

FLASHPHOTOLYSIS OF STILBENES AT 77°K IN RIGID EPA

G. Heinrich, H. Blume and D. Schulte-Frohlinde

Institut für Strahlenchemie

Kernforschungszentrum Karlsruhe

(Received in UK 14 August 1967)

We have investigated stilbene in rigid EPA at 77°K by flashphotolysis technique and observed the reversible formation of a transient spectrum with vibrational fine structure (table I). Similar results have been obtained on 4-methoxy- and 4-methoxy-4'-nitro-stilbene (table I). The decay kinetics are of the first order in all cases.

TABLE I

Transient Absorption Spectra in rigid EPA at 77°K. Conc.  $\sim 10^{-4}$  -  $10^{-5}$  moles/l; degassed;  $\sim 250$  Joules per Flash, Filter: Schott a. Gen., Mainz, UG 11, 1.5 mm

compound	spectrum (peaks $m\mu$ ) <sup>(+)</sup>	lifetime (sec)
stilbene	<u>379</u> /360/343	$22.0 \times 10^{-3}$
4-OCH <sub>3</sub> -	<u>400</u> /382.5/(365)	$23.5 \times 10^{-3}$
4-OCH <sub>3</sub> -4'-NO <sub>2</sub> -	<u>645</u> /612/(540)/(490)/450	$15.0 \times 10^{-3}$
naphthalene	<u>416</u> /393/373	2.6
1-OCH <sub>3</sub> -	490/465/ <u>440</u> /420/395/370	2.3
1-OCH <sub>3</sub> -4-CN-	522.5/495/ <u>469</u> /450/425	2.2
phenanthrene (1)	<u>492</u> /461/432	3.3

(+)<sup>Weak shoulders in parenthesis; max. absorption wave length underlined</sup>

From the observation that the transient of stilbene is obtained only from the trans-form but not from the cis-form we conclude that the transient is not caused by the formation of 4a,4b-dihydrophenanthrene. Therefore it seems probable that the intermediate is the long missed triplet state of trans-stilbene (2). In agreement with this interpretation the lifetimes of the transients do not depend on polar substitution (table I). The same result has been found in the naphthalene series (table I).

#### REFERENCES

- (1) D.P. Craig and I.G. Ross, J. Chem. Soc. (London), 1589 (1954)
- (2) W.G. Herkstroeter and G.S. Hammond, J. Amer. Chem. Soc. 88, 4771 (1966)