U.V. Irradiation-induced Fission of a C=C or C≡C Bond adsorbed on TiO_2

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Summary The major products of the photohydrogenation of alkenes or alkynes on TiO_2 are alkanes formed *via* the fission of the C=C or C≡C bond, which is caused by the interaction of the bonds with the O^- hole centres.

ALTHOUGH the reactivities of O^- hole centres formed by u.v. irradiation of oxides have been discussed by a number of workers,[1] there are few or no reports concerning their reactivities towards the scission of the bonds between carbon atoms. The present communication deals with this topic.

Water vapour was adsorbed, under various conditions (Table), onto TiO_2 (P-25 from the Japan Aerosil Co., surface area 40 m^2 g^{-1}) which had been subjected to oxygen treatment at 720 K Alkenes or alkynes were then introduced and irradiated by a high pressure mercury lamp without a filter.

TABLE. TiO_2–A · Water vapour was adsorbed at room temperature until a pressure of a few mmHg was reached, after which the evacuation was carried out at room temperature. Catalyst, 300 mg; reactant 63 μmol. TiO_2–β · As A, except the amount of water vapour introduced was insufficient to form a monolayer. Catalyst, 50 mg; reactant, 8·8 μmol.

Catalyst	Reactants	Products (μmol)
TiO_2–A	CH≡CH	C_2H_4 (2·49), CH_4 (1·66), $C_2H_5CH{=}CH_2$ (0·39)
	$CH_3C{\equiv}CH$	C_2H_6 (4·90), $C_2H_5CH{=}CH_2$ (1·96), CH_4 (1·09)
	$C_2H_5C{\equiv}CH$	C_3H_8 (4·65), $CH_2{=}C{=}CHCH_3$ (0·38)
	$CH_2{=}CH_2$	CH_4 (0·30), C_2H_6 (0·045), C_3H_8 (0·01)
	$CH_3CH{=}CH_2$	C_2H_6 (0·625), C_3H_8 (0·23), CH_4 (0·048)
TiO_2–B	$CH_2{=}CHCH{=}CH_2$	$CH_3CH{=}CH_2$ (0·0385), C_3H_8 (0·0143), CH_4 (traces)
	$(CH_3)_2C{=}CH_2$	C_3H_8 (0·0203), CH_4 (0·0105)
	$CH_3CH{=}CH_2$	C_2H_6 (0·0085), CH_4 (traces)
	$CH_2{=}CH_2$	CH_4 (0·0017)

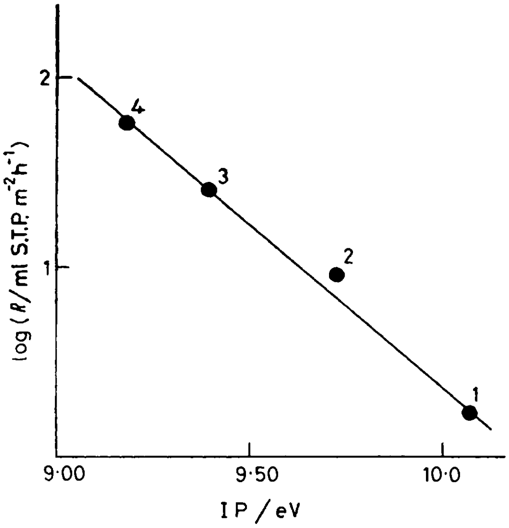

FIGURE. Log(rate of cleavage of C=C bond, *R*) *vs.* ionization potentials of olefins. 1, $CH_2{=}CH_2$; 2, $CH_3CH{=}CH_2$; 3, $(CH_3)_2CH{=}CH_2$; 4, $CH_2{=}CHCH{=}CH_2$.

With $CH_3C{\equiv}CH$ and $C_2H_5C{\equiv}CH$ on TiO_2–A, the major products are alkanes, formed by hydrogenation accompanied by scission of the C≡C bond (Table). With $CH_2{=}CH_2$ and $CH_3CH{=}CH_2$, in addition to these alkanes, alkanes formed without C=C bond fission are produced. The Table also shows the major products obtained using TiO_2–B. Alkanes are again formed by hydrogenation accompanied by scission of the C=C bond. If the C–C bond were cleaved, elimination of CH_3 groups would occur, and C_2H_4 and C_3H_6 would be formed in the reaction of C_3H_6 and C_4H_8 respectively. The lack of formation of these compounds confirms that C=C bond fission takes place, but not C–C bond fission Increasing the temperature of evacuation after water vapour adsorption led to markedly decreased amounts of alkanes produced. The extent of this effect was much less for the formation of CH_4 than for the formation of alkanes of higher molecular weight.

Boonstra *et al.*[2] have proposed that the H atoms produced by u.v. irradiation of Ti-OH groups play a significant role in the photohydrogenation of ethene. There is no doubt that the hydrogen necessary for the formation of alkanes comes from Ti-OH groups, although the mechanism of alkane formation is unclear. However, it seems very difficult to attribute the occurrence of the C=C or the C≡C bond fission to the formation of H atoms. Furthermore, the OH radicals formed by hole trapping of the OH groups are not expected to exhibit such a reactivity towards bond scission. Accordingly, O^- hole centres formed by u.v. irradiation appear to be important in this bond fission. As a result of the interaction of O^- hole centres with alkenes or alkynes, weakening of the C=C or the C≡C bond will occur during hydrogenation. As seen in the Figure, a linear relationship holds between the ionization potentials of the alkenes and the rates of cleavage of the C=C bond. Such a correlation is expected on the basis of the concept that electron transfer from alkenes to O^- hole centres is involved in the weakening of the C=C bond.

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