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Received September 9, 1975

Time Resolved Electron Spin Resonance Spectroscopy. III. Electron Spin Resonance Emission from the Hydrated Electron. Possible Evidence for Reaction to the Triplet State[1]

Sir

In time-resolved ESR experiments carried out on pulse irradiated aqueous solutions we have found that the presence of certain other radicals causes the ESR line of the hydrated electron, e_{aq}^-, to appear in emission. The radical-pair theory of CIDEP[2,3] which is used to explain abnormal ESR intensities in systems of homogeneously reacting radicals, is capable of explaining emission for one radical of an unlike pair (and corresponding enhanced absorption for the other) as a result of differing g factors for the two kinds of radicals. In the present case, however, the sense of the effect—emission for the radical (e_{aq}^-) with the lower g factor—is opposite to that expected on the basis of the usual assumptions (see below). It is the purpose of this paper to describe the experimental results and to offer a tentative explanation for the observed effect.

The ESR spectrum of the hydrated electron was first reported by Avery et al. who found a single ESR line at $g = 2.0002 \pm 0.0002$ in basic methanol solutions.[4] In the course of similar time-resolved ESR studies[5,6] we have examined the ESR signal of e_{aq}^- in a number of chemical systems. Because the radiolysis of water produces approximately equal yields of e_{aq}^- and OH[7] it is necessary to study e_{aq}^- in a mixed radical system. In addition to pure water where OH is the "counter radical" to e_{aq}^-, it is possible to find a number of reactants for OH which do not react rapidly with e_{aq}^- and so can be used to change the nature of the counter radical. As will be described, the behavior of the ESR signal of e_{aq}^- varies considerably depending on the counter radical.

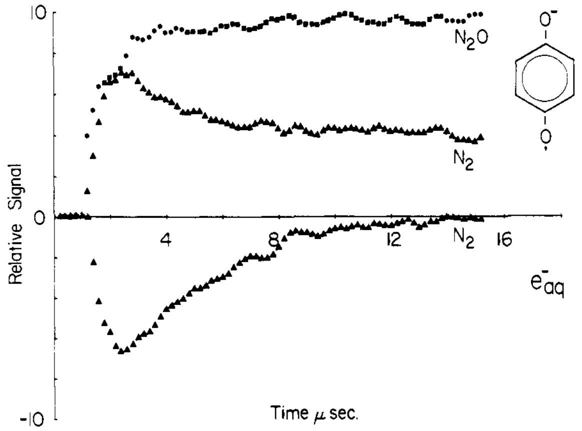

Figure 1. Time dependence of the ESR signals of e_{aq}^- and p-benzosemiquinone ion in a solution of 2 mM hydroquinone (pH 11.9). The lower trace gives the signal for e_{aq}^- in N_2 saturated solution while the center trace shows the central line of the semiquinone ion for the same conditions. The upper trace gives the signal for the semiquinone ion in N_2O saturated solution where the yield is roughly twice as great. Most of the decay of the central trace is relaxation of an enhanced absorption and not chemical decay since the long term level is nearly 50% that in the N_2O solution.

ESR experiments were carried out with an improved version of the fast-response ESR spectrometer described earlier.[5,8] Initial experiments used the OH scavengers methanol and SO_3^{2-}, and in each case a strong ESR signal was found at $g = 2.00033 \pm 0.00003$. This signal is clearly that of e_{aq}^- as is shown by its absence when the solution was saturated with N_2O.[9] The time profile at the center of resonance showed a rise to a maximum at ~4 μsec and a subsequent exponential decay with a half-life of ~6 μsec.[10] The disappearance of e_{aq}^- can be the result of reactions with impurities,[11] radiation induced products, and radicals. That radical-radical reactions are probably involved is shown by the fact that at lower doses (per pulse) both the rise and the decay are somewhat slower.[12] After the ESR signal of e_{aq}^- had been located it was found possible to observe it in basic water with no OH scavenger. Under these conditions the signal maximum was only about 20% as intense.

A number of other reactants for OH were tried with varying results. Methanol and sulfite gave nearly identical curves for e_{aq}^- under the same dose conditions. Ethylene, formate, and *tert*-butyl alcohol also behaved similarly but gave a 40% larger maximum height than sulfite or methanol and a somewhat faster decay. Bromide and ferrocyanide gave smaller signals than sulfite. With the systems of carbonate (counter radical $CO_3\cdot^-$), phosphite ($\overline{P}O_3^{2-}$), hypophosphite ($H\dot{P}O_2^-$), phenol (pH 11, phenoxyl), and hydroquinone (pH 11, benzosemiquinone ion) the ESR signal of the electron appeared in emission. With CO_3^{2-} the maximum amplitude of the emission occurred at 2-3 μsec (a shorter time than for the absorption signals) and was 60% stronger than the signal with sulfite at the same dose rate. The amplitude of the emission curve was approximately linearly dependent on dose rate. Even at the lowest dose rates the curves did not cross into absorption out to at least 20 μsec where the signal was comparable to the noise level. A typical emission curve is shown in Figure 1 for hydroquinone as OH scavenger. Here it was possible to detect the lines of the semiquinone ion counter radical formed by OH. The initial peak and subsequent decay of this radical (center trace) show that, as required by the theory, this ESR signal experiences an enhanced absorption[13] which is complementary to the emission of e_{aq}^-.

CIDEP for systems of homogeneously reacting radicals has been successfully explained by the radical-pair model[2,3] which considers the evolution of the electronic wave function for a pair of radicals during diffusive encounters and reencounters. In a single radical system the low field hyperfine lines usually tend toward emission[13] and this effect is explained by the theory if preferential reaction into the electronic singlet state of the product occurs. When two unlike radicals react, the difference in Zeeman energies caused by any g factor difference can act in the same way, producing emission for the radical of higher g factor. Trifunac and Thurnauer[15] seem to have observed such a behavior. A major difficulty arises in the case of e_{aq}^- in that the effect, emission from e_{aq}^- (and enhanced absorption for the counter radical with benzosemiquinone ion), is opposite to that described above. All of the counter radicals which lead to emission from e_{aq}^- (and indeed nearly all common radicals) have g factors considerably above that of e_{aq}^- (2.0003). Thus if the radical-pair model is to be used to explain the five cases showing emission it must be under the assumption that *reaction between* e_{aq}^- *and the counter radical occurs preferentially into the triplet state* of the product.

We believe that this proposed preference for the triplet state of the product molecule is correct and that it can be understood, qualitatively at least, on the basis of the arguments put forth by Henglein.[16] He has suggested that reactions of e_{aq}^- involve tunneling and that one must consider the matching of the energy levels which the electron will leave with those which it will occupy in the acceptor system, much as in the Franck-Condon principle. Henglein has placed the center of the occupied levels corresponding to e_{aq}^- at −1.7 eV with respect to the mobile electron. Because of the high ionization potential of the products in the systems used such as $CO_3\cdot^-$-CO_3^{2-} or $C_6H_5\dot{O}$-$C_6H_5O^-$ the unoccupied ground state levels of the acceptor system will be at much more negative energies than −1.7 eV so that little reaction into the ground state is likely. If an excited state of the reactant system exists near the levels of e_{aq}^- then reaction can occur. Differences between various counter radicals can arise, therefore, because of their differing excited states. It would not be surprising if aromatics such as phenoxide ion and hydroquinone (the products with phenoxyl and benzosemiquinone ion radicals) had triplet excited states such that a reasonable match with e_{aq}^- occurred thus giving preferential rapid reaction into this triplet state.

Further work on the ESR of e_{aq}^- is being carried out in an attempt to account quantitatively for the time profile of the ESR signal using a modified Bloch equation[10] and to explore further the implications of the model suggested here to explain the preference for recombination to the triplet state.

Acknowledgment. The authors are pleased to acknowledge discussion of this problem with A. Henglein.

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(1) Supported in part by the U.S. Energy Research and Development Administration.

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(7) The yields of e_{aq}^-, OH, and H are about 2.8, 2.8, and 0.6 radicals per 100 eV absorbed.

(8) As before[5] no field modulation was used so the spectra correspond directly to absorption. For determining the time profile, the ESR signal following each radiolysis pulse was digitized with a Biomation 8100 transient recorder and averaged by means of a PDP-8 minicomputer. The response time of the spectrometer was about 0.3 μsec. The magnetic field was also controlled by the computer.

(9) The reaction $e_{aq}^- + H_2O + N_2O \rightarrow OH + OH^- + N_2$ removes e_{aq}^- and converts it to additional OH. A corresponding increase in the ESR signal of the OH reaction product, $\dot{S}O_3^-$, is found in sulfite solutions saturated with N_2O.

(10) It is important to recognize that the slow *growth* of the ESR signal is a natural result of spin relaxation and in no way represents a chemical process. The detailed curve could be duplicated very closely by a calculation based on a modified Bloch equation similar to that employed earlier.[6]

(11) Optical pulse radiolysis experiments on similar solutions showed an electron half-life of about 35 μsec.

(12) The total radical concentration is estimated to be $\sim 3 \times 10^{-5}$ *M* under the dose conditions used. This value is consistent with the observed half-life being controlled by radical–radical reaction.

(13) Some of the decay of the signal of benzosemiquinone ion radical must be the result of radical–radical reaction. However, most of the radical does not react by this path as shown by the fact that the signal at 15 μsec is still nearly half that for the N_2O saturated solution (upper trace) where the yield is twice as large.

(14) That is, the low field-lines are weaker than the corresponding lines at high field. If the radical reaction rate is rapid enough as in pulse experiments[5] the low field lines actually appear in emission.

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Received August 18, 1975

Correlation of STO-3G Calculated Substituent Effects on the Proton Affinity of Benzene with σ^+ Parameters

Sir:

Linear free energy relationships have had an enormous impact on the direction which physical organic chemistry has taken in the last quarter century. Early attempts by Hammett and Taft among others to find a simple means of classifying the effects of substituents on chemical reactions have led directly to many of the now familiar concepts of bonding and structure.[1] Most of this multitude of reactions that have been correlated successfully by Hammett-Taft type schemes are entirely solution processes. Thus, interpretation of linear-free-energy correlations—or deviations therefrom—purely in terms of electronic arguments may at times be hazardous. With the advent of gas phase ion cyclotron resonance spectroscopy and of reliable nonempirical molecular orbital calculations—both of which may be used to provide energetic data on molecules and ions in their "dilute gas" phase—it should now be possible to separate the components of linear-free-energy correlations which are of a fundamental electronic origin from those that depend on the presence of solvent. Nevertheless, previous attempts to interpret electronic effects of substituents in quantitative terms by molecular orbital approaches have not been successful, undoubtedly because of the severe limitations of the semiempirical methods used.[2] In this communication we report the preliminary results of our ab initio theoretical investigations into the effects of meta and para substituents on the stability of protonated benzene.

The minimal basis set STO-3G method[3,4] was used to derive energies for the *isodesmic* process,[5] for comparison with the empirical σ^+ constants originally proposed by Brown and Okamoto[6] to correlate electrophilic aromatic substitution reactions. The STO-3G basis set has been shown previously to describe satisfactorily the energies of