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# PHOTO-OXIDATION OF ALKANES BY METAL OXIDE SEMICONDUCTORS

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ABSTRACT : The partial conversion of alkanes to the corresponding ketones has been achieved by irradiation of a suspension of semiconductor powder in oxygen-saturated alkanes. The reactivity of thermally and chemicallydoped semiconductor and the effect of chemisorbed water have also been studied.

The photocatalytic reactionsof semiconductors have been the subject of various studies during the last few years$^{(1)}$. A photon whose energy is at least equal to the band gap of the semiconductor promotes an electron to the conduction band, permitting redox reactions to be achieved.

We have studied alkane oxidation with a series of semiconductors. In a typical experiment the semiconductor (0.1g) was stirred in neat cyclohexane (3 ml) saturated with oxygen, and irradiated with a Hg-Xe lamp (1000W) for 20h . Cyclohexanone was always the major oxidised organic compound. It was characterised as its 2,4-dinitrophenylhydrazone and the yield was estimated by G.L.C. against an internal reference . The yield of $CO_2$ was determined after conversion to Ba $CO_3$.

The reaction with rutile $TiO_2$, anatase $TiO_2$, $WO_3$ and ZnO gave respectively 24 and 25, 60 and 220, 14 and 0, 22 and 21 μmoles of cyclohexanone and $CO_2$. As previously reported$^{(2)}$ anatase $TiO_2$ was more reactive than rutile $TiO_2$. We have also studied the activity of semiconductors loaded with platinum , prepared according to published procedures . The oxides and $H_2PtCl_6$ used are from Prolabo. The yield ( in μmoles) of cyclohexanone and $CO_2$ were 88 and 180 with Pt(10%) -$TiO_2$$^{(3)}$;132 and 350 with Pt (10%) -$TiO_2$$^{(4)}$ ; 57 and 109 with Pt (10%)-$TiO_2$$^{(5)}$ ; 62 and 75 with Pt (10%)-$WO_3$$^{(5)}$ ; 20 and 10 with Pt(10%)-ZnO$^{(4)}$. The yield of oxidised compounds increased when $TiO_2$ and $WO_3$ were loaded with platinum. The best yield was obtained with anatase Pt-$TiO_2$$^{(4)}$ (17% based on $TiO_2$ and 278% based on Pt).
As can be noted , $WO_3$ was less active than $TiO_2$ but it selectively oxidised cyclohexane to cyclohexanone without the concurrent formation of $CO_2$.

When Pt-$TiO_2$ was loaded with $RuO_2$$^{(6)}$ a good catalyt for water oxidation , the yield decreased (15 μmoles of cyclohexanone and 5 μmoles of $CO_2$).

The yield of oxidised materials increased when $TiO_2$ was thermally doped $^{(7)}$ (cyclohexanone : 125 μ moles ; $CO_2$ : 360 μ moles) . However , thermally doped $WO_3$$^{(8)}$ gave lower yield ( 6 μ moles of cyclohexanone).

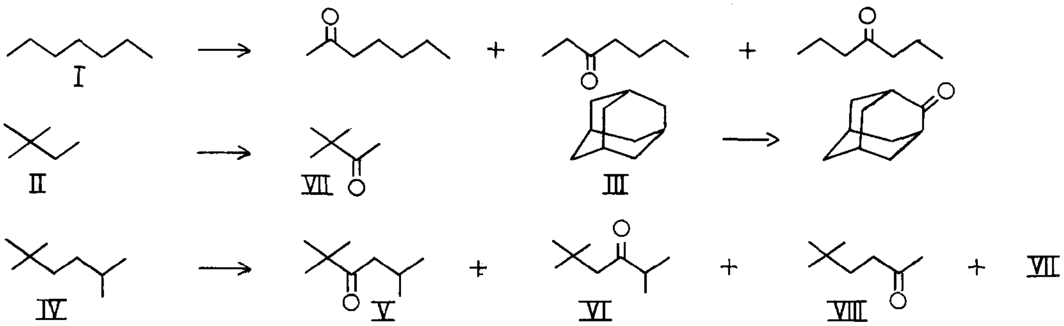
No difference was observed when water was adsorbed on the surface of the catalyst

Moreover, when an excess of water was added to the reaction mixture, in the case of anatase $TiO_2$ the yield of oxidation products actually decreased (3 and 4 µmoles of cyclohexanone and $CO_2$). The major organic product was always the ketone and not the alcohol as reported by Bard et al(9). Little or no oxidation was observed with the following semiconductors : $Fe_2O_3$, $In_2O_3$, CdS, CdSe, $Nb_2O_5$, $SrTiO_3$, Rh loaded on $SrTiO_3$ colloïdal $TiO_2$ and CdS, and Co loaded on colloïdal $TiO_2$.

Using $Pt/TiO_2$ and $Pt/WO_3$ we studied the selectivity of the oxidation towards primary and secondary carbon under the standard experimental conditions (Scheme I). In all the cases, the major oxidised compounds were ketones, characterised by the mass spectrum and the melting point of the corresponding 2,4-dinitrophenylhydrazones.

Three ketones were obtained from n-heptane (I) and no organic products resulting from oxidation of primary carbons were detected. With 2,2-dimethylbutane (II) and with adamantane (III) , the products result from the oxidation on secondary carbon. 2,2,5-Trimethylhexane (IV) leads to the formation of the two oxidised products (V) and (VI) on secondary carbon as before. Two other products, the 3,3-dimethyl-2-butanone (VII) and the 5,5-dimethyl-2-hexanone (VIII) were also found. For the latter , a mechanism of the type described by Teichner *et al.*(10) for the photo-oxidation of vapour phase hydrocarbon could be involved . Small amounts of alcohol can be detected by G.L.C. but the ratio alcohol/ketone decreased with the reaction time, so the ketone may be formed *via* the alcohol.

In contrast to the results previously reported by Teichner *et al.*(10) and Pichat *et al.*(11) for vapour phase alkane oxidation, all the oxidised products result from the attack on a secondary carbon. Oxidation on primary carbon leads probably to the total oxidation of the substrate by a photo-Kolbe mechanism (9).



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