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Acid-Induced Free-Radical Decomposition of Hydroperoxides: Quantal Calculations

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Acid-Induced Free-Radical Decomposition of Hydroperoxides: Quantal Calculations

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ABSTRACT

Quantum mechanical calculations using the GAUSSIAN 76 system of programs are used to suggest a possible mechanism for the acid-induced free-radical decomposition of hydroperoxides.

INTRODUCTION

Recent work in this laboratory [1, 2] and elsewhere has shown that the acid-induced decomposition of organic hydroperoxides can proceed via a free radical mechanism as well as the widely accepted heterolytic pathway. One important piece of experimental evidence in support of the homolytic mechanism is that certain hydroperoxides in strongly acidic media are efficient free-radical initiators of vinyl polymerization under conditions at which neither the acid nor the hydroperoxide alone will induce polymerization. In the case of polymerization of methyl methacrylate with t-butyl hydroperoxide and sulfuric acid at 25° C, the initiating species have been identified as the t-butoxy and hydroxy radicals [2]. This suggests that the mechanism of radical formation involves a simple O–O bond homolysis and that this process is facilitated by protonation of the hydroperoxide.

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The compounds used in the experimental work [2] were readily available and included: t-butyl hydroperoxide (1), n-pentyl hydroperoxide (2), 2-pentyl hydroperoxide (3), 3-cyclohexenyl hydroperoxide (4), and hydrogen peroxide (5) together with di-t-butyl peroxide (6). Compounds (5) and (6) did induce polymerization but at a much slower rate than the others. We have now performed a series of quantum mechanical calculations in order to test whether the protonated forms of the hydroperoxides have a lower energy pathway to free radicals than the corresponding neutral species. Because of the expense of computing reaction pathways for large molecules, the calculations were carried out on methylhydroperoxide and hydrogen peroxide. The results are reported in this article and are used to suggest a possible mechanism for the acid-induced free-radical deoomposition of hydroperoxides.

RESULTS AND DISCUSSION

All of the calculations reported here were done using the GAUSSIAN 76 system of programs [3] on the CSIRO CYBER 76, and a standard 4-31G basis set. The initial geometries of the molecules were taken, where possible, from the tabulation of Lathan et al. [4], and when the

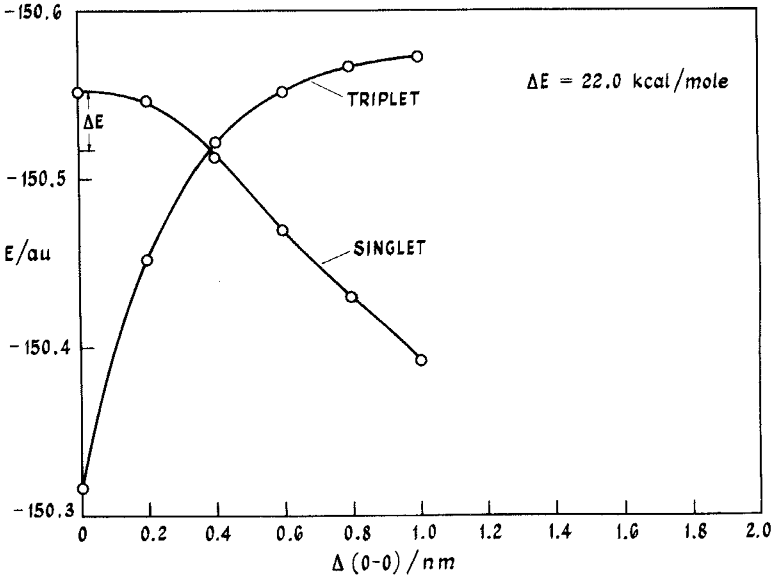

FIG. 1. Plot of total energy against the change in O–O distance for H_2O_2.

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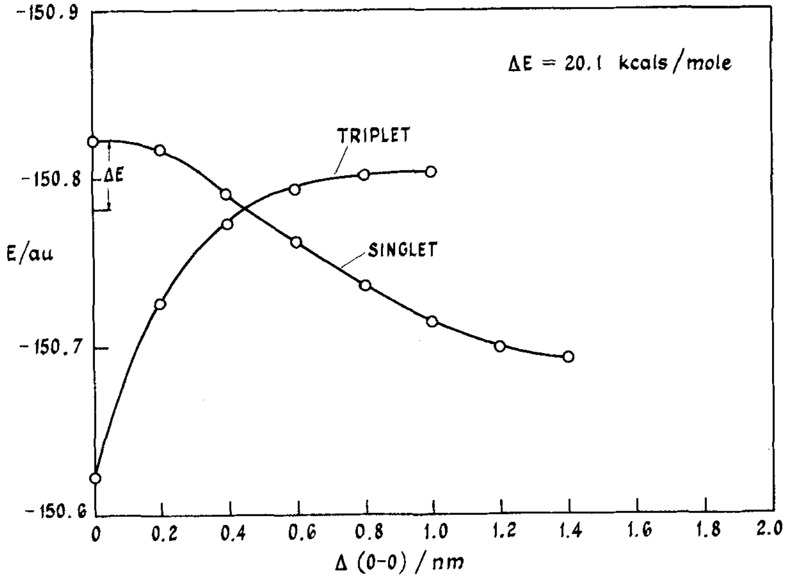

FIG. 2. Plot of total energy against the change in O–O distance for $H_3O_2^+$.

molecule was not included in this tabulation we optimized the geometry. In each calculation the O–O bond distance was increased in steps of 0.2 nm until the total energy of the system was approximately constant. Calculations were performed on the singlet and triplet states of H_2O_2, $H_3O_2^+$, CH_3OOH, $CH_3\overset{+}{O}(H)OH$, and $CH_3OOH_2^+$. The results are presented graphically in Figs. 1 to 5. The singlet states of the molecules form ions whereas the triplet states separate into free radicals.

The results show that for hydrogen peroxide there is not a significant difference in the amount of energy needed to form two radicals from the protonated and nonprotonated forms. It should be noted that the energies involved in these transitions are rather high when compared with thermal energy at room temperature. The molecule CH_3OOH can be protonated in two positions. The $CH_3\overset{+}{O}(H)OH$ is more stable than $CH_3OOH_2^+$ by about 6 kcal/mol. It is the behavior of the triplet states of these two ions which gives an insight into the possible mechanism of the acid-induced free-radical decomposition of hydroperoxides. The thermal energy required to separate $CH_3OOH_2^+$ into its free radicals along the path ABC in Fig. 5 is less than 3 kcal/mol. Thus the total energy for the two stage mechanism $CH_3\overset{+}{O}(H)OH \longrightarrow CH_3OOH_2^+ \longrightarrow$ free radicals is considerably less than for the nonprotonated reaction $CH_3OOH \longrightarrow$ free radicals (path ABC in Fig. 3).

This two-stage path is available to Compounds (1) to (4) above,

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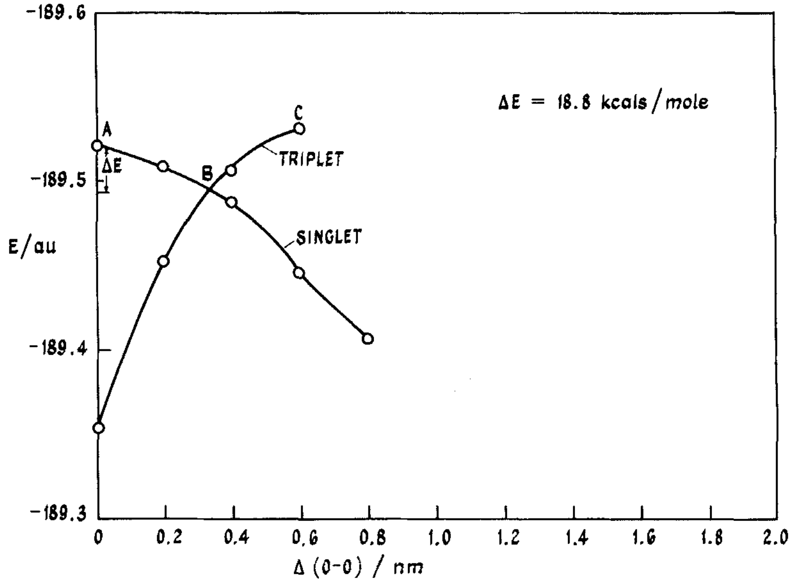

FIG. 3. Plot of total energy against the change in O–O distance for CH_3OOH.

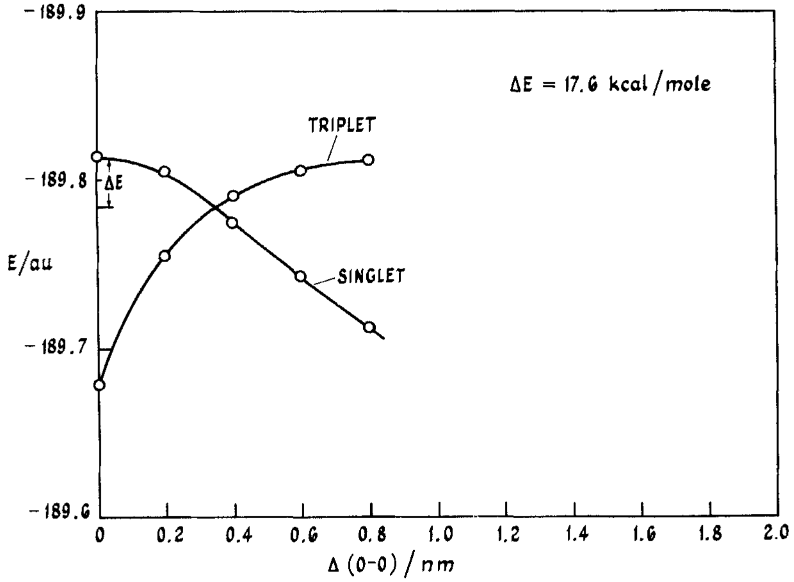

FIG. 4. Plot of total energy against the change in O–O distance for $CH_3\overset{+}{O}(H)OH$.

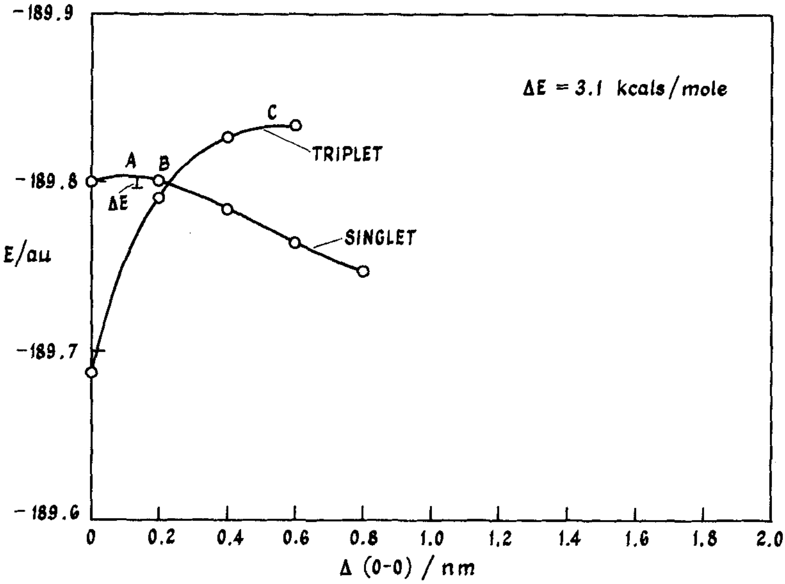

FIG. 5. Plot of total energy against the change in O–O distance for $CH_3OOH_2^+$.

all of which induce, at a reasonable rate, the polymerization of methyl methacrylate in the presence of a strong acid. It is not available to H_2O_2 nor to di-t-butyl peroxide, and this is in keeping with the observation that these compounds induce the polymerization of methyl methacrylate in acid solution only very slowly.

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REFERENCES

[1] E. Rizzardo and D. H. Solomon, J. Macromol. Sci.–Chem., A11, 1697 (1977).
[2] E. Rizzardo and D. H. Solomon, Ibid., A14, 33 (1980).

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[3] J. S. Buckley, R. A. Whitehead, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, Quantum Chem. Program Exchange, 10, 368 (1978).
[4] W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, Prog. Phys. Org. Chem., 11, 175 (1974).

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