dation of DMDS with OH indicates the occurrence of the reaction

$$CH_3SOH + O_2 \xrightarrow{M} CH_3SO_3H \qquad (22)$$

Atmospheric Implications. Reduced-sulfur compounds have aroused much interest since the estimation of the global sulfur budget[38-40] requires considerable quantities of these emissions to balance the budget. Several papers which dealt with model studies about the sulfur cycle in the atmosphere introduced DMS as a key component.[2,7] As pointed out by Chameides et al.[41] DMDS and other reduced-sulfur compounds should also be treated as significant components of S-containing compounds in the atmosphere since their emissions from biogenic or anthropogenic sources are reported.[1,5] In most modeling studies the yield of SO_2 from the oxidation of DMS is dealt with as unity[7,8] except for the estimation by Sze and Ko.[2] As mentioned already, however, the yield SO_2 is 20, 29, and 22% from OH reactions of DMS, CH_3SH, and DMDS, respectively. Methanesulfonic acid is a stable compound, so that it should precipitate as it is or as sulfonate $CH_3SO_3^-$. Detection of CH_3SO_3H in ambient aerosols by Panter and Penzhorn[42] provides strong evidence for this contention. This information requires revisions of the former models which described the sulfur cycle by only H_2S, SO_2, and SO_4^{2-}.

Acknowledgment. We thank Mr. H. Takagi of the Engineering Division at the National Institute for Environmental Studies for assistance in conducting the GC/MS analysis.

Registry No. OH, 3352-57-6; SO_2, 7446-09-5; CH_3SNO, 22223-61-6; H_2SO_4, 7664-93-9; CH_3OH, 67-56-1; C_2H_5ONO, 109-95-5; CH_3SH, 74-93-1; CH_3SO_3H, 75-75-2; CH_3S, 7175-75-9; CH_3SOH, 62965-22-4; HCHO, 50-00-0; DMDS, 624-92-0; DMS, 75-18-3.

---

[38] W. W. Kelog, R. D. Cadle, E. R. Allen, A. L. Larzrus, and E. A. Martell, *Science*, 175, 587 (1972).

[39] J. P. Friend, "Chemistry of the Lower Atmosphere", S. I. Rasool, Ed., Plenum Press, New York, 1973.

[40] L. Granat, H. Rodhe, and R. O. Hallberg, *Ecol. Bull.*, 22, 89 (1976).

[41] W. L. Chameides, P. H. Wine, and A. R. Ravishankara, *Eos Trans. AGU*, 62, 289 (1981).

[42] R. Panter and R.-D. Penzhorn, *Atmos. Environ.*, 14, 149 (1980).

A Comparison of the Carbon-13 Hyperfine Constants of Carboxylated Cyclohexadienyl and Hydroxycyclohexadienyl Radicals[1]

Robert N. Sangster,[2] Keith P. Madden, and Robert H. Schuler*

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

(Received: October 28, 1982)

^{13}C ESR spectra of the H atom adducts to pyromellitic and benzenepentacarboxylic acids have been observed. Comparison of the ^{13}C hyperfine constants with those previously obtained for the OH adducts shows essentially identical values at the carboxyl positions and significant differences for the ring atoms only at the C_3 and C_6 positions. The spin density distribution in the π system is clearly not affected to any significant extent by OH substitution. In spite of this the ^{13}C hyperfine coupling constants for C_6, the site of addition, are 13 and 23% lower, respectively, in the OH adducts. This finding is at variance with correlation of ^{13}C couplings strictly in terms of the local and adjacent π spin densities. Since there is no appreciable loss of spin density from the π system the effects of OH substitution cannot arise directly from transfer of spin density to the C_6 position. Rather these effects must result from changes in the interactions between the σ and π systems introduced by the substitution. It is suggested that the differences noted here, and the related drop of ~35% in the proton hyperfine constants at C_6, result mainly from the loss of symmetry in the OH substituted radicals.

Introduction

Eiben and Schuler[3] have reported ^{13}C ESR spectra of a number of hydroxycyclohexadienyl polycarboxylates in aqueous solutions and were able to assign specific ^{13}C hyperfine constants both to the carboxyl substituents and to the ring positions. These data show that the carboxyl ^{13}C hyperfine constants provide a good measure of the distribution of unpaired spin density over the conjugated system in essentially the same way that the proton hyperfine constants do for the analogous unsubstituted radicals. The hyperfine constants of the ring carbon atoms largely reflect this distribution according to a Karplus–Fraenkel relationship[4] of the form

$$a^c = Q_l\rho_l + Q_a(\rho_a + \rho_a') \qquad (1)$$

which includes contributions from both local (ρ_l) and adjacent (ρ_a) spin densities. In the Karplus–Fraenkel description Q_l and Q_a are complicated proportionality constants made up of a number of terms which take into account different contributions to the hyperfine interactions and have, respectively, values ~36 and ~−14 G for aromatic systems. The proton data for cyclohexadienyl and hydroxycyclohexadienyl radicals indicate that OH substitution at the C_6 position does not affect the distribution of unpaired spin density over the π system to any appreciable extent. However, the hyperfine constant of the proton at C_6 is appreciably lower in the OH substituted radical (e.g., 48.0 G in cyclohexadienyl and 34.5 G in hy-

---

[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2391 from the Notre Dame Radiation Laboratory.

[2] Work-study student from University of Waterloo, Waterloo, Ontario.

[3] Eiben, K.; Schuler, R. H. *J. Chem. Phys.* 1975, *62*, 3093.

[4] Karplus, M.; Fraenkel, G. K. *J. Chem. Phys.* 1961, *35*, 1312.

0022-3654/83/2087-2395$01.50/0 © 1983 American Chemical Society

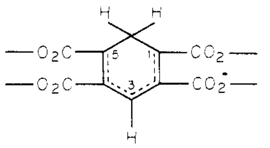
drocyclohexadienyl) so that it is clear that OH substitution perturbs the electronic wave function in the vicinity of C_6 very significantly. Because of this difference it is of particular interest to have comparative hyperfine data on the ring carbon atoms in these two types of radicals. At the time of the previous measurements the signal-to-noise ratio attainable in experiments designed to examine ^{13}C spectra of cyclohexadienyl radicals was insufficient to make the necessary observations at natural abundance levels. Recent improvements[5] in the spectrometer used in the in situ radiolysis–ESR experiment have increased the sensitivity by a factor $\sim$5 and now make some such measurements feasible. We have been able to observe the ^{13}C hyperfine structure of the carboxylated cyclohexadienyl radicals produced by H atom addition to pyromellitic and benzenepentacarboxylic acids. Most of the ^{13}C hyperfine constants are similar to those for the analogous OH adduct. However, the value for the carbon atom at the C_6 position is observed to be significantly higher for the H adduct although the spin densities at the C_1 and C_5 positions are not appreciably affected by the nature of the substituents. The data presented here represent an extremely critical test of various factors responsible for ^{13}C hyperfine interactions and emphasize that the hyperfine splittings and spin densities cannot be correlated simply by an equation of the form of eq 1.

Experimental Section

The experimental methods employed here were very similar to those used by Eiben and Schuler.[3] ESR measurements were made at X-band (9.2 GHz) by using in situ electron beam radiolysis to maintain a radical concentration in excess of 10^{-4} M. Improvements in the spectrometer[5] include computer control of magnetic field scan, which permits scan rates as low as 0.06 G min^{-1} allowing time constants of $\sim$20 s to be used effectively, and addition of a low noise microwave preamplifier to the microwave bridge. These improvements have resulted in roughly a fivefold increase in the available signal-to-noise ratio. A flow system was used with irradiation of the sample directly in the ESR cavity by a $\sim$10-μA beam of 2.8-MeV electrons. The pyromellitic and benzenepentacarboxylic acids were from Aldrich. Aqueous solutions were $\sim$5 mM in the acid, with 0.1 M NaH_2PO_4–Na_2HPO_4 buffer added to convert e_{aq}^- to H atoms. The pH was 7, sufficiently high to assure that the carboxyl groups were fully ionized. Solutions were purged with N_2 to remove dissolved oxygen. Flow rates were $\sim$0.5 cm^3/s and residence times of the sample within the cavity $\sim$50 ms. Radical lifetimes of the polycarboxylates were of the order of the residence times so that concentrations were largely controlled by the production rate ($\sim$0.01 M/s).

Results and Discussion

The low-field ^{13}C hyperfine structure observed for cyclohexdienyl-1,2,4,5-tetracarboxylate radical (I) produced by addition of H atoms to a proton position of pyromellitic acid is illustrated in Figure 1. Six different isotopically labeled radicals are observed, two with line intensities of $\sim$0.6% and four with intensities of $\sim$1.2% of that of the main lines, as expected from the relative isotopic abundance of these radicals (relative natural abundance per carbon atom is 0.011/0.90 = 0.012). The related ESR spectrum observed for the OH addition product from a N_2O-saturated solution at pH $\sim$13 and and eightfold lower gain is also given in Figure 1 for comparison. Except for several peaks of lower intensity due to impurities the latter is as reported previously[3] and does not exhibit coupling to the OH proton because of rapid exchange with the water. For the H adducts lines were observed at the positions indicated in a number of different experiments and mirror image patterns were also observed at high field so that one is reasonably assured that these lines are properly assigned to the radical in question. ^{13}C spectra of similar intensity were also observed for cyclohexadienyl-1,2,3,4,5-pentacarboxylate (produced by H addition to benzenepentacarboxylic acid). Certain of the much less intense lines of the H atom adduct to trimesic and prehnitic acids were also observed but the spectra are more complex so that in the absence of the entire spectrum the individual lines could not be assigned to specific atoms with certainty.



I

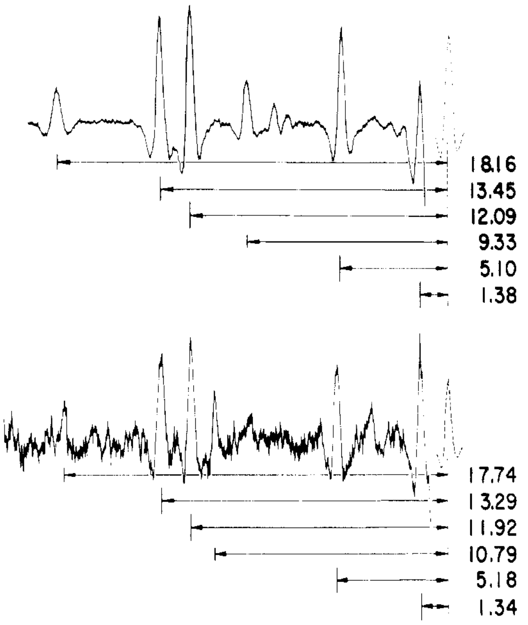


Figure 1. Second-derivative ESR spectra of low-field region of (upper) 1,2,4,5-tetracarboxyhydroxycyclohexadienyl and (lower) -cyclohexadienyl radicals, produced, respectively, by OH and H addition to pyromellitic acid. The ^{13}C spectra are recorded at 100× the gain of the main proton lines given as the dotted curves on the right. The ^{13}C half splittings are indicated by the stick figures under the ESR spectra with the ^{13}C hyperfine coupling constants being given at the right in gauss. Both spectra were recorded at $\sim$20 °C. The lowest field lies of the spectra of the nonlabeled radicals are aligned so as to illustrate the similarities and differences in the ^{13}C structure.

It is seen in Figure 1 that the overall ^{13}C patterns for the H and OH adducts are very similar. The splitting of the outermost line is somewhat larger and that of the fourth line considerably smaller in the OH substituted radical. The other splittings are essentially the same in the two radicals. The hyperfine data for each of the cyclohexadienyl radicals observed in the present study are summarized in Table I along with comparative data on the corresponding hydroxycyclohexadienyl radicals. These hyperfine constants are judged to be accurate to ±0.03 G (standard deviation of determinations from at least seven recordings).

Assignments to the carboxyl groups are based on argu-

---

(5) Verma, N. C.; Fessenden, R. W. *J. Chem. Phys.* **1976**, *65*, 2139, Hornak, J.; Fessenden, R. W., in press.

TABLE I: ^{13}C Hyperfine Constants (G) of Carboxylated Cyclohexadienyl and Hydroxycyclohexadienyl Radicals[a]

		ring system[b]				carboxyl substituents[c]		
source	adduct	C_1 C_5	C_2 C_4	C_3	C_6	$C_1(CO_2^-)$[a] $C_5(CO_2^-)$	$C_2(CO_2^-)$ $C_4(CO_2^-)$	$C_3(CO_2^-)$
benzenepentacarboxylic acid	H	12.70	11.69	18.67	10.38	4.83	1.30	6.79
	OH	12.79	11.72	19.35	8.33	4.75	1.28	6.82
pyromellitic acid	H	13.29	11.92	17.74	10.79	5.18	1.34	(11.80)[d]
	OH	13.45	12.09	18.16	9.33	5.10	1.38	(12.13)[d]
benzene	H					(9.00)	(2.69)	(13.14)
	OH					(8.92)	(2.74)	(13.14)

[a] Data for hydroxycyclohexadienyl radicals are from Eiben and Schuler (ref 3). Assignments are as given in that paper. There were at least seven measurements of each ^{13}C splitting with the standard deviation within each set being ~0.03 G. [b] See ref 3 for comments on the assignments to the C_1, C_5 and C_2, C_4 pairs. [c] Values in parentheses are the proton hyperfine couplings at the indicated ring positions. [d] The small difference between these values was confirmed during the present study.

ments given in the previous study and are virtually certain. It is seen that these hyperfine constants are essentially unaffected by OH substitution, as is also largely the case for the proton hyperfine constants of the adducts to benzene, so that is clear that in these instances the distribution of unpaired spin density over the conjugated system is very similar for the two types of radicals. It is particularly noted that there appears to be virtually no loss of spin density from the π system on substitution.

As with the OH adducts each of the radicals studied here exhibits two unique ring carbon atoms with hyperfine constants ~18 and 10 G. Assignments of the larger of these values to C_3 are based on estimates ~18 G from eq 1, as made for the hydroxylated radicals (taking $Q_l \sim 36$ G and $Q_a \sim -14$ G). One would expect the hyperfine interactions at C_3 to be affected by OH substitution only to the extent that the π system is perturbed while a considerably greater effect is possible at C_6, particularly in view of the large differences previously noted in the proton hyperfine constants at this latter position. Of the two unique hyperfine constants assignable to the ring carbon atoms the smaller is affected substantially by substitution, in confirmation of the previous assignment of this value to C_6 (and the larger to C_3) in hydroxycyclohexadienyl radical. For the radicals produced from pyromellitic acid the difference of 2.4% between the remaining hyperfine values for C_3, in fact, parallels the change of 2.8% in the value noted for the proton attached at this position. In the case of the pentacarboxylate radicals a slightly larger difference in C_3 is observed (3.6%) although the coupling to the carboxyl group indicates that the spin density at this position is unaffected by substitution within experimental error. Within the level of these slight differences, OH substitution must affect the interactions between the π spin density and the H and CO_2^- substituents somewhat differently. Because the C_3 atom is quite remote from the position of substitution any such effect must, however, be rather indirect. We note that the proton hyperfine constants for the various carboxyl derivatives of cyclohexadienyl, but not for cyclohexadienyl itself, are all slightly greater in their hydroxylated analogues. One possible explanation is that there is somewhat less loss of spin density to the carboxyl groups in the hydroxylated radicals but there is no evidence for this in the case of the pentacarboxylates or in the effect of substitution on the *g* factor.[2] More probably the out-of-plane wagging of the H_3 atom samples the wave function asymmetry produced by the OH (see below) more extensively than does the carboxyl group. If so the latter provides a better probe of the spin density at C_3. While the differences are small, these data emphasize that the hyperfine constants of carbon atoms in a π system can be affected at the few percent level by factors other than the local and adjacent spin densities.

The two doubly intense lines, corresponding to hyperfine constants ~13 and 12 G, are readily assigned to the C_1 (C_5) and C_2 (C_4) positions by reference to the almost identical values observed in the hydroxylated radical. While the specific assignment could be inverted (cf. ref 3 for comments on this point) such a change would not alter the present arguments since neither hyperfine constants is affected to any significant extent by substitution. The lack of effect at C_2 (and C_4) is as expected since there is a position of low (negative) spin density so that the hyperfine interaction is developed mainly from the spin densities at C_1 and C_3, which are similar in the two radicals, with little possibility for any direct effect of OH substitution. Even though the carboxyl groups indicate similar spin density at C_1 (and C_5) in the substituted and unsubstituted radicals one might expect to see some difference in the ^{13}C hyperfine constants of the ring atom at this position because of its proximity to the substituent, but little is observed. Apparently effects of perturbation of the π system by the OH largely cancel at these positions. The hyperfine data for the carbon atoms in the conjugated system, therefore, completely confirm the conclusion from the substituent probes that the spin density distribution in the π system is not appreciably affected by OH substitution at C_6.

For both radicals the remaining ~10-G hyperfine constant can be assigned quite readily to the unique carbon atom at C_6. The values observed in this case are 13 and 23% higher than those for the hydroxylated radicals even though the spin density at the adjacent positions, as measured by the carboxyl probes and also by the ring atoms, does not change appreciably. It has long been known[6] that the proton hyperfine coupling at the C_6 position of hydroxycyclohexadienyl radical is 25% lower than that of cyclohexadienyl even though the magnitudes of both are expected to be controlled by the sum of the spin densities on C_1 and C_5 (more accurately by the magnitude of the sum of the wave functions).[7] Substitution of OH for H clearly distorts the interaction between the π system and substituents at C_6 with the effects of this distortion also being felt quite strongly at this carbon nucleus. This conclusion very dramatically illustrates that additional terms must be added to eq 1 to take into account special features of the radicals. It is noted at this point that the hyperfine constant for C_6 is undoubtedly negative.[8] The decrease in its magnitude observed on OH

---

(6) Eiben, K.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 1186.

(7) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

(8) Chipman, D. M. *J. Chem. Phys.* **1979**, *71*, 761, and submitted for publication.

substitution therefore corresponds to additional positive contributions which must, from the above arguments, result rather indirectly. The OH substituent, of course, introduces asymmetry with respect to the plane of the ring. Apparently this asymmetry does not affect the π orbitals associated with the conjugated system significantly. The effects of C_6 could, however, be different because of the sp^3 hybridization at this position. Chipman[9] has also pointed out that in hydroxycyclohexadienyl radical rotational motion of the OH group could effectively induce some unpaired spin density at C_6. These sorts of effects are not included in the arguments on which eq 1 is based.

While the previous ^{13}C ring carbon data[3] on the different carboxylated cyclohexadienyl radicals could not be completely correlated in terms of eq 1, it was possible that complications in the spin distribution could have been introduced by the OH substituent, as is manifested by the data for the protons at C_6. It is clear from the present data on the unsubstituted radical that this is not the explanation. From arguments as previously given[10] (cf. Table IV in ref 10) one can estimate an upper limit to the spin density at C_6 as ~0.06 (i.e., 70% of 0.08). Using this value in the explicit relationship for $a(C_6)$, with the values for $Q^{C}_{CC'}$ and $Q^{C}_{C'C}$ taken from the work of Fraenkel and coworkers[4,11] and $Q^{C}_{CH} = -17.8$ G for the saturated systems as deduced from the data on ethyl radical,[12] we find $a(C_6)$ is predicted to be −1.3 G vs. the experimental value of −10.4 G. This means a further negative contribution must be added to eq 1, perhaps involving nonlinear terms between the spin densities and hyperfine constant, as suggested by Whiffen's comments.[3] One clearly needs more theoretical work to provide further insight into the σ–π interactions and ultimately into their effects on the hyperfine data. Current studies in these laboratories are aimed at building a data base to test these calculations over a wide range of hydrocarbon radicals.

Acknowledgment. The authors thank Drs. R. W. Fessenden and D. M. Chipman for many helpful discussions.

Registry No. I, 85304-45-6; cyclohexadienyl-1,2,3,4,5-pentacarboxylate radical, 85304-46-7.

---

(9) Chipman, D. M., private communication.

(10) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *38*, 773, **1963**, *39*, 2147.

(11) Strauss, H.; Fraenkel, G. K. *J. Chem. Phys.* **1961**, *35*, 1738.

(12) Fessenden, R. W. *J. Phys. Chem.* **1967**, *71*, 74.

Surface Tensions and Micellization of ω-Cyclohexylalkanoic Acids and Their Sodium Salts

Arne Skauge[†] and Jan J. Spitzer[*]

Department of Chemistry and Oil Sands Research Laboratory, The University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4

(Received: August 3, 1982; In Final Form: December 1, 1982)

The surface properties of a homologous series of ω-cyclohexylalkanoic acids and their sodium salts of general formula $C_6H_{11}(CH_2)_nCOOH$ with $n = 0, 1, 2, 3$ were determined at 25 °C. For sodium carboxylates with $n = 1, 2, 3$ the critical micelle concentrations (cmc) were found to be 1.0, 0.53, and 0.26 M. Surface tension measurements on aqueous solutions of these compounds were used to calculate the saturation areas per molecule, the free energies of adsorption, and the efficiency and effectiveness of adsorption. The cyclohexyl ring in these compounds makes the saturation areas larger than those of the corresponding straight-chain acids and salts. This effect diminishes with the increasing number of CH_2 groups in the alkyl chain. A "rule of two" ($-RT \ln 2$) is found to be valid for the standard free energy of adsorption per CH_2 group to a charged air/solution interface as compared to the "rule of three" ($-RT \ln 3$) that is typical of uncharged interfaces. These are the same rules that are known to apply to the free energies of micellization of CH_2 groups into ionic and nonionic micelles.

Introduction

The dependence of interfacial activity and micellization on the structure of the hydrophobic part of a surfactant molecule has not been much studied. The large number of literature data are limited to compounds that have various hydrophilic groups attached to straight paraffinic chains. In a few studies on isomers of alkylbenzenesulfonates,[1-3] on branched alkyl sulfates,[4] on dialkylresorcinol ethers,[5] and on dialkyl sulfosuccinates[6] the effects of branching or doubling of the alkyl chain were investigated. Rosen[7] has recently summarized the effects of a number of variables on both adsorption and micellization, while an older review limited to micellization is also available.[8] The lack of data about the effects of hydrophobic structures has persisted[9] in spite of Hartley's original suggestion[5] that the interfacial activity of a surfactant can be increased (sometimes to a point of spontaneous

---

[†] Visiting Scientist, Department of Chemistry, University of Bergen, Bergen, Norway.

[*] Address correspondence to this author at the Department of Chemistry, The University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4.

(1) H. A. Neville and C. A. Jeanson, *J. Phys. Chem.*, **37**, 1001 (1933).

(2) R. G. Paquette, E. C. Lingafelter, and H. V. Tartar, *J. Am. Chem. Soc.*, **65**, 686 (1943).

(3) J. J. Meister in "Solution Chemistry of Surfactants", Vol. 2, K. L. Mittal, Ed., Plenum Press, New York, 1979, p 841.

(4) E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.*, **36**, 611 (1944).

(5) G. S. Hartley, *Trans. Faraday Soc.*, **37**, 130 (1941).

(6) E. F. Williams, N. T. Woodberry, and J. K. Dixon, *J. Colloid Interface Sci.*, **12**, 452 (1957).

(7) M. J. Rosen in "Solution Chemistry of Surfactants", K. L. Mittal Ed., Plenum Press, New York, 1978, p 45.

(8) H. B. Klevens, *J. Am. Oil Chem. Soc.*, **30**, 74 (1953).

(9) J. L. Moilliet, B. Collie, and W. Black, "Surface Activity", 2nd ed., E. & F. Spon Ltd., London, 1971, p 41.

0022-3654/83/2087-2398$01.50/0