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A Theoretical Study of the Initiation of the Direct Synthesis of H_2O_2

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A study, by the all-valence-electron SCMO method, is presented of the initiating steps in the direct reaction between equimolar proportions of H_2 and O_2 to form H_2O_2. A number of possible mechanisms are examined and it is concluded that the most likely is one which involves essentially primary fission of the H-H bond.

Introduction

Hydrogen peroxide is at present prepared industrially by electrolytic formation and hydrolysis of the peroxodisulphate ion or by continuous autoxidation of an anthraquinol. The possibility of synthesising the material by direct reaction of molecular H_2 and O_2 has been of great interest for some time and, indeed, the reaction $H_2 + O_2 = H_2O_2$ is thermodynamically feasible. In practice the formation of water suppresses the reaction under any easily attainable reaction conditions.

The series of reaction between possible species in the system is complex and hence, in the present paper, we have focussed attention on possible initiating steps in the reaction. Hence we have investigated theoretically a set of possible mechanisms involving the two species in order to try to deduce what kind of initiating process would be likely to require least activation energy. The theoretical method used throughout was a modified version of the well-known CNDO technique.[1] This has been fully described previously and the parameters for hydrogen and oxygen used in the calculation have been listed.[1] The equilibrium geometry[2] of H_2O_2 taken was H–O = 0.096 nm, O–O, 0.148 nm, and $\widehat{HOO} = 100°$: the molecule has C_2 symmetry, being twisted about the O–O bond with an angle of twist equal to 90° 12′

The method of invetigation was to allow the reacting molecules to approach each other along specified pathways and to examine the energy changes which ensued. The system possesses several degrees of freedom and hence we decided to limit these by assuming that all the processes were concerted. This still leaves open the choice of intermolecular distance at which the reaction is considered to 'start' and so we first established at what distance significant interaction between the molecules begins. Figure 1 shows the total energy variation when a hydrogen and an oxygen molecule, separated initially by 2 nm, are allowed to approach mutually. It is immediately obvious that perturbation of the molecular orbitals of the reactants commences when they are separated by ~ 0.5 nm. Thus, all subsequent sets of calculations started with the molecules held at this distance apart. This procedure also further diminishes the number of calculations necessary to the reaction coordinate.

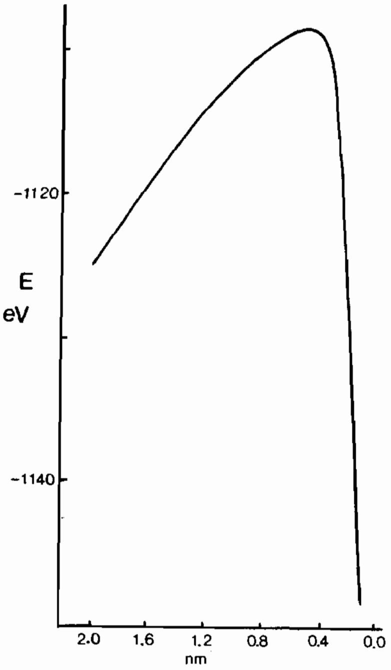

Figure 1. Energy Changes in Reaction at Large Distances.

As stated above, all the processes studied were considered to be concerted: variation of intermolecular distance was brought about at a constant rate concomitantly with bond angle and length distortions, as the system went through the transition state and relaxed into the equilibrium final, H_2O_2 configuration. By considering the process this way, we obtain a

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(1) J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys.*, *43*, S, 129, (1965); D.R. Armstrong, P.G. Perkins and J.J.P. Stewart, *J. Chem. Soc.*, *A*, 3674, (1971).

(2) 'Organic Peroxides' Vol. II, Ed. D. Swern, Wiley, New York, 1971 p. 642.

one-dimensional energy curve with the reaction coordinate as an extended normal coordinate. Hence, the overall calculation of each process was carried out in a sequence of eight steps, (each corresponding to an equal geometrical change in bond lengths and angles), starting with the initial configuration defined as above and ending with the equilibrium configuration of H_2O_2 (except of course in reaction (a)). The effect of third bodies such as inert gases, other molecules of H_2, O_2, or H_2O_2, or the walls of the reaction vessel were ignored in all cases considered. These are all known to affect the course of the reaction[3] but at this stage we wished to avoid such complications.

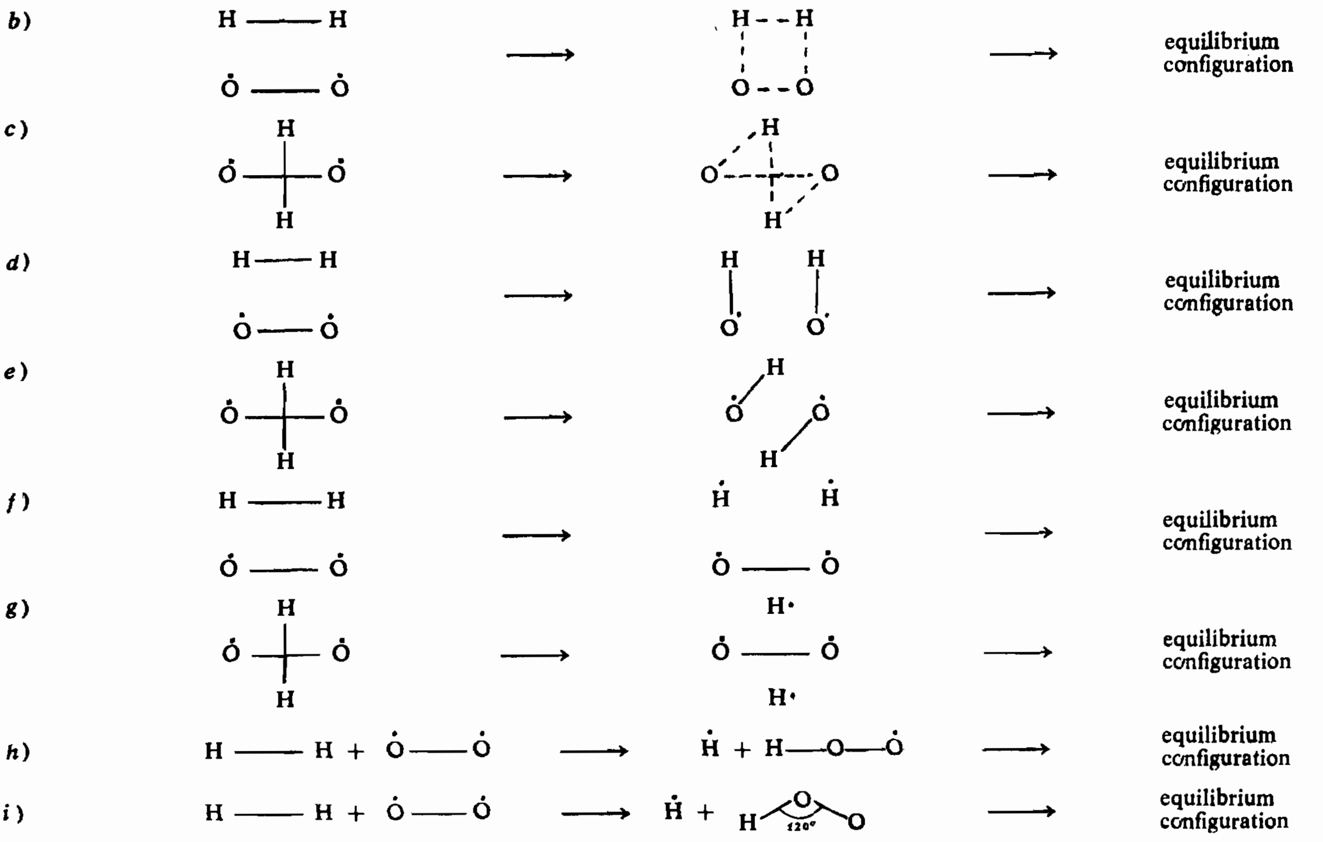
Table I. Computed Activation Energies *Ea* and Heats of Reaction, ΔH.

Mechanism	E_a*	ΔH
a	1.00	0.87
b	1.00	0.87
c	0.91	0.87
d	4.91	1.82
e	6.09	1.82
f	0.91	3.64
g	0.91	2.36
h	16.36	0.91
i	18.18	3·64

* All the energy values are scaled (arbitrarily) to E_a (for reaction *a*) = 1.00.

The mechanisms studied were

i.e., giving the trapezium structure of the H_2O_2 molecule.



The free-radical reactions were studied by the Pople-Nesbet method.[4]

Results and Discussion

Plots of total energy (eV) against reaction coordinate are shown in Figures 2-5 and the derived quantities ΔH and energy of activation (E_a) are listed in Table I. It is emphasised that because of the nature of the CNDO approach the energies in Table I have no *absolute* significance — the interesting point here is their intercomparability. As can be seen immediately, the results for the three concerted reactions, *a, b* and *c* are very similar and have similar values for E_a and ΔH. On the basis of Table I, reaction *f* appears to most favoured. A somewhat surprising result is that obtained from reactions *h* and *i*, and these suggest that the $HO_2^{\cdot}$ radical will not be formed in the initial stage of the reaction. This is somewhat unexpected, since the species $ROO^{\cdot}$ are common in

(3) D.E. Hoare, J.B. Protheroe and A.D. Walsh, *Trans. Farad. Soc.*, *55*, 548, (1959).
(4) J.A. Pople and R.K. Nesbet, *J. Chem. Phys.*, *22*, 5711, (1954).

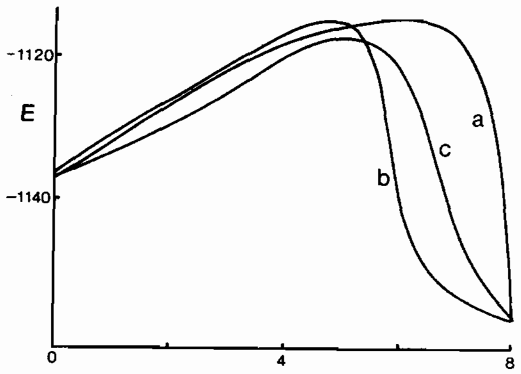


Figure 2. Energy Profiles for Reactions a), b), c).

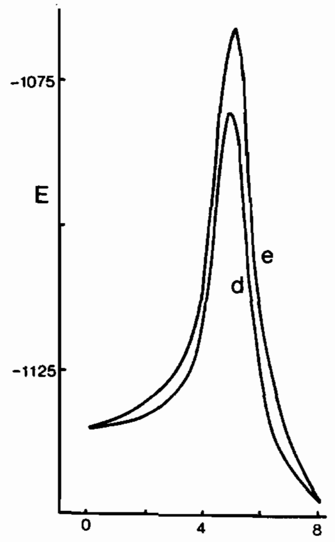


Figure 3. Energy Profiles for Reactions d), e).

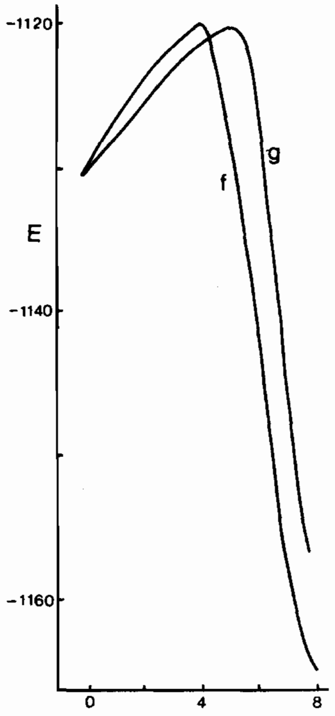


Figure 4. Energy Profiles for Reactions f), g).

peroxide chemistry. The result, therefore implies that a third body is required to effect the production of $HO_2^{\cdot}$. The two reactions *d* and *e*, in which the O-O bond is broken, also require a great deal of energy This encourages the view that one requires for this reaction a catalyst which absorbs H_2 and weakens the H-H bond whilst at the same time leaving O-O unaffected.

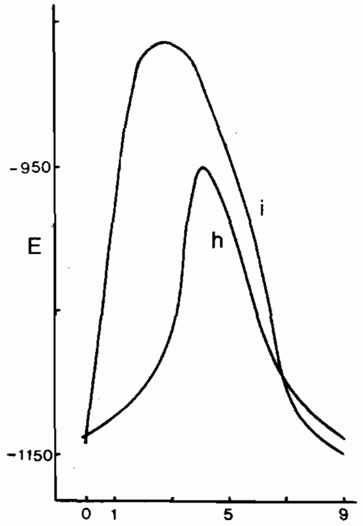


Figure 5. Energy Profiles for Reactions h), i).

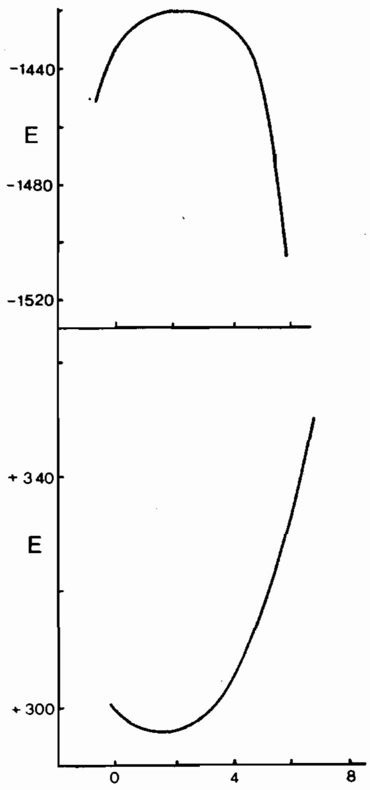


Figure 6. Nuclear and Total Energy Changes in Reaction f).

We now look at reaction *f* in a little more detail, to see how the individual energies change in the process. In this reaction there is a reduction of nuclear energy at the start of the process which is accompanied by a sharp increase (negatively) in electronic energy. Together, these produce an increase in total energy of the system (Figure 6). However, as the maximum and minimum in the electronic and nuclear energy curves are passed, the system as a whole gains stability rapidly and the activation peak is small. An informative correlation of the energy changes with bond orders in the system may be effected by a study of Figure 7. The latter shows that there is a sharp drop in H-H bond order concomitant with a rise in O-H bond order. The latter corresponds to the formation of effectively delocalized m.o.'s of H_2O_2. Moreover, these drastic changes occur at the stage in the process immediately following formation of the transition state.

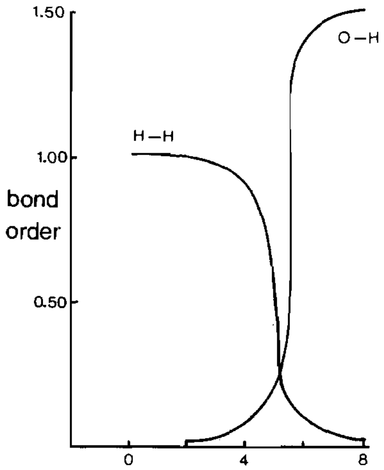


Figure 7. Bond Order Changes for Reaction f).

The results of this study show that catalysis of the initiation should be effected by systems which facilitate H-H scission, since this obviously constitutes the activation barrier. Hence, metals such as palladium or, possibly, mercury, should be effective. However, inert gases or H_2O_2 product may act as third bodies bringing about the decomposition of H_2O_2 and removal of products on formation will be necessary.