# The Photoreduction of Polyacenes by Tri-*n*-Butyl Stannane

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(Received September 23, 1971)

There have been previous reports on the photoreduction of anthracene derivatives[1] and some polyacenes[2,3] by tri-*n*-butyl stannane. This reaction gives one of the few examples of hydrogen-atom abstraction in a pure $\pi$-$\pi^*$ excited state. Preliminary experiments have shown that the lowest triplet state is susceptible to photoreduction. It is interesting to investigate the mechanism of this reaction and the reactivity of polyacene. Fortunately, the flash-photolysis method gives direct information on the reactivity of the lowest triplet state toward photoreduction. In this communication, we wish to report that some polyacenes were photoreduced in the presence of stannane and that the rate constants of hydrogen abstraction reactions *via* the lowest triplet state were determined by this method.

Prior to kinetical experiments, we investigated the photochemical behavior of deaerated *n*-hexane solutions of polyacenes in the presence of stannane. The samples degassed by repeating a freeze-pump-thaw cycle six times in the dark were irradiated for a series of known time intervals, and the spectral changes were recorded with a Shimadzu SV-50A spectrophotometer for each interval. The results will now be presented. Phenanthrene, naphthacene, 1,2-benzanthracene and chrysene containing stannane were found to lose their characteristic absorption bands in the ultraviolet and the visible regions. For phenanthrene and naphthacene, new bands, which seemed to be assignable to 9,10-dihydrophenanthrene and 5,12-dihydronaphthacene respectively, appeared in the ultraviolet region. However, we haven't yet identified the photochemical products of 1,2-benzanthracene and chrysene. Under the same conditions, though, Brimage and Davidson[3] have recently reported that phenanthrene and 1,2-benzanthracene gave 9,10-dihydrophenanthrene and 7,12-dihydro-1,2-benzanthracene respectively; therefore, we consider that chrysene will be similarly photoreduced to the corresponding dihydro-product.

The flash photolytic experiments were done in deoxygenated benzene solutions of polyacenes containing various concentrations of stannane at room temperature. The decay curves of the lowest triplets after the flash were obtained by observing the transmittance changes at the triplet-triplet-absorption maximum wave lengths: 481 m$\mu$ (phenanthrene), 460 m$\mu$ (naphthacene), 492 m$\mu$ (1,2-benzanthracene), and 570 m$\mu$ (chrysene).[4] The apparent rate constants, $k$, calculated from these curves disregarding the triplet-triplet annihilation, may be related to the photoreduction rate constants, $k_r$, as follows:

$$k = k_d + k_r[Q]$$

where $k_d$ is the decay constant in the absence of stannane and where $[Q]$ is the concentration of stannane. By plotting $k$ *versus* $[Q]$, the relationship between $k$ and $[Q]$ was found to be almost linear, and from the slopes, we obtained the photoreduction rate constants, $k_r = 1.8\times10^5\text{M}^{-1}\text{sec}^{-1}$ for phenanthrene ($10^{-3}$M), $k_r \leqq 10^4\text{M}^{-1}\cdot\text{sec}^{-1}$ for naphthacene ($4\times10^{-5}$M), $k_r = 1.5\times10^4\text{M}^{-1}\text{sec}^{-1}$ for 1,2-benzanthracene ($10^{-4}$M), and $k_r = 1.5\times10^5\text{M}^{-1}\cdot\text{sec}^{-1}$ for chrysene ($10^{-4}$M).

On the other hand, Brimage and Davidson[3] obtained $k_r = 4.7\times10^5\text{M}^{-1}\text{sec}^{-1}$ for phenanthrene and $k_r = 1.8\times10^5\text{M}^{-1}\text{sec}^{-1}$ for 1,2-benzanthracene using steady illumination; we also got $k_r = 7.1\times10^4\text{M}^{-1}\text{sec}^{-1}$ for naphthacene and $k_r = 9.4\times10^4\text{M}^{-1}\text{sec}^{-1}$ for 1,2-benzanthracene by their method.

In comparison with these results, the values obtained by the flash-photolysis method were smaller than those obtained by the steady-state method in any compound. The reason for this is not obvious, but this is a very interesting fact. Particularly, there is a noticeable discrepancy between the values obtained by the two methods for naphthacene. This may suggest that there exists another excited state (or states) which is more reactive than the lowest triplet state. More investigations of the other compounds will offer clear information on the reactive excited states of cata-condensed aromatic hydrocarbons.

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1) J. Osugi, S. Kusuhara, and S. Hirayama, *Rev. Phys. Chem. Jap.*, **37**, 94 (1967).

2) J. Osugi, S. Kusuhara, and S. Hirayama, Preprints for the Symposium of Photochemistry, Japan (October, 1968), No. 25.

3) D. R. G. Brimage and R. S. Davidson, *Chem. Commun.*, **1971**, 281.

4) G. Porter and M. W. Windsor, *Proc. Roy. Soc., Ser. A*, **245**, 238 (1958).