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MNDO Study of the Mechanism of $O_2(^1\Delta)$ Formation by Reaction of Cl_2 with Basic H_2O_2

Donn M. Storch, Chester J. Dymek, Jr.,* and Larry P. Davis

Contribution from the Department of Chemistry and the Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, Colorado 80840. *Received July 19, 1982*

Abstract: The MNDO method has been used to study potential mechanisms for the reaction of Cl_2 with a basic hydrogen peroxide solution which produces $O_2(^1\Delta)$. Several steps were found which yield $O_2(^1\Delta)$ with little or no activation. The calculations also indicate that there is little chance for intersystem crossing to produce triplet oxygen; thus we predict close to 100% $O_2(^1\Delta)$ yield. Two alternative explanations for the decrease in $O_2(^1\Delta)$ production at lower pHs are discussed.

Introduction

When gaseous Cl_2 is mixed with concentrated basic H_2O_2, a high percentage of the O_2 formed is in the electronically excited $^1\Delta$ state. Gaseous $O_2(^1\Delta)$ generated by this reaction has been used to pump an atomic iodine laser on the $I(^2P_{1/2})-I(^2P_{3/2})$ transition at 1.315 μm.[1,2] Efficient operation of this laser requires that the O_2 mixed with I_2 in the cavity contains significantly more than the minimum 17% of $O_2(^1\Delta)$ required to produce a population inversion in the atomic iodine. This is partly due to the requirement to optimize the energy output/fuel ratio and partly due to the fact that some of the $O_2(^1\Delta)$ is used to dissociate I_2.

Efforts to produce efficient generators of $O_2(^1\Delta)$ using this reaction suggest that the percent of $O_2(^1\Delta)$ generated at the reaction site approaches 100%.[3,4] Reduction to the approximately 50% $O_2(^1\Delta)$ delivered to the laser cavity appears to be due to a combination of (a) liquid-phase deactivation to ground state $O_2(^3\Sigma)$ as the $O_2(^1\Delta)$ diffuses out of the liquid in which it is formed, (b) deactivation by surfaces enroute from the reaction solution to the cavity, and (c) gas-phase deactivation by quenchers emanating from the solution. Because of its 45-min radiative half-life, simple radiative decay is not a significant source of $O_2(^1\Delta)$ loss.

Wherever the key to optimizing $O_2(^1\Delta)$ yield lies, an understanding of the formation mechanism would be a valuable input into development of an efficient generator. The overall stoichiometry of the formation reaction is

$$Cl_2 + H_2O_2 + 2OH^- \rightarrow O_2(^1\Delta) + 2H_2O + 2Cl^- \qquad (1)$$

The OH^- is typically introduced by mixing equal volumes of about 6 M NaOH or KOH and 90% H_2O_2. While different techniques for mixing the $Cl_2(g)$ with the basic H_2O_2 solution have been used, in each case the $Cl_2(g)$ must enter the liquid phase where reaction 1 occurs. The $O_2(^1\Delta)$ formed in solution must then diffuse back toward the gas–liquid interface through a liquid in which, on the basis of comparison with pure H_2O, it has a lifetime on the order of microseconds.[5] The fact that yields as high as 50% can be delivered by this process indicates that the reaction is indeed very fast; i.e., most of the Cl_2 reacts after diffusing only a very short distance into the liquid phase.

In connection with deactivation processes, some experimental results should be noted. The percent of $O_2(^1\Delta)$ formed and the efficiency of Cl_2 utilization are functions of the pH of the liquid reaction mixture.[6] The percent of $O_2(^1\Delta)$ formed decreases as pH decreases from an optimum range of 8–9 to about 5, at which point Cl_2 utilization drops to near zero rather abruptly and O_2 production virtually ceases. This suggests that as the concentration of basic species decreases, the $O_2(^1\Delta)$ is formed deeper in the liquid phase, resulting in more deactivation as it diffuses out. When the concentration becomes sufficiently low, any conversion of Cl_2 to O_2 probably proceeds by the mechanism proposed for acidic solutions by Connick.[16]

Our approach has been to use MNDO calculations to study the energetics of the reactions that might occur between species believed to be present in the liquid reaction zone, at the gas–liquid interface.

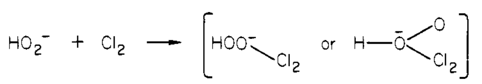
When Cl_2 is dissolved in basic aqueous solution, the equilibrium

$$Cl_2 + 2OH^- = Cl^- + ClO^- + H_2O \qquad (2)$$

is rapidly established with $K = 7.5 \times 10^{15}$. Because of unfavorable equilibrium constants and/or kinetics, other ClO_n^- ions are likely to be at negligible concentrations at the less than 0 °C temperatures employed in $O_2(^1\Delta)$ reactors.[7] The reaction of ClO^- with dilute basic H_2O_2 was found to be fast and yielded essentially 100% of $O_2(^1\Delta)$.[8] While some ClO^- will be formed by reaction 2, the equilibrium

$$OH^- + H_2O_2 = HO_2^- + H_2O \qquad (3)$$

should favor HO_2^- over OH^- by about 2 orders of magnitude on the basis of the relative acidity/basicity of H_2O and H_2O_2[9] and the relative concentrations of H_2O_2 and OH^- used in the reactor. Thus reaction 2 may be a far less favored route for Cl_2 reaction than reaction between Cl_2 and HO_2^-. The reactions between these two species were proposed as eq 4 and 5 by Hurst.[10] A similar mechanism was proposed by Goldberg[10] in which step 4 is followed by steps 6–8. An aim of this work was to determine the feasibility of these mechanisms and compare them with other possible reactions. Although MNDO cannot calculate solvent effects, the magnitude of such effects can generally be estimated by conventional arguments. Thus we believe that MNDO calculations



(4)

[I]

$$[I] \rightarrow H^+ + 2Cl^- + O_2(^1\Delta) \qquad (5)$$

$$[I] \rightarrow HOOCl + Cl^- \qquad (6)$$

$$HOOCl + HO_2^- \rightarrow H_2O_2 + OOCl^- \qquad (7)$$

$$ClOO^- \rightarrow Cl^- + O_2(^1\Delta) \qquad (8)$$

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are useful in testing whether the intermediate [I] is energetically feasible. They can test whether the intermediate, if it is formed, will dissociate into $O_2(^1\Delta)$ as proposed. They are also useful in determining whether reactions 4 and 5 as well as other reactions that may lead to $O_2(^1\Delta)$ formation occur with significant energies of activation. Finally, MNDO calculations can be made on both singlet and triplet reaction surfaces to investigate the possibility of intersystem crossing from the singlet to triplet surface as a cause of less than 100% $O_2(^1\Delta)$ yields.

Theoretical Data

All calculations were performed with the MNDO (modified neglect of diatomic overlap) method developed by Dewar et al.[11] The original version contained parameters for the elements hydrogen, carbon, nitrogen, and oxygen.[12] Recently Dewar has published parameters for chlorine.[13]

MNDO, like its predecessor MINDO/3, has proved to be quite useful in studying possible reaction pathways.[14] For studying reaction pathways, we fixed a geometric variable (usually the distance between two atoms, one on each of the two reacting species) as the reaction coordinate. The position of the remaining atoms of the two molecules was allowed to optimize. This reaction coordinate was then changed to a new fixed value and the calculation repeated until the whole reaction pathway had been done. If a particular reaction pathway indicated a transition state, a force constant calculation was performed on the transition-state geometry to show that the stationary point was indeed a true transition state by the calculation of one, and only one, negative eigenvalue of the force constant matrix.

Since all molecular orbital calculations are performed on isolated molecules, it is not obvious that calculations on a complex multiphase reaction such as ours are meaningful. Dewar has shown that MNDO calculations can be useful in interpreting solution reactions if the solvation enthalpy of the reactant is not changed appreciably by replacing one of the solvent molecules with the second reactant.[15] Thus the results of calculations on isolated systems have at least a qualitative correspondence with solution reactions. When possible, we will comment on the potential effects of solvation on each of the reactions studied. In general, we expect that the polar solvents H_2O and H_2O_2 should stabilize any intermediates formed.

All calculations on single molecules were performed with complete geometry optimization. The resultant standard heats of formation ($\Delta H_f°$ at 25 °C) were then used to determine $\Delta H°$'s for various possible reactions. Since all reactants are in singlet states, yet the primary product (O_2) is a triplet in its ground state, it was necessary to consider the possibility of intersystem crossing in all reactions producing O_2. For these reactions, geometry optimization as previously described was done for each reaction coordinate point on the ground-state singlet surface. The corresponding triplet energies were calculated with the optimized, fixed single state geometry. If a triplet state was found to be at lower energy than the singlet, the triplet geometry was then allowed to optimize. This procedure models the actual physical reaction pathway since all reactants come together on a singlet surface, but when the triplet surface approaches the singlet surface in energy, intersystem crossing can occur. All triplet calculations were done with at least the 10 lowest energy CI states.

Results and Discussion

The starting liquid-phase reactants are H_2O, NaOH(aq), and H_2O_2(aq). Reactions among these species can be summarized as acid–base processes. When Cl_2 is introduced into the solution, other acid–base processes must also be considered. Cl_2 can react with the species in these acid–base equilibria in several different ways. As more species are formed, more reactions are possible, some of which produce O_2. Therefore, the reactions we will consider can be divided into three groups: acid–base equilibria, reactions between Cl_2 gas and the liquid-phase species involved in these equilibria, and reactions producing O_2.

Table I. Enthalpies of Formation for Species Investigated

	$\Delta H_f°$, kcal/mol		$\Delta H_f°$ (exptl),[a] kcal/mol	
species	singlet	triplet	gas phase	solvated
HCl	−15.32		−22.06	−39.95
HO^-	−5.77	+86.09	−33.67	−54.97
HO_2^-	−17.76	+28.53		−38.32
HOCl	−15.02	+37.58	−22.00[b]	
$HO_2Cl_2^-$	−79.89	−6.14		
H_2O	−60.94	+62.65	−57.80	−68.32
H_2O_2	−38.12	+55.09	−32.58	−45.69
H_3O^+	+134.23		+138.9[b]	
Cl^-	−54.92		−58.8	−39.95
ClO^-	−7.82			−25.6
Cl_2	−10.73	+31.19	0.00	−5.6
Cl_2O	+31.32		+21.0[b]	
O_2	+12.15 ($^1\Delta$)	−15.42 ($^3\Sigma_g$)	0.00	−2.8

[a] Experimental values from: *NBS Tech. Note (U.S.)* **1968**, *No.* 270-3, except as noted. [b] "JANAF Thermochemical Tables and supplements"; Dow Chemical Co.: Midland, MI (continuously updated).

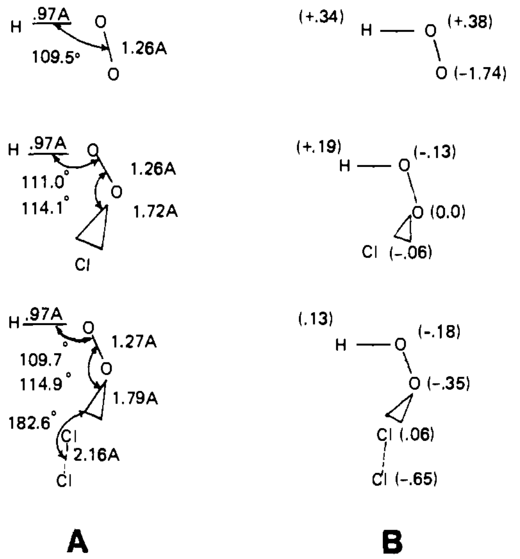

Figure 1. Possible intermediate species: A, bond lengths and angles; B, charge distribution.

As a first step in analyzing possible reaction steps, we calculated $\Delta H_f°$ for all species we expect to be in the solution. These values are contained in Table I. Experimental values (where available) are included for comparison. The hydroxide ion is calculated by MNDO to be less stable than it actually is by about 28 kcal/mol. This error does not, however, affect the conclusions reached in this paper.

In addition we have included the optimized geometries and charge distribution for the species, HO_2^-, HO_2Cl, and $HO_2Cl_2^-$ in Figure 1. This information will be useful in evaluating proposed mechanisms.

I. Acid–Base Reactions. Within the starting solution, the only reactive species present in significant concentration are shown in reaction A in Table II. Once Cl_2 reacts with the basic solution, formation of HOCl is possible. The calculated enthalpies in Table II indicate, and the equilibrium constants confirm, that any HOCl produced will be converted to OCl^- by reactions B or C.

Table II includes equilibrium constants calculated from the individual acid dissociation constants. Since MNDO is parameterized to produce good enthalpies of formation (ca. ±5 kcal

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Table II. Acid-Base Equilibria

	H_{rxn}(MNDO), kcal	K_{rxn}(exptl)
(A) $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	−34.81	2×10^2
(B) $HO_2^- + HOCl \rightarrow H_2O_2 + OCl^-$	−12.56	1.6×10^4
(C) $OH^- + HOCl \rightarrow H_2O + OCl^-$	−47.37	3.2×10^6

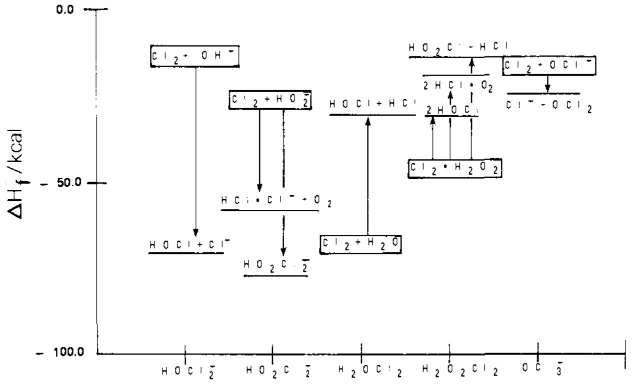

Figure 2. Calculated enthalpies of formation of Cl_2 with various solution species and their probable reaction products.

mol^{-1}) and entropy effects in these acid-base reactions are expected to be small, we expect, and find, that the calculated enthalpies of reaction do predict the trend found in the equilibrium constants. Thus the predominant basic species in the solution before Cl_2 is introduced is OOH^-. To the extent that any HOCl is formed, its predominant form is OCl^-.

II. Chlorine as a Reactant. Figure 2 related enthalpies of various combinations of solution species with Cl_2 to the enthalpies of their probable products. In the three processes favored by enthalpy ($Cl_2 + OH^-$, $Cl_2 + HO_2^-$, $Cl_2 + OCl^-$), chlorine reacts with basic anions. In contrast, the possible reactions of Cl_2 with water or hydrogen peroxide are not favored by enthalpy. Although solvation effects could make these reactions more favorable, entropy effects are unfavorable because one of the reactants is a gas. Note that MNDO correctly predicts that the reaction with hydroxide produces HOCl. However, since the starting mixture is only 3 M in NaOH and since HO_2^- is a weaker base, very little hydroxide should be in solution; therefore, only a small amount of HOCl should be produced. Even if some HOCl is produced, OCl^- is the favored form (see Table I) and this is likely to react with chlorine to form OCl_2, which will further reduce the HOCl concentration.

The most enthalpy-favored reaction is $Cl_2 + HO_2^-$. The enthalpy-favored product is a loosely bound complex of HOOCl with a chloride ion, $HO_2Cl_2^-$ (see Figure 1). This pathway occurs when there are no constraints on the direction of the Cl_2 approach to the HO_2^-. However, there is a second mechanism that leads directly to O_2. The direct reaction of Cl_2 on the proton of HO_2^- leads to products that are more stable than the reactants yet less stable than the large complex $HO_2Cl_2^-$. This reaction pathway occurs, according to the calculations, when the Cl–Cl–H angle is constrained to 180°. If this angle is free to optimize, the Cl_2 swings around and attacks the terminal oxygen to produce the large complex $HOOCl_2^-$. In a solvent environment, this freedom may be significantly restricted, so that attack on the hydrogen may proceed as calculated to form O_2 directly.

III. Oxygen as a Product. Figure 3 relates enthalpies of possible products that include O_2 to the enthalpies of the reactants that produced them. In every possible mechanism except one, the production of O_2 is favored by enthalpy—even for the singlet oxygen. Most of the favored processes involve a base attack on HO_2Cl or $HO_2Cl_2^-$. The one oxygen-producing reaction where formation of O_2 is not the most exothermic process possible is the direct reaction of chlorine on the proton of HO_2^-. However, the product of the most exothermic process for this set of reactants, i.e., $HO_2Cl_2^-$, which forms when the Cl–Cl–H angle is not constrained, is converted to O_2 by reaction with either OH^- or HO_2^-.

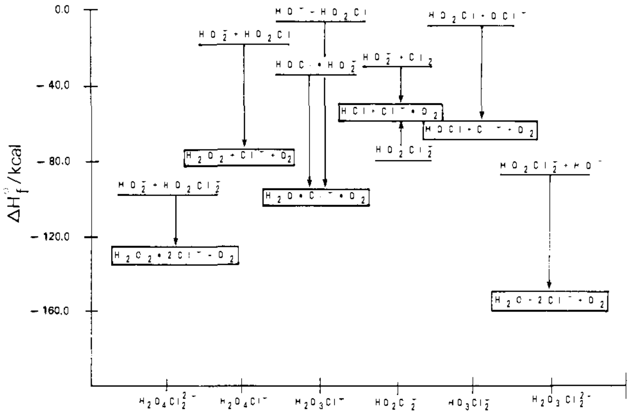

Figure 3. Calculated enthalpies of formation of O_2 with various reaction products and their probable precursors.

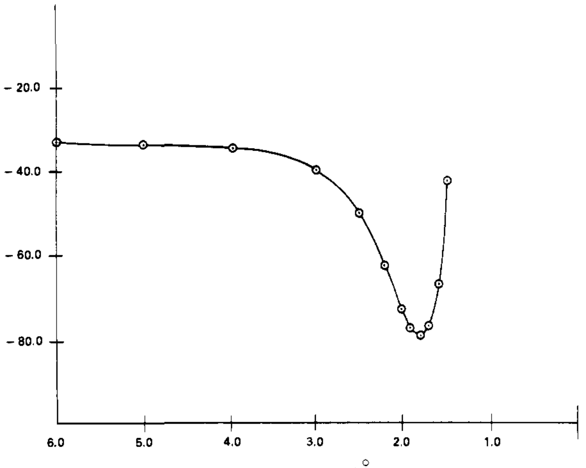

Figure 4. Reaction profile for the reaction of $Cl_2 + HO_2^-$. The reaction coordinate is chlorine approaching the terminal oxygen.

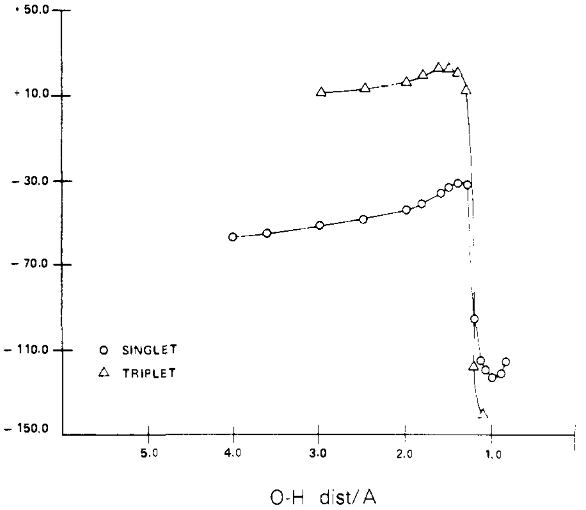

Figure 5. Reaction profile for the reaction of $HO_2^- + HO_2Cl_2^-$. The reaction coordinate is the terminal oxygen of HO_2^- approaching the hydrogen on $HO_2Cl_2^-$.

IV. Reaction Mechanisms. The reaction of most interest is between Cl_2 and the predominant basic species in solution HO_2^-. Figure 4 shows the reaction profile calculated for the reaction coordinate being the Cl–O distance. This reaction proceeds directly, with no activation barrier, to form the species $HO_2Cl_2^-$. This appears to be a stable intermediate. The terminal chlorine atom is loosely bound (with a Cl–Cl bond order of 0.3). We have calculated a barrier to removal of Cl^- from the complex of 24.6 kcal/mol. There is some question of whether solution effects will

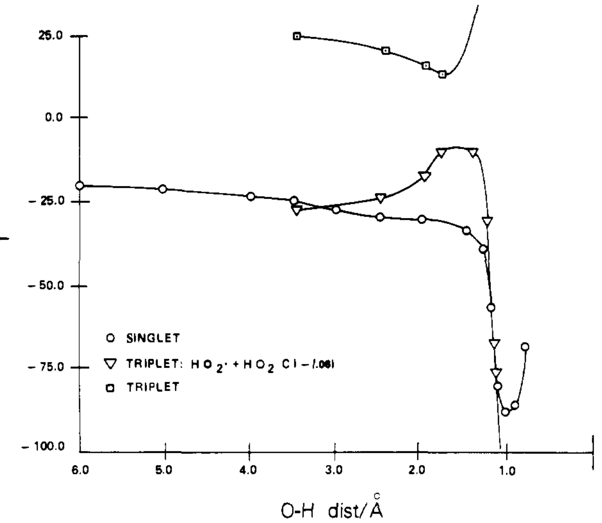

Figure 6. Reaction profile for the reaction of HO_2^- + HO_2Cl. The reaction coordinate is the terminal oxygen of HO_2^- approaching the hydrogen on HO_2Cl.

favor break up of the complex to produce HO_2Cl and Cl^-. However, as we will show, this question has little bearing on the overall process.

Figure 5 shows the reaction profile for the reaction of HO_2^- with $HO_2Cl_2^-$. For this calculation, the reaction coordinate is the distance between the terminal oxygen on the HO_2^- and the hydrogen on the $HO_2Cl_2^-$. In this step, the hydroperoxide ion acts as a base to remove the proton on the large complex. The apparent activation barrier is actually the Coulombic repulsion that is encountered by bringing two negatively charged species together in the gas phase. The solvent, acting as a dielectric, reduces this repulsion and may remove most of the barrier. Once the barrier has been surmounted, the reaction proceeds rapidly to produce $O_2(^1\Delta)$, H_2O_2, and two Cl^-.

In the event that the large complex $HO_2Cl_2^-$ is not stable in solution, i.e., reaction 6 occurs, HO_2Cl would then be the more probable reacting species. Figure 6 shows the energetics of HO_2^- reacting with HO_2Cl. Now there is no barrier to the reaction that produces $O_2(^1\Delta)$, H_2O_2, and Cl^-.

Therefore, whether $HO_2Cl_2^-$ or HO_2Cl is the predominant species in solution, the primary base HO_2^- will attack either to produce singlet molecular oxygen easily. Indeed, any charged base seems to be effective in this process. We have examined analogous reactions using OH^- and OCl^-, and each can remove the proton to produce $O_2(^1\Delta)$.

As we mentioned above, there appears to be an alternate pathway for the initial reaction of Cl_2 with HO_2^- (Figure 7). If the chlorine is prevented from approaching the negatively charged oxygen and, instead, attacks the proton, the reaction proceeds with no activation barrier to produce $O_2(^1\Delta)$, HCl, and Cl^-. The constraint imposed on the reactant (preventing reaction with the oxygen) may seem artificial. However, in light of the two-phase reaction environment, such a constraint might be consistent with the gas–liquid interface. Moreover, this process may be favored over Cl_2 attack on the oxygen by solvent effects in that it would encounter a relatively lower barrier due to solvent interactions with the HO_2^-. The strongly negative terminal oxygen (see Figure 1) would form stronger hydrogen bonds with solvent molecules H_2O_2 and H_2O.

One process we investigated which seems to be relevant is shown in Figure 8. In the reaction of HOCl with HO_2^- we see what appears to be a true transition state with an activation energy of 32 kcal/mol. Since we are not dealing here with two similarly charged species, we feel that this activation barrier will persist in solution.

MNDO calculations allow us to examine another aspect of this system. Because one of the products is O_2 and because $O_2(^3\Sigma)$ is the more stable form of oxygen, we searched for possible points of intersystem crossing. In our system only O_2 has a triplet state

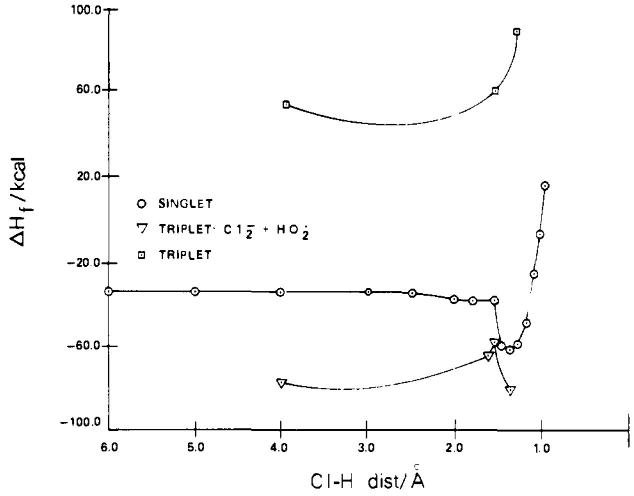

Figure 7. Reaction profile for the reaction Cl_2 + HO_2^-. The reaction coordinate is chlorine approaching the hydrogen on HO_2^-. In this process, the chlorine has been constrained to approach along a straight line (180° angle Cl–H–O). Unconstrained approach results in the profile given in Figure 4.

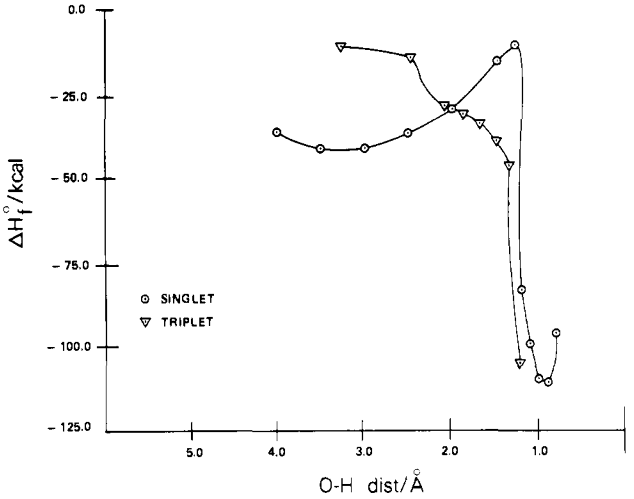

Figure 8. Reaction profile for the reaction HO_2^- + HOCl. The reaction coordinate is the terminal oxygen of HO_2^- approaching the hydrogen of HOCl. This profile has been included primarily as an example where intersystem crossing could successfully result in significant amounts of $O_2(^3\Sigma)$.

lower in energy than the singlet, and therefore we only considered triplet states for the reactions that produced O_2 (Figures 5 through 8). In the reaction of HO_2^- and $HO_2Cl_2^-$ (Figure 5) the triplet reaction surface crosses the singlet surface only after molecular O_2 has been produced. Therefore the probability of intersystem crossing is approximately the probability of the transition from $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$. Similarly, the reaction of HO_2^- with HO_2Cl (Figure 6) crosses only after oxygen has been split off.

As a slight contrast, the direct reaction of Cl_2 with HO_2^- (Figure 7) does not have any point of crossing between the singlet and triplet surfaces. The lowest triplet surface that corresponds to the species Cl_2^- and HO_2 does not intersect the singlet surface at all. The next triplet surface (corresponding to the true reactants Cl_2 and HO_2^-) lies much higher and does not approach the singlet reaction surface.

The one reaction that does exhibit a potential for intersystem crossing is the reaction of HOCl with HO_2^- (Figure 8). In this reaction, the triplet surface crosses well ahead of the transition state. However, in this case, two factors probably keep the reaction from being of major importance, at least in very basic media. First, HOCl concentrations will be low because HOCl is a stronger acid than the other weak acids present, H_2O_2 and H_2O. Only after the solution becomes more acidic will HOCl become an important species in solution. Also, even if intersystem crossing occurs, it occurs at an energy approximately 3.0 kcal above the reactant energies. Since other processes have been shown to proceed with no activation, it is unlikely that this process will be very important. It does, however, offer another possible explanation for the experimentally observed decrease in both total O_2 production and $O_2(^1\Delta)$ percentage as the solution pH decreases.

Conclusions

Calculations have shown that several possible processes produce $O_2(^1\Delta)$ with little or no activation. Most of these involve a two-step mechanism in which Cl_2 first reacts with basic species present in solution to form intermediates. These intermediates can then be attacked by basic species to yield $O_2(^1\Delta)$.

On the basis of our calculations, we believe that a plausible picture of what happens in the reaction zone as Cl_2 is bubbled through concentrated basic hydrogen peroxide is as follows:

(1) Cl_2 rapidly reacts ($E_a \simeq 0$) with HO_2^- (the most concentrated reactive species present) to form either (a) $HO_2Cl_2^-$ if the Cl_2 attacks the terminal O atom or (b) $HCl + Cl^- + O_2(^1\Delta)$, if the Cl_2 attacks the H atom. This supports the mechanism proposed by Hurst (reactions 4 and 5).

(2) Any $HO_2Cl_2^-$ formed will react with base, either OH^- or HO_2^-, to form $O_2(^1\Delta)$, two Cl^-, and either H_2O or H_2O_2. This is consistent with Goldberg's proposed mechanism (reactions 6–8), in that reaction of a base with the H on the intermediate (either as HOOCl alone or with the Cl^- loosely bound) is a key step in subsequent O_2 formation. MNDO calculations indicate that $OOCl^-$ is not stable in the gas phase but spontaneously decomposes to O_2 and Cl^-, so that steps 7 and 8 may be more properly combined into a single elementary step. However, in solution, $OOCl^-$ may be slightly stabilized by polar solvents, so that it may exist briefly as an intermediate.

(3) The $O_2(^1\Delta)$ diffuses into the gas phase, being deactivated to $O_2(^3\Sigma)$ to some unknown extent (but probably less than 20% deactivated based on extrapolated data) in the process.

(4) As base is consumed, as in a batch reactor, the Cl_2 must diffuse deeper into the solution to encounter reactive basic species. Thus $O_2(^1\Delta)$ undergoes more deactivation as it diffuses the longer distance into the gas phase. Furthermore, reactions involving acidic species, e.g., H_2O, H_2O_2, and HOCl, occur to a greater extent. Then reactions for which the triplet and singlet surfaces cross (see Figure 8) may cause the observed lowering of $O_2(^1\Delta)$ output at lower pH.

Acknowledgment. We wish to thank Professor M. J. S. Dewar of the University of Texas at Austin and Dr. William F. McDermott of Air Force Weapons Laboratory for helpful discussions. The USAF Academy Educational Research Computer Center (DFSEC) generously provided the computation time. We also greatly appreciate the expert typing of Mrs. B. J. Darcy.

Registry No. Chlorine, 7782-50-5; hydrogen peroxide, 7722-84-1; oxygen, 7782-44-7.

Hartree–Fock Calculations on Negative Ion States of Chromium Hexacarbonyl

L. G. Vanquickenborne* and J. Verhulst

Contribution from the Department of Chemistry, University of Leuven, 3030 Heverlee, Belgium.
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Abstract: Restricted Hartree–Fock calculations (RHF) have been carried out on the ground state of neutral chromium hexacarbonyl and on a number of low-lying unstable anion states of $Cr(CO)_6^-$. The results are analyzed and compared to recent electron transmission spectral data.

If the ground-state energy of a negative ion is higher than the ground-state energy of the corresponding neutral molecule, the ion is unstable with respect to spontaneous electron loss and the molecule is characterized by a negative electron affinity. The existence of these unstable negative ion states is observable, albeit somewhat indirectly, by electron transmission spectroscopy (ETS). Indeed, in electron–molecule collisions, the scattering cross section changes abruptly when the impacting electron has just enough energy to be temporarily captured into an unstable ion. This phenomenon is usually referred to as a resonance.[1,2]

Although there are several types of resonances, we will only be concerned with the so-called shape resonances, where the projectile electron may be said to be briefly retained into a normally vacant orbital of the target; such a resonance can be looked upon as a state where the electron is temporarily captured into a potential well, whose attractive portion consists of Coulomb forces, while its repulsive portion is due to the centrifugal potential associated with the angular momentum of the electron. The typical lifetime of a shape resonance is of the order 10^{-12}–10^{-15} s. Shape resonances have been observed for atoms, diatomic and triatomic molecules,[3] for unsaturated hydrocarbons, and very recently[4] also for the transition-metal hexacarbonyl compounds $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.

From a theoretical point of view, the study of resonances requires the proper description of both the target and the projectile. Different aproximate methods have been developed to calculate the wave functions, energies, and lifetimes of the resonances.[5]

Instead, it is the purpose of the present work to discuss the results of a Hartree–Fock calculation of certain stationary negative ion states of $Cr(CO)_6^-$. Since resonances are not true bound states, such a calculation cannot be quantitative nor complete. Yet, wave functions of bound-state form that closely resemble the temporary ion states should yield a reasonable first estimate of the resonance energies. Preliminary calculations of this same type, using the $X\alpha$ formalism, have been presented by Giordan et al.[4]

Neutral $Cr(CO)_6$ Molecule

SCF calculations have been carried out within the framework of Roothaan's RHF open-shell formalism,[6] using the SYMOL program.[7,8] The $Cr(CO)_6$ molecule was taken to be perfectly

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