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TIME-RESOLVED ABSORPTION SPECTROSCOPIC DETECTION OF 10,10-DIMETHYL-10-SILAANTHRACEN-9(10H)-ONE OXIDE

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Laser-photolysis studies have been carried out on a solution of 9-diazo-10,10-dimethyl-10-sila-9(10H)-anthracene in cyclohexane. In aerated solutions, the triplet 10,10-dimethyl-10-silaanthracen-9(10H)-ylidene was quenched with oxygen ($k_q = 2 \times 10^9$ $M^{-1}s^{-1}$) to give a characteristic absorption (λ_{max} at 425 nm) due to the corresponding carbonyl oxide.

Carboxyl oxides are accepted as a key intermediate in the ozonolysis of olefins and in the photooxidation of diazo compounds.[1)] Although oxygen-atom-transfer reactions of the oxides have been the subject of recent active investigations, and some theoretical work on the intriguing molecular structure has been reported, not many spectroscopic studies have appeared in the literature.[2)] We wish to report here a time-resolved spectroscopic investigation on the photolysis of a diazo compound in the presence of oxygen and, to our knowledge, the first spectroscopic characterization of a carbonyl oxide formed by the reaction of a triplet carbene with oxygen.

As the carbenic species, we chose 10,10-dimethyl-10-silaanthracen-9(10H)-ylidene (**2**) generated by the photolysis of the corresponding diazo compound (**1**).[3)] In the preceding paper,[4)] **2** was shown to be in the ground triplet state which exhibited an absorption maximum at 343 nm and had a lifetime of 866 ± 54 ns in degassed cyclohexane at room temperature.

Laser-photolysis measurement was carried out on a non-degassed cyclohexane solution (1.02×10^{-3} M) by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser (pulse width of 5 ns) as the exciting light source.[5)] The lifetime of triplet **2** was now only 180 ns, and a broad absorption band with a maximum at 425 nm appeared (Fig. 1). The absorption (λ_{max} at 354 nm) due to the doublet species (**3**) was not observable under these conditions. The rate of increase in absorbance at 425 nm was practically the same as that of decay of the peak at 343 nm, showing that triplet **2** was quenched with oxygen to form a new species. The solution became yellow after the experiment and formation of ketone **4** was indicated by its absorption spectrum (λ_{max} at 363 nm).[3)]

Addition of methanol (1.48×10^{-1} M) accelerated the decay of the absorbance at 425 nm from 2.2×10^4 to 2.6×10^4 s^{-1}, suggesting the quenching of a carbonyl oxide with methanol to give an α-methoxy hydroperoxide. All these results support the assignment of the new species to carbonyl oxide **5**. By combining the pseudo-first order formation rate constant of **5** (5.6×10^6 s^{-1}) with the concentration of dissolved oxygen in cyclohexane (2.3×10^{-3} M), the quenching rate constant of **2** with oxygen is estimated to be 2×10^9 $M^{-1}s^{-1}$ which is within typical diffusional quenching constants.

Zwitterionic and diradical structures are proposed to carbonyl oxides. The observed absorption maximum resembles the ketyl radical (λ_{max} at 444 nm) rather than the conjugate acid (λ_{max} at 351 nm) of anthrone,[6)] suggesting the diradical structure of **5**.

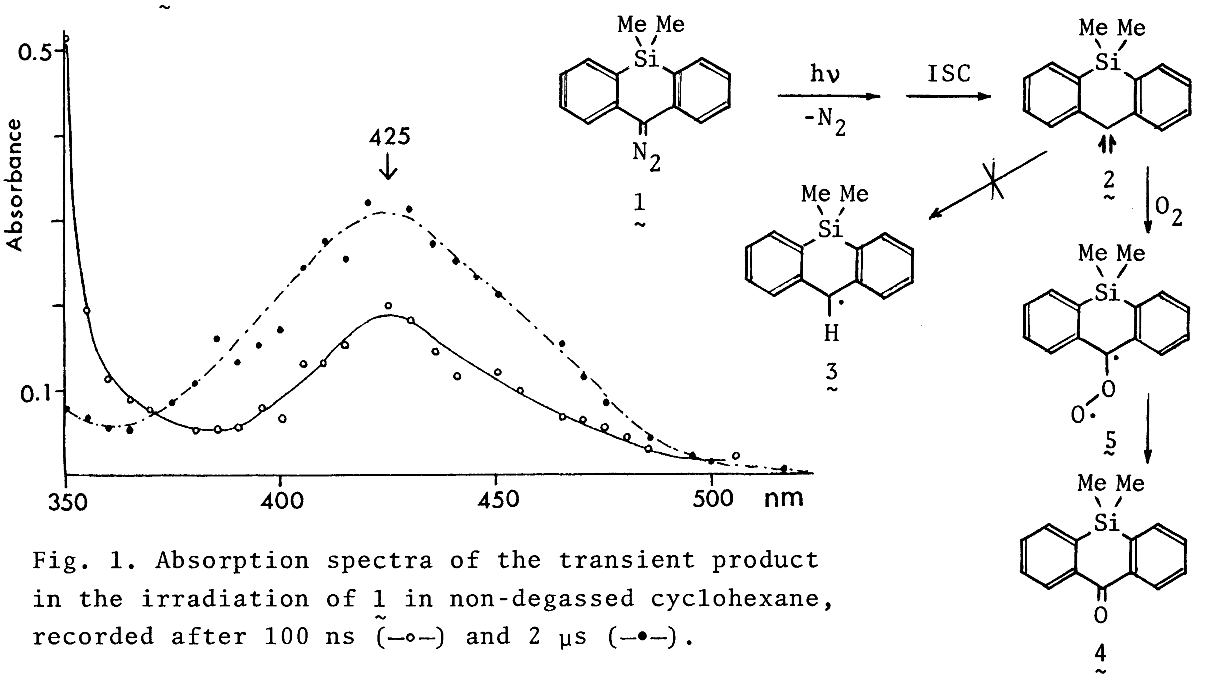

Fig. 1. Absorption spectra of the transient product in the irradiation of **1** in non-degassed cyclohexane, recorded after 100 ns (—○—) and 2 μs (—•—).

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