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UNIVERSITY COLL CORK (IRELAND) DEPT OF CHEMISTRY
ENERGY MIGRATION INVOLVING IRRADIATED SOLIDS.(U)
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February 28, 1977

FINAL SCIENTIFIC REPORT

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ENERGY MIGRATION INVOLVING IRRADIATED SOLIDS

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Professor Joseph Cunningham,
University College Cork,
Ireland.



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20. Abstract Results are presented which point to surface sites involving O ₂ ions and/or hydroxyls as important locations for transfer of energy via radiationless process between uv-illuminated metal oxides and probe molecules adsorbed on their surfaces. Attempted passivation of the surfaces by treatment with water vapor enhanced rather than decreased, the extent of interaction between irradiated solid and various probe molecules, including nitrous oxide or methyl halides as electron-accepting probe molecules or C ₂ D ₅ OD as an electron donating probe molecule. ↗		

TECHNICAL SUMMARY

The research carried out under this short low-cost grant mainly represents an extension of a research effort previously funded under AFOSR-71-2148E. Since the Interim and Final Scientific Reports of that preceding grant provide a detailed account of the extensive publications and scientific communications arising from earlier phases of this research, such information is not repeated here, but the earlier reports should be referred to for an overall view of this research effort. In this extension of that research effort experiments have been designed and carried out to examine the exact nature of sites on the surface of irradiated solids which facilitate the transfer of radiation energy to gaseous 'probe' molecules present over the irradiated solids. In line with the agreed statement of work, these studies have included investigations of zinc oxide, magnesium oxide and titanium oxide as irradiated solid substrates; whilst nitrous oxide and alcohols have been used as gaseous probe molecules. This report includes a preprint of a paper describing results of such studies and entitled:

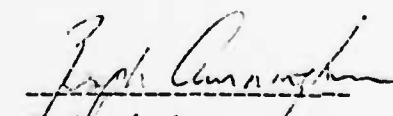
"Reactions Involving Electron Transfer at Semiconducting Surfaces, Part VII. Interactions of Nitrous Oxide and C₂-C₄ alcohols on ZnO and TiO₂ at Room Temperature".

That paper has been submitted for publication and it details evidence to support the conclusion that, for dehydroxylated ZnO or TiO₂ surfaces, the formation of O⁻-type surface intermediates and their subsequent reactions with adsorbed probe molecules (such as aliphatic alcohols) represent a sequence of radiationless processes which effectively convert energy absorbed from incident UV radiation into chemical changes in the adsorbed probe molecules. The preprint also demonstrates that attempted "passivation" of the ZnO and TiO₂ surfaces by treatment with water vapour at 623 K did not affect the reactivity of the dark or uv-illuminated TiO₂ surfaces but did markedly increase the activity of ZnO surfaces for dissociation of nitrous oxide both in the dark and

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and additionally under UV-illumination. Although not reported in the preprint, it has also been found that such attempted passivation of MgO surfaces increased their photocatalytic activity for N₂O dissociation, but did so only for photons with $\lambda > 254$ nm. These results upon attempted passivation of ZnO, TiO₂ and MgO surfaces strongly suggest: (i) that surface locations involving a "dangling" surface hydroxyl (which are not known to form on TiO₂ in our conditions) can act as effective sites for transfer of electrons from ZnO or MgO; (ii) that for semiconducting substrates such as Zinc oxides with significant densities (10^{14} - 10^{18} cm⁻³) of electrons already in the conduction band at room temperature in the absence of uv-illumination, these sites involving dangling hydroxyls allow electron-transfer to probe molecules in the dark; (iii) for insulating substrates such as MgO which lack conduction band electrons, electron transfer becomes possible from sites involving dangling hydroxyls wherever they interact with surface excitons.

The validity of these ideas has been further tested by experiments with methyl halides CH₃Cl and CD₃I, which were selected because, like N₂O, they were reported to be reactive towards electrons but not towards the radical species OH or H. A total absence of photocatalysed dissociation of the methyl halides was noted over uv-illuminated TiO₂ surfaces, which again appeared consistent with absence of hydroxyl-containing surface sites for electron transfer on TiO₂. On dehydroxylated MgO surfaces photocatalysed dissociation of the methyl halides occurred to methane (80%) plus ethane (20%) but the same surface, after rehydroxylation produced only methane product. The results were consistent with the idea detailed above that presence of surface hydroxyls facilitate reaction of surface excitons with the electron-trapping probe molecules. An important role for surface sites involving hydroxyls has thus been established in energy transfer from irradiated ZnO and MgO to N₂O and methyl halide probe molecules.


J. Cunningham
Principal Investigator

"Reactions Involving Electron Transfer at Semiconducting Surfaces¹:
VII, Interactions of nitrous oxide and C₂ -C₄ alcohols on ZnO and TiO₂
at Room Temperature"

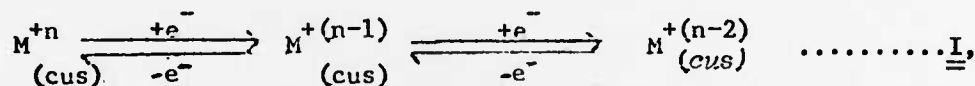
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Department of Chemistry, University College, Cork. Ireland.

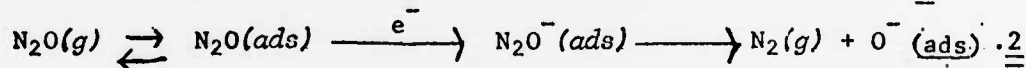
ABSTRACT

Trace amounts of dehydration product desorbed from ZnO or TiO₂ surfaces upon exposure to t-butanol at room temperature whereas alkene products from dehydration of ethanol or isopropanol were only detected following thermally assisted desorption. Dehydration product was not enhanced by nitrous oxide which did, however, increase extent of alcohol dehydrogenation and yield additional nitrogen product from N₂O dissociation. Extent of dehydrogenation and of additional nitrogen formation correlated well with reported reactivity of alcohols towards O⁻ fragments, which are here attributed to N₂O dissociation. Illuminating the Alcohol/Metal Oxide interfaces with photons at 254 nm in a dynamic system with on-line mass spectrometric analysis showed that, with N₂O present, illumination further enhanced dehydrogenation and nitrogen formation. Results are consistent with an important role for coordinatively unsaturated oxygen ion sites in dehydrogenation and with their conversion to surface O⁻ species by hole trapping. Dehydration was largely unaffected by uv-illumination whilst presence of N₂O influenced it in opposite sense to dehydrogenation. Sites active in dehydration are tentatively identified as Lewis acid type metal ion sites on the surfaces.

Earlier papers in this series considered electron-transfer from semiconducting ZnO or TiO₂ to adsorbed molecules, both in terms of *indirect* electron transfer based on collective-electron Band Theory models, and in terms of *direct* electron transfer from isolated electron-donating sites on the ZnO or TiO₂ surfaces^{2,5}. Metal-ion sites possessing lower-than-usual charge and higher-than-usual degree of coordinative unsaturation i.e. $M_{(cus)}^{(n-1)+}$, were identified as sites effective in direct electron-transfer to adsorbed N₂O or O₂. Examples were Ti³⁺ ions adjacent to oxygen vacancies on the surface⁵ of TiO₂ and interstitial Zn⁺_Δ on the surface^{2,3} of ZnO. It was recognised that if equilibration of electrons between such sites and the conduction band of these n-type semiconducting solids occurred rapidly via. I,



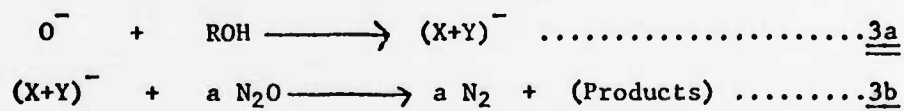
then the electron-donating power of these surface metal-ion sites should vary with position of the Fermi level. This prediction was confirmed^{2,5} by careful measurement of the very small amounts of nitrogen product evolved from surfaces of various zinc oxides by dissociative-electron-attachment to nitrous oxide at room temperature according to 2,



Other lines of evidence have also indicated electron exchange between bulk and surface locations of zinc oxides^{6,7} but evidence has been lacking for corresponding exchange processes in TiO₂. Surfaces of TiO₂ powders have, however, been shown to donate^{8,9,10} or accept^{11,12} electrons from adsorbed organic molecules in certain conditions.

The present work extends to aliphatic alcohols our approach of utilising room-temperature reaction of surfaces with appropriate probe

molecules as a means of assessing number and nature of highly active surface sites. This extension of the approach was prompted by, and was designed to test, the following ideas advanced by previous workers in relation to surface activity for dehydrogenation and dehydration of aliphatic alcohols: *firstly*, the idea that primary and secondary alcohols are good reagents for electronic holes at surfaces of ZnO, either through direct interaction^{1,3,14} or after hole capture by OH^{15,16}. The validity of these suggestions was of particular interest since, if correct, they would establish that alcohols could be used as hole-probes in similar manner to that already demonstrated for N₂O as an electron-probe in examining charge-localization at these semiconductor surfaces. Since concentrations of surface-localised holes were expected to be low for our n-type ZnO and TiO₂ samples in the dark at room temperature, present experimental tests of these suggestions include an examination of the interactions of alcohols with uv-illuminated samples having large concentrations of photogenerated holes. Such electronic holes in an array of lattice O²⁻ ions should possess some of the characteristics of O⁻ species⁷; *Secondly*, the idea that O⁻ exhibits selective reactivity towards primary and secondary, but not tertiary, alcohols, as previously postulated by Warman^{1,7,18}. Warman further suggested that, when N₂O is used as the source of O⁻ species, secondary reactions 3a and 3b occur in the presence of primary or secondary alcohols and produce additional dissociation of N₂O.



Insufficient information prevented identification of the ionic intermediates, (X+Y)⁻, in the gas-phase reactions studied by Warman. However,

it was hoped that examination of analagous reactions on ZnO and TiO₂ surfaces in the present study would reveal surface processes similar to 3a and 3b and might clarify the nature of ionic intermediates and products on the metal oxide surfaces.

EXPERIMENTAL

Materials: Powdered, high-purity metal oxides were identical to the ZnO (SP500) and TiO₂ (Rutile MR-128) used in previous studies²⁻⁵ and were obtained by courtesy of New Jersey Zinc Co. Thin polycrystalline layers on quartz substrates were prepared and activated at 623K as previously described. Alcohols were Analar reagent grade dried over freshly dehydrated molecular sieve and purified by trap-to-trap distillations, except for anhydrous C₂D₅OD or "C₂D₅OD + 5% D₂O" which were used as supplied by Stohler Isotopes. High purity nitrous oxide, BOC Grade X, was used as obtained.

Procedures for non-illuminated samples: Observations on the gas phase above non-illuminated samples were made with the closed quartz reactor and associated greaseless high-vacuum system depicted in Fig.1a, wherein products were detected from room temperature interactions of alcohols and/or nitrous oxide with metal oxides previously activated for 16 hr. in vacuo at 623K. Products non-condensable (n.c.) at 77K were measured with Pirani or Ionization gauges and identified with a CEC type 21-620A mass spectrometer during periodic freezing-out of reactants into a trap at 77K. Since such measurements could only monitor growth of those products which desorbed from the catalyst surface at room temperature, a sequence of "desorption/pressure - measurement/mass analysis" was carried out with the system shown in Fig.1a while the catalyst, which had been exposed to

Alcohol and/or nitrous oxide at room temperature, was heated in vacuo by 50° increments to 623K. Electron spin resonance spectra were taken with a Decca X-1 spectrometer or a Varian model-, upon TiO_2 samples to which alcohol was admitted as a vapour at room temperature.

Photoassisted Surface Reactions: Interfaces between Metal Oxide sample and Alcohol or (Alcohol+N₂O), which had completed the fast 'dark-reaction' characteristic of initial 0.5h contact times⁵, were then illuminated by the low intensity output of a 15-watt low pressure Hg-arc lamp with emission mainly at 254 nm. Lamp configuration relative to the sample within an MgO-coated cavity was arranged to limit any possible surface heating effect to <5° temperature rise which, if induced thermally, did not significantly disturb the dark-equilibrated behaviour. Growth of any product which desorbed into the gas-phase at room temperature was followed and analysed over periods of illumination up to 6 hr. Photon flux at the sample position was determined by calibration with potassium ferrioxalate actinometer. Results obtained at illuminated interfaces are indicated by use of an asterisk e.g. N₂O/ ZnO^* or $\text{C}_2\text{H}_5\text{OH}/\text{TiO}_2^*$. Photoassisted products were monitored *either* in the same system as for dark reaction (see Fig. 1a) *or* more directly in the dynamic flow system depicted in Fig. 1b. In this latter system, gases emerging from the reactor at pressures ca. 10^{-4} N m^{-2} entered into the ion source of a Micromass 6 mass analyser located 15 cm from the catalyst sample via. a high conductance path. Photoassisted changes in composition of the gas flow could thus be very rapidly detected and monitored.

RESULTS AND DISCUSSION

Section I: Formation and Desorption of Products in static reactors.

I.1. Nitrogen product from N_2O/ZnO and $(N_2O + Alcohol)/ZnO$ interfaces at room temperature:

Figure 2A(i) illustrates the rapid growth of gaseous product non-condensable at 77K which occurred during the first hour of contact at room temperature between freshly activated ZnO and nitrous oxide. Plot (i) of Fig. 2B demonstrates that formation of noncondensable product over the same ZnO surface in the dark at room temperature was slightly reduced when t-butanol was premixed with N_2O prior to contacting the freshly activated surface. Plots (ii) of Fig. 2A and 2B demonstrate, however, that the limiting yield of noncondensable product, $V(N_2)_{lim}$ as observed at room-temperature contact times >60 min, was greatly enhanced when either ethanol or isopropanol was premixed with N_2O in 1:1 mole ratio and simultaneously contacted with the metal oxide. Mass spectrometric analysis of the noncondensable product established that it was $>98\%$ nitrogen and that no nitric oxide or oxygen was detectable. Empirical kinetic analysis showed that the increase in nitrogen product, $V(N_2)_t$ detected after dark contact time t , obeyed the first-order type expression,

$$\log \left(\frac{V(N_2)_{lim}}{V(N_2)_{lim} - V(N_2)_t} \right) = k_d t \quad (4),$$

for contact times 5 - 30 mins. Table I summarises the values of $V(N_2)_{lim}$ and k_d which gave the "best fit" of data to this expression. These data point to two significant differences between the influence of tertiary as distinct from primary or secondary alcohol at the N_2O/ZnO interface:

(a) Nett nitrogen product formation from nitrous oxide at contact times

TABLE I

Limiting yields of Nitrogen Produced and desorbed over ZnO at room temperature

SYSTEM	$P_0(P_{\text{React}})$ N_m	$V(N_2)_{\text{Lim}}$ $\text{mls}/\text{m}^2 \times 10^{-5}$	$t_{\frac{1}{2}}$ (Min)	θ_0	k_d (Min^{-1})
N_2O/ZnO	45.0	4.16	8.1	0.011	8.6×10^{-2}
$N_2O + C_2H_5OH/ZnO$	45.0 (each)	7.73	7.7	0.019	9.0×10^{-2}
$N_2O + (CH_3)_2CHOH/ZnO$	45.0 (each)	7.76	8.4	0.019	8.3×10^{-2}
$N_2O + (CH_3)_3COH/ZnO$	45.0 (each)	3.53	4.1	0.009	16.9×10^{-2}

>1 hr., $V(N_2)_{lim}$, was approximately doubled by premixing ethanol or isopropanol with the nitrous oxide admitted to the freshly activated ZnO surface; whereas admixture of t-butanol slightly reduced $V(N_2)_{lim}$; (b) the apparently first-order rate constant, k_d , for dissociation of N_2O to N_2 at the 'dark' ZnO surfaces was not significantly affected by premixed ethanol or isopropanol, whereas t-butanol increased k_d , despite its overall inhibiting effect on $V(N_2)_{lim}$.

The effects noted for ethanol and isopropanol so strongly resemble those reported by Warman^{1,2,10} (see Introduction) that a similar interpretation was suggested, viz. that initial dissociation of N_2O occurred via (2) on the metal oxide and that the resultant $O^- (ads)$ species reacted rapidly with alcohol, producing surface intermediates, $(X+Y)^-$, which in turn rapidly dissociated other N_2O molecules via 3a and 3b. Such a mechanism, with process 2 containing the slow rate-determining step, would account for the overall rate constant k_d remaining unaffected by ethanol or isopropanol whilst the nitrogen yield $V(N_2)_{lim}$ doubled, since each type (2) event leads eventually via 3 to dissociation of at least two N_2O molecules. Our observation that t-butanol did not increase $V(N_2)_{lim}$ appeared consistent with Warman's conclusion that tertiary alcohols do not undergo type 3 reaction with O^- , and hence cannot lead to additional N_2O dissociation.

Data points to the right of an arrow on each plot in Fig. 2 show that illumination by UV light mainly at 254 nm caused additional photo-assisted dissociation to nitrogen product at ZnO interfaces which previously had attained their limiting value of $V(N_2)_{lim}$ in the dark. Two

contributions to this photoassisted dissociation can be distinguished on the traces in Fig. 2A: a slow linear growth of $V(N_2)^*$ with duration of illumination, which was the sole photoassisted process for N_2O/ZnO^* ; and an initial rapid photoassisted growth $V(N_2)^*$, of nitrogen persisting only during the initial $\frac{1}{2}$ hr. of illumination at the $(N_2O + EtOH)/ZnO^*$ interface. For this latter interface the rate of photoassisted N_2 formation returned to that characteristic of N_2O/ZnO^* interfaces at illumination times $>\frac{1}{2}$ hr.

Data to the right of the arrows in Fig. 2B for mixtures of N_2O with isopropanol or t-butanol over the illuminated ZnO surface, also appear consistent with contributions by both an initial fast photoassisted process and a slower continuing process to growth of $V(N_2)^*$. Mass spectrometric analysis demonstrated that the apparent increase in n.c. product from illuminated t-butanol/ ZnO^* interface shown in Fig. 2B originated from photoassisted formation of methane and not N_2 . This was the only illuminated interface found to yield appreciable desorption of methane product at room temperature and the significance of this observation is discussed in a later section.

Previous infra-red studies indicated a high degree of dehydroxylation for ZnO surfaces pretreated in vacuo at the 623-673K temperatures employed in the present study.¹⁹ Isotopic composition of the methanes produced at such ZnO surfaces by interaction with CDI was likewise previously shown to be consistent with extensive dehydroxylation of ZnO activated at these temperatures.⁴ Consequently the data in Fig. 2 for N_2 formation from N_2O/ZnO interfaces approximate to the situation for a dehydroxylated surface. It

TABLE 2

Limiting Yields of Nitrogen Produced and Desorbed over TiO_2 at Room Temperature

SYSTEM	P_{O_2} (React) Nm^{-2}	$V(\text{N}_2)_{\text{lim}}$ $\text{mls/m}^2 \times 10^{-4}$	$t_{\frac{1}{2}}$ (Min)	θ_{O}	k_d (min^{-1})
$\text{N}_2\text{O}/\text{TiO}_2$	45.0	2.34	11.5	0.057	6.02×10^{-2}
$\text{N}_2\text{O} + \text{C}_2\text{H}_5\text{OH}/\text{TiO}_2$	45.0 (each)	6.90	5.1	0.176	1.36×10^{-1}
$\text{N}_2\text{O} + (\text{CH}_3)_2\text{CHOH}/\text{TiO}_2$	45.0 (each)	6.89	4.7	0.174	1.49×10^{-1}
$\text{N}_2\text{O} + (\text{CH}_3)_3\text{COH}/\text{TiO}_2$	45.0 (each)	2.01	5.7	0.049	1.23×10^{-1}

was of interest to rehydroxylate such ZnO surfaces and again observe extent of nitrogen formation, in view of suggestions that surface hydroxyls on metal oxides represent active surface sites. The ZnO surfaces were rehydroxylated by baking in water vapour at 623 for 2 hrs. after which water was pumped away at 623 and the sample cooled to room temperature. The growth of nitrogen product over this rehydroxylated surface in the absence of illumination is represented by curve(ii) of Fig.3A. Comparison with the initial 80 min. of curve(i), which was obtained on the same ZnO layer prior to its rehydroxylation, leaves no doubt that rehydroxylation yielded additional surface sites on ZnO which were active for N_2O dissociation to N_2 at room temperature in the static reactor. Curve(iii) of Fig.3A illustrates that UV illumination of the interface between N_2O and rehydroxylated ZnO caused a further large enhancement in the rate of N_2O dissociation. Thus it is clear that rehydroxylated ZnO surfaces were much more active than dehydroxylated ZnO for N_2O dissociation both in the dark and particularly under UV illumination.

1.2. *Nitrogen product from N_2O/TiO_2 and $(N_2O+Alcohol)TiO_2$ interfaces at room temperature;*

Data to the left of the arrows in Figure 4 illustrates growth of nitrogen product during the first hour of contact of freshly-activated non-illuminated TiO_2 with N_2O or with $(N_2O+Alcohol)$. Empirical kinetic analysis again established that data for contact times 5-30 min. could be adequately fitted to the first-order type expression 4. Table 2 lists values so determined for $V(N_2)_{lim}$ and k_d over the TiO_2 surface. Inspection of the $V(N_2)_{lim}$ values reveals that, at room temperature, t -butanol failed to enhance nitrogen product formation at the dark N_2O/TiO_2 interface, whereas admixture of ethanol or isopropanol greatly enhanced $V(N_2)_{lim}$ relative to that with only N_2O present. Comparison

of data in Table 2 with Table 1 reveals that admixtures of ethanol or isopropanol with N_2O trebled the limiting yield of nitrogen product $V(N_2)_{lim}$ observed when contacted with TiO_2 , in contrast to the doubling upon contact with ZnO . Since enhancement by a factor of 3 was just that noted by Warman^{17, 18} for reaction with gas-phase O^- , this observation suggested that O^- intermediates on TiO_2 surfaces reacted with these alcohols with stoichiometry similar to that reported for processes 3a and 3b in the gas phase. The smaller enhancement of (N_2) noted in Table I for corresponding ZnO interfaces could arise *either* from loss of some fraction of surface O^- radicals into the ZnO bulk by hole migration (which recent results of Lundsford support⁷) or by the blocking of some active sites on ZnO through rapid and irreversible chemisorption of alcohol (see below).

In contrast to ZnO interfaces, at which only t-butanol increased the apparently first-order rate constant k_d for N_2 formation from N_2O , all the alcohols caused k_d over $(N_2O+Alcohol)/TiO_2$ interfaces to increase to similar values approximately double those over N_2O/TiO_2 . Unchanged values for $V(N_2)_{lim}$ with admixtures of t-butanol gave no evidence for occurrence of processes 3a or 3b with this alcohol. Consequently it appeared that only process 2 could contain a slow r.d.s. common to the three systems and that each alcohol enhanced this r.d.s. to comparable extent on TiO_2 . Process 2 involves the sequence:- N_2O adsorption dissociation of N_2O within the surface; and finally, N_2 desorption. Data additional to those on rate of N_2 appearance in the gas phase would be necessary to determine which of these steps was enhanced by the alcohols to give rise to observed increases in k_d . Evidence on

this question is discussed in a later section.

Data to the right of an arrow in Fig. 4 were taken with photons of $\lambda=254$ nm incident onto the previously dark-equilibrated interfaces. The lack of any significant photoassisted dissociation to N_2 at the N_2O/TiO_2^* interface argued against significant photocatalysis of Process 2 at that interface. Consequently no photoassisted formation of additional $O_{(ads)}^-$ intermediates from N_2O was thought to occur at N_2O/TiO_2^* interfaces. Plots 4A(ii) and 4B(ii) demonstrate, however, that readily measurable rates of N_2 production were observed when ethanol or isopropanol were simultaneously present with N_2O at the illuminated TiO_2 surface. A working hypothesis capable of explaining these observations was that illumination of the TiO_2 surface directly produced surface $O_{(ads)}^-$ intermediates without the need to photodissociate N_2O , (e.g. by trapping photo-generated holes at pre-existing coordinatively unsaturated O^{2-} ions²⁰). Reaction of adsorbed alcohol with such O^- entities via 3a to produce secondary surface radicals capable of reacting with N_2O via 3b, would account for the additional N_2 observed upon illumination despite the absence of O^- fragments from N_2O photodissociation. Absence of any photoassisted nitrogen product formation in the presence of t-butanol (see plot 4B (i) to the right of the arrow), is consistent with reported low reactivity of O^- towards this tertiary alcohol (recall that the photoassisted increase in noncondensable products from t-butanol/ TiO_2 shown in Fig. 4 B plot (i) was due to formation of methane and not N_2).

Negative results of experiments aimed at establishing whether rehydroxylation of the TiO_2 surfaces enhanced N_2O dissociation to nitrogen are summarised in Fig. 3 B, which shows that growth of N_2 product followed

almost identical curves for dehydroxylated and 'rehydroxylated' TiO_2 surface previously activated in vacuo at 623 for 16 hr. was carried out in the same manner as for ZnO (viz. 2 hrs. in water vapour at 623K) but figure 5.b. makes clear that this treatment caused neither any increase in N_2 formation in the dark nor any photoassisted N_2O dissociation. This result makes it improbable that the enhanced dissociation of N_2O here observed in the presence of alcohol over the non-illuminated TiO_2 surface could have arisen from any rehydroxylation of the surface by the alcohol. However, some workers report lack of success in attempts to rehydroxylate TiO_2 surfaces²¹ and the conclusion that surface hydroxyls on TiO_2 are inactive for N_2O dissociation must remain tentative until direct evidence becomes available on the extent of surface rehydroxylation achieved with H_2O or alcohol. Results of studies on the interaction of N_2O and alcohols over ZnO or TiO_2 surfaces obtained on static systems by other techniques are described in the following paragraphs.

I. 3. *Products released by thermally-assisted desorption from ZnO or TiO_2 interfaces previously exposed to alcohol and/or N_2O .*

The t-butanol/ ZnO interface was the only case in which release of product into the gas phase accompanied room-temperature adsorption of alcohol onto ZnO or TiO_2 surfaces previously activated in vacuo at 623°K (cf. Table 3). Our failure to detect aldehyde or ketone products from the other alcohols in the gas phase above the surfaces of these n-type semiconducting solids did not appear fully consistent with previous claims^{22, 23} that a high Fermi level should promote dehydrogenation.

TABLE 3

Extent of Room-temperature Product formation at Alcohol Vapour/Metal Oxide Interfaces - as deduced from thermal desorption in vacuo.

SYSTEM	Reaction Conditions at 390K	DESORBED PRODUCTS ^a			
		(-H ₂ O)	(-H ₂)	(Diss)	H ₂ (g)
Alcohol/Metal Oxide					
C ₂ H ₅ OH/ZnO ^e	dark	4.7	-	1.4 ^b	17.0
"	+hv	5.0	-	1.9 ^b	18.0
"	+N ₂ O	3.2	-	2.6 ^b	14.0
"	hv+N ₂ O	4.4	-	2.7	15.0
C ₂ H ₅ OH/TiO ₂ ^f	dark	19.0	-	13.0 ^b	0.6
"	+hv	19.0	-	4.1 ^b	2.1
"	+N ₂ O	5.8	-	30.0 ^b	0.2
"	hv+N ₂ O	2.6	-	12.0 ^b	-
(CH ₃) ₂ CHOH/ZnO ^e	dark	3.9	1.9	-	16.0
"	+hv	3.8	2.2	-	11.0
"	+N ₂ O	2.8	2.8	-	8.7
"	hv+N ₂ O	2.5	5.7	-	7.3
(CH ₃) ₂ CHOH/TiO ₂ ^f	dark	69.1	-	6.8 ^c	-
"	+hv	58.0	0.5	14.0	-
"	+N ₂ O	47.0	0.2	4.5 ^c	-
"	hv+N ₂ O	44.0	1.6	9.9	-
(CH ₃) ₃ COH/ZnO ^e	dark	16.0	-	-	CH ₄
"	+hv	18.0	-	0.02 ^d	-
"	+N ₂ O	16.0	-	0.01 ^d	-
"	N ₂ O+h	17.0	-	0.12 ^d	-
"	dark	0.06 ^g	-	-	-
"	+hv	0.09 ^g	-	0.06 ^g	0.07 ^g
"	N ₂ O+hv	-	-	0.20 ^g	0.09 ^g
(CH ₃) ₃ COH/TiO ₂ ^f	dark	81.0	-	- ^d	-
"	+hv	100	-	1.5	-
"	+N ₂ O	70.0	-	-	-
"	hv+N ₂ O	100	-	3.4	-
"	hv	4.2 ^g	-	-	0.10 ^g
"	N ₂ O+hv	1.7 ^g	-	-	0.15 ^g

a) Normalised to μl of product gas (STP) desorbing per m^2 of oxide surface.

b) Detected as butadiene + CO₂ + methyl acetylene + propene.

c) Detected as acetaldehyde.

d) Detected as acetone.

e) Alkene and H₂ desorbed 300-460° but aldehyde on ketone 460-620K.

f) All product except acetone desorbed 300-510K but acetone desorbed 460-620K

g) Desorbed at room temperature.

Efforts were therefore made to detect the expected dehydrogenation products by thermal desorption after gas phase and any physisorbed alcohol had been pumped away at 300K away under continuous evacuation at $< 10^{-4}$ Nm⁻².

Data on these effects, which are summarised in Table 3, do not provide reliable absolute values for surface densities of sites active for alcohol dehydration or dehydrogenation at room temperature, because of possibilities for additional reaction during the thermal desorption procedure. They do, however, provide 'baseline' values for comparison with amounts of product thermally desorbed from the same interfaces in different conditions e.g., when exposed to uv-illumination or to nitrous oxide admixed with the alcohol.

Significant numbers of 'active sites' capable of alcohol dehydration were indicated by thermal desorption of corresponding alkene in readily measurable amount, (tabled under -H₂O in Table 3). This was true for both ZnO and TiO₂, but the specific activity of TiO₂ was greater in all cases. For the TiO₂ surface, extent-of-dehydration increased in the sequence, t-butanol>isopropanol>>ethanol, which is the same as that usually observed for alcohol dehydration by acid-type centres in homogeneous or heterogeneous catalysis. Appearance of the olefine product at temperatures much below those previously reported indicates that some at least, of the dehydration sites were of unusually high activity.

As expected, no dehydrogenated product was obtained for t-butanol but the ratio,(dehydrogenation/dehydration),increased for isopropanol and ethanol. Thermally assisted desorption of the anticipated dehydrogenation products,(acetone or acetaldehyde from isopropanol or ethanol respectively),occurred to lesser extent than release of dehydrated products or of molecular hydrogen at temperatures $<498\text{K}$. The histograms in Fig. 5 illustrate the higher desorption temperatures required for release of acetone product than for propene or hydrogen desorption from the isopropanol/ZnO interface. The acetone histogram also represents (by the fully blackened sections) the thermal desorption behaviour noted for the same surface when acetone rather than alcohol was initially absorbed at room temperature. At the higher temperatures required for desorption of aldehydes or ketones, thermally-assisted rearrangements occurred - as evidenced by partial conversion of preadsorbed acetone to isobutene or of preadsorbed acetaldehyde to 1, 3 butadiene. Extent of ethanol dissociation corresponding to products related to adsorbed acetaldehyde is tabled under (Diss) in Table 3. This latter observation contrasts with a report by McArthur²⁴ that acetaldehyde desorbed readily from ZnO and the difference suggests that ethanol selectively displaced acetaldehyde at the temperatures employed in McArthur's study.

Admixture of nitrous oxide with the ethanol admitted to dark ZnO or TiO₂ caused a definite increase in products attributable to acetaldehyde (which then suffered further degradation

upon thermal desorption). This observation, and a smaller increase in acetone from isopropanol, appeared consistent with the working hypothesis developed in Section I, according to which nitrous oxide dissociated on the surfaces to yield O^- fragments which enhanced dehydrogenation by then abstracting α -hydrogen from primary or secondary alcohol. Data in Table 3 also show that dehydration products experienced a decrease when N_2O was admixed with primary or secondary alcohols, in contrast to the increases which N_2O brought about in dehydrogenation.

A slight increase in extent of dehydration was observed for t-butanol under illumination at either ZnO or TiO_2 surfaces but nitrous oxide did not further enhance this photodehydration. Comparison of the first and second data rows for other Alcohol/Metal Oxide systems in Table 3 reveals that no significant enhancement of dehydrated or dehydrogenated product above the baseline values resulted from illumination of the interfaces through a quartz wall with the output of a 15 watt low pressure mercury arc lamp. Photons of λ 254 nm predominated in this output and such photons had sufficient energy to create holes and electrons in surface and sub-surface regions of the ZnO or TiO_2 layers. Reports by previous workers, to the effect that alcohols reacted with electronic holes at uv-illuminated ZnO surfaces, had led us to expect additional oxidation of alcohols at that illuminated interface relative to the baseline values observed in the dark. Our failure to detect ^{such} addition-

al photoassisted dissociation of ethanol or isopropanol vapour casts serious doubts on the idea that electronic holes promote alcohol oxidation. The last data line for the t-Butanol/Metal Oxide system in Table 3 supports a similar negative conclusion, even when nitrous oxide and t-butanol were simultaneously present over these uv-illuminated interfaces. Particular importance attaches to this latter observation because N_2O represented a reducible, and t-butanol an oxidisable, reagent. In terms of electronic theories²², photogenerated holes and hole-hole-electron pairs should promote their photoreduction and photooxidation respectively. Consequently this negative result argues against an important role of electronic factors at the interfaces between illuminated ZnO or TiO_2 and (t-Butanol + nitrous oxide).

1.4. ESR measurements:

Further evidence of the small influence of adsorbed alcohol upon electron localization/delocalization at the metal oxide interface emerges from the ESR spectra shown in Fig. 6. Spectrum (i) was measured at 77K on a sample of TiO_2 which had been outgassed in vacuo at 623K and it corresponds well to broad anisotropic adsorption band usually attributed to paramagnetic Ti^{3+} centres at the TiO_2 surface. Spectrum (ii) was not significantly altered if the sample was warmed in vacuo to 300K and again cooled to 77K but a new spectrum (ii) resulted if such samples were exposed to the saturation vapour pressure of

ethanol or sec-2-butanol for 10 min. and re-evacuated at 300K before recooling to 77K. When such samples were subsequently heated to 623K under continuous evacuation and remeasured at 77K spectrum (i) was again obtained. The reversible nature of the change brought about by brief exposure to alcohol vapour at room temperature would be consistent with chemisorption of the alcohol. It must however be concluded from the small differences between spectra (i) and (ii), either in respect of integrated intensity or magnetic parameters, that surface paramagnetic Ti^{3+} centres were not markedly affected by the chemisorbed alcohol. The changes in shape of the resonance would be consistent with weak dipolar interaction between chemisorbed alcohol and Ti^{3+} , resulting in a slight increase in g_{11} of the latter.

The absence of any marked change in integrated intensity of the spectrum certainly would not be consistent with extensive charge transfer between alcohol and the vacuum-activated TiO_2 surface. Thus if chemisorbed alcohol acted as a donor increase in Ti^{3+} centres would be expected. Conversely decrease in their number should have occurred if Ti^{3+} centres transferred electrons to chemisorbed alcohol.

SECTION II

Reactions of alcohols and/or (Alcohol+N₂O) mixtures at illuminated ZnO and TiO_2 surfaces under dynamic conditions.

Since results in Section 1 showed that aldehyde and ketone products from alcohol dehydrogenation reactions remained adsorbed on non-illuminated ZnO and TiO_2 surfaces in the static

reaction system and were only gradually desorbed on heating to 625°K in vacuo, experiments were carried out in dynamic conditions to determine if products of photoassisted elimination reactions then remained adsorbed in similar manner, or if they were released to the gas phase at room temperature. Oxide samples were therefore prepared and pre-treated as described above and then exposed to low dynamic pressures of reactant gas(es) at ca 10^{-4} Nm⁻², which were established over the samples as a balance between inlet leak-rate of reactants through a metal variable leak valve and their removal by a continuously operating ion-pump with pumping speed of 50 litres sec⁻¹. A micromass 6 mass analyser located 15 cm from the oxide surfaces along a high conductance path was employed for on-line gas analysis. Reactant alcohols, or (alcohol+N₂O) mixtures in approximately 1:1 mole ratio, were mass-analysed at various time intervals, prior to the commencement of illumination, until reproducible reactant spectra were obtained. Continuous illumination of the GAS/SOLID interface was then commenced and the gaseous phase mass-analysed at various times during an illumination period of approximately three hours. Interfaces were illuminated through a quartz envelope by the unfiltered output of a 15-watt low pressure Hg lamp with output concentrated principally at 254 nm. and results are summarised in Figures 7A and 7B.

II. 1. Photoproducts from Isopropanol/Metal Oxide interfaces:

On-line mass analysis provided no evidence for measurable enhancement of peaks at m/e values corresponding to propene, the dehydration product detected from ZnO interfaces by thermal desorption (cf. Section 1). Exposure of the illuminated ZnO surface

to alcohol was, however, several orders of magnitude less in these on-line analyses (ca 4×10^{-3} torr sec) than for typical exposures (ca 10^3 torr sec) in the static reactor experiments.

The lower curve of Fig. 7A illustrates photo-assisted production of acetone dehydrogenation product upon illumination of an *isopropanol/ZnO* interface through quartz. Note the rapid initial increase in gas-phase acetone, reaching a maximum approximately 4 minutes after the commencement of uv illumination. This increase was followed by a slow decrease in dynamic pressure of acetone until, at times ~ 170 min. after the commencement of illumination, photoproduction of acetone had ceased. These results indicated that, as illumination proceeded in the presence of isopropanol, surface sites capable of photoassisted dehydrogenation were progressively removed. The results would be consistent with photogeneration of surface O^- sites and their reaction with isopropanol to yield dehydrogenated product plus inactive surface hydroxyls. Recent publications on reactivity of O^- show the requisite high rate constants for abstraction of α^- hydrogen^{17, 25}.

Data to the left of the arrow in the diagrams in Fig. 7 were obtained prior to the commencement of u.v. illumination and show that presence of N_2O and isopropanol in 1:1 mole ratio as the gas phase flowing over the 'dark' ZnO interface resulted in a larger pre-illumination level of acetone formation (Fig. 7A upper plot). Data to the right of the arrow in the upper plot show that the initial photoenhanced formation of acetone was larger and was sustained for longer times in the presence of N_2O .

These observations are consistent with some production of additional O^- species from N_2O on the dark or illuminated ZnO interface and reaction of these O^- species to yield dehydrogenated products via reactions of type 3a and 3b. Data on the upper plot of Fig. 7A at times >60 min. illumination indicate a small nett increase in acetone, corresponding to some small rate of photoassisted dehydrogenation in the photostationary state via 3a and 3b. Nitrogen corresponding to this process was detected in the static photo-reactions (see Fig. 2A ii).

Data in Fig. 7B illustrate the photoassisted growth of both the dehydration product, propene, and the dehydrogenation product, acetone, above a uv-illuminated isopropanol/ TiO_2^* interface. Comparison of Figures 7A and 7B confirm the greater activity of the TiO_2 surface for these photoassisted elimination reactions involving isopropanol. Since ESR measurements on a previous study on the ZnO and TiO_2 samples used in this work showed much greater surface concentration of metal-excess centres on TiO_2 than on ZnO, such Ti^{3+} centres are suggested as the active sites responsible for the greater dehydration on TiO_2 .

II.2 *Comparison of photoassisted elimination reactions for primary, secondary and tertiary Butanols.*

summarises results of on-line mass analysis of photoproducts detected above uv-illuminated interfaces of TiO_2 with primary, secondary or tertiary butanol. Extent of observed photo-dehydration may be seen to lie qualitatively in the sequence expected on the basis of ease of alcohol dehydration, viz. tertiary >secondary>>primary. Since a quantitative measure of the extent of each photoassisted elimination reaction was desirable, values

for the total amount of gaseous photo-products which desorbed from the illuminated interfaces over the observed time-intervals were derived using equation (5),

$$\text{Amount desorbed} = \frac{1}{ARTo} V\Delta P(t) + S \int_0^t \Delta p dt \quad (5)$$

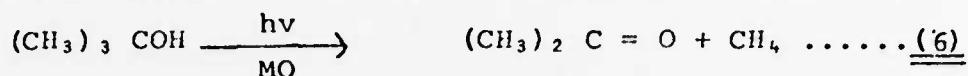
In this equation, as developed in 1953 by Becker and Hartmann²⁶ A = surface area of adsorbent; To = gas temperature; V = volume of reaction system; S = pumping speed and $\int_0^t \Delta p dt$ is the area under pressure-versus-time curves such as are shown in figures 7 and 8. Increases in peak height obtained experimentally for various mass numbers were converted to pressure changes Δp , and substituted into equation (5), thereby yielding values for the total number of molecules of each product desorbing in a given time interval, (usually 0-170 min. after the commencement by uv. illumination). These values are tabulated in Table 4 for the Alcohol/Metal Oxide systems studied. In relation to photodehydration, these data show that extent of reaction of tertiary butanol was an order of magnitude greater than for secondary alcohols at the same interface, whilst primary alcohols did not experience photodehydration to measurable extent. Extent of photodehydrogenation (see columns headed "-H₂" in Table 4) did not show such large variations with the nature of the alcohols, which indicates that extent of this photoassisted elimination process depended more upon the number of active sites provided by the illuminated TiO₂ or ZnO surface than upon ease of alcohol dehydrogenation. Tertiary butanol represented an obvious exception to this behaviour since dehydrogenation via. an initial α -hydrogen abstraction was not possible. Our observations showed that acetone was the second major photoproduct from t-butanol/

TABLE 4

Extent of room temperature dehydration and dehydrogenation at alcohol vapour/
metal oxide illuminated interfaces under dynamic conditions.

Reactant	ZnO*			TiO ₂ *		
	(-H ₂ O)	(-H ₂)	(-CH ₄)	(-H ₂ O)	(-H ₂)	(-CH ₄)
C ₂ H ₅ OH	-	2.5x10 ¹⁹	-	-	1.1x10 ²⁰	-
N ₂ O+C ₂ H ₅ OH	-	6.9x10 ¹⁹	-	-	2.3x10 ²⁰	-
(CH ₃) ₂ CHOH	-	3.6x10 ¹⁹	-	1.9x10 ¹⁹	1.4x10 ²⁰	-
N ₂ O+(CH ₃) ₂ CHOH	-	7.7x10 ¹⁹	-	-	2.6x10 ²⁰	-
(CH ₃) ₃ COH	1.1x10 ²⁰	-	7.4x10 ¹⁹	1.8x10 ²⁰	-	1.8x10 ²⁰
N ₂ O+(CH ₃) ₃ COH	8.4x10 ¹⁹	-	9.9x10 ¹⁹	6.1x10 ¹⁹	-	3.4x10 ²⁰
(CH ₃) ₂ CHCH ₂ OH	-	2.9x10 ¹⁹	-	-	7.8x10 ¹⁹	-
CH ₃ CH ₂ CH(OH)CH ₃	1.0x10 ¹⁹	4.3x10 ¹⁹	-	1.5x10 ¹⁹	1.3x10 ²⁰	-

Metal Oxide* systems, in addition to isobutene. The overall stoichiometry of acetone formation may be expressed as in (6).



A reaction with this stoichiometry would be consistent with the relatively large amounts of methane obtained on illumination of the *t*-butanol/metal oxide interface in the static reaction system (see Table 3). Such photoassisted reaction may be described as "(-CH₄)", i.e. a photoelimination of methane. Data listed under that heading in Table 4 indicate the amount of acetone detected by on-line mass analysis. It was originally felt that the formation of acetone at the *t*-butanol/ZnO* interface might be the result of secondary reactions such as oxidation of isobutene photoproduct by lattice oxygen. However, test experiments with mixture of (N₂O+isobutene) present over illuminated ZnO or TiO₂ surfaces under either static or dynamic conditions did not result in significant photooxidation of the isobutene. Dehydration followed by oxidative cleavage of the double bond is therefore discounted as a route to photoassisted elimination of the methane observed from *t*-butanol. In effect the process has the characteristics of a reverse Grignard reaction, which suggests involvement of co-ordinatively unsaturated metal ion sites on the catalyst surface. Further studies will be necessary before the nature of the sites active for this process can be identified with confidence.

II.3 Influence of water vapour in dynamic conditions.

Since analysis with the on-line mass analyses offered a more sensitive procedure (than static techniques) for examining

the influence of coadsorbed water upon photocatalytic activity, comparison was made of the extent of photoassisted formation of CD_3CDO from anhydrous $\text{C}_2\text{D}_5\text{OD}$ and from $\text{C}_2\text{D}_5\text{OD}$ containing 5% D_2O . Results are summarised in Fig. 8 for both ZnO and TiO_2 surfaces exposed to continuous illumination at 254nm. It is clear from these data that the presence of D_2O enhanced the extent of alcohol photo dehydrogenation. This is similar to reports by Stone et al¹⁶ that rehydroxylation of a TiO_2 surface resulted in increased photodehydrogenation of isopropanol to acetone.

CONCLUSIONS

Results obtained in this study for the extent of N_2O dissociation at vacuum-activated ZnO or TiO_2 surfaces are fully consistent with the interpretation previously advanced that electron transfer to N_2O from unsaturated metal ion sites i.e., $\text{M}_{\text{cus}}^{+(z-1)} \xrightarrow{\text{N}_2\text{O}} (\text{M}^{+z} - \text{O}^-)_{\text{cus}} + \text{N}_2$, represents the main channel for nitrogen production at room temperature in the absence of uv-illumination. This model for surface reactivity is extended by the new data here presented on further dissociation of N_2O in the presence of primary or secondary alcohol, allied to the evidence for enhanced alcohol dehydrogenation when N_2O was present. Together, these observations are consistent with secondary reactions of the O^- ions formed from N_2O in this process. A necessary corollary to its efficient occurrence in the presence of N_2O is that other reactions requiring $\text{M}_{\text{cus}}^{+(z-1)}$ sites should be inhibited. The inhibition of alcohol

dehydration here observed at surfaces also exposed to N_2O may thus be understood.

Results obtained here on photoassisted elimination reactions from alcohol vapours at ZnO or TiO_2 surfaces exposed to uv-illumination in static or dynamic conditions demonstrate the occurrence of other surface sites capable of interacting directly with alcohol when activated by illumination. Results with alcohols are consistent with identification of these sites as O_{cus}^{2-} and with their conversion to O_{cus}^- by hole-trapping during illumination. The enhancing effect of 5% D_2O upon photo-dehydrogenation of C_2D_5OD in dynamic conditions would be consistent with D_2O acting as an electron trap to complement such hole trapping. Present results do not, however, support the proposal that adsorbed alcohol act as efficient hole traps on ZnO or TiO_2 , even when N_2O was simultaneously present as an electron trap.

Results here presented on changes in surface reactivity effected by treatments designed to rehydroxylate the vacuum-activated ZnO or TiO_2 surfaces point to important differences between the sites so produced on TiO_2 from those on ZnO , with only the latter effective for N_2O dissociation. Further study will be necessary to fully characterise such sites and determine if they are in agreement with recent suggestions²⁷ that O_{cus}^{2-} adjacent to surface OH^- can act as electron donor sites on ZnO and NO_2 .

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Captions to Figures

Figure 1

Vacuum systems for study of gaseous products evolved from interfaces of ZnO and TiO₂ with N₂O and/or aliphatic alcohols:

1(a) Static reactor with pumping line, P; gas handling line, L; pirani gauge, G; variable leak valve, V; metal valves, M; cold fingers, C; and metal oxide sample, M.O.

1(b) Dynamic reactor with inlet leak valve, I; metal oxide layer, M.O.; stainless steel tubing, E; glass walled photo-reactor, C; micromass 6 mass analyser, M.A.; pressure gauge, B; and ion pump.

Figure 2

Evolution of N₂ product from ZnO surfaces at 293K (position of arrow denotes commencement of illumination):

- 2A (i) N₂O/ZnO with $P_{N_2O} = 45 \text{ Nm}^{-2}$.
(ii) N₂O + C₂H₅OH/ZnO with $P_{N_2O} = 45 \text{ Nm}^{-2}$
 $P_{C_2H_5OH} = 45 \text{ Nm}^{-2}$.

- 2B (i) N₂O + (CH₃)₃COH/ZnO with $P_{N_2O} = 45 \text{ Nm}^{-2}$
 $P_{(CH_3)_3COH} = 45 \text{ Nm}^{-2}$.
(ii) N₂O + (CH₃)₂CHOH/ZnO with $P_{N_2O} = 45 \text{ Nm}^{-2}$
 $(CH_3)_2CHOH = 45 \text{ Nm}^{-2}$.

Figure 3

Effects of surface rehydroxylation upon N₂O dissociation on ZnO or TiO₂ at 293K:

- 3A (i) N₂ evolution on ZnO surface pretreated in vacuo at 623K for 16 hours (arrow denotes start of illumination).
(ii) As for (i) except surface rehydroxylated by treatment in 50 Nm⁻² H₂O at 623K for 2 hours.
(iii) As for (ii) except u.v. illumination commenced at time indicated by the arrow.
- 3B (i) N₂ from TiO₂ surface pretreated in vacuo at 623K for 16 hours
(ii) As for (i) except surface rehydroxylated at 623K in 0.5 torr H₂O.

Figure 4

Evolution of N_2 product from TiO_2 surfaces at 293K:

- 4A (i) N_2O/TiO_2 ;
(ii) $N_2O + C_2H_5OH/TiO_2$;
- 4B (i) $N_2O + (CH_3)_3COH/TiO_2$;
(ii) $N_2O + (CH_3)_2CHOH/TiO_2$.

Figure 5

Histograms for thermal desorption of various products from $(CH_3)_2CHOH/ZnO$ interfaces on heating to 623K:

- (i) H_2 evolution; (ii) propene;
(iii) Acetone (darkened sections represents thermal desorption of $(CH_3)_2CO$ from a $(CH_3)_2CO/ZnO$ interface.

Figure 6

E.S.R. spectra of TiO_2 at 77K:

- (i) After activation for 16 hours at 77K.
(ii) After exposure for 10 min. to C_2H_5OH at 293K followed by evacuation.

Figure 7

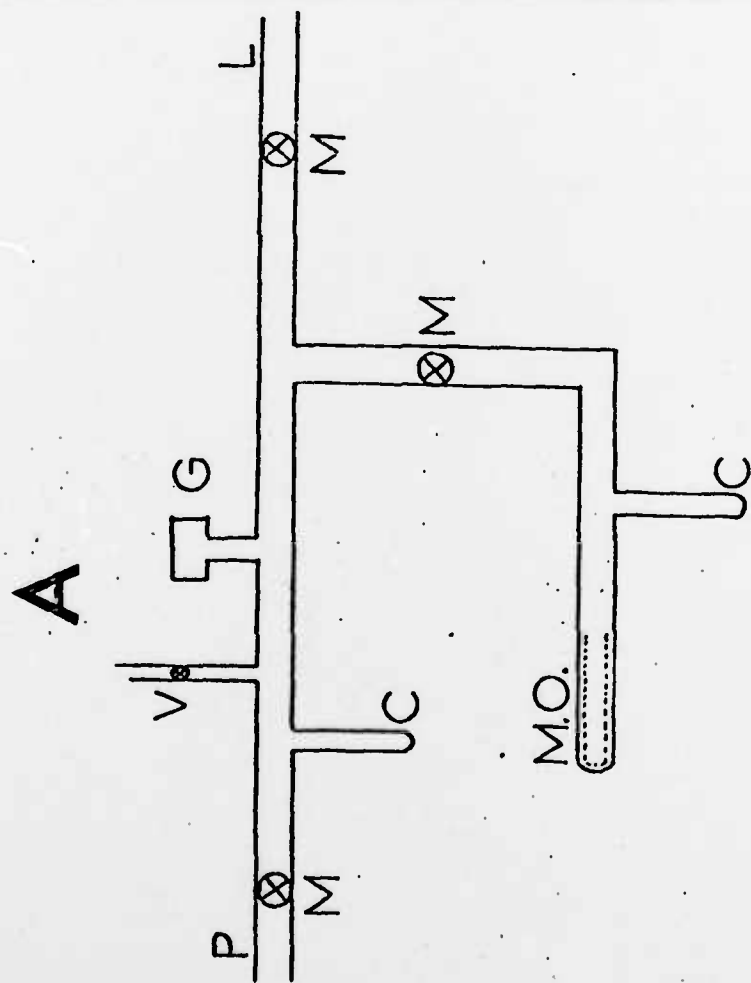
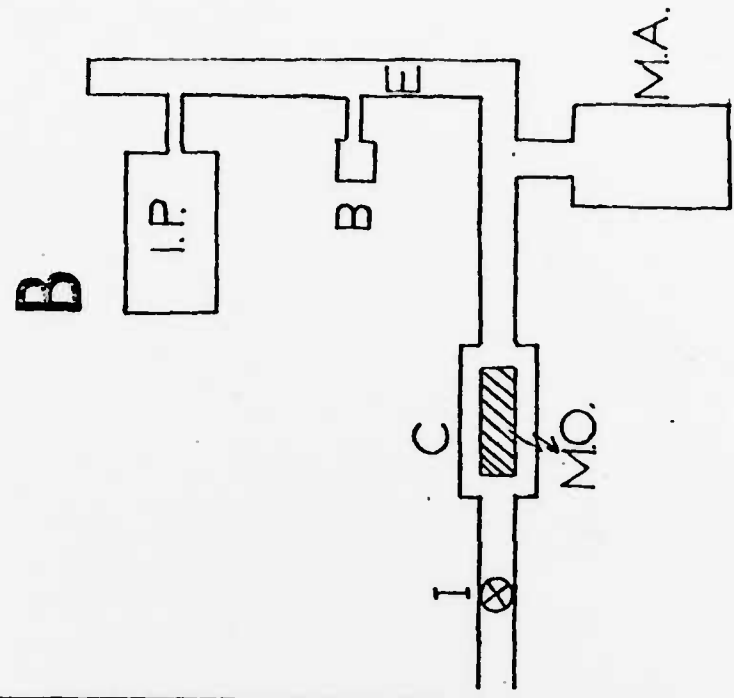
Time profiles for appearance of various products in the gas-phase, as detected with Micromass 6 mass analyser with isopropanol flowing over the metal-oxide catalyst at $2 \times 10^{-4} Nm^{-2}$. Arrows denote the start of continuous illumination with photons at 254 n.m.

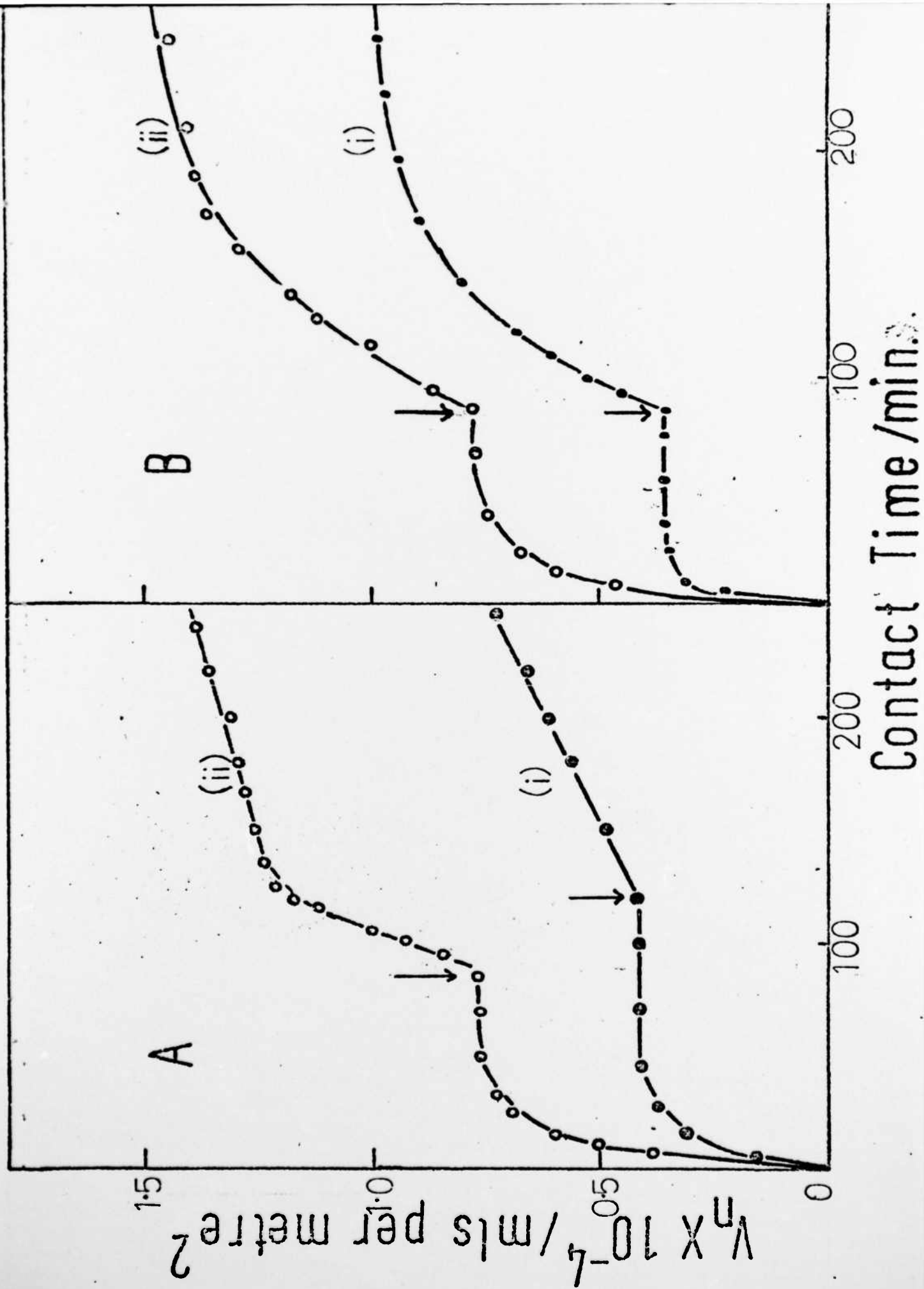
- 7A (i) Acetone from isopropanol/ ZnO^* .
(ii) Acetone from $N_2O +$ isopropanol/ ZnO^* .
- 7B (i) Acetone from isopropanol/ TiO_2^*

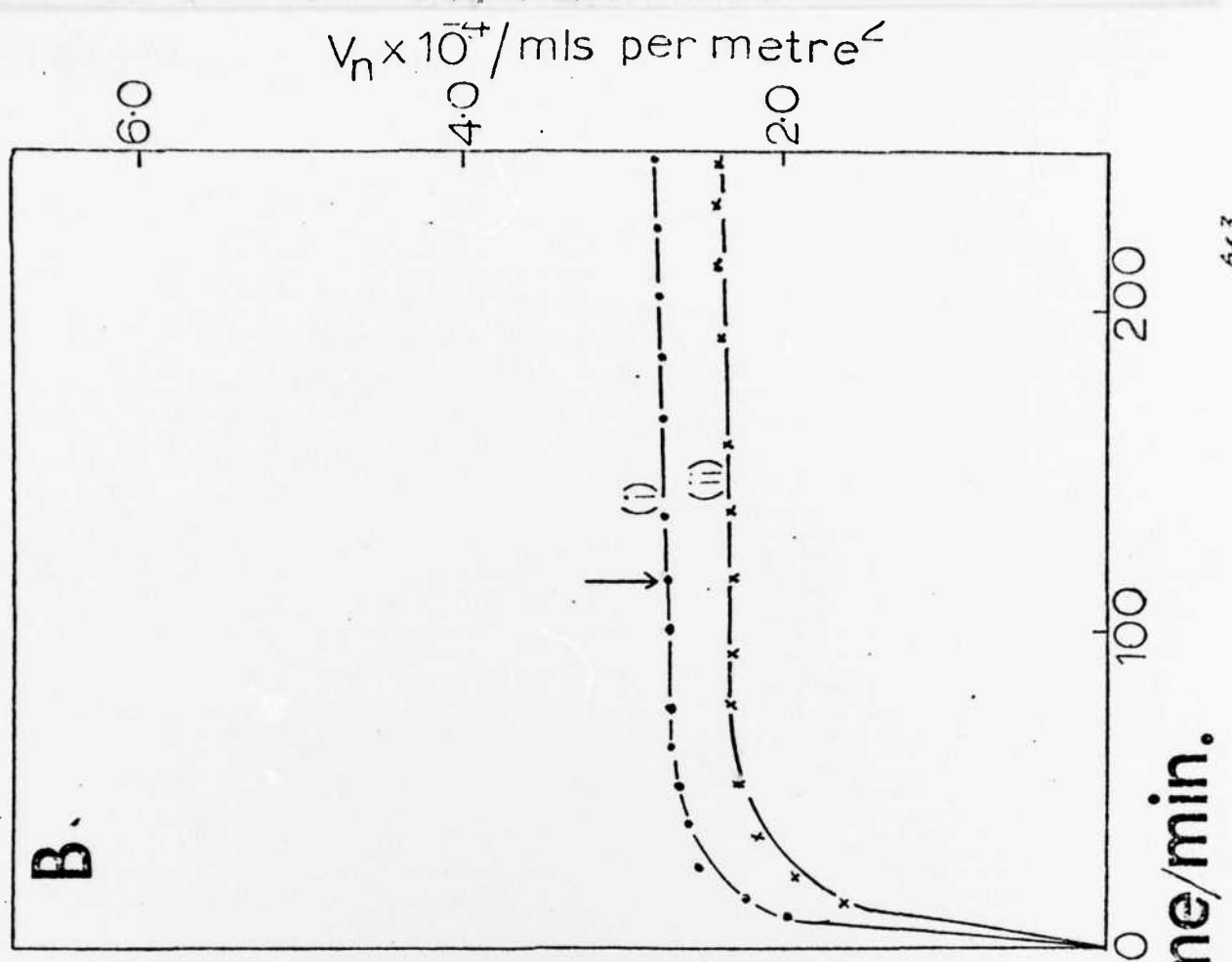
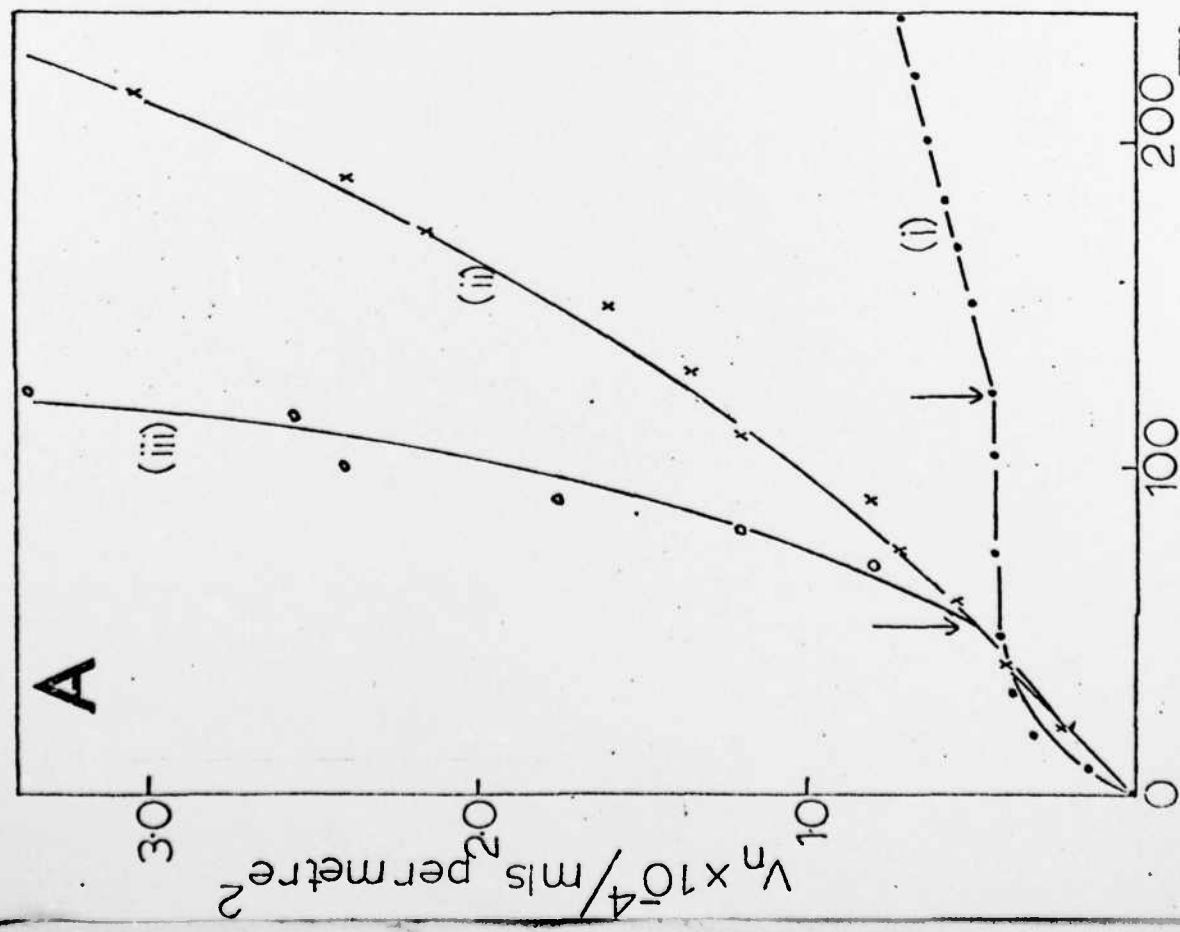
Figure 8

Influence of a 5% water content upon photodehydrogenation of ethanol over ZnO and TiO_2 surfaces illuminated by 254 n.m. photons in a dynamic quartz photoreactor.

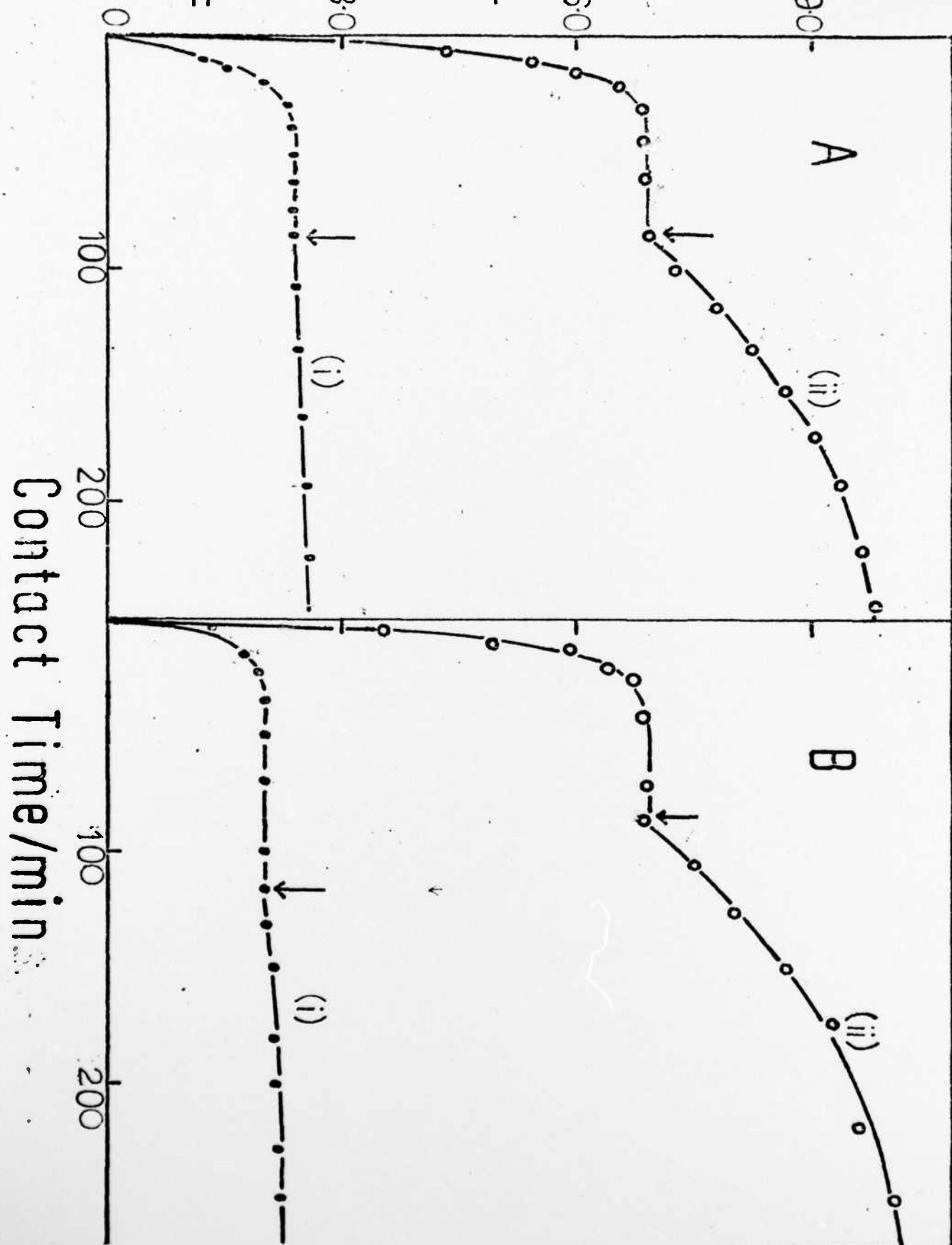
- 8A (i) CD_3CDO from C_2D_5OD/ZnO^*
(ii) CD_3CDO from $C_2D_5OD + 5\%D_2O/ZnO^*$.
- 8B (i) CD_3CDO from C_2D_5OD/TiO_2^*
(ii) CD_3CDO from $C_2D_5OD + 5\%D_2O/TiO_2^*$.

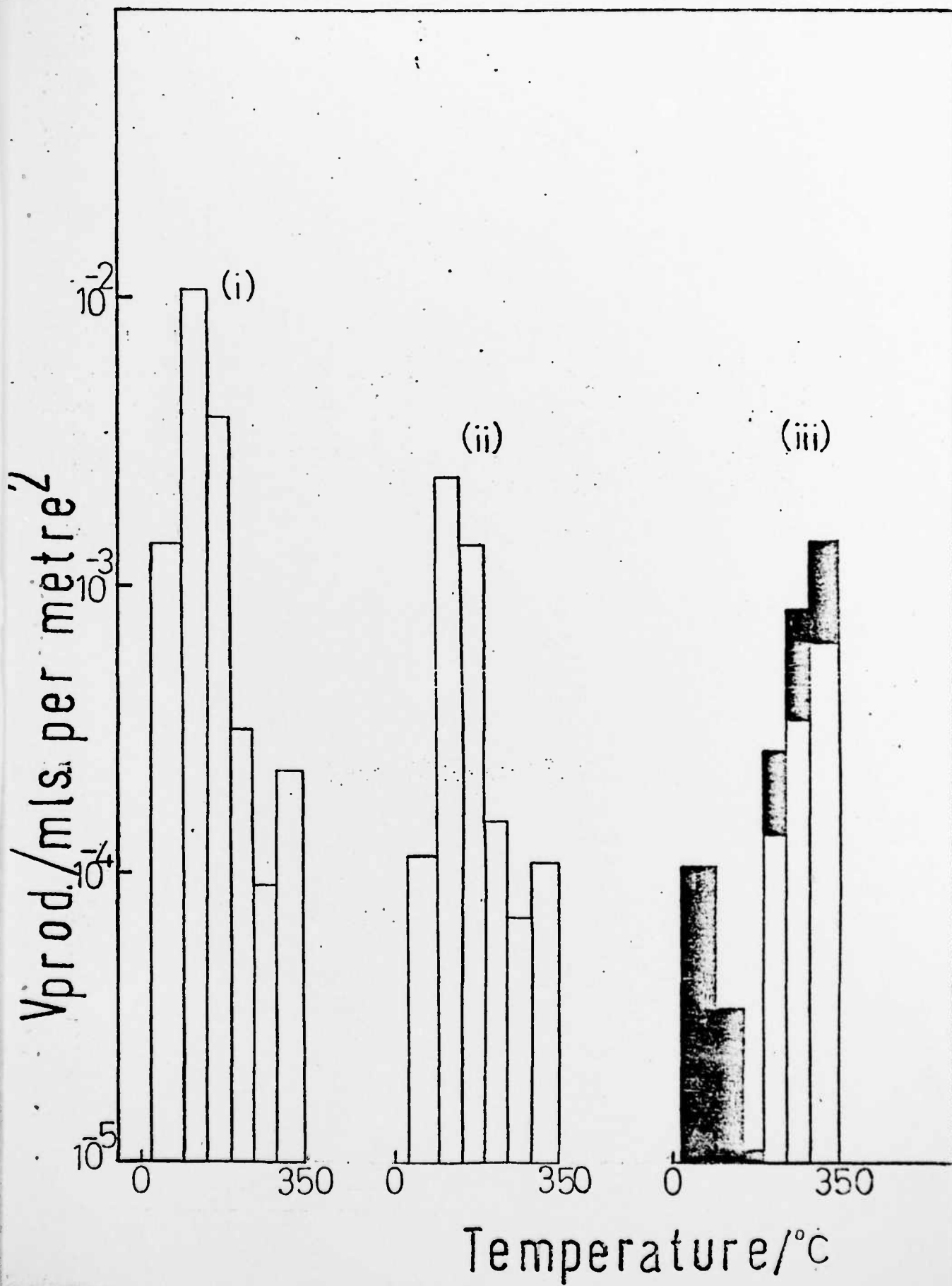


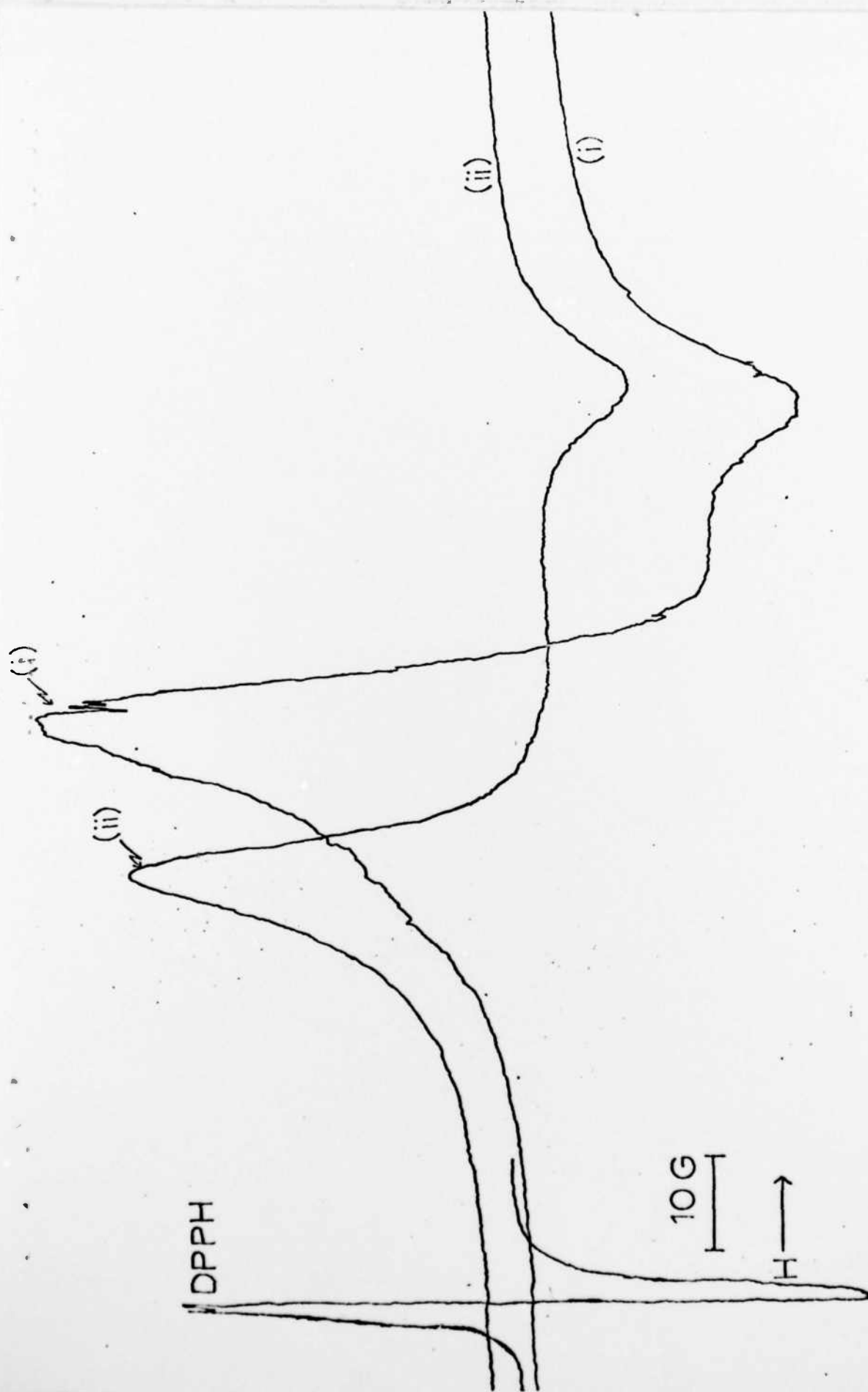


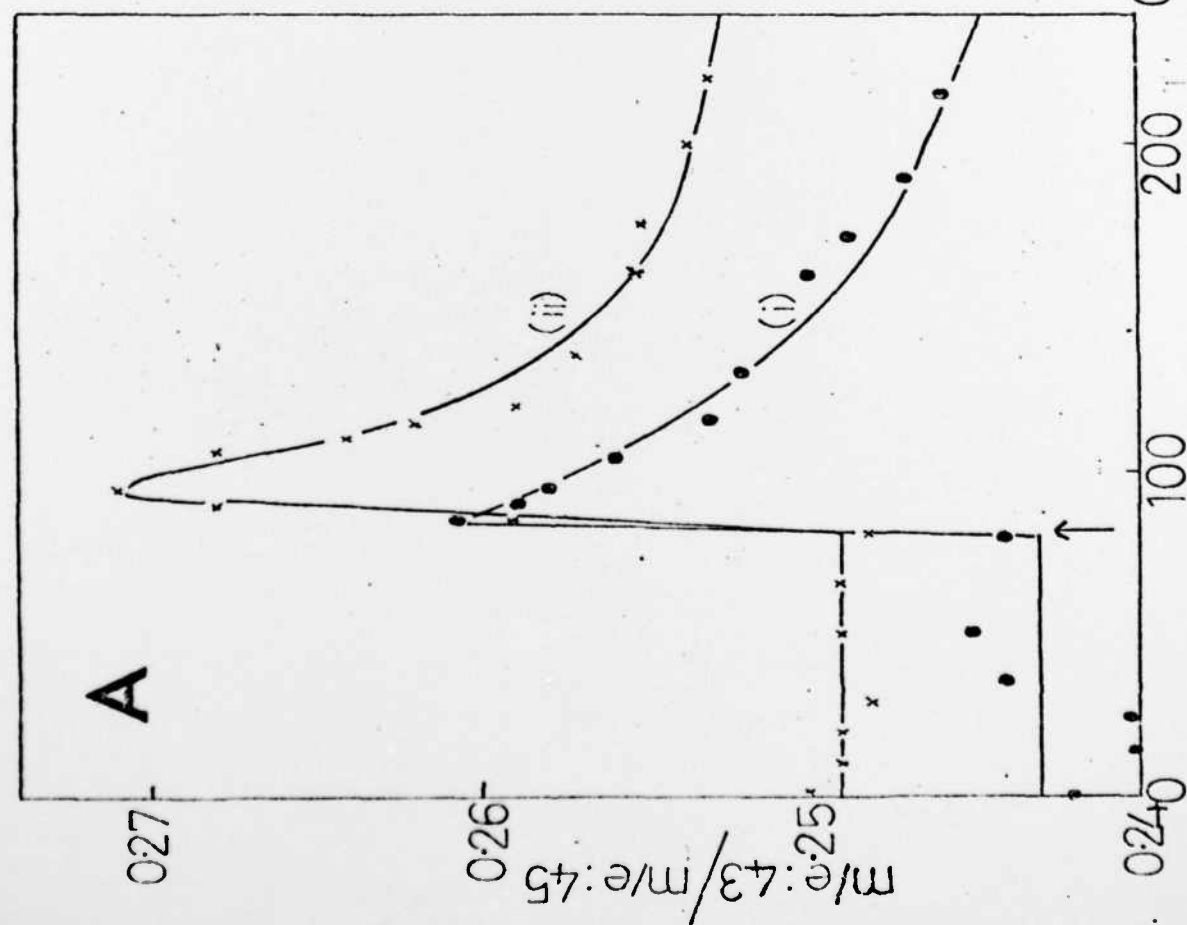
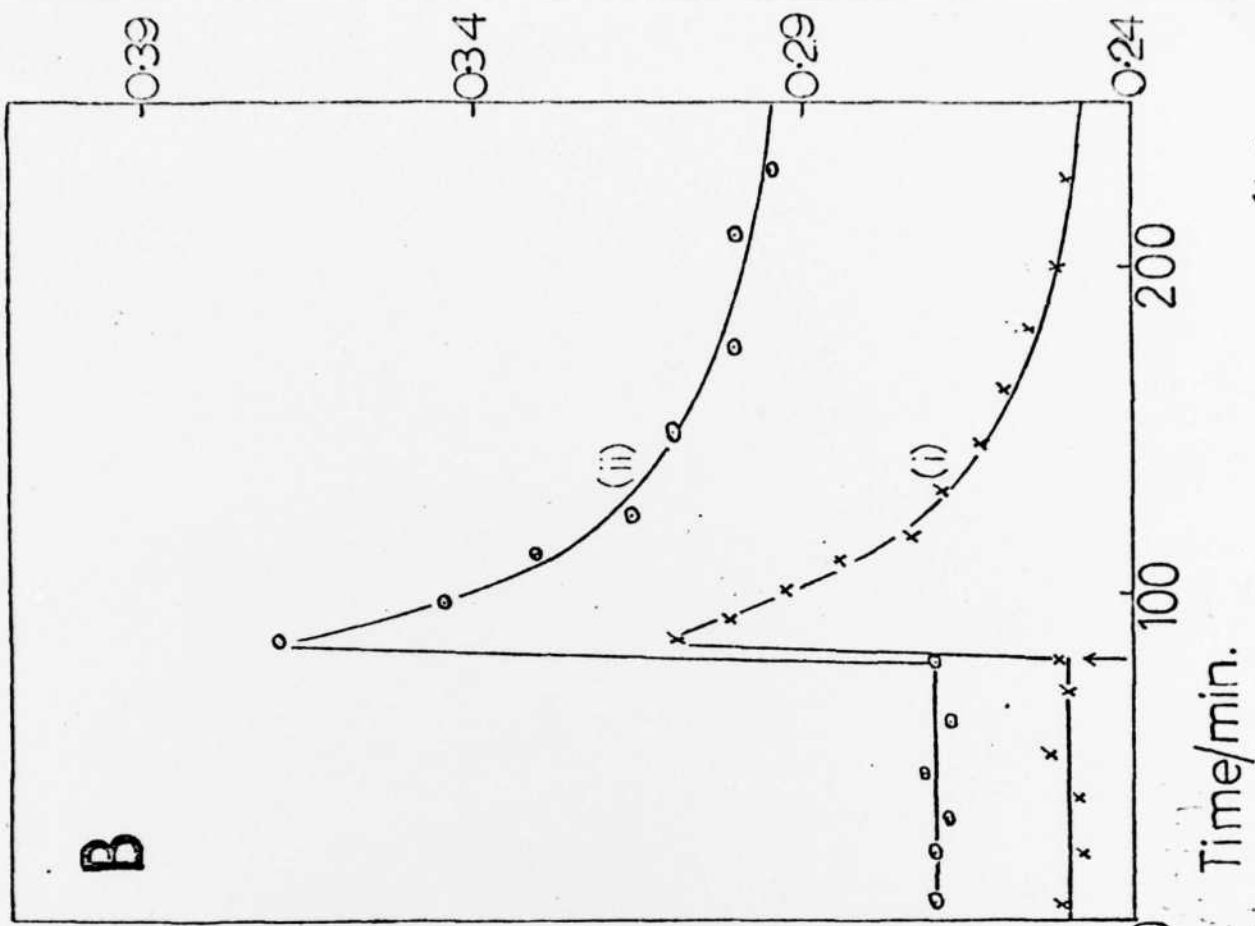


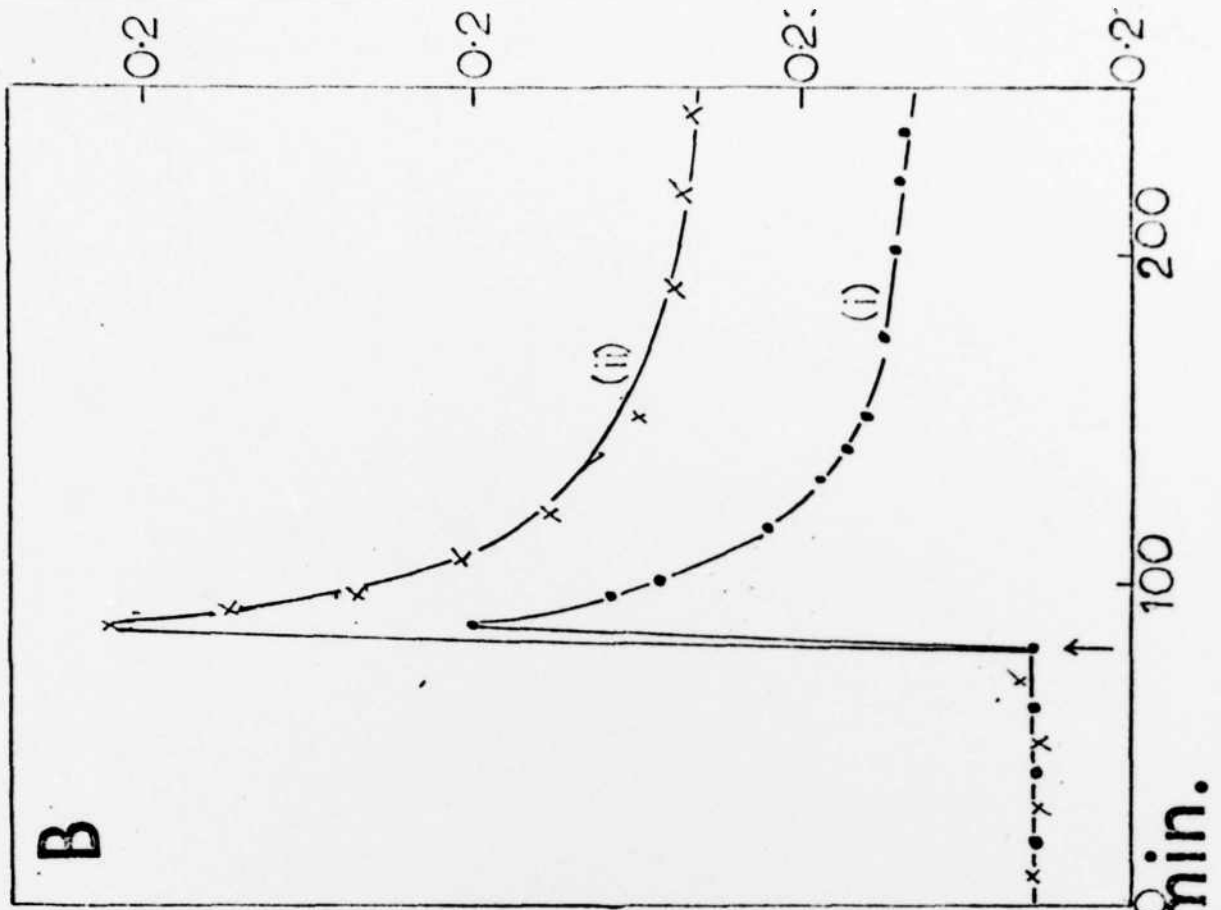
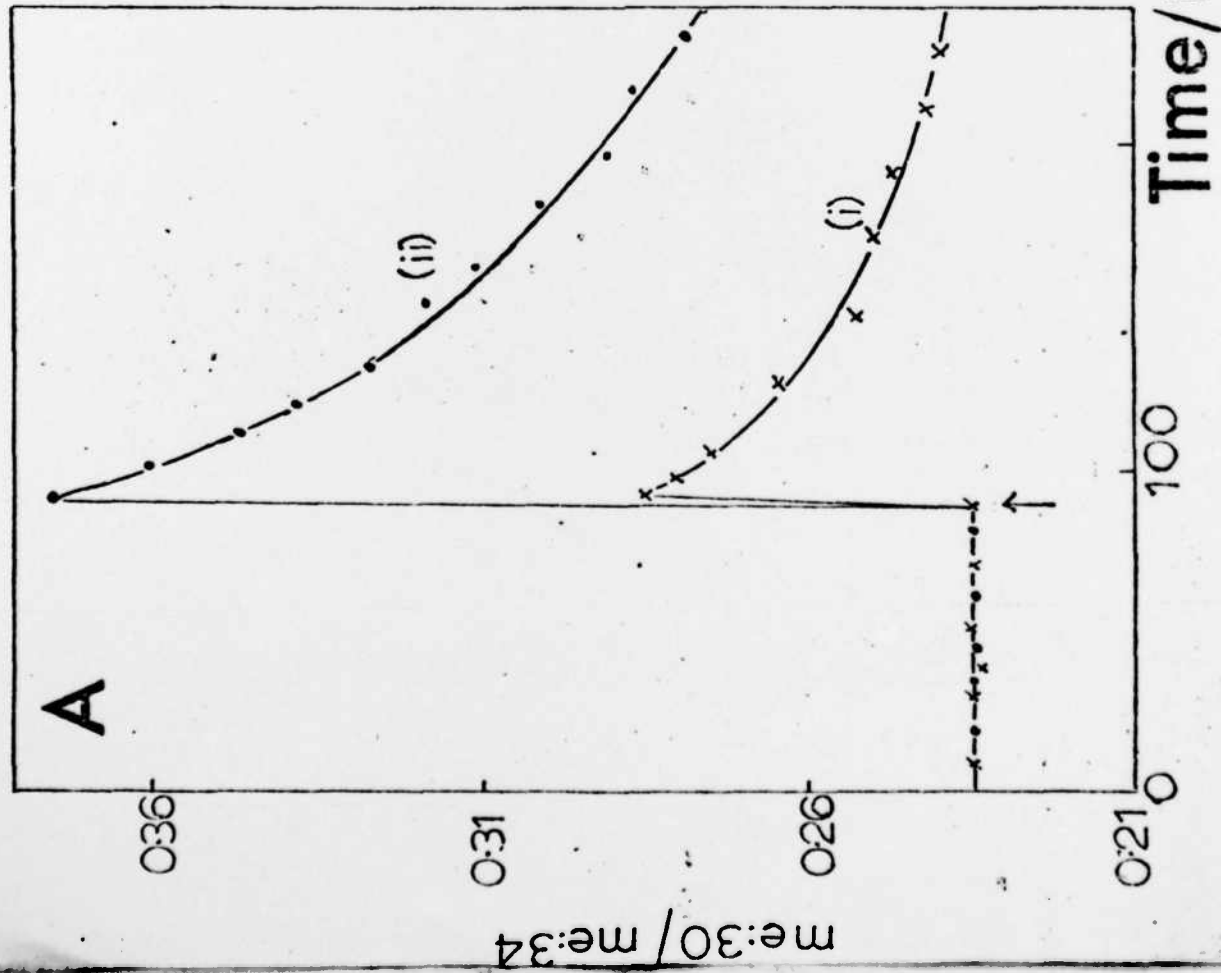
$V_n \times 10^{-4} / \text{ml s per metre}^2$











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