Chemically Induced Dynamic Electron Polarization in Pulse Radiolysis. $S-T_{\pm 1}$ Polarization from Hydrogen Radical Reactions[1]

Sir:

For some time now, there have been a number of theoretical suggestions regarding electron spin polarization pathways in the radicals produced by pulse radiolysis. Wan and co-workers[2–4] have presented the theory of "initial spin polarization" in H and D atoms[2,3] and have broadened this to include the CIDEP observed in alkyl radicals.[4] Early experimental data have been regarded by these workers as supportive of their views.[5] While the original study of H radical CIDEP showed no difference between the low field emission and high field enhanced absorption lines,[6] recent reports have established greater low field line intensity as compared to the high field line,[7] leading to renewed interest in the above mentioned theories.

We have reported CIDEP studies in microsecond[8] and submicrosecond[9] time domains which clearly illustrate the dominance of radical pairs ($S-T_0$) polarization pathways in radiolytic systems. However, until now no adequate theory buttressed with experiments has been presented to explain anomalous polarization in H radicals.

We have been able to study CIDEP of the radical produced by OH abstraction for acetate.[9] In acidic solution the e_{aq}^- produced is converted to H and the dominant radicals in acidic aqueous acetate solution are $\cdot CH_2COOH$ and H.[10] The spectrum of the $\cdot CH_2COOH$ radical (at 2 μs) in acidic solutions is shown in Figure 1. The usual $S-T_0$ CIDEP spectrum in neutral solutions shows the low field line in emission, an unpolarized central line, and the high field line in enhanced absorption. The intensities of the high and low field lines are either identical or the low field line is somewhat less intense than the high field line when electron spin relaxation sets in.[9] The upper spectrum in Figure 1 most closely resembles this. With decreased pH intensity changes in the three lines become increasingly evident. The lowering of pH increases the conversion of e_{aq}^- to H.[10] The line intensities in the lowest spectrum in Figure 1 clearly illustrate that the low field line is more intensely in emission, the central line is in emission, and the high field line is in enhanced absorption but considerably less intense relative to the other lines. This is similar to what can be observed in the two lines of the H radical where the low field emission is slightly greater than the high field absorption.[7] However, the effect in acetate (Figure 1) is more noticeable.

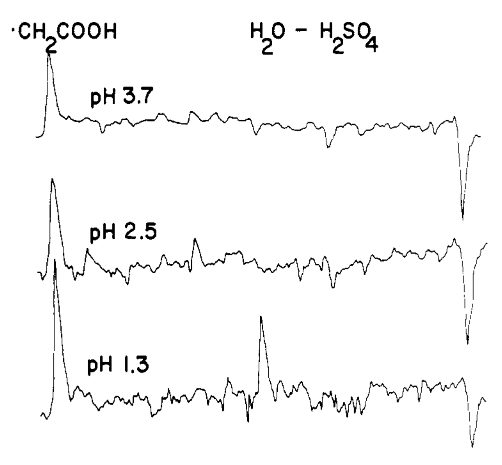

Figure 1. Sodium acetate, 0.33 M (H_2O, 50 G sweep, He, H_2SO_4): upper to lower, pH 3.7, 2.5, 1.3. In both figures field increases left to right. All spectra are taken at 2 μs. In all figures positive signals mean emission and negative signals mean absorption.

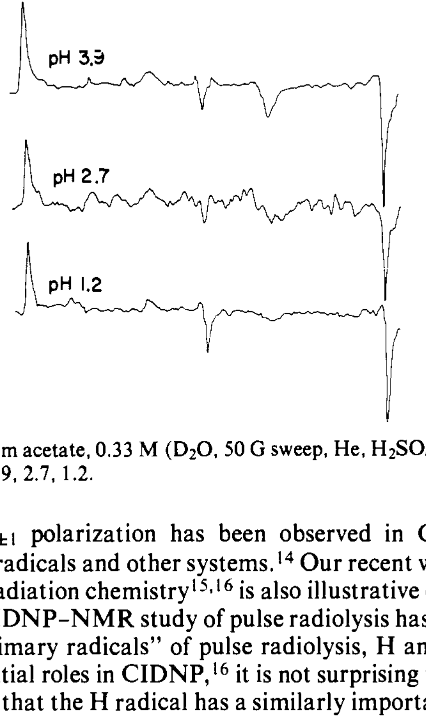

Figure 2. Sodium acetate, 0.33 M (D_2O, 50 G sweep, He, H_2SO_4): upper to lower, pH 3.9, 2.7, 1.2.

When the identical experiment was carried out in D_2O the spectra in Figure 2 were observed. These are essentially "normal" CIDEP spectra of the $\cdot CH_2COOH$ radical.

The H and D radicals have identical *g* factors[11] and all the experimental conditions are otherwise identical. The explanation of this unusual polarization in the $\cdot CH_2COOH$ radical and H radical[7] is that substantial hyperfine coupling in the H radical is responsible for making the $S-T_{-1}$ polarization[12] pathway feasible in the radical pairs involving H radicals. The hyperfine coupling splits the T_{+1} and T_{-1} levels while the T_0 level is not effected in the first order. Thus not only is the $S-T_{-1}$ energy gap substantially decreased but also differentiation of $T_{\pm 1}$ levels allows the $S-T_{\pm 1}$ polarization pathways to contribute to the usual $S-T_0$ polarization. The D radical has hyperfine coupling that is substantially smaller than that of H (77.54 vs. 506.6 G[11]) and no appreciable $S-T_{-1}$ mixing is observed from the radical pairs involving D.

No other reports of $S-T_{\pm 1}$ polarization pathways in CIDEP exist. The only other example of $S-T_{\pm 1}$ CIDEP can be found in our study of aqueous micellar solutions,[13] where the constraints of micellar aggregation reduce diffusion and thus enhance the $S-T_{\pm 1}$ polarization pathway.

The $S-T_{\pm 1}$ polarization has been observed in CIDNP studies of biradicals and other systems.[14] Our recent work on CIDNP in radiation chemistry[15,16] is also illustrative of that. Since our CIDNP-NMR study of pulse radiolysis has shown that the "primary radicals" of pulse radiolysis, H and e_{aq}^-, have substantial roles in CIDNP,[16] it is not surprising that we now observe that the H radical has a similarly important role in the CIDEP of these same systems.

As we have shown by this study and our previous work[8,9] the radical pair model of CIDEP quite adequately explains all the observed electron spin polarization in radiolytic systems.

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Relative Rates of Halogen Addition to Double and Triple Bonds. The Bromination of *trans*-Cinnamic and Phenylpropiolic Acids and Their Esters

Sir:

The difference in reactivity of olefinic and acetylenic double bonds in addition reactions has long been considered noteworthy and is important for a better understanding of the mechanisms of these reactions.[1,2] As a contribution to this problem, we wish to report data on the bromination of *trans*-cinnamic and phenylpropiolic acids, and their methyl esters, under well-defined kinetic conditions.

The 3-hexenes react about 3 × 10^5 times faster than 3-hexyne, and *trans*-1-phenylpropene 5000 times faster than phenylmethylacetylene, with bromine in acetic acid.[2] These and similar large differences in bromination and chlorination have usually been ascribed to the higher energy of the vinyl cation intermediates (bridged or open), as compared with the intermediates in olefinic halogenation.[3] In other addition reactions, e.g., in hydration, the differences are much reduced.

However, some of the data on which rate differences are based may not be free from ambiguities. In the presence of bromide ion some of the bromination reactions follow two-term rate expressions (see below). The two terms need to be sorted out, because they probably correspond to different mechanisms of addition, depending on whether the substrate is an olefin or an acetylene.

trans-Cinnamic acid and phenylpropiolic acid and their methyl esters were brominated under identical conditions in 75% aqueous acetic acid (by volume) in the presence of varying amounts of sodium bromide (0.02–0.5 M), and at a constant ionic strength (0.5 M, $\mathrm{NaClO_4}$). Under these conditions the rate expression is $-\mathrm{d}(\mathrm{Br_2})_\mathrm{T}/\mathrm{d}t = k_{\mathrm{obsd}}(\mathrm{Br_2})_\mathrm{T}(\mathrm{A})$, where $(\mathrm{Br_2})_\mathrm{T}$ is the titratable bromine, and A the substrate. In the presence of bromide ion the total rate of bromination can be expressed by eq 1.

$$-\mathrm{d}(\mathrm{Br_2})_\mathrm{T}/\mathrm{d}t = k_2(\mathrm{Br_2})_{\mathrm{free}}(\mathrm{A}) + k_3(\mathrm{Br_2})_{\mathrm{free}}(\mathrm{Br^-})(\mathrm{A}) \quad (1)$$

The second term is written as a bromide ion catalyzed reaction and involves a termolecular attack of bromine and bromide ion (Ad3), as first demonstrated by Pincock and Yates for bromination of acetylenes.[4] This interpretation of the second term also applies to acetylenic iodinations[5] and hydrochlorinations,[6] and is strongly supported by product composition.

However, the second term in eq 1 is indistinguishable kinetically from a reaction involving the tribromide ion, $k_{\mathrm{Br_3^-}}(\mathrm{Br_3^-})(\mathrm{A})$, and $k_3K = k_{\mathrm{Br_3^-}}$, where K is the dissociation constant for the tribromide ion. In olefinic halogenation this term has usually been interpreted as an electrophilic attack by the tribromide ion, as first shown by Bartlett and Tarbell.[7] The second terms, therefore, refer to different mechanisms of halogenation and their magnitudes cannot be compared.[8] If one is interested in the relative rates of halogenation, one must compare the first terms only, which unambiguously represent an electrophilic attack by molecular bromine on the substrate ($\mathrm{Ad_E2}$).

The different rate constants can be obtained from the equation $k_{\mathrm{obsd}}(K + \mathrm{Br^-})/K = k_2 + k_3(\mathrm{Br^-})$, by plotting the term on the left against the bromide ion concentration. The rate constant k_2 is 1.97 ± 0.02 $\mathrm{M^{-1}\,s^{-1}}$ for bromination of phenylpropiolic acid and (2.86 ± 0.08) × 10^{-1} $\mathrm{M^{-1}\,s^{-1}}$ for bromination of *trans*-cinnamic acid. The acetylenic acid reacts about seven times faster than the olefinic acid. This, however, is not a true comparison. It is thought that the bromination of both of the acids proceeds through their respective anions, and K_a for phenylpropiolic acid in water is over 100 times greater than that for *trans*-cinnamic acid.[9] Hence more of the anionic acetylenic substrate will be present, which would account for its greater rate of reaction. But in the bromination of the respective methyl esters, k_2 is (4.75 ± 0.68) × 10^{-3} $\mathrm{M^{-1}\,s^{-1}}$ for the bromination of methyl phenylpropiolate and (1.30 ± 0.04) × 10^{-1} $\mathrm{M^{-1}\,s^{-1}}$ for that of methyl *trans*-cinnamate. The olefinic ester reacts 27 times faster than the acetylenic one.[10] Thus, the difference in relative reactivities of these unsaturated esters and acids has been greatly reduced when compared to the data on hydrocarbons quoted in the introduction. These results support the suggestion, first advanced by Robertson,[11] that the difference in reactivity of acetylenes and olefins in halogenation depends on the substituents attached to the unsaturated center, and that the halogenation of olefins is affected to a greater extent by the nature of the substituents than that of acetylenes.[1,12] The quoted reduction in the ratio to 5000, when an electron-attracting phenyl substituent is present,[2] agrees with this interpretation.

The two kinetic terms on which the rate comparison is based are not only kinetically equivalent but must involve similar mechanistic pathways. The products of the reaction in the absence of bromide ion, when only the first term in eq 1 is applicable, reveal the presence of a cationic intermediate capable of reacting with the solvent. Under those conditions, phenylpropiolic acid affords a small amount of a mixture of *cis*- and *trans*-dibromocinnamic acids and extensive decarboxylation products, characteristic of a vinyl cation,[5] and ethyl phenylpropiolate affords *cis*- and *trans*-dibromo esters (13 and 23%) and solvent-incorporated products (64%) including ethyl bromobenzoylacetate. *trans*-Cinnamic acid and its ester yield in about equal amounts dibromides and bromohydrins (*erythro*-2-bromo-3-hydoxy-3-phenylpropanoic acid and ester) derived from *anti*- addition.[13] The exact nature of the intermediate ion cannot be specified with precision, but it is probably best represented as an open vinyl cation in the case of the acetylenic compound, and an unsymmetrical, weakly bridged carbonium ion in the case of the olefinic substrate.[14]

Details of the kinetics and product composition of these reactions will be discussed in forthcoming publications.

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