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A CIDEP Study of the Addition of Trialkylsilyl Radicals to Substituted *p*-Benzoquinones

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Synopsis. Evidence has been obtained through the combined ESR and CIDEP techniques for the two distinct pathways in which trialkylsilyl radicals add to substituted *p*-benzoquinones *via* the carbonyl oxygen as well as the ring carbon–carbon double bonds. The results represent the first observation of CIDEP from organic radicals containing an organosilyl group in solution.

The reaction of organosilyl radicals with carbonyl compounds has received considerable attention in the past decade.[1–4] While it is generally accepted that the most *stable* adduct formed between a trialkylsilyl radical and 2,6-di-*t*-butyl-*p*-benzoquinone (DTBQ) at room temperature is the adduct to the carbonyl oxygen, recent experiments at low temperature with 3,6-dimethylthieno[3,2-*b*]thiophen-2,5-dione[5] indicate that the faster reaction is the addition of the trialkylsilyl radicals to the ring carbon–carbon double bond. Although CIDEP has been detected previously from trialkylsilyl radicals in solution, it is possible that in a fast reaction involving a primarily polarized organosilyl radical and a quinone the secondary racical adduct may retain and exhibit the initial polarization. In an ideal case, the magnitude of the secondary polarization is a direct measure of the relative efficiencies of the different reaction pathways. We wish to report here the first observation of CIDEP of the trialkylsilyl radical adducts to DTBQ formed by two distinct mechanisms.

When *t*-butylbenzene solutions of DTBQ and triethylsilane were photolyzed in the microwave cavity of an ESR spectrometer at −50 °C a first derivative spectrum (Fig. 1a) was observed which showed *a* triplet attributable to the oxygen adduct (**1**) (a_H=1.08 G (1G ≈10^{-4})) and *a* broad doublet due to the ring adduct (**2**) (a_H=7.03 G).

The polarization spectrum of the same system obtained in the CIDEP experiment is shown in Fig. 1b. The totally emissive character of the polarization spectrum is consistent with the photochemistry of the triplet DTBQ which must lead to the formation of two primary, emissive radicals, $\mathrm{DT\dot{B}QH^*}$ and $\mathrm{R_3\dot{S}i^*}$. In the present system with excess benzoquinone, the addition reactions of $\mathrm{R_3\dot{S}i^*}$ to the ground state benzoquinone molecules are so rapid (faster or comparable to the spin lattice relaxation rate of $\mathrm{R_3\dot{S}i^*}$) that only the radical adducts (**1**) and (**2**) are observed in the cw spectrum. However, in the polarization spectrum, additional emissive lines due to the semiquinone radical $\mathrm{DTB\dot{Q}H^*}$ are also apparent. In order to avoid the complication of the polarization spectrum due to the overlapping semiquinone radicals, triethylsilane was replaced with hexamethyldisilane as the reactant. In such a system the overall reaction can be represented by the following steps:

[1] $\mathrm{^3DTBQ^* + Me_3SiSiMe_3 \longrightarrow DTBQ\text{-}SiMe_3^* + Me_3\dot{S}i^*}$,

[2] $\mathrm{Me_3\dot{S}i^* + DTBQ \longrightarrow}$ (**1**) and (**2**).

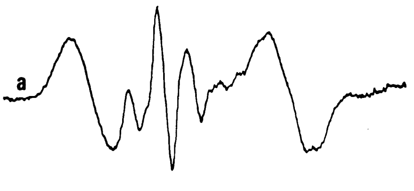
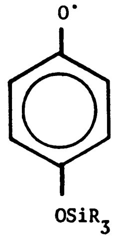
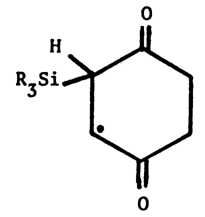


Fig. 1a. Cw ESR first derivative spectrum observed during the photolysis of DTBQ and triethylsilane in *t*-butylbenzene at −50 °C;



(**1**)



(**2**)

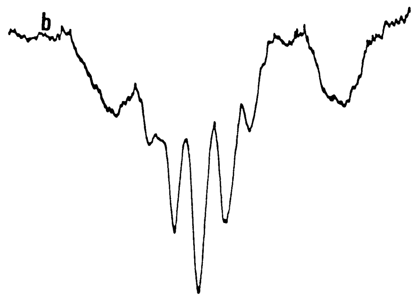


Fig. 1b. Polarization spectrum of the same system in 1a at −50 °C;

The cw and the polarization spectra of the DTBQ/hexamethyldisilane system at 23 °C are shown in Fig. 1c and 1d, respectively. At room temperature, the predominant radical adduct was (**1**), while a weak polarized spectrum of the ring adduct (**2**) was observable in the CIDEP experiment.

The present results clearly establish that there are two distinct pathways for the addition of trialkylsilyl radicals to *p*-benzoquinones. The variation of temperature in the reaction system further confirms that the most thermally stable adduct is the oxygen adduct. At room temperature with DTBQ most of our previous

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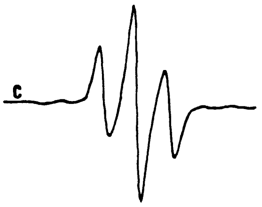

Fig. 1c. Cw ESR first derivative spectrum observed during the photolysis of DTBQ and hexamethyldisilane at 23 °C;

Fig. 1c. Polarization spectrum of the same system in 1c at 23 °C.

studies of the reactions of organometallic radicals, $\dot{M}R_3$, indicate the predominant formation of adducts of the type (**1**). In a more interesting study of the photochemical and thermal reactions of Me_3Sn–$\dot{M}n(CO)_5$, we have shown⁽⁶⁾ that at room temperature the two primary radicals, $Me_3\dot{S}n$ and $\dot{M}n(CO)_5$ behaved very differently towards the addition mechanism to DTBQ: The $Me_3\dot{S}n$ radicals added to the carbonyl oxygen of DTBQ while the $\dot{M}n(CO)_5$ radicals attacked only at the carbon–carbon double bond of the ring. These results can be explained by the reversibility and endothermicity of the addition of stannyl radicals to ethylenic double bonds.⁷⁾

Experimental

Cw ESR spectra were recorded on a Varian E-3 X-band spectrometer with 100 kHz field modulation. Irradiation in cw experiments was accomplished by using a 200 watt super pressure mercury lamp. For CIDEP experiments, a Molectron nitrogen laser (1 MW) was used as the excitation source and the ESR transients were directly detected without modulation using a Hewlett Packard wide band preamplifier and a Princeton Applied Research model 162 boxcar integrator and a Nicolet microcomputer controlled digital oscilloscope with a Hewlett Packard 7475A digital plotter.

Chemicals were supplied by Aldrich, the *p*-benzoquinone was sublimed and the tertiary butylbenzene distilled before use.

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