

A mass spectrum of the trimethylsilyl (TMS) derivative of dilipoxyl hydroxylamine (**3c**) contained a strong molecular ion at the expected m/e 609 and an intense fragment ion at m/e 519 from loss of TMS-OH. This m/e 519 peak (high-resolution $519.43006 = C_{32}H_{57}NO_4$) is the highest mass in the spectrum of the *O*-acetyl derivative **3b** resulting from an apparent loss of acetic acid to give the enamine ion, $[C_{14}H_{25}O_2CH_2CH=NC_{16}H_{29}O_2]^+$. In both spectra the m/e 519 ion then fragments by α -ketone cleavage and β -ketone McLafferty rearrangements.

An attempt to *O*-methylate **3** with CH_3I in acetone and K_2CO_3 gave instead the β -elimination product **4**, which we call lipox-1-ene. Lipox-1-ene is an oil showing new vinyl ketone absorptions at ν_{max}^{neat} 1670 and 1610 cm^{-1} in its ir spectrum and vinyl protons at δ 5.7–6.4 in its pmr spectrum. A high-resolution mass spectrum showed a molecular ion at m/e 252.2085 ($C_{16}H_{28}O_2$) for **4**.

Periodate–permanganate oxidation of the vinyl ketone, **4**, gave the previously unknown acid, 12-methyl-8-oxotridecanoic acid (**5**). This compound was synthesized using the cadmium Grignard reagent of 1-bromo-4-methylpentane (**6**) and ω -carboxy-suberoyl chloride (**7**). The acid **5** obtained by synthesis ($C_{14}H_{26}O_3$, molecular ion 242.1878, mp 59.5–62.3°) gave ir and pmr spectra identical with those of the acid obtained by degradation. Mass spectra of both acids show identical molecular ions and fragmentation patterns.

These data substantiate structure **1** for lipoxamycin, a novel *N*-diketoalkyl-substituted hydroxamic acid with potent antifungal properties.

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Howard A. Whaley

Infectious Diseases Research, The Upjohn Company
Kalamazoo, Michigan 49001

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Electron Spin Resonance Studies of Equilibria in Semiquinone–Alkali Metal Ion Systems

Sir:

It has recently been suggested¹ that an endor-induced esr study of solutions of the durosemiquinone anion supports an earlier esr study of the system,² despite the fact that the work of ref 2 has been reinterpreted by others.³ The purpose of this communication is to suggest that the endor work is consistent with our reinterpretation and also supports our claim that the spectra of ref 2 were incorrectly interpreted.

In our studies of semiquinone systems, we have generally found that spectra from the "free" ions⁴ and

(1) R. D. Allendoerfer and R. J. Papez, *J. Amer. Chem. Soc.*, **92**, 6971 (1970).

(2) M. P. Khakhar, B. S. Prabhananda, and M. R. Das, *ibid.*, **89**, 3100 (1967).

(3) T. A. Claxton, J. Oakes, and M. C. R. Symons, *Nature (London)*, **216**, 914 (1967); J. Oakes and M. C. R. Symons, *Trans. Faraday Soc.*, **66**, 10 (1970).

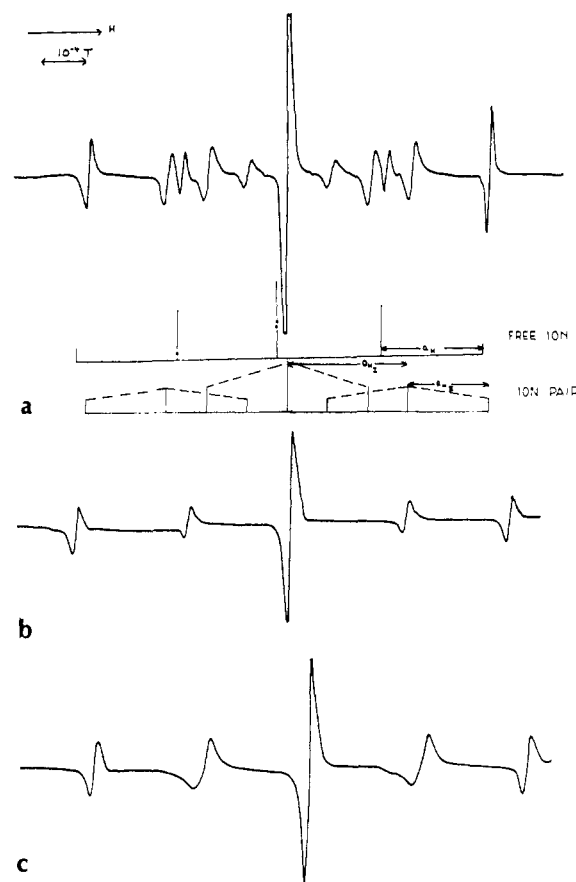


Figure 1. ESR spectra for potassium *p*-benzo-semiquinone at various temperatures: (a) at 183°K, showing a quintet for the "free" anion and a triplet of triplets for the ion pair; (b) at 240°K, the "free" ion spectrum remains unchanged, but certain features of the ion-pair spectrum have broadened; (c) at 263°K, the spectrum of the "free" anion is coincident with that of the ion pair for which marked line-width alternation is apparent.

ion pairs are detected simultaneously.^{3,5,6} What was disputed was the suggestion² that a third species, possibly a solvent-separated ion pair, was also present. We have shown that *no* new spectral features were present, the effect being an unfortunate artifact.³ The endor results confirm our conclusion.

In all our studies of alkali metal salts of *p*-benzo-semiquinone,^{3,5} 2,6-dimethyl-*p*-benzo-semiquinone,⁶ and durosemiquinone^{3,5} the low-temperature spectra ($\sim 180^\circ K$) comprise narrow lines from the "free" anions and narrow lines from the asymmetric ion pairs.^{3,5,6} As the temperature is raised, certain lines for the ion pairs broaden and merge to give spectra comparable with those of the "free" anion, but with alternating narrow and broad features, while the lines for the "free" anion remain narrow.

We conclude that "free" anions are not involved in the broadening process and that the rate of interconversion of the "free" anions and ion pairs is slow ($< 10^6 \text{ sec}^{-1}$). This reinforces our view that the normally accepted model of intramolecular oscillation of

(4) These were identified as "free" or solvated anions and not solvent-separated ion pairs on the basis of (i) dilution experiments and (ii) independence of the spectrum from the counterion.

(5) J. Oakes, Ph.D. Thesis, University of Leicester, 1967.

(6) T. A. Claxton, J. Oakes, and M. C. R. Symons, *Trans. Faraday Soc.*, **64**, 596 (1968).

the cation between the oxygen atoms of the semiquinones is the source of line broadening.^{3,5,6}

Typical spectra illustrating these observations are depicted in Figure 1.

J. Oakes,* M. C. R. Symons, T. A. Claxton

Basic Division, Unilever Research Port Sunlight Laboratory
Unilever Ltd., Port Sunlight, Cheshire L62 4XN, England

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The Kinetic Deuterium Isotope Criterion for Concertedness

Sir:

The magnitude of the kinetic, primary deuterium isotope effect has been proposed as a criterion of transition-state structure stemming from theoretical considerations by Westheimer¹ and by Bigeleisen.² On the basis of these derivations it is currently presumed that a fully symmetrical transition state will manifest a "maximum" kinetic isotope effect,³ whereas asymmetric transition states (which are either more product or more reactant-like) will tend to exhibit smaller values of k_H/k_D .

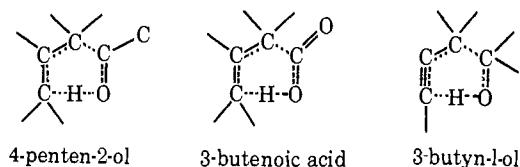
A number of reservations have been expressed as to the applicability of this correlation. Willi and Wolfsberg⁴ have suggested that low isotope effects could be a consequence of high hydrogen force constants in the transition state. Bader^{5a} has emphasized this occurrence resulting from large antisymmetrical vibrations in a symmetrical transition state.^{5b} The presumption that contributions from valency bending forces may be cancelled out by tunneling⁶ (or otherwise) represents a further possible limitation. Saunders⁷ has developed a model of the transition state for H transfer which suggests that proton coupling with other atomic motions has a significant influence on the isotope effect, a conclusion which is at variance with the very basis of Westheimer's¹ and Bigeleisen's² earlier derivations. On the other hand, a model calculation by O'Ferrall and Kouba⁸ appears to provide strong support for the correlation of transition-state symmetry and the magnitude of k_H/k_D but *only* for systems where H is transferred from carbon. The claim is made that in the transfer of H from oxygen the bending vibrations in the transition state are too large to be ignored.

The theoretical debate⁴⁻⁸ over the parameters affecting the kinetic isotope effect has generated remarkably little experimental data which might afford a basis for decision among conflicting claims. Moreover, contemporary interest in concerted reaction mechanisms⁹ presents the urgent necessity for a reliable criterion of the symmetrical transition state. Thus, an es-

timate of the degree of concertedness in cases of sigmatropic hydrogen migration⁹ might be realized by measurement of k_H/k_D . Of similar importance is the fact that the magnitude of the primary isotope effect has often been used¹⁰ as an index to transition-state structure in reactions where proton transfer is rate limiting. A recent communication in this journal,¹¹ however, has challenged the validity of this application.^{10d}

We have undertaken the measurement of k_H/k_D as a function of temperature in the thermolysis of three substrates broadly classifiable as β -hydroxyolefins. The members of this series represent significant variation in the nature of the hydroxyl bond, and the hybridization of both the C-1 and the C-4 (terminal carbon) to which H is transferred. Two of these reactions (see Chart I) have been described^{12,13} as more or less

Chart I. Transition States for Thermolysis of Various β -Hydroxyolefins



concerted in nature on the basis of the product formed from the deuterated substrate,¹⁰ and kinetic order and activation parameter¹¹ criteria. The third case, namely, the thermolytic fragmentation of 3-butyne-1-ol, though no report of previous studies seems to exist, nonetheless proceeds in very similar fashion and is characterized by activation parameters which are nearly identical with those of the other two. Moreover, the very fact that all three reactions show almost the same rates at all temperatures, despite the very considerable range of substituent and structural variation, is of itself a coincidence which strongly suggests a truly concerted, sigmatropic transition state.

We have also shown that the reaction in each case proceeds with no evident medium dielectric influence on rate, and occurs with equal facility in the gas and liquid phase where wall effects can be considered to be entirely absent. Clearly, therefore, the transfer of hydrogen between the carbon and oxygen termini cannot be attended by any significant degree of charge development on any of the atoms involved in the transition state. The presence of a high concentration of water vapor in all instances exerts no effect on the rate.

Reaction rates were measured in a flow system¹⁴ under circumstances where the substrate was highly diluted with very "dry" helium and passed into a thermostated, gold coil reactor characterized by only negligible wall effects.¹² Several experimental difficulties had to be confronted in measuring k_H/k_D over a large temperature range (ca. 100°C). For one, the extent of deuteration of the substrate hydroxyl function had

(10) A few common examples are: (a) C. G. Swain and E. R. Thornton, *ibid.*, **84**, 817 (1962); (b) K. C. Brown and W. H. Saunders, Jr., *ibid.*, **92**, 4292 (1970); (c) E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962); (d) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

(11) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971).

(12) R. T. Arnold and G. Smolinsky, *ibid.*, **81**, 6433 (1959); *J. Org. Chem.*, **25**, 129 (1960).

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(14) H. Kwart, S. Sarnar, and J. Olson, *J. Phys. Chem.*, **73**, 4056 (1969).

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(2) J. Bigeleisen, *Pure Appl. Chem.*, **8** (3-4), 217 (1964).

(3) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(4) A. V. Willi and M. Wolfsberg, *Chem. Ind. (London)*, 2097 (1964).

(5) (a) R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964). (b) The symmetrical transition state is essentially defined by the assumption² of a maximum deuterium isotope effect, namely, the arrangement of maximum energy content on the reaction path in which the H vibrations to C and O (C...H...O) are immobilized; that is to say, the arrangement in which all C-H stretching vibrational energy is lost.

(6) R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1965).

(7) W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **91**, 16 (1969).

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