surfaces of the powdered metal oxides were preoxidised by exposure to $p(O_2) \approx$ 380 Torr at the reaction temperature for several hours prior to introduction of oxygenated alcohol vapour. Photoactivation was achieved by exposure of the metal-oxide powder (spread as a thin layer on a fritted disc) to the output of a 125 W medium-pressure Hg arc lamp filtered through a Pyrex water-cooled jacket.

RESULTS AND DISCUSSION

PHOTOEFFECTS AT HIGH T.A.P.S*.

Results obtained with 20 Torr of propan-2-ol as the alcohol reactant, flowing together with argon and with 380 Torr of O_2 over the indicated metal oxides, are summarised in table 1, the second column of which lists any thermally assisted conversions detected at 350 K. At this relatively low temperature, thermal activation of the (alcohol + O_2)–metal-oxide interfaces in the dark was apparently too weak to bring about a significant level of elimination reactions during the short contact-time allowed by the flow procedure (except for MnO_2 surfaces, which yielded small but continuing activity for dehydrogenation at a rate of 1.2 μmol min^{-1} per 200 mg of MnO_2).

† 1 Torr $\equiv$ 101 325/760 Pa.

TABLE 1.—STEADY-STATE CATALYTIC ACTIVITIES OF METAL-OXIDE SURFACES FOR ELIMINATION REACTIONS FROM PROPAN-2-OL IN THE DARK AND UNDER U.V. ILLUMINATION

metal oxide (1)	surface area /m² g⁻¹ (2)	at 350 K, u.v. illumination		dark		at 475 K, u.v. illumination		
		$\Delta^*(C_\alpha{-}C_\beta)^a$ (3)	$\Delta^*(-H_2)^a$ (4)	$(-H_2)^b$ (5)	$(-H_2O)^b$ (6)	$\Delta^*(C_\alpha{-}C_\beta)^a$ (7)	$\Delta^*(-H_2)^a$ (8)	$\Delta^*(-H_8O)^a$ (9)
TiO_2^a	50	1.212	0.98	5.2	5.5	1.4943	1.9924	0.9962
$V_2O_5^{d,e}$	2.6	—	—	0.35	0.88	—	—	—
$Cr_2O_3^d$	55	—	(0.03)	3.2	0.19	—	—	—
MnO_2^d	27	—	(0.35)	2.7	2.6	—	—	—
$Fe_2O_3^d$	4.6	—	—	0.04	3.1	—	(0.046)	—
$Co_3O_4^d$	3.4	—	—	1.3	0.2	—	—	-0.3387
NiO^d	1.9	—	—	0.9	0.68	—	-(0.454)	-(0.265)
CuO^d	2.2	—	—	0.9	0.007	—	—	—
ZnO^f	4.1	0.14	0.04	0.3	0.30	1.225	—	0.147

[a] Dark rates expressed as μmol min⁻¹ per 200 mg sample; [b] photoenhancement expressed as μmol min⁻¹ per 200 mg sample; [c] Degussa (P-25); [d] Spex (99.99%); [e] rates for V_2O_5 are at 415 K; [f] NJZ-SP500.

Note: for the whole experiment: $p(O_2) = 380$ Torr; $p(ROH) = 20$ Torr; feed-gas flow rate = 40 cm³ min⁻¹, photon flux = 5×10^{16} s⁻¹ at wavelengths 300-800 nm.

At 350 K and in the absence of illumination none of the oxides caused detectable steady-state rates of conversion to acetaldehyde product, whose formation would formally require $(C_\alpha-C_\beta)$ bond cleavage. The third and fourth columns of table 1 summarise, under the headings $\Delta^*(C_\alpha-C_\beta)$ and $\Delta^*(-H_2)$, respectively, any new or enhanced activity for these processes detected whenever the interfaces were exposed to a flux of *ca.* 5×10^{16} photon s^{-1} at 350 K. The choice of 200 mg of oxide as the reference amount on which to base any differences between activity in the dark and under illumination was indicated by previous results[3] showing that the u.v. photons had access only to that amount of sample in the photocatalytic reactor. Unequivocal evidence for significant photoassisted production of acetaldehyde as a $(C_\alpha-C_\beta)$ photoproduct from propan-2-ol was obtained only over the diamagnetic oxides TiO_2 and ZnO, whose photoactivity at 350 K yielded acetone as a $(-H_2)$ photoproduct as well as acetaldehyde. These observations were reminiscent of the occurrence of parallel pathways to $(-H_2)$ and $(C_\alpha-C_\beta)$ products identified in the literature as electron-transfer-initiated processes in reactions of organometallic complexes with secondary alcohols.[12]

Results with butan-2-ol were qualitatively very similar to those with propan-2-ol and again gave unequivocal evidence of photoactivity at 350 K only for ZnO and TiO_2 samples. This contrasted sharply with the complete lack of any type of photoactivity detectable by this procedure at 350 K over V_2O_5, Cr_2O_3, Fe_2O_3, Co_3O_4, NiO or CuO towards either propan-2-ol or butan-2-ol in the presence of 380 Torr of O_2. Manganese oxide emerged (*cf.* table 1) as the only $3d$ oxide which exhibited both cations with partially filled d levels *and* a susceptibility towards the photoenhancement of dehydrogenation of propan-2-ol or butan-2-ol at significant levels. This interesting observation should be qualified at this stage by our feeling that increases of the magnitude shown for $\Delta^*(-H_2)$ in table 1 may not be sufficiently enhanced relative to the strongly temperature-dependent thermally assisted activity of this interface in the dark as to exclude minor *surface* heating by the flux of photons $(300 < \lambda/nm < 800)$ or photodesorption of poisons such as CO_2 as possible sources of $\Delta^*(-H_2)$ on manganese oxides. For these reasons the value of $\Delta^*(-H_2)$ for MnO_2 is bracketted in table 1. Similar reservations are attached to additional bracketted values, shown for $\Delta^*(-H_2)$ for Cr_2O_3 and Fe_2O_3 in table 1, not only because of their rather small absolute magnitude (see later results on photoreaction in the surface monolayer) but also because of their failure to disappear immediately when illumination is ended.

Details of the significant thermally activated dark activities of the metal oxides in table 1 towards propan-2-ol at 475 K in the absence of oxygen were recently presented elsewhere,[13] together with activation energies for the $(-H_2)$ and/or $(-H_2O)$ processes. In view of indications thereby received that the relative importance of differing pathways for thermally activated elimination reactions of the alcohol could vary strongly with temperature, it became apparent that reliable values of any differences between photoactivated and thermally activated catalytic activities at 475 K [*i.e.* $\Delta^*(-H_2)$, $\Delta^*(-H_2O)$ or $\Delta^*(C_\alpha-C_\beta)$] ideally would require: first, the determination at 475 K of the steady-state dark activity under selected pressures of alcohol and oxygen (*cf.* columns 5 and 6 of table 1); secondly, a determination of the extent to which illumination at 475 K altered this; and thirdly, a test of whether illumination changed the interface irreversibly by photolysis or photodesorption by checking whether the activity returned to its preillumination steady-state value upon ceasing illumination. Results from such a sequence of measurements with $p(ROH) = 20$ Torr and $p(O_2) = 380$ Torr are summarised in the last three columns of table 1. Dark activities for acetaldehyde production were furthermore below detection for all the

oxides studied, except for V_2O_5, MnO_2 and Cr_2O_3. For the latter pair of oxides at 475 K, the thermally assisted conversions corresponded to 3.5×10^{14} and 3.5×10^{15} (molecules of CH_3CHO produced) $m^{-2}\ s^{-1}$, respectively, and were not detectably enhanced by illumination. On the other hand, the significant enhancements of acetaldehyde product detected upon illumination of ZnO or TiO_2 at 475 K at the levels listed in the seventh column of table 1 confirm the existence of a photoinitiated pathway to CH_3CHO, which had likewise been evident on these diamagnetic oxides at 350 K in the presence of 380 Torr of O_2. Suggestions by other workers[14] that such pathways involve alkene formation, followed by oxidative scission of the newly formed C=C double bond, were examined by comparing dark and photoassisted rates of propene production at 475 K in the presence or absence of oxygen. For TiO_2 and ZnO in the dark, the introduction of O_2 at 380 Torr increased rather than decreased the steady-state conversion to propene and did not cause the appearance of detectable acetaldehyde product (thereby arguing against thermally assisted oxidative scission involving gas-phase O_2). For illuminated $(CH_3)_2CHOH$–TiO_2 interfaces the extent of photo-assisted conversions to $(-H_2)$, $(C_\alpha$—$C_\beta)$, and $(-H_2O)$ products were first measured in the presence of 380 Torr of O_2, which was then replaced by 380 Torr of argon carrier gas. Such removal of O_2 caused the $(C_\alpha$—$C_\beta)$ conversion to decline rapidly almost to zero, whilst the small conversion to propene increased slightly. Upon reintroducing 380 Torr of O_2 into the gas flow over the illuminated interface the conversions to $(C_\alpha$—$C_\beta)$ and $(-H_2)$ products increased to their original values, whilst propene declined abruptly at first, but then re-approached the earlier value with oxygenated reactant. In addition to demonstrating the oxygen-reversible nature of the photo-activity, the results established that the changes in $(-H_2)$ and $(C_\alpha$—$C_\beta)$ were an order of magnitude greater than the small and opposite changes in $(-H_2O)$ product, thereby indicating that the photoassisted oxidation of propene by gas-phase O_2 could not be responsible for all the $(C_\alpha$—$C_\beta)$ yield. The results do not, however, exclude photo-activation of surface oxygen. Finally, a comparison was made of the magnitude of any changes in $(C_\alpha$—$C_\beta)$ and $(-H_2)$ and $(-H_2O)$ yields in the presence of a continuous flow of O_2 whenever illumination was commenced. For zinc oxide at 475 K the observed increase in $\Delta^*(C_\alpha$—$C_\beta)$ was an order of magnitude greater than the decrease, $\Delta^*(-H_2O)$, in propene caused by commencing illumination with O_2 present. The cumulative effect of these observations provides evidence for an alternative photo-assisted pathway to $(C_\alpha$—$C_\beta)$ involving neither gaseous O_2 nor gas-phase propene as an intermediate. One final point to be noted from the values in column 7 is the confirmation they provide that only for the diamagnetic oxides TiO_2 and ZnO did the data provide unequivocal evidence for $(C_\alpha$—$C_\beta)$-type photoactivity, there being no detectable photoenhancement of acetaldehyde product over any of the oxides featuring cations with partially filled $3d$ levels.

A working hypothesis capable of explaining the observed restriction to ZnO and TiO_2 of $(C_\alpha$—$C_\beta)$ photoactivity among the $3d$ metal oxides investigated here can be developed from the view put forward in our earlier publications[1-3] that photoactivity requires the close coupling of two processes, $viz.$ (i) photoinitiated localization of a hole upon a surface oxide anion and (ii) reaction of the resultant O^--type surface site with alcohol species arriving thereon either from the gas phase or by migration across the adsorbate layer. Those earlier interpretations recognised not only the selective activity of O^--type species towards secondary and primary alcohols, but also the difficulty of distinguishing this from reactivity of the protonated analogues, $i.e.$ surface hydroxy radicals. Similar uncertainties persist in the present work concerning O^- and OH, since the latter may result either from photoinitiated localization of holes on pre-existing OH^- surface groups or by proton-transfer to O^- from alcohol. For convenience the

following interpretation is given in terms of O^--type intermediates, but OH is not excluded. Earlier workers reported that the substitution of Ti^{4+} cations in oxides by cations with incomplete $3d$ shells inhibited photoinduced charge transfer at the surface.[15] In attempting to explain the similar sharp decline in photocatalytic activity here reported when switching from ZnO or TiO_2 to metal oxides with incomplete $3d$ shells, the following aspects of points (i) and (ii) merit particular attention: the relative ease with which photons may generate O^--type surface species, and the relative susceptibility of any such photogenerated O^--species to rapid degradation into other surface species lacking the specific reactivity of O^- towards alcohols. Since recent studies on TiO_2[16] and ZnO[17, 18] single crystals show an absence of states in the band-gap, photogenerated holes in TiO_2 and ZnO relate predominantly to energy bands derived from $2p$ orbitals of the oxygen-anion sublattice, and correspond to itinerant O^--type electronic arrangements. (This can apply whether the holes are free or are coupled as hole–electron pairs.) However, for the other oxides examined in this study the wavelengths present in the photon flux used ($300 \geqslant \lambda/\text{nm} \leqslant 800$) were more likely to result in the photogeneration of excited states relating to orbitals derived from the cations[19] than to O^--type species (e.g. in Fe_2O_3 photons of energy ca. 2.0 eV can produce Fe^{4+}–Fe^{2+} cation pairs, but charge-transfer from O^{2-} to Fe^{3+} requires 5.7 eV). Even if photoexcitation of some of the other oxides initially produced O^--type configurations, rapid trapping of such holes by occupied states lying in the band-gap and derived from $3d$ levels of the variable-valency cations should rapidly convert the holes to electronic configurations differing from O^- and lacking its selective reactivity towards alcohols.

PHOTOEFFECTS AT LOW T.A.P.S*.

In an effort to achieve higher sensitivity for detection of photoinitiated oxidation of propan-2-ol over the various metal oxides, some experiments were carried out under low pressures (0.1 Torr) of $^{18}O_2$ and $(CH_3)_2CHOH$ and with mass-spectrometric (m.s.) rather than gas-chromatographic (g.c.) detection. Such experiments demonstrated an unmistakable photoassisted rate of oxidation of alcohol at room temperature whenever Cr_2O_3(red), Fe_2O_3(red), ZnO and TiO_2 were simultaneously exposed to u.v. illumination, alcohol vapour and $^{18}O_2$. Furthermore, the acetone photoproduct from these systems was found to be enriched to $30 \pm 10\%$ in oxygen-18. The apparent contradiction between this unequivocal m.s. evidence of photoassisted ($-H_2$) reaction over Cr_2O_3 and Fe_2O_3 and the absence of any such evidence from g.c. studies is believed to have its origins in the differing experimental conditions for the two sets of experiments. Thus the continuous-flow g.c. experiments were weighted in favour of the detection of photoproducts arising from truly photocatalytic processes i.e. those capable of yielding photoproducts equivalent to a high turnover per surface site. The m.s. experiments under low pressures in a static reactor were, on the other hand, weighted in favour of the detection of photoproducts arising from photoinitiated reactions with surface monolayers of the metal oxides. Similar observations of photoassisted ($-H_2$) reaction to sub-monolayer equivalence have previously been observed by infrared spectroscopy for propan-2-ol on ZnO and Al_2O_3.[20] Such observations need not imply a photocatalytic process continuing to high t.a.p.s*. Thus the former could proceed via direct photoactivation of surface ions and a once-only reaction with alcohol$+O_2$, whereas the latter imply hole formation in sub-surface regions and repeated activation of surface sites following their migration to the surface. Blank experiments made by introducing an admixture of $^{18}O_2 + (CH_3)_2CO$ over the metal-oxide surfaces followed by illumination established that the observed extents of incorporation of oxyen-18 into the acetone product from propan-2-ol could not

have arisen by either dark or photoassisted oxygen isotope exchange between $^{18}O_2$ and acetone after its production. Furthermore, the yield of acetone appeared too large in some cases (such as Fe_2O_3, which yielded no detectable propene in the dark or under illumination in the absence of O_2) to be explicable in full in terms of any photoassisted attack by $^{18}O_2$ upon an alkene intermediate formed by a $(-H_2O)$ process. Consequently, the probable existence of some other photoassisted pathway to $(CH_3)_2C^{18}O$ in the presence of $^{18}O_2(g)$ could be inferred from these low-turnover results.

Experiments were made to test the possibility that this alternative mechanism might involve, initially, the photoassisted formation of $H_2^{18}O$ as in eqn ($1a$) (which itself is a multistep process involving O^-)

$$(CH_3)_2CH^{16}OH + \tfrac{1}{2}{}^{18}O_2 \xrightarrow[MO]{h\nu} (CH_3)_2C^{16}O + H_2^{18}O \qquad (1a)$$
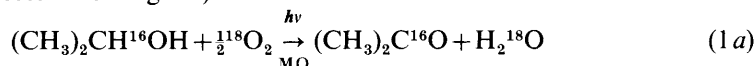
and that oxygen-18 subsequently became scrambled between acetone and water *via* ($1b$)

$$(CH_3)_2C^{16}O + H_2^{18}O \rightleftharpoons (CH_3)_2C^{18}O + H_2^{16}O \qquad (1b)$$
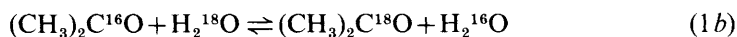
in the photoactivated reaction monolayer. In order to test this alternative mechanism, rates of oxygen-18 exchange were monitored when $(CH_3)_2C^{16}O$ plus water enriched to 38% in oxygen-18 were introduced over metal oxide samples at room temperature. The samples had been pretreated *in vacuo* or in oxygen in a fashion identical to those employed to study alcohol reactions, but they had not been exposed to alcohol. Upon illumination of these $[(CH_3)_2C^{16}O + H_2^{18}O]$–metal-oxide interfaces by the same photon flux as employed to study alcohol $+ {}^{18}O_2$ systems, the fast scrambling of oxygen-18 between acetone and H_2O was observed over ZnO and Cr_2O_3. Our experimental observations that photodehydrogenation of propan-2-ol to acetone was always accompanied by ^{18}O-incorporation in low-turnover conditions can thus be accounted for by an important role being played by a mechanism involving reactions ($1a$) and ($1b$). Furthermore, the importance of reactions ($1a$) plus ($1b$) also allows a reinterpretation of our earlier observations[2] on the complete loss of the $-{}^{18}OH$ label from 2-methylpropan-2-ol when converted to acetone upon illumination over preoxidised TiO_2 in the presence of $^{18}O_2$. Process ($1a$) in those conditions would lead to the loss of the ^{18}O label from acetone *after its formation* from 2-methylpropan-2-ol by photoassisted $(C_\alpha - C_\beta)$ bond cleavage.

In the particular instance of zinc oxide, some support for the model just summarised for photoactivity was derived earlier from demonstrations that creation of additional O^--type surface species (from $N_2O + e^- \rightarrow N_2 + O^-$) enhanced elimination reactions at (alcohol $+ N_2O$)–ZnO interfaces under illumination.[21] Conversely, inhibiting effects upon ZnO photoactivity were to be expected from incorporation of hole-trapping species capable either of reacting more rapidly than alcohol with O^--type holes or of directly capturing photogenerated holes more efficiently than surface O^{2-} species. Surface species capable of promoting hole–electron recombination may also lower $[O^-]$. The following data describe *inhibition* of ZnO photoactivity by species selected for their likely ability to affect $[O^-]$ by one-electron-transfer events at the surface. In this context pyrene and tetracyanoethylene (TCNE) were selected as adsorbates likely to interfere with photoactivation of O^{2-} *via* one-hole-transfer interactions. The g.c. technique was modified[3] to allow for: (i) the introduction of individual pulses of alcohol vapour plus oxygen over a clean, illuminated ZnO surface in order to characterise its photoactivity towards several successive pulses; and (ii) the adsorption of pyrene or TCNE or other adsorbates onto the ZnO surfaces followed by characterization of the photoactivity of these 'poisoned' ZnO surfaces towards successive pulses of $[(CH_3)_2CHOH + O_2]$. Fig. $1(a)$ illustrates the strongly inhibiting
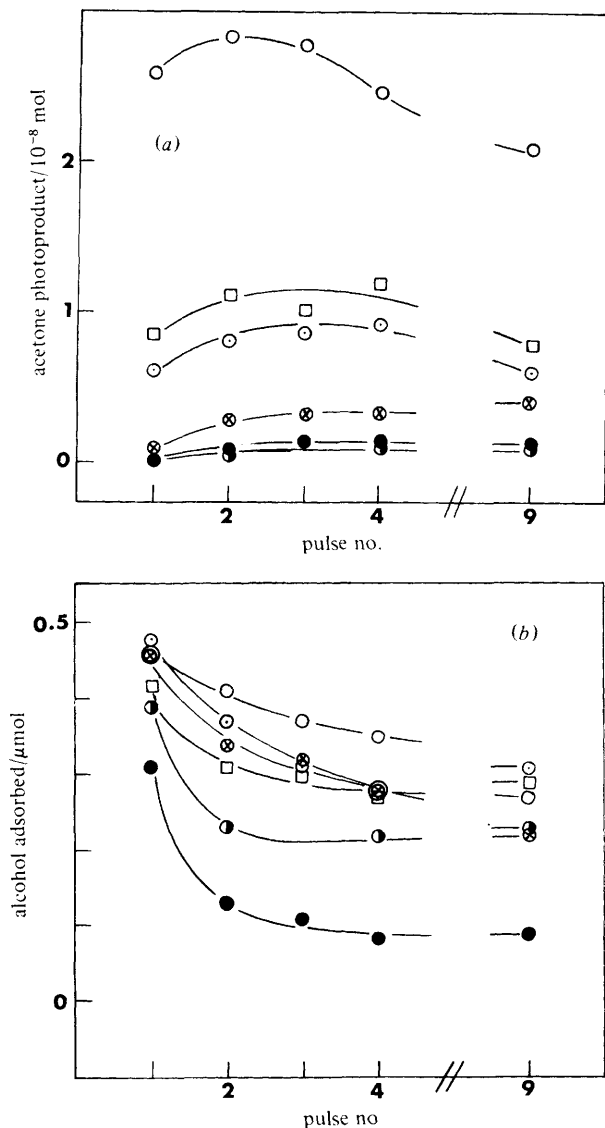
FIG. 1.—(a) Amounts of acetone produced from pulses of standard alcohol + oxygen mixtures passed over ZnO samples pretreated with ●, TCNE vapour; ◑, TCNE from benzene solution; ⊗, pyrene vapour; ⊙, pyrene from benzene solution and □, benzene. The symbol ○ represents measurements made with ZnO exposed only to (CH₃)₂CHOH as adsorbate. (b) Effects of: ●, TCNE vapour; ◑, TCNE from benzene solution; ⊗, pyrene vapour; ⊙, pyrene from benzene solution and, □, benzene preadsorbed on to ZnO on the extent of subsequent propan-2-ol adsorption from standard reactant pulses fed to the reactor at 35 min intervals. ○, Measurements made with a ZnO sample exposed only to alcohol adsorbate.

influence of preadsorbed pyrene or TCNE upon the rate of production of acetone over the illuminated ZnO surfaces, with comparable large decreases resulting from the preadsorption of pyrene from its vapour and of TCNE from its vapour or from benzene solution. Table 2 summarises, in the form of percentage activities of the poisoned surfaces relative to activity over an illuminated clean ZnO control, these

TABLE 2.—RELATIVE ACTIVITIES OF CLEAN AND POISONED $(CH_3)_2CHOH$–ZnO INTERFACES FOR THE INDICATED *PHOTOASSISTED PROCESSES AT 350 K[a] AND FOR ALCOHOL ADSORPTION IN THE DARK[b]

poison	$[-(H_2)^*]^c$ (%)	$[-(C_\alpha—C_\beta)^*]^d$ (%)	$[-(H_2O)^*]^e$ (%)	$[(CH_3)_2CHOH(ads.)]$ (%)	
				pulse 1	other
none	100	100	100	100	—
pyrene$_{(v)}$	10	32	5	95	80 ± 10
TCNE$_{(v)}$	< 5	5	0	40	40
TCNE					
Δ (ex. C_6H_6)	< 5	5	0	75	—
$CH_3COOH_{(v)}$	0	0	0	0	0
C_6H_5OH	0	14	8	0	0
$C_6H_5NH_2$	20	39	30	100	60 ± 20
anisole	20	47	10	100	60 ± 20

[a] Photoactivities assessed from the extent of conversion averaged over the first four reactant pulses of $[(CH_3)_2CHOH + O_2]$ passed over the illuminated ZnO surface at 350 K; [b] extent of adsorption assessed from amount of alcohol retained by ZnO from pulse 1 of alcohol or from other pulses (see text); [c] photodehydrogenation activity expressed as percentage of the higher continuing activity noted over a clean ZnO sample in similar conditions, viz. [d] photoassisted $(C_\alpha—C_\beta)$ bond cleavage expressed relative to rate of 4.4×10^{-9} mol CH_3CHO per min over clean ZnO or, [e] photodehydration expressed relative to rate of 4×10^{-10} mol C_3H_6 per min over clean ZnO.

inhibiting effects upon $(-H_2)$-type activity and also upon $(-H_2O)^*$ and $(C_\alpha—C_\beta)$ activities at the illuminated interfaces. Activities in each case were the average of the first four reactant pulses. Whilst those data for pyrene and TCNE adsorbates do show inhibiting effects which could be consistent with the interference of these adsorbates in one-electron-transfer processes, other data in table 2 for the effects of other classes of adsorbates demonstrate that other modes of action of the adsorbates should also be taken into account. Thus acidic preadsorbates such as acetic acid or phenol, which may interact with the surface as Brönsted or Lewis acids, may be seen from table 2 to have caused strong inhibition. However, the probable method of interference of those acidic preadsorbates could be shown, by appropriate use of the reactant pulse technique,[13] to be via inhibition of irreversible propan-2-ol adsorption [cf. fig. 1(b)]. Such effectively complete inhibition of alcohol adsorption by these acidic preadsorbates may be contrasted with effects of the one-electron-transfer preadsorbates upon alcohol adsorption. The levels to which irreversible propan-2-ol adsorption was reduced by preadsorption of TCNE (40%), or of pyrene (95%), would be quite insufficient (if only Langmuir-type adsorption processes occurred) to explain the much larger percentage inhibitions those preadsorbates exerted on photoactivity (cf. table 2). Basic preadsorbates, such as pyridine or anisole, which may interact with the ZnO surface as Brönsted or Lewis bases, were notably less effective than acidic adsorbates or TCNE in inhibiting photoactivity towards propan-2-ol or adsorptive capacity (cf. table 2). However, our additional observations of an absence of any significant inhibiting effect upon alcohol adsorption in the *first* pulse following exposure to the basic adsorbates, and the contrasting evidence for some inhibition of alcohol adsorption in subsequent pulses, points towards more complicated surface interactions in these cases (e.g. possibly a base-catalysed conversion of alcohol with an associated induction period).

Further work will be necessary if these more complex interactions involving bases are to be understood. However, the present results with likely one-electron-transfer adsorbates provide some new indirect support for the involvement of one-electron-transfer processes in the photoactivity of $[(CH_3)_2CHOH + O_2] - ZnO^*$. This in turn is consistent with the view put forward here that the especially high and often observed photoactivity of ZnO (and TiO_2) may be understood in terms of persistent O^--type character of photogenerated holes made possible by the absence of occupied states related to d orbitals in the band-gap.

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