Temperature Dependence of Regioselectivity and Excimer Equilibrium in the Photodimerization of 9-Methylanthracene

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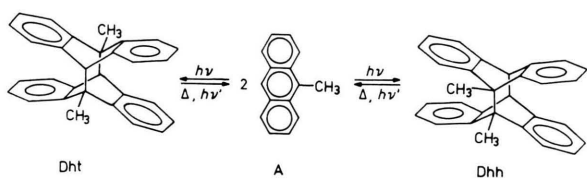Universität-Gesamthochschule-Siegen, Physikalische Chemie, Siegen

The temperature dependence of the ratio of formation of the two isomeric products (head-to-tail- and head-to-head-photodimer) of the photodimerization of 9-methylanthracene was measured in chloroform, ethanol, diethyl ether, and methylcyclohexane as solvents. The ratio increases or decreases with temperature depending on the solvent. One of the isomeric photoproducts was converted photochemically into the other one, indicating an equilibrium of excimer precursors of the products.

Photodimerization of anthracenes and photocleavages of the dimers have been studied intensively [1–13] since Förster [2] proposed the involvement of excimers. Direct flash spectroscopic evidence for the intermediacy of excimers was given only in the photocleavage of dimers [3]. Less directly in the photodimerization of solid anthracene the involvement of excimers was deduced from emission and dimerization quantum yields at different temperatures [4, 13]. However, Kaupp and Teufel suggested another possible mechanism involving radical intermediates [5], and although most of the authors accept Förster's proposal the dimerization mechanism is still under discussion [6–8]. Recently it has been shown that regioselectivity occurs in the photodimerizations of 9-substituted anthracenes depending on the solvent [1, 5, 9, 10, 11]. In the case of the nonpolar 9-methylanthracene (**A**) the formation of the head-to-tail-photodimer (**Dht**) exceeds the formation of the head-to-head-photodimer (**Dhh**) (cf. scheme 1) in most of the solvents investigated [9]. The present note reports on the formation of **Dhh** on irradiation of **Dht** which supports the assumption of excimer intermediates, and on the temperature dependence of the ratio of product formation (ΦDht/ΦDhh) after irradiation of **A** in the solvents chloroform, ethanol, diethyl ether, and methylcyclohexane.

Solutions containing between 5×10^{-4} and 2×10^{-3} M of **A** at temperatures varied from 223 K to 295 K were saturated with nitrogen and irradiated using light of 366 nm wavelength not absorbed by the dimers formed. The concentrations were chosen corresponding to the solubilities of **A**, **Dht**, and **Dhh** in the various solvents at the different temperatures. Less than 10% of **A** were converted during the irradiation time which in no case exceeded the time within which significant amounts of the thermodynamically labile Dhh-isomer may decay (cf. [9]). Ratios of the quantum yields of the isomeric products ΦDht/ΦDhh were determined as described previously [9]. The results are given in Fig. 1 in the form of diagrams $\ln(\Phi\text{Dht}/\Phi\text{Dhh})$ vs. reciprocal temperature. From inspection of the figure it follows that the ratio ΦDht/ΦDhh is distinct for each solvent at a given temperature and that the sequence of increasing ratios in various solvents may change with temperature as the plots intersect. Therefore, no obvious dependence of the ratio ΦDht/ΦDhh on solvent parameters like polarity, polarizability, viscosity, or availability of protons is discernable. Overall dimerization quantum yields ΦD = ΦDht + ΦDhh differ with temperature as diffusion is slower at lower temperatures.

Scheme 1

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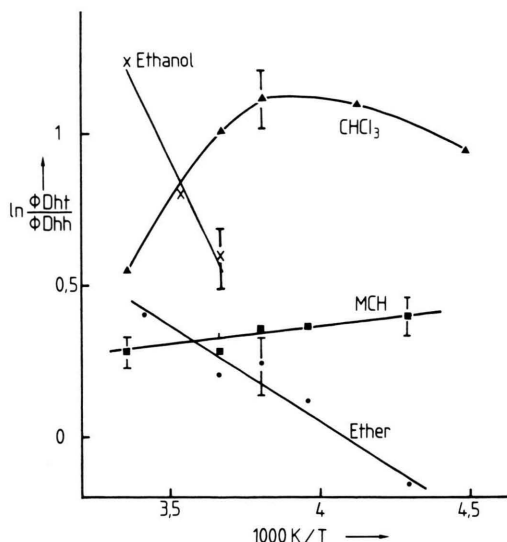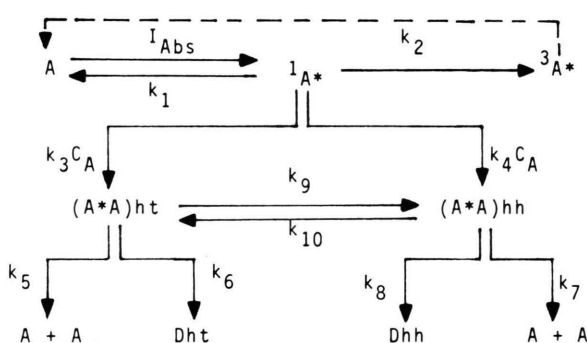
Fig. 1. Logarithmic dependence of the ratio of the quantum yields of isomeric photodimers of 9-methylanthracene $\ln(\Phi \text{Dht}/\Phi \text{Dhh})$ on reciprocal temperature in the solvents chloroform (▲), ethanol (×), diethyl ether (●), and methylcyclohexane (■).

The results are in agreement with the following kinetic scheme:

Scheme 2

The k_i denote the rate constants of reaction steps i, (A*A)ht and (A*A)hh the excimer precursors of Dht and Dhh, respectively. The postulation of the equilibrium k_9/k_{10} between the two excimers is to a great extent based on the results of reference [9]. Without inclusion of the equilibrium any solvent effect on any reaction step would necessarily result in either an increase or a decrease of ΦD, unless several effects compensate each other which is unlikely. The observed small effects on ΦD (see

Fig. 3 in [9]) cannot account for the differences in $\Phi \text{Dht}/\Phi \text{Dhh}$ at room temperature: ΦD-values of 0.0108 and 0.0112 were determined at monomer concentrations of 0.00140 and 0.00144 M in cyclohexane and diethyl ether, respectively. The corresponding $\Phi \text{Dht}/\Phi \text{Dhh}$-values were 1.0 in cyclohexane and 1.5 in diethyl ether. If upon changing from cyclohexane to diethyl ether the difference in $\Phi \text{Dht}/\Phi \text{Dhh}$ were due to a decrease in k_8 — i.e. ΦDhh is smaller at constant ΦDht —, a ΦD-value of 0.009 in diethyl ether must be expected which differs from the measured value 0.0112 more than the error limits in ΦD ($\pm$ 7%) allow.

The existence of an equilibrium k_9/k_{10} is further supported by the following experiments: photochemically prepared and recrystallized Dht was irradiated in 10^{-5} M solutions of n-hexane and diethyl ether at room temperature. The wavelength of 280 nm was chosen for these experiments since the extinction coefficient of A and Dht are similar at this wavelength while at all other wavelengths the extinction coefficient of A exceeds that of Dht by far. The wavelength of 280 nm was selected from the emission of a mercury lamp by means of an interference filter (Oriel No. 5336). About 10% of Dht was converted into A by irradiations. Besides, significant amounts of Dhh were detected in the irradiated solutions by the method described previously [1, 9]. Considering the absorption conditions, the low concentration of A, and the dimerization quantum yields [9] it is impossible that Dhh was formed in a bimolecular process by reirradiation of A. Therefore, a conversion of Dht to Dhh via the excited singlet state Dht*, the excimer (A*A)ht and reactions steps 8 and 9 is likely.

From Scheme 2 the following expressions for ΦDht and ΦDhh can be deduced assuming quasi-stationarity:

$$\Phi \text{Dht} = \frac{k_6}{k_5 + k_6 + k_9}\,\Phi(\text{A*A})\text{ht},\qquad (1\,\text{a})$$

$$\Phi \text{Dhh} = \frac{k_8}{k_7 + k_8 + k_{10}}\,\Phi(\text{A*A})\text{hh}.\qquad (1\,\text{b})$$

If the equilibrium k_9/k_{10} is established, we may assume

$$k_9 \gg k_5 + k_6 \quad \text{and} \quad k_{10} \gg k_7 + k_8. \qquad (2\,\text{a, b})$$

Excimer emission is probably the main contribution to the reaction steps 5 and 7. It was not observed

under the reaction conditions and is known to be a slow process: 200 ns were measured for the excimer emission lifetime at low temperatures [3]. Another reasonable assumption is $k_3 \approx k_4$ and therefore $\Phi(A^*A)ht \approx \Phi(A^*A)hh$ since otherwise solvent effects on ΦD have to be expected. Then

$$\Phi Dht/\Phi Dhh \approx (k_6/k_8) K, \qquad (3)$$

where K denotes the equilibrium constant for k_9/k_{10}. Plots of $\ln(\Phi Dht/\Phi Dhh)$ vs. $1/T$ should result in straight lines according to

$$\ln(\Phi Dht/\Phi Dhh) \qquad\qquad (4)$$
$$= \ln(k_6^0/k_8^0) - (E_6 - E_8)/RT + \Delta S^\ominus/R - \Delta H^\ominus/RT.$$

Here E_i is the activation energy of reaction step i, k_i^0 the frequency factor, and $\Delta S^\ominus$ and $\Delta H^\ominus$ are the standard entropy and standard enthalpy, respectively, of formation of (A*A)ht. With the exception of the measurements in $CHCl_3$ the plots in Fig. 1 are in agreement with the linear relationship.

Although in $CHCl_3$ as in the other solvents no excimer emission was detected under the reaction conditions (the home made spectrometer was not designed for high sensitivity), at higher concentrations of A $(4 \times 10^{-2}$ M) and at 223 K in all solvents used excimer emission was found exhibiting emis-sion maxima around 550 nm (cf. [3]). In $CHCl_3$ this excimer emission was more intense by a factor of about 10 compared to the other solvents indicat-ing that excimer emission competes more effectively with photodimerization and that the assumptions (2a, b) may be invalid in this solvent at low tem-peratures. It was not possible to distinguish between the emissions of the two isomeric excimers.

In conclusion, the observed temperature depen-dence of the ratios $\Phi Dht/\Phi Dhh$ in different solvents can be understood assuming an equilibrium of excimer precursors of the products. This assump-tion is supported by the observation of a direct photochemical conversion of the Dht-isomer to the Dhh-isomer. A mechanism involving biradical intermediates [5] is less likely as these cannot be equilibrated easily.

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