UCRL-16045

University of California

Ernest O. Lawrence Radiation Laboratory

THE ELECTRON SPIN RESONANCE SPECTRUM OF THE RADICAL ANION 1, 3, 5-CYCLOHEPTATRIENE AND THE SPIN POLARIZATION CONSTANT $Q_{C'CH}{}^{H}$

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Journal of Chemical Physics

UCRL-16045

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE ELECTRON SPIN RESONANCE SPECTRUM OF THE RADICAL ANION OF 1, 3, 5 - CYCLOHEPTATRIENE AND THE SPIN POLARIZATION CONSTANT $Q_{C'CH}^{H}$

Donald H. Levy and Rollie J. Myers

April 1965

The Electron Spin Resonance Spectrum of the Radical Anion of 1, 3, 5 - Cycloheptatriene and the Spin Polarization Constant $Q_{C'CH}^{H}$

by Donald H. Levy* and Rollie J. Myers

Department of Chemistry, and Inorganic Materials Research Division,
Lawrence Radiation Laboratory, University of California,
Berkeley, California

Abstract

The radical anion of 1, 3, 5 - cycloheptatriene has been prepared by electrolysis in liquid ammonia. The proton hyperfine structure of its electron spin resonance spectrum was assigned with A(1,6) = 7.64, A(2,5) = 0.59, A(3,4) = 4.90 and A(7) = 2.16 gauss. Satisfactory agreement between calculated and observed coupling constants is only obtained if the radical anion is assumed to have a non-planar boat conformation and if the methylene coupling is assumed to arise primarily from spin polarization by the spin density on adjacent carbon atoms. A value for this spin polarization constant is obtained and we find that either $Q_{C'CH}^{H}$ = 4.33 or -3.09 gauss. The recent data of Morton are in good agreement with the positive value, but the theoretical calculation by Colpa and de Boer indicate that it should be probably negative in sign.

Introduction

The origin of the proton hyperfine splittings in aromatic radical anions has been well understood for some time. These protons lie in the nodal plane of the pi-electron system and the hyperfine coupling between them and the odd electron is generally accepted as being due to a spin exchange polarization between the odd pi-electron and the sigma-electrons in the carbon-hydrogen bond.[1-3] Considerable interest has also been shown in the origin of the proton hyperfine coupling from methyl and methylene groups substituted on pi-radicals. These substituent protons do not lie in the pi-electron nodal plane and consequently there are two possible mechanisms that will give rise to hyperfine splittings. The first is a spin exchange polarization mechanism similar to that which produces aromatic proton splittings, and the second is a hyperconjugation mechanism[4] which leads to a non-zero pi-electron spin density at the substituent protons.

Several workers have postulated that the hyperconjugation mechanism is by far the more important. Bolton and co-workers[5] showed that the pairing principle of Hückel theory,[6-7] which predicts that the radical cations and anions of a given alternant hydrocarbon should have very similar ESR spectra, would be carried over to methyl coupling constants if these coupling constants arose via a spin polarization mechanism. However, if hyperconjugation were the principal mechanism there would be no reason for cation and anion methyl coupling constants to be equal. They took the experimental fact that they are not equal as evidence that the principal mechanism was indeed hyperconjugation. Using a hyperconjugation model they calculated a series of ratios A(methyl cation)/A(methyl anion) which were in good agreement with the experimental ratios.

Colpa and de Boer[8] pointed out that while the particular model of Bolton et al. could predict the proper cation/anion ratios, the absolute magnitudes of the coupling constants predicted by this theory were far too small. They developed a different hyperconjugation model which successfully predicted both the cation/anion ratio and the absolute magnitude of the coupling constants in a number of cases. In addition, they performed a configuration interaction calculation on the $C'-CH_2$ fragment (C' being the unsaturated carbon to which the methylene group is attached) to obtain an estimate of the magnitude of the spin exchange polarization mechanism. They found that the spin polarization contribution to methylene coupling constants should be given by

$$A(H) = Q_{C'CH}^{H} \rho_{C'} \qquad (1)$$

and that this Q value was far too small to account for the large coupling constants observed. They point out that the approximations in such a calculation naturally leave the numerical results in some doubt. Nonetheless they felt that the order of magnitude of the results substantiated their main argument.

These two treatments give a good indication that hyperconjugation is the predominant mechanism for hyperfine coupling in methyl and methylene substituted aromatics. However, it would seem desirable to have a case in which the hyperconjugation and spin polarization mechanisms are clearly separated. This would provide direct evidence for the importance of hyperconjugation in these radicals and in addition would provide a quantitative experimental measure of the spin polarization mechanism. The radical anion of cycloheptatriene provides such a case.

The usefulness of this radical anion is due to the fact that as long as pi-electron-electron interactions are neglected symmetry considerations require the first anti-bonding molecular orbital of cycloheptatriene to have a node passing down the symmetry axis which goes through the methylene carbon. This means that within this approximation there can be no hyperconjugation contribution to the methylene coupling constant, and consequently any coupling constant can only be the result of spin polarization. Even if one includes electron correlation effects the contribution of hyperconjugation is small and can be estimated by an approximate SCF calculation. Thus the methylene proton coupling constant in this radical anion gives a direct experimental measurement of the magnitude of the spin polarization mechanism.

Experimental Results

We have prepared the cycloheptatriene radical anion by electrolyzing a three millimolar solution of the parent hydrocarbon dissolved in a solution of liquid ammonia. The solution was saturated with tetramethylammonium iodide. The electrolysis apparatus and spectrometer have been previously described.[9-10] The spectrum is shown in Fig. 1a.

The spectrum has four coupling constants but the assignment is made considerably easier by the fact that the two outermost triplets are so well resolved. One coupling constant is given by the distance between the two triplets, and the second is given by the spacing within either triplet. The total width of the spectrum determines the fourth coupling constant if the first three are known, and the remaining coupling constant

was assigned by trial and error with very little difficulty. The resulting assignment is given in Table I, and the theoretical spectrum[9] calculated from this assignment is shown in Fig. 1b. As can be seen there is excellent agreement between the theoretical and experimental spectra.

With no further experiments it is impossible to assign which of the coupling constants are associated with which protons. As can be seen from Fig. 1 the molecule contains four sets of two symmetrically equivalent protons each. The radical anion of cycloheptatriene in which one of the methylene protons had been replaced by deuterium was prepared.[11] In Fig. 2 we show the experimental spectrum for C_7H_7D and a calculated one with the deuterium coupling assigned to position 7 as given in Table I. It can be seen that there was negligible proton exchange with the solvent and that the methylene coupling constant must be 2.16 gauss as given in Table I.

Discussion

The assignment of the coupling constants in Table I to the three vinyl hydrogen positions requires some further discussion. The electron diffraction[12] and nmr[13] data indicate that 1, 3, 5 - cycloheptatriene does not have a planar structure. It has a boat conformation which is consistent with the bond angles expected for the sigma-system of such a molecule. In this structure the carbon atoms 1, 2 and 5, 6 as shown in Fig. 1 form a plane. The methylene carbon 7 and the carbon atoms 3, 4 are bent above this plane to form a boat conformation. In this structure

perfect pi-overlap would be provided between positions 3-4 but the pi-overlap between the other adjacent carbon atoms depends upon the exact structure of the molecule. In the simple valence bond structure shown in Fig. 1 the major reduction in pi-overlap would be between positions 2-3 and 4-5. In the case of cyclooctatetraene there is some evidence[14,15] that the mono- and di-anions are planar. This is taken as confirmation of the 4n + 2 rule, but since these considerations do not apply to 1, 3, 5 - cycloheptatriene it seems likely that its radical anion is still non-planar and in a boat conformation similar to the parent hydrocarbon.

We have used the approximate SCF theory of McLachlan[16] together with the matrix elements of Coulson and Crawford[17] to estimate the effect of electron correlation in the methylene group. Because of the nodal properties of the one-electron functions of simple Hückel theory the methylene group can not hyperconjugate with the odd electron unless electron correlation is included. We have calculated coupling constants for one Hückel case and for two SCF cases and the results are shown in Table I.

In the Hückel case we have assumed a planar structure so that the pi-overlap is the same between all adjacent positions except for the methylene group where Coulson and Crawford's[17] matrix elements were used. There is fair agreement in this case between the calculated and observed coupling constants and the methylene group coupling constant is zero as required by symmetry. In the SCF planar case we have used McLachlan's[16] technique and negative spin densities are obtained at positions 2, 5 and

at the methylene group. It can be seen that the calculated coupling constant of the methylene group, even when electron correlation is included, is much too small to explain the observed value of 2.16 gauss.

The interesting fact about the SCF planar calculation is that it predicts too large a coupling constant at positions 1, 6 and too small a one at positions 3, 4. The effects of non-planarity would be to decrease the pi-overlap between positions 2-3 and 4-5 and also possibly between positions 1-2 and 5-6. A structure of alternating single and double bonds as shown in Fig. 1 would only allow a decrease in the pi-overlap between positions 2-3 and 4-5, but it is also possible for all four positions to have decreased pi-overlap. If it is assumed that the pi-overlap of positions 1-2, 2-3, 4-5 and 5-6 are all equally decreased then a SCF calculation does not give better agreement with the observed coupling constants at positions 1,6 and 3,4. If, on the other hand, one only decreases the pi-overlap between positions 2-3 and 4-5 an improved agreement is obtained as shown in the last column of Table I. The best agreement was obtained with $\beta(2\text{-}3) = 0.7\ \beta(3\text{-}4)$. If one assumes that the resonance integral is proportional to the cosine of the angle between the p_Z orbitals then this angle should be close to 45°. Molecular models of cycloheptatriene, with alternate single and double bonds and in a boat conformation, show a considerable twist between the p_Z orbitals on positions 2-3 and 4-5 and angles close to 45° can be obtained. Thus the observed coupling constants at positions 1, 6 and 3, 4 seem to clearly show that this radical anion, like the parent hydrocarbon, is non-planar.

It is also interesting to observe that a norcaradiene structure[13] cannot explain the observed coupling constants. In the norcaradiene structure there is a bond between positions 1 and 6 so that carbon atoms 1, 6 and 7 form a cyclopropane ring fused to a cyclohexadiene ring. The pi-system in norcaradiene would be that of a 1, 3 - butadiene but with some hyperconjugation to the orbitals on positions 1, 6. This is very similar to 1, 3 - cyclohexadiene and its radical anion has been observed.[10] Its coupling constants are 11.1, 8.2 and 2.0 gauss where the largest one is due to the methylene groups. A comparison with Table I shows that a norcaradiene structure with a pi-system similar to 1, 3 - cyclohexadiene could not explain the observed spectrum without an unreasonable adjustment of both Q and the hyperconjugation parameters.

Spin Polarization Constant

The methylene coupling constant observed in Table I is much larger than that calculated even if the SCF corrections are made. This same SCF calculation has been made for a number of radicals containing methyl and methylene groups[10] and in all other cases the matrix elements of Coulson and Crawford yield satisfactory agreement with experiment. Spin polarization by the large spin density on the nearby carbon atoms must be the source of this discrepancy, for electron correlation in cycloheptatriene radical anion could never be expected to yield a coupling constant of 2.16 gauss at the methylene position.

The fact that hyperconjugation is not effective in this radical allows us to obtain an experimental value for the constant $Q_{C'CH^{H}}$. The SCF McLachlan calculation predicts that essentially all the spin

density is in the unsaturated part of the molecule and that the spin density at all positions is positive for the non-planar conformation. Assuming that this is correct we can obtain a value of Q for the unsaturated part of the molecule by the equation

$$|Q| = \sum_{n=1}^{6} A_i = 26.26 \qquad (2)$$

Using this Q, the experimental coupling constant A_1, and McConnell's relationship[1-3] $A_i = Q\rho_i$, one finds the unpaired spin density on carbon atom 1 is 0.291 and the total unpaired spin density adjacent to the methylene group is 0.582. The total methylene coupling constant consists of a small hyperconjugation part and a larger spin polarization part. The hyperconjugation part was estimated in Table I to be -0.36 gauss.

Colpa and de Boer[8] performed an approximate calculation of $Q_{C'CH}^{H}$ which indicated that it was negative in sign. If this were true, then the spin polarization and electron correlation contribution to the observed methylene coupling constant in Table I are of the same sign. However, the data of Morton[18] give a value for the spin polarization constant that is positive in sign. We shall make both assumptions and for our first calculation we shall assume that $Q_{C'CH}^{H}$ is positive. With this assumption we have for the spin polarization coupling constant

$$|A(\text{spin pol.})| = \big||A(\text{obs.})| + |A(\text{hypercon.})|\big| = 2.52 \text{ gauss} \qquad (3)$$

This coupling constant and the adjacent spin density of 0.582 gives from eq. (1) the experimental value $Q_{C'CH}^{H} = 4.33$ gauss. If the spin polarization constant is negative in sign then the hyperconjugation contribution has to be substracted from the observed coupling and $Q_{C'CH}^{H} = -3.09$ gauss.

Morton[18] used the postulated equation

$$A_{\beta}(\theta) = B_0 + B_2\cos^2\theta \qquad (4)$$

for the β- hydrogen coupling constants in irradiated organic acids. The constant B_0 in eq. (4) is equivalent to our $Q_{C'CH}^{H}$. He finds that B_0 and B_2 have the same sign and he finds from two determinations that $B_0 = 3.9 \pm 0.7$ gauss. Since B_2 must be positive in sign then B_0 must also be positive according to Morton's data.[19] The agreement between our value of 4.33 and Morton's 3.9 gauss is strong support for the fact that $Q_{C'CH}^{H}$ must be positive, since it is difficult to believe that Morton's use of eq. (4) could yield the correct value of B_0 but one which was wrong in sign.

In their calculation, Colpa and de Boer[8] find that $Q_{C'CH}^{H}$ is the sum of two terms. One of these terms is negative and one is positive. The negative term is the direct spin polarization of the CH bond by the spin density of the atom C′. This term is similar to the usual spin polarization mechanism in aromatic hydrocarbons but it should be quite small due to the decrease in the exchange integrals. Colpa and de Boer estimate a -1.76 gauss contribution from this term. The second term

appears as a second-order term and it is due to the spin polarization in the CH bond caused by the spin density in the C′C bond. The spin density in the C′C bond comes from direct spin polarization and they use Karplus and Fraenkel's[20] value of $Q_{C'C}^{C} = -14$ gauss.

This value of $Q_{C'C}^{C}$ was derived by Karplus and Fraenkel for the 2s contribution for C^{13} interaction through spin polarization of an sp^2 orbital. It is not appropriate for proton interaction through spin polarization of its 1s orbital unless if multiplied by the factor[20] 3 x 507.6/1191. This slightly modifies Colpa and de Boer's second-order term to +0.83 and the resulting theoretical value is $Q_{C'C}^{H} = -0.9$ gauss.

Colpa and de Boer make several serious approximations in their calculation and in addition their calculation does not exactly apply to our case. Their calculation is for sp^2 hybridization with the H-atom in the usual pi-electron nodal plane while our determination is for sp^3 hybridization with the H-atoms in a nodal plane between two pi-orbitals. The first-order contribution can be quite different in the two cases for the exchange integrals between the pi-electron and the C-H orbitals are dependent upon the angle between them. It is quite possible, however, that the McLachlan calculation given in Table I contains most of the correction for the C-H bond not being in the usual pi-electron nodal plane. If this is the case, then the agreement between Morton's value and our positive value of $Q_{C'CH}^{H}$ is good evidence that the Colpa and de Boer calculation gives the wrong sign for spin polarization.

Acknowledgments

We are indebted to Professor F. R. Jensen for supplying our first sample of cycloheptatriene and for help with the deuteration. Miss Carolyn Talcott prepared the deuterated species and did some of the computer calculations. This work was supported by a grant from the U.S. Atomic Energy Commission.

References

* Present address: Department of Theoretical Chemistry, Cambridge, England.

(1) H. M. McConnell, J. Chem. Phys. 24, 764 (1956); S. I. Weissman, J. Chem. Phys. 25, 890 (1956); H. S. Jarrett, J. Chem. Phys. 25, 1289 (1956).

(2) H. M. McConnell and H. H. Dearman, J. Chem. Phys. 28, 51 (1958).

(3) H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107 (1958).

(4) R. S. Mulliken, C. A. Rieke and W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).

(5) J. R. Bolton, A. Carrington and A. D. McLachlan, Mol. Phys. 5, 31 (1962).

(6) A. D. McLachlan, Mol. Phys. 2, 271 (1959).

(7) E. de Boer and S. I. Weissman, J. Am. Chem. Soc. 80, 4549 (1958).

(8) J. P. Colpa and E. de Boer, Mol. Phys. 7, 333 (1964).

(9) D. H. Levy and R. J. Myers, J. Chem. Phys. 41, 1062 (1964).

(10) D. H. Levy, thesis, University of California, Berkeley, 1965; Lawrence Radiation Laboratory Report UCRL-11864.

(11) The synthesis is described in ref. 10. The n.m.r. spectrum of the deuterated species agreed with that of ref. 13.

(12) M. Traetteberg, J. Am. Chem. Soc. 86, 4265 (1964).

(13) F. R. Jensen and L. A. Smith, J. Am. Chem. Soc. 86, 956 (1964).

(14) H. L. Strauss, T. J. Katz and G. K. Fraenkel, J. Am. Chem. Soc. 85, 2360 (1963).

(15) See also A. Carrington, H. C. Longuet-Higgins and P. F. Todd, Mol. Phys. 8, 45 (1964) and T. J. Katz private communication - submitted for publication.

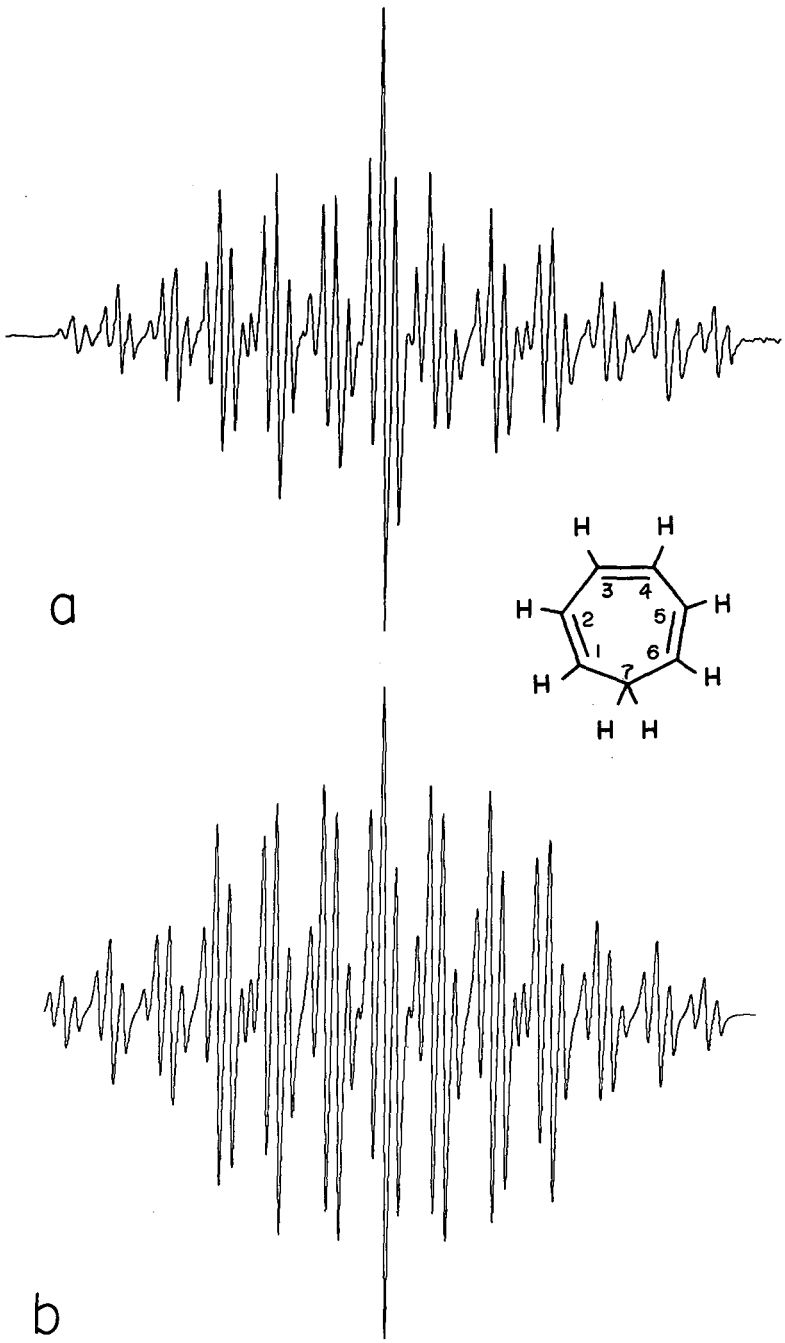
(16) A. D. McLachlan, Mol. Phys. 3, 233 (1960).

(17) C. A. Coulson and V. A. Crawford, J. Chem. Soc. 1953, 2052.

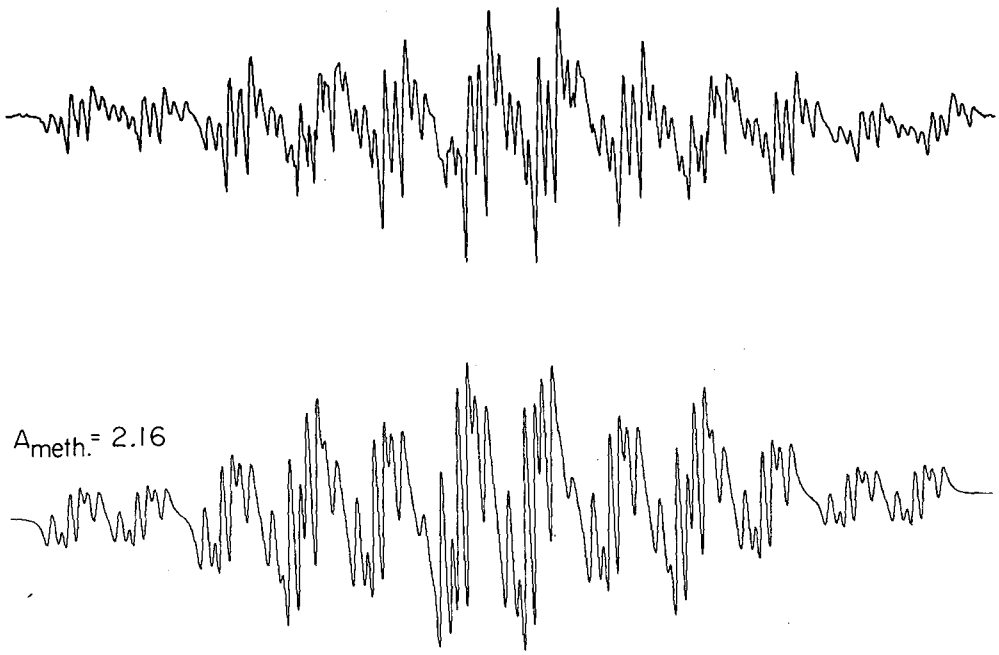
(18) J. R. Morton, J. Chem. Phys. 41, 2956 (1964).

(19) J. R. Morton, private communication.

(20) M. Karplus and G. K. Fraenkel, J. Chem. Phys. 35, 1312 (1961).



MUB-5799



MUB-6568

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.