3790 J. Phys. Chem. 1988, 92, 3790–3792

^{13}C Hyperfine Interactions in Terephthalate Trianion Radical[1]

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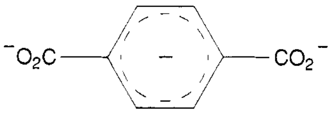
(Received: November 19, 1987; In Final Form: January 21, 1988)

Sufficiently high concentrations of terephthalate radical trianion can be produced by reduction of terephthalate with acetone ketyl radical anion in in situ radiolysis experiments that ESR spectra of the radicals containing ^{13}C at natural abundance levels can be recorded readily. The ^{13}C hyperfine constant for the carbon atoms at the four equivalent ring positions is (−)1.46 G. Hyperfine constants of 1.37 and 4.64 G are observed for the other two pairs of equivalent carbon atoms with the smaller value found to apply to the carboxyl carbons from studies of a sample with the carboxyl group enriched in ^{13}C. Application of the Karplus–Fraenkel relation indicates that there is an unpaired spin population of ∼0.26 on each of the ring carbon atoms adjacent to the carboxyl groups. This high-spin population is reflected in somewhat broadened lines of the radicals with ^{13}C at these ring positions. The signals of this radical saturate relatively easily, indicating a longitudinal relaxation period considerably longer than for most transient radicals.

During the course of radiolytic studies of the reduction of terephthalic acid,[2] we have found that its radical trianion



can be prepared at sufficiently high concentrations by electron transfer from acetone ketyl radical anion that ESR signals from the radicals containing ^{13}C at natural abundance levels can be readily observed at steady state in in situ radiolysis experiments. These ESR studies, presented here, make available information on ^{13}C hyperfine interactions in aqueous solution for a class of radical anions where only proton data have been available to date.[3]

Experimental Section

Steady-state in situ radiolysis ESR studies were carried out by methods similar to those described by Eiben and Fessenden[4] and used in other more recent studies in this laboratory.[5,6] Second-derivative spectra were recorded at X band (9.2 GHz) by using phase-sensitive detection with field modulations of 200 Hz and 100 kHz. Recent improvements in the ESR apparatus[7] implement digital recording of ESR traces and allow averaging and detailed analysis after data collection. ESR parameters were determined as previously described[4] with the g factor measured by reference to that of sulfite radical anion ($g = 2.00307$).[8] A flow system was used with the sample residence time in the ESR cavity being 50 ms. Solutions were at ∼19 °C. Radical production rates were 0.01 M s^{-1} so that radical concentrations were $\sim 10^{-4}$ M. Sodium terephthalate was from Aldrich. [α,α'-$^{13}C_2$]Terephthalic acid, obtained from MSD Isotopes, had a carboxyl enrichment of ∼99% in ^{13}C so that signals from the unlabeled or ∼2% singly labeled impurities did not contribute significantly to the observed spectra. Reduction of the terephthalate was carried either directly by e_{aq}^- in a N_2-purged solution containing 0.1 M *tert*-butyl alcohol to remove OH or by acetone ketyl radical anion ($(CH_3)_2CO^-$) prepared by H atom abstraction from 0.1 M 2-propanol in a N_2O-purged solution at pH >11.

Results and Discussion

Reduction of terephthalate ion by e_{aq}^- in aqueous solution is rapid, $k(e^- + C_6H_4(CO_2^-)_2) = 8.5 \times 10^9$ M^{-1} s^{-1},[2] so that the proton hyperfine structure of the radical trianion can be readily observed during continuous radiolysis of N_2-purged terephthalate solutions.[3] In the present study weak lines of the magnitude expected for the ^{13}C-containing radicals were also observed. These latter lines were found to be considerably more intense in 2-propanol solutions at high pH. In this case H atoms and OH radicals are converted to acetone ketyl radical anions which subsequently transfer electrons to the terephthalate. Pulse radiolysis experiments show that in the absence of significant production of other radicals there is very little decay of terephthalate radical trianion on the millisecond time scale, i.e., that second-order decay is very slow ($<10^7$ M^{-1} s^{-1}).[2] Because of the long lifetime of this radical, the steady-state concentration can be maintained sufficiently high during continuous electron irradiation that one can readily observe all of the lines of the ^{13}C-containing radicals with intensities well above noise level. However, since electron transfer from the ketyl radical to terephthalate is relatively slow [$k(CH_3)_2CO^- + C_6H_4(CO_2^-)_2 = 2 \times 10^7$ M^{-1} s^{-1}],[2] the signal intensity is maximized only at relatively high terephthalate concentrations (∼10 mM). The ESR spectrum observed for a N_2O-purged 10 mM terephthalate solution containing 0.1 M 2-propanol at pH 13 is illustrated in Figure 1. The main quintuplet is described by $g = 2.00329$ and $a_H = 1.52$ for each of four equivalent protons. These values are essentially as previously reported by Neta and Fessenden.[3] The weaker lines, displayed in Figure 1, bottom, at a 30-fold higher gain, are of the magnitude expected for the radicals containing ^{13}C at natural abundance levels. One particularly notes in Figure 1 that only two satellites with intensities appropriate to ^{13}C structure are observed at fields below the main quintuplet and that these are separated approximately by the proton hyperfine constant. There are no other lines of the expected intensity in the spectrum. The outermost of these lines is ∼1% as intense as its corresponding line in the main quintuplet and is readily attributed to one of the radicals containing ^{13}C at the natural abundance (1.1%) at one of two equivalent positions. The observed splitting corresponds to a ^{13}C hyperfine constant of 4.64 G. Analysis of the remaining structure requires further information and detailed examination of the line shapes.

In order to determine the hyperfine constant of the carboxyl carbon atom, the radical produced from a sample with the CO_2 groups 99% enriched in ^{13}C was examined, and the spectrum observed is given in Figure 2. Because of the high enrichment, essentially all (∼98%) of the radicals are doubly labeled so that contributions from singly labeled radicals are not apparent in the spectrum. The spectrum of Figure 2 shows the additional structure

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[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3039 from the Notre Dame Radiation Laboratory.

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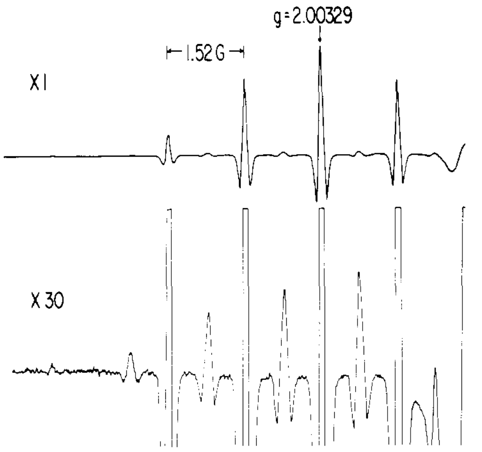

Figure 1. Second-derivative ESR spectrum of terephthalate trianion radical observed during continuous irradiation of a 10 mM solution of terephthalate at pH 13. Solution was purged by bubbling with N_2O and contained 0.1 M isopropyl alcohol to convert OH radicals to acetone ketyl radical anions. Signals were recorded digitally and are displayed at a 30-fold increased gain in the lower spectrum. Note that the relative amplitudes of the four observed lines of the principal quintuplet, which are split by 1.52 G, are in the ratio 1:3.4:4.4:3.3. The highest field line is obscured by the signal from irradiated quartz. This anomalous ratio results from the relatively greater saturation of the inner lines of the spectrum at the power level used and approaches the expected 1:4:6:4:(1) ratio at a 20-dB lower power level.

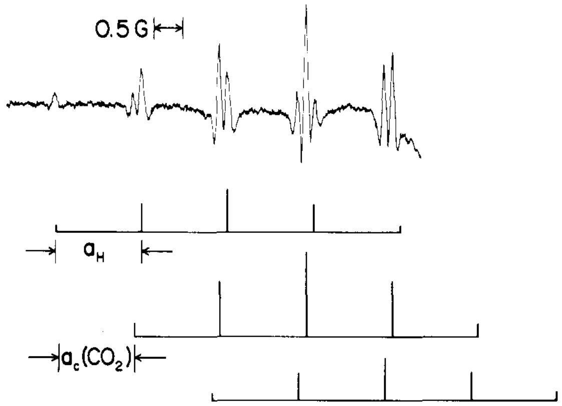

Figure 2. ESR spectrum of the radical trianion derived from [α,α'-$^{13}C_2$]terephthalic acid. Solution was 1 mM in terephthalate and 0.1 M *tert*-butyl alcohol at pH 13 and N_2 purged. Lines of the central quintuplet are at the positions indicated in Figure 1 for the unlabeled radical (a_H = 1.52 G). The additional splitting by the enriched carboxyl carbon corresponds to $a_C(CO_2)$ = 1.37 G.

expected for a radical with two equivalent carboxyl ^{13}C atoms, each having a hyperfine constant of 1.37 G. This assignment of the carboxyl hyperfine constant requires that the 4.64-G ^{13}C hyperfine constant be assigned to the radical containing ^{13}C at C_1 since the radicals labeled at C_2 should have a 2-fold greater intensity. These hyperfine constants are accurate to ~0.01 G.

Signal-averaging methods were used to record the ^{13}C structure present at a higher signal-to-noise ratio. The averages of nine scans (scanned at a rate of 0.01 G min^{-1} with the time constant ~8 s) recorded at the normal power level used in this type of experiment are displayed in Figure 3. The positions of the lines, as given by the above parameters, for the radicals containing ^{13}C at C_1 and in the carboxyl group are indicated by the stick spectra. The relatively high intensity of the ^{13}C structure in the central region requires that there be additional contributions from lines of the radicals with ^{13}C at C_2 in these regions at approximately the positions indicated for these in Figure 3.

Figure 3. ^{13}C ESR lines observed at high power. Recordings averaged nine scans recorded digitally. Lines of the different ^{13}C components are at the positions indicated by the stick spectra (solid lines for the radicals with ^{13}C and C_1, dashed at C_2, and dotted at CO_2) taking a_H = 1.52 G, $a_C(C_1)$ = 4.64 G, $a_C(C_2)$ = 1.46 G, and $a_C(CO_2)$ = 1.37 G. Simulated spectra were produced as described in text.

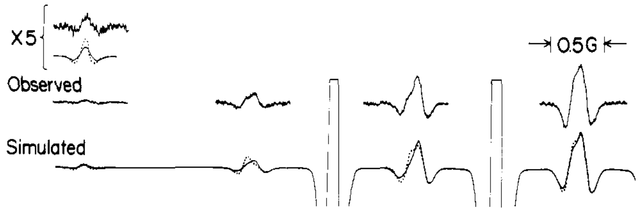

Figure 4. ^{13}C ESR lines as observed at low power. Note difference in line shapes from those in Figure 3, particularly in the second group of ^{13}C lines. Dotted simulations assume line shape of radicals having ^{13}C at C_1 are identical with those of the other ^{13}C-containing radicals. Solid simulation takes into account 25% increase in width of these lines.

Before attempting detailed analysis of the line shapes resulting from the overlapping contributions from the different ^{13}C-containing radicals, we note that the lines associated with the proton hyperfine structure are narrow and that they power saturate very easily. At the power levels normally used in our radiolysis experiments the relative amplitudes of the four observed lines of the main quintuplet are 1:3.4:4.4:3.3 rather than the expected ratio of 1:4:6:4:(1) (see Figure 1).[9] From the observed ratio one infers that there must be a small but subtle difference between the shapes of the different lines of the quintuplet. With reduction of the power level by 20 dB the expected ratio is approached. At low power and low modulation the limiting line width observed in these radiolysis experiments (0.1 G) is effectively limited by magnetic inhomogeneities so that the lines have appreciable (~85%) Gaussian character. From the observed saturation behavior one concludes that the central lines of the quintuplet saturate more readily than the outer lines. At low radical concentrations the relative line intensities are more nearly as expected even at high power levels. This observation indicates that the relaxation rates resulting from Heisenburg spin exchange are relatively more important for the radicals with high total nuclear angular momenta.

The shapes of the multicomponent ^{13}C lines were simulated by summing appropriate Lorentzian and Gaussian contributions with the amplitudes chosen to correspond to the main quintuplet as indicated above. The lines of the radicals having ^{13}C at C_1 were, however, somewhat broader (~10%) than the unit intensity line of the quintuplet, and this additional width is reflected in the simulations of Figure 3. The hyperfine constants corresponding to the simulations are a_H = 1.52 G, $a_C(C_1)$ = 4.64 G, $a_C(C_2)$ = 1.46 G, and $a_C(CO_2^-)$ = 1.37 G.

Studies at lower power levels are difficult because the signals are comparable to the noise. Recordings which averaged data from eight scans at low modulations and low power, given in Figure 4, show that the unit lines due to the radicals containing ^{13}C at C_1 have an amplitude only ~50% of that expected. They are, however, somewhat broader (~25%) than the remaining lines so that the integrated intensities are about as expected. As a result,

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[9] Second-order splittings (see: Fessenden, R. W. *J. Chem. Phys.* **1962**, *37*, 747) are very small (~0.002 G) and are insufficient to explain the noted intensity ratios.

the shapes of the complex components in Figure 4 differ appreciably from those in Figure 3 where the differences in intrinsic line width are to a large extent masked by the effects of saturation. It is noted that the line shape of these complex lines is extremely sensitive to slight differences in the widths of the components as is particularly seen by comparing both the experimentally observed and simulated shapes of the second group of ^{13}C lines in Figure 3 and 4. In Figure 4 the ^{13}C structure of the central lines is dominated by the hyperfine constant of the radicals having ^{13}C at C_2 so that $a_C(C_2)$ can be determined from detailed analysis of the experiments at low power to be 1.46 G (i.e., ±0.02 G). The fact that the lines with ^{13}C at C_1 are appreciably broader than the other components implies that there is a high degree of anisotropy at this position.

The ^{13}C hyperfine constants noted here are closely related to those reported by Rieger et al.[10] for the terephthalonitrile radical anion in *N,N*-dimethylformamide solution as determined in electrochemical experiments ($a_H = 1.59$ G, $a_C(C_1) = 8.81$ G, $a_C(C_2) = 1.98$ G, $a_N = 1.81$ G, and $a_C(CN) = 7.83$ G). The values of a_H and $a_C(C_2)$ are very similar and clearly indicate similar unpaired spin distribution on the ring of the two radicals. The observed proton hyperfine constant (−1.52 G) indicates, from the McConnell relationship[11] with $Q_H = -25$ G, that ρ_2, the unpaired spin population at C_2, is 0.06. This value is similar to the estimate of 0.067 for ρ_2 in the terephthalonitrile radical anion.[12] From the Karplus–Fraenkel relation,[13] since $\rho_3 = \rho_2$, the hyperfine constant of the carbon at C_2 should be described by

$$a_C(C_2) = (Q_l + Q_a)\rho_2 + Q_a\rho_1 \qquad (1)$$

where ρ_1 is the unpaired spin population at C_1 and Q_l and Q_a are σ–π parameters relating the observed ^{13}C coupling to the contributions resulting from π spin population on the local and adjacent atoms. Q_l and Q_a are found in other systems to be respectively ~28 and −10 G.[14] Since ρ_2 is small (0.06), the contribution of the first term in eq 1 (1.1 G) is less than the observed splitting (1.46 G). Application of the Karplus–Fraenkel relation, therefore, indicates that ρ_1 must be either 0.26 or −0.04, depending on whether $a_C(C_2)$ is negative or positive. The latter choice would place essentially all of the unpaired spin population on the carboxyl groups and is unrealistic so we conclude that the sign of $a_C(C_2)$ must be negative and that ρ_1 is ~0.26. These values place ~76% of the unpaired spin on the ring, indicating that ~12% is on each of the carboxyl groups. Similar conclusions for the terephthalonitrile radical anion were reached by Reiger and Fraenkel from considerations of the magnitude of the ^{13}C splittings observed in that case. We note here that the observation that the lines of the radicals labeled at C_1 are more anisotropic than the other lines is in accord with the high local spin population at this position.

From the unpaired spin on the ring, one predicts from the Karplus–Fraenkel relationship that $a_C(C_1)$ should be ~5.8 G. The smaller value observed here (4.64 G) and the larger value in the case of the terephthalonitrile radical anion (8.8 G) presumably reflect differences derived from unpaired spin on the adjacent CO_2^- and CN groups. The contribution to a_C from spin on adjacent carboxyl groups ($Q_a(CO_2) = -10$ G) is, therefore, comparable to that on other adjacent carbon atoms. The larger value for $a_C(C_1) = 8.81$ G noted by Rieger et al. for terephthalonitrile anion implies that Q_a derived from unpaired spin on the CN group is positive and of the magnitude of ~15 G.

Eiben and Schuler[5] found in studies of carboxylated cyclohexadienyl radicals that the carboxyl ^{13}C hyperfine constant probed the unpaired spin population on the adjacent ring carbon atoms in much the same way as the proton values, i.e.

$$a_C(CO_2^-) = Q(CO_2^-)\rho \qquad (2)$$

where $Q(CO_2^-)$ can be taken as ~15.8 G. This relation breaks down in the present case where the observed value for $a_C(CO_2^-) = 1.4$ G is much smaller than the ~4 G predicted. It is clear from this that in the present case a contribution must be added to eq 3 to take into account the significant population of unpaired spin on the carboxyl group and that this contribution must be of opposite sign to that derived from spin on the ring carbon.

Acknowledgment. We thank Prof. R. W. Fessenden for discussions on these studies.

Registry No. ^{13}C, 14762-74-4; $[C_6H_4(CO_2)_2]^{3-}$, 40680-12-4.

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Accurate Measurement of Vibrational Transition Energies for a Wide Range of *v*, *J* States Using CARS Spectroscopy of Chemical Reaction Products: Spectroscopy of H_2 from the H + HI Reaction

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$Q_v(J)$ transition energies of H_2 are measured for $v = 0$–4, $J = 0$–18 by coherent anti-Stokes Raman scattering (CARS) spectroscopy of rovibrationally excited H_2 from the $H + HI \rightarrow H_2 + I$ reaction at high collision energies. The accuracy of the measurements reported here is 0.05 cm^{-1}, limited by the bandwidth of the laser sources used. The measured transition energies generally agree with those predicted by ab initio quantum calculations and with previous less precise measurements based on H_2 electronic spectroscopy. However, discrepancies outside mutual uncertainties are common, and the accuracy of the ab initio calculations appears to be somewhat less than the 0.015 cm^{-1} claimed. Measurements with an accuracy of 0.0005 cm^{-1}, much greater than that of the present measurements, are possible with the methods described here by using narrow-bandwidth laser sources for CARS spectroscopy.

Introduction

In a recent publication,[1] Nieh and Valentini reported the use of coherent anti-Stokes Raman scattering (CARS) spectroscopy to obtain spectra of high *v*, *J* states of photofragments under collisionless conditions. In their experiments extensive rotational and vibrational spectroscopic constants and a potential energy curve were obtained for $O_2(^1\Delta_g)$. Here we report an extension and generalization of this approach, using reactive collisions of translationally hot hydrogen atoms with HI to generate high *v*, *J* states of H_2 and using CARS to accurately measure the energies

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