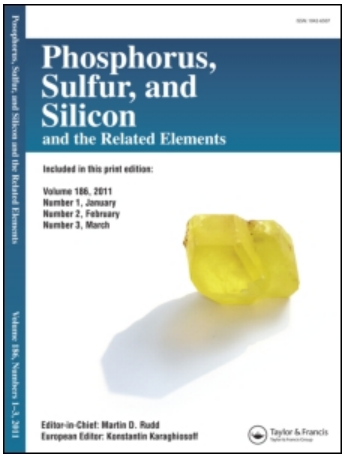

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AN ESR-CIDEP STUDY OF THE FREE-RADICAL INTERMEDIATES IN THE SULFURIZATION OF 2,5-DIMETHYL-*P*-BENZOQUINONE WITH LAWESSON REAGENT IN TRIFLUOROACETIC ACID

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SHORT COMMUNICATION
AN ESR-CIDEP STUDY OF THE FREE-RADICAL INTERMEDIATES IN THE SULFURIZATION OF 2,5-DIMETHYL-*P*-BENZOQUINONE WITH LAWESSON REAGENT IN TRIFLUOROACETIC ACID

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Substituted *p*-benzoquinones undergo rapid sulfurization with Lawesson reagent in triflouroacetic acid. The ESR observations of the radical intermediates and the time-resolved CIDEP results afford some insights into these complex reactions.

In the past decade extensive and systematic studies of the substituted-quinone model systems in our laboratory have demonstrated the usefulness and potential applications of the combined ESR-time-resolved CIDEP techniques towards the understanding of the free-radical processes involved in the quinone reactions.[1-3] One of the recent applications established the primary charge-transfer process between a polarized benzoquinone radical cation and some sulfur heterocyclic compounds in trifluoroacetic acid.[4] The use of trifluoroacetic acid as solvent appeared to afford the best "stability" of the radical cations generated in the charge-transfer processes.[5-7] Although the popular Lawesson reagent has been extensively employed as a sulfurizing reagent with many classes of organic compounds,[8-10] we are not aware of any published reports dealing with the sulfurization of substituted *p*-quinones using Lawesson reagent. Furthermore, in the Lawesson-reagent reactions, the exact nature of the processes is not well understood. By using the 2,5-dimethyl-*p*-benzoquinone (Q) as the model system in the sulfurization reaction with Lawesson reagent, we report here the interesting ESR and CIDEP observations on the radical-cation intermediates involved in this process. The positive identification of the radical cation's involvement and the time-resolved CIDEP results of the radical-cation intermediates lead to the first insight in the nature of the radical processes of this important class of reaction which will be of great general interest.

When 2,5-dimethyl-*p*-benzoquinone (Q) was dissolved in pure trifluoroacetic acid, a weak thermal radical signal was observed which could be substantially enhanced by UV irradiation. The typical ESR spectrum (Fig. 1a) which did not change when trifluoroacetic acid-d_1 was used, was assigned to the radical-cation structure of the parent quinone ($\dot{Q}^+$) (Table I). The addition of Lawesson reagent to the solution

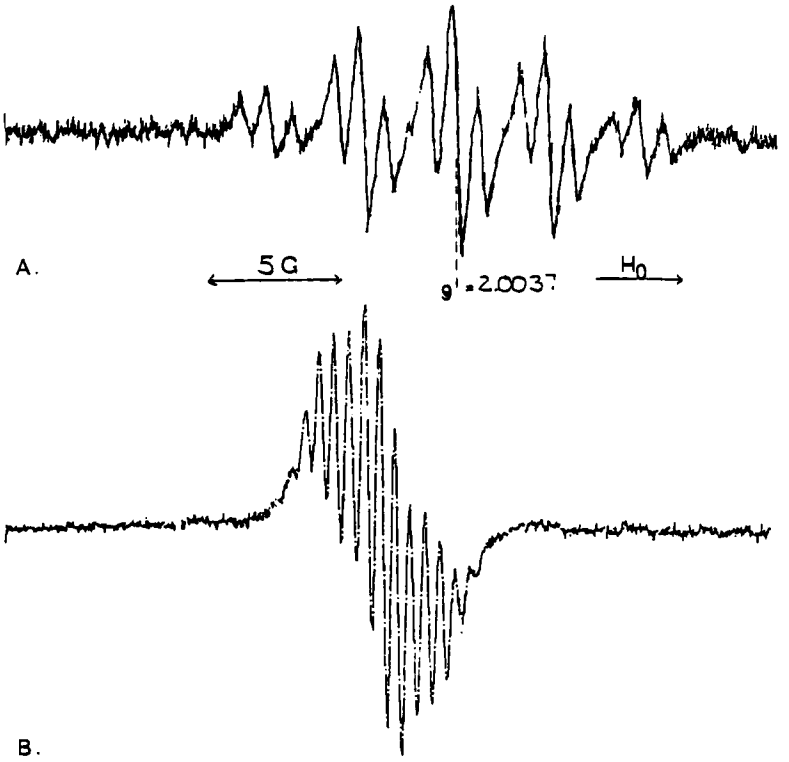


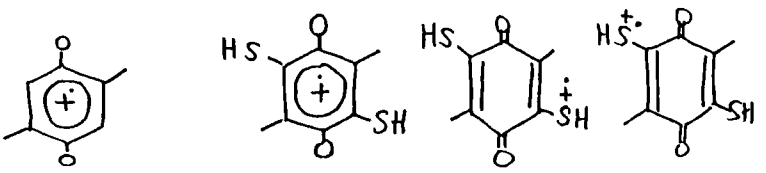
FIGURE 1 C.w. ESR spectra observed at room temperature: (a) $\dot{Q}^+$ alone in trifluoroacetic acid, (b) the new radical cation $Q\dot{S}H^+$ when Lawesson reagent was added.

immediately produced a drastic change in the ESR observation (Fig. 1b) in which a new ESR signal with significant *g*-shift appeared. At low concentrations of Lawesson reagent, it was possible to observe some residual signal (under high sensitivity) due to the "unreacted" $\dot{Q}^+$. The assignment of this new species to the sulfurized-quinone radical cation $Q\dot{S}H^+$ (Table I) is supported by the following facts: (1) The significant *g*-shift and (2) the drastic change in the proton hyperfine couplings. It is reasonable that some resonance structures such as *I* are involved in the overall assignment of the $Q\dot{S}H^+$ radical cation (Table I). The contribution of such a resonance structure accounts for the large *g*-shift observed. It also enhanced the spin density at the ring positions in which the SH substitution occurred. Thus, the SH proton coupling constant is larger than the methyl protons. This assignment was confirmed when trifluoroacetic acid-d_1 was used. In this case, the radical cation expected would be the $Q\dot{S}D^+$ which the replacement of deuterium in the SH groups led to the "collapse" of the hyperfine pattern into a single broad line.

Although it appeared that the thermal reactions between $\dot{Q}^+$ and Lawesson reagent to form $Q\dot{S}H^+$ were rapid, it remained uncertain whether the process actually involved the Q^+ cation. To delineate this problem, we have carried out the reaction in a time-resolved CIDEP experiment.[11] As shown in previous charge-transfer reactions between $\dot{Q}^+$ and sulfur heterocyclic compounds,[4] the secondary radical

TABLE I

Assignments and ESR parameters of radical cations in the sulfurization reaction of 2,5-dimethyl-*p*-quinone with Lawesson reagent



	$\dot{Q}^+$	$QS\dot{H}^+$ $\dot{Q}^+$	I $QS\dot{H}^+$
g-factor		2.0037 ± 0.0002	2.0057
$\underline{a}_H^{CH_3}$ (6 H)		3.32¡0.03 gauss	0.59 gauss
$\underline{a}$ (2 H) (ring)		0.9 gauss	—
$\underline{a}$ (2 H) (SH)		—	1.66

cation could only be polarized if it was formed by direct reaction with the primary polarized quinone cation. In the present study, the results showed that 2,5-dimethyl-*p*-benzoquinone radical cation was totally emissively polarized via the "triplet mechanism"[1] in trifluoroacetic acid, either alone or in the presence of Lawesson reagent. In the latter case, substantial polarization was also observed for the $QS\dot{H}^+$ at a lower magnetic field owing to the *g*-shift. These results clearly established the participation of the polarized parent $\dot{Q}^+$ radical cation in the charge-transfer-sulfurization processes. Although detailed mechanisms of the whole process must await further experimental studies, including identification of the final diamagnetic products, for the first time a free-radical process and the nature of the radical intermediates are confirmed in this interesting and general class of reactions. It is noteworthy to mention that with the corresponding hydroquinone (QH_2) under identical conditions, the formation of sulfurized radical cations was not observed.

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