

A Simple Nuclear Magnetic Resonance Method for the Study of Stable Free Radicals

By IAN BAXTER and JEREMY K. M. SANDERS*

(*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW*)

Summary N.m.r. spectra of stable free radicals undergoing fast exchange with their related molecular species demonstrate selective line broadening; this observation

provides the basis of a method for the determination of the sites of free electron density in organic compounds.

THE use of e.s.r. spectroscopy in studies of free radicals is well established,¹ but the potential of n.m.r. spectroscopy is almost wholly unexplored. For example, although it is known that radical anions²⁻⁴ and radical cations⁵ undergoing rapid electron exchange with their related neutral species give rise to broadened n.m.r. spectra, the specificity of the broadening and its potential uses in organic chemistry have not been previously described.

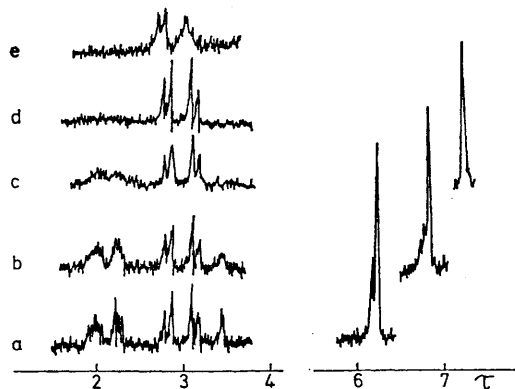
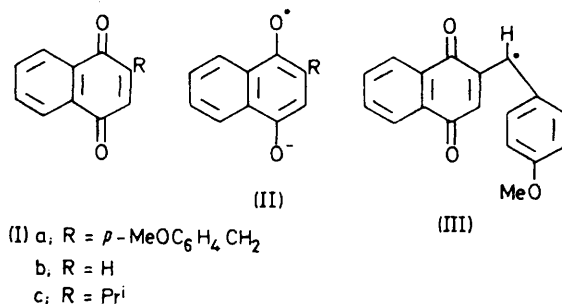


FIGURE. 100 MHz ^1H n.m.r. spectra of (Ia) in deuteriomethanol in the presence of increasing concentrations of *t*-butylamine (a) no added amine, (b) $5 \times 10^{-4}\text{M}$, (c) $3 \times 10^{-3}\text{M}$, (d) $2 \times 10^{-2}\text{M}$, (e) $1 \times 10^{-1}\text{M}$. Methoxy-regions of spectra (b) and (c) are offset by 0.5 and 1.0 p.p.m. respectively.

Addition of increasing concentrations of *t*-butylamine to solutions of the naphthoquinone (Ia) in deuteriomethanol causes selective and increasing line broadening in the ^1H n.m.r. spectrum (see Figure) without affecting solvent resonances. Thus, $5 \times 10^{-4}\text{M}$ amine causes significant broadening of the quinonoid (τ 3.5) and aliphatic benzyl (τ 6.18) resonances but has little effect on other resonances which are, however, broadened by higher amine concentrations. In the examples we have studied, shifts have not been observed. Acid quenching of the solutions restores the original spectrum of the quinone (Ia) with no detectable deuterium incorporation.

These observations are best explained by invoking the presence of the naphthosemiquinone radical anion (IIa) in fast exchange with a large excess of the naphthoquinone (Ia). The observed spectra exhibit characteristics of both species, and therefore the quinonoid and aliphatic benzyl

protons, being closest to unpaired electron density, are most broadened, while the aromatic protons of the naphthoquinone fragment (τ 2.3, 2.0) are less broadened. This is consistent with the results of e.s.r. studies.¹ Most important is the relative sharpness of the benzyl AA'BB' signals, clearly ruling out the existence of substantial amounts of the highly stabilised benzyl radical (III). At the highest *t*-butylamine concentrations used, these signals also begin to broaden (Figure, spectrum e) but whether this is due to exchange effects³ or the presence of a second radical species is not clear.



The relative broadening induced by *t*-butylamine in spectra of the naphthoquinones (Ia), (Ib), and (Ic) is *ca.* 1:10:10⁻². This presumably does not reflect relative stabilities of the derived radical anions but the ease of their formation: hydroxide ion-catalysed formation of semiquinones from quinones is believed to proceed *via* nucleophilic attack at a free quinonoid position,⁶ and an analogous pathway in the amine-catalysed reaction would be expected to be subject to steric influences at the 2-position. These results also reflect relative reactivities of the naphthoquinones under these conditions.⁷

The results described here provide the basis of a simple method for the determination of the site of free electron density in organic compounds without the need for analysis of complex e.s.r. spectra, and should, therefore, prove useful in mechanistic studies. The use of sterically less demanding reagents for radical production could also provide an n.m.r. method for the determination of oxidation-reduction potentials by competition experiments.

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¹ See for example, A. R. Forrester, J. M. Hay, and R. H. Thomson, 'The Organic Chemistry of Stable Free Radicals,' Academic Press, 1968, ch. 1.

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