

## Preliminary Note

Photochemistry of *trans*-stilbene adsorbed on chromatographic aluminas

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As an extension of our earlier work on chemisorbed stilbene [1], we studied the post-irradiation behavior of *trans*-stilbene dispersed by grinding on chromatographic aluminas and various other metal oxide surfaces. The adsorbents were used as received or mildly activated by heating in air at 120 °C. The stilbene was assumed to be in a physically adsorbed state. The isothermal dark reaction following irradiation with the 313 nm mercury line was followed by measurement of the diffuse reflectance, with the Kubelka-Munk function  $f(R) = (1 - R)^2/2R$  being used as a quantitative measure of the absorbance.

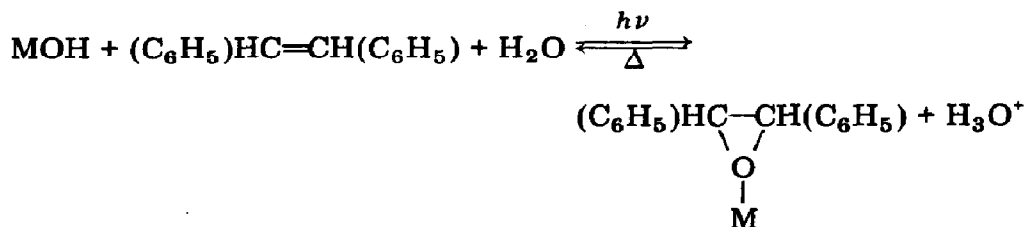
The irradiation of *trans*-stilbene on neutral alumina produced a photochromic change which was largely reversible on standing. A plot of  $\log \{f(R)_\infty - f(R)_t\}$  against time  $t$  showed a distinct non-linearity, indicating a complex dark reaction. Analysis assuming two parallel first-order processes, where the rate constant for the first reaction is about an order of magnitude larger than that for the second, was quite satisfactory. Temperature-dependent studies gave activation energies of  $54 \pm 13 \text{ kJ mol}^{-1}$  and  $71 \pm 8 \text{ kJ mol}^{-1}$  respectively for the two reactions. Mild activation of the adsorbent reduced the quantum yield and decreased the rate of the dark reactions. The more rapid reaction is apparently suppressed when acid-washed alumina is used as the adsorbent, whereas the quantum yields and rate constants for both reactions are greatly reduced on basic alumina.

Photochromism was also observed in *trans*-stilbene on silica gel, MgO and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (a 26%  $\text{Al}_2\text{O}_3$  fluid cracking catalyst kindly supplied by Akzo Chemie N.V.). The dark reactions appeared to be single first-order processes in each of these cases.

It is unlikely that a detailed explanation of the complex dark reaction of irradiated *trans*-stilbene on the chromatographic aluminas can be given, since the surface structure of these adsorbents is not well known. They are presumed to be mixtures of various phases, including the  $\gamma$  and  $\eta$  phases which compose the so-called catalytic aluminas. The latter have been more thoroughly investigated and are known to contain as many as five distinct types of hydroxyl groups [2]. Recently Knözinger and Ratnasamy [3] have

shown that the five hydroxyl sites may be identified with various surface structures on the 100, 110 and 111 faces of  $\gamma$  and  $\eta$  alumina. We assume that some of these hydroxyl sites are also present on the chromatographic alumina surfaces.

Photoexcitation apparently leads to a complete loss of conjugation across the olefinic bond in the surface-bound stilbene, as has been already reported [1]. It is well known [4] that surface oxygen atoms on silver can react with ethylene to form ethylene oxide and we suggest that a somewhat analogous reaction



might be involved in the present case. The radiation possibly leads to the formation of surface peroxides, which are known to yield epoxides through interaction with olefins [5].

Although the surface structure may be rather complex and dependent on the prior history of the sample, IR studies indicate there is only one type of hydroxyl group on  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  or  $\text{MgO}$  [6]. However, the hydroxyl groups on catalytic aluminas are distinct, having different acidities and correspondingly different IR frequencies [2, 3]. Whether the complex reaction we observed on aluminas is caused by the involvement of different hydroxyl types, or possibly caused by adsorption on different crystalline faces, is not yet known. Similar studies with  $\gamma$  and  $\eta$  aluminas are in progress and should allow a more definitive interpretation to be given.

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