

THEORETICAL DESCRIPTION OF THE ${}^2A''$ AND ${}^2A'$ STATES OF THE PEROXYFORMYL RADICAL[☆]

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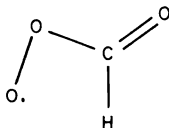
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We use simple orbital ideas to describe the lowest two states (${}^2A''$ and ${}^2A'$) of the peroxyformyl radical and report ab initio Hartree-Fock calculations in these states. We find that both states may be formed exothermically by association of O_2 and HCO in their ground states; however, the excited state may decompose readily to OH and CO_2 . The possible role of such processes in oxidation of aldehydes is discussed.

1. Introduction

In examining mechanisms for the photochemistry of polluted atmospheres [1-3], models of the stratosphere [4,5], and the martian atmosphere [6], we became interested in the possible importance of the peroxyformyl radical



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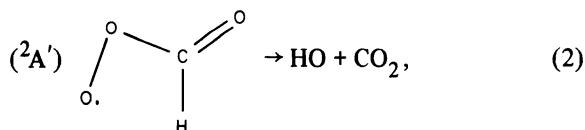
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(hereafter HCO_3) formed from association of O_2 and HCO,



From simple ideas of bonding [7] and from calculations [8,9] on HO_2 , it was evident that association of O_2 and HCO (both in their ground states) also could lead to exothermic formation of the first excited state (${}^2A'$) of HCO_3 . These considerations suggested that this excited state of HCO_3 would be far more reactive (than the ground state) and in particular that it might undergo a highly exothermic decomposition



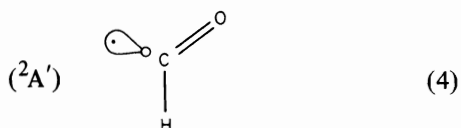
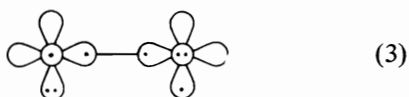
whereas this process would be quite unfavorable for

the ground state.

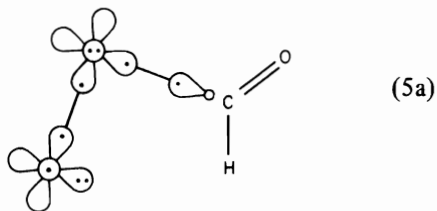
In order to form a basis for considering the possible role of HCO_3 and its excited state in various oxidation processes, we carried out accurate ab initio calculations on each state. These results are presented following a qualitative description of the bonding in HCO_3 .

2. The qualitative description

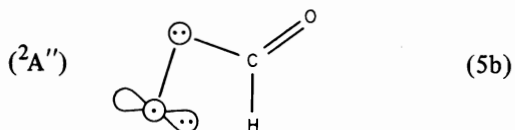
In the generalized valence bond description [7], the ground states of the O_2 and HCO molecules are viewed as



where (a) p orbitals perpendicular to the plane of the paper are represented by circles, (b) p orbitals and sp hybrids in the plane are indicated by lobed figures, and (c) the dots indicate how many electrons are in the orbitals. Bonding the O_2 of (3) to the HCO of (4) then leads to the $^2A''$ state of HCO_3 ,



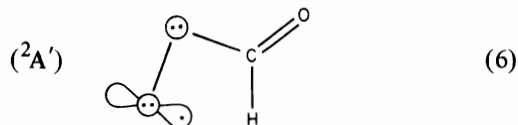
which we will simplify as



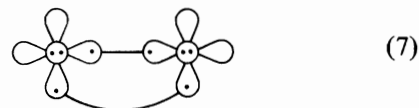
where bonding pairs are represented by lines.

A low-lying excited state of (5) is obtained by ex-

iting from the lone pair orbital into the singly occupied orbital, leading to the $^2A'$ state



Pulling the HCO from (6) leads[‡] to the



configuration of O_2 , corresponding to a *singlet* (excited) state of O_2 . Based on the $^1\Delta_g \leftarrow ^3\Sigma_g^-$ energy separation in O_2 (0.98 eV), one would expect the excitation energy $^2A' \leftarrow ^2A''$ to be about 1 eV. In fact, as will be shown, the calculations predict an excitation energy in the range of 0.4 to 0.9 eV. For the $^2A'$ state of HCO_3 given by (6) the radical electron is in a $p\sigma$ orbital pointing at the H. Consequently for the $^2A'$ state we expect only a small energy barrier for shifting the H from the C to the terminal O. This leads (quite exothermically) to the products $\text{OH} + \text{CO}_2$. On the other hand for the ground state ($^2A''$) of HCO_3 the doubly-occupied lone pair orbital points at the H and the radical electron is in a π orbital. In this case there should be a very large energy barrier for the decomposition (2). (This corresponds to a $2s + 2s$ 1, 3 sigma-tropic shift, forbidden by the Woodward-Hoffmann rules [10] (and by the orbital phase continuity principle) [11].)

3. Results

The Hartree-Fock (HF) wavefunctions for the lowest $^2A'$ and $^2A''$ states of HCO_3 were calculated

[‡] The description of reactions, dissociations, and associations obtained from generalized valence bond [7] (GVB) calculations and from our simple orbital representations is essentially a diabatic one. The description of real dynamic processes must of course allow the system to make use of the various diabatic surfaces. For example, retaining the planar geometry and pulling the O_2 from the excited state of HCO_3 in (6) leads to $^1\text{O}_2$, however the physical process of dissociation of vibrationally excited $\text{HCO}_3(^2A')$ can also lead to $^3\text{O}_2$.

Table 1
Hartree-Fock energies using the [4s2p] basis

| Molecule | State | Energy (au) |
|------------------|--|--------------|
| HCO ₃ | ² A'' | -262.8289 a) |
| HCO ₃ | ² A' | -262.8137 a) |
| HCO | ² A' | -113.1998 b) |
| O ₂ | ³ Σ _g ⁻ | -149.5712 c) |
| CO ₂ | ¹ Σ _g ⁺ | -187.5534 d) |
| OH | ² Π | - 75.3817 e) |

a) The geometry of HCO₃ was based on comparisons with bond lengths and bond angles of HCOOH, H₂O₂, MeOOME, and CH₃CHO. We have used $R_{C=O} = 1.202$ Å, $R_{C-O} = 1.343$ Å, $R_{CH} = 1.097$ Å, $R_{O-O} = 1.40$ Å, $\angle HCO = 124.1^\circ$, $\angle O=C-O = 124.9^\circ$, and $\angle C-O-O = 103^\circ$.

b) $R_{C=O} = 1.08$ Å, $R_{C-H} = 1.198$ Å, $\angle HCO = 119.5^\circ$.

c) $R_{OO} = 1.2074$ Å.

d) $R_{C=O} = 1.1621$ Å, $\angle OCO = 180^\circ$.

e) $R_{OH} = 0.9706$ Å.

in the [4s2p/2s] contracted gaussian basis set of Dunning [12] using the Hunt-Hay-Goddard [13] open-shell program.

As expected the calculations (see table 1) show the ground state to be ²A'' with the ²A' state only 0.4 eV higher. Since these states have very similar electronic structure with the same number of open shells, the correlation energies are expected to be similar and the HF energy difference is expected to be a good approximation to the excitation energy of the ²A' state. Goddard and Dunning [8] carried out both HF and extensive CI calculations on the corresponding states of HO₂ including polarization (3d) basis functions; they find an HF excitation energy of 0.4 eV and a CI excitation energy of 0.9 eV. We expect a similar effect for HCO₃ and hence the excitation energy of HCO₃ is expected to be 9 to 20 kcal.

Plots of the open shell molecular orbitals for both states ($2p\pi$ from ²A'' and $2p\sigma$ orbital of the ²A') are presented in fig. 1. As expected from the qualitative concepts discussed in the preceding section, these orbitals are concentrated mainly on the first (left) oxygen, but they do have some contributions on the other centers. From fig. 1b it is clear that the radical $2p\sigma$ orbital of the ²A' state does point towards the hydrogen atom, suggesting that in the ²A' state there should be only a small barrier for hydrogen migration. Comparison with the $2p\sigma$ orbital from the ²A'' ground state (not shown) indicates the radical orbital (fig. 1b)

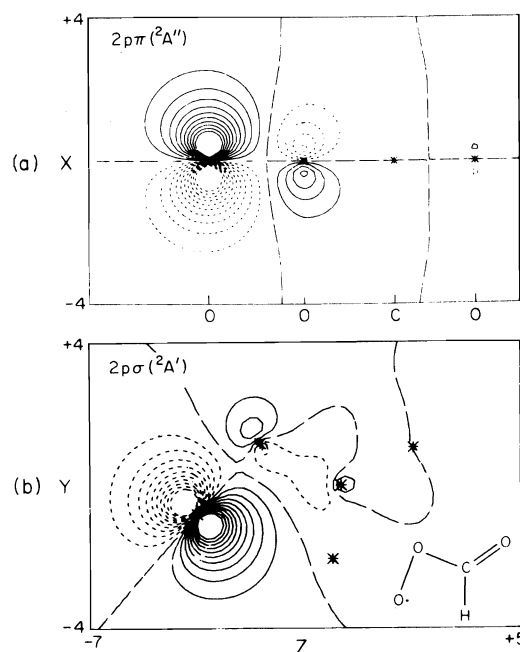
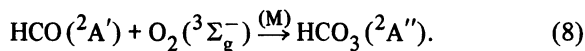


Fig. 1. Contour plots of the singly-occupied orbitals for the (a) ²A'' and (b) ²A' states of HCO₃. Long dashed lines indicate nodal planes; solid and dotted lines represent positive and negative contours respectively (increments of 0.05 au). The open shell π -orbital (a) is plotted in three planes perpendicular to the molecule and passing through the O-O, O-C, and C=O bonds. These three plots were joined at the mutual nuclear centers. The open shell σ -orbital (b) is plotted in the molecular plane.

contracts slightly when doubly occupied.

In order to estimate heats of formation for various processes in the atmosphere that can lead to the formation of HCO₃, we carried out Hartree-Fock calculations on HCO, O₂, OH, and CO₂ using the same gaussian basis set, obtaining results indicated in table 1.

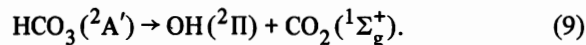
As discussed in the previous section, the HCO₃ radical can be formed from the reaction



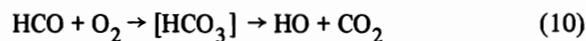
Using the results of table 1 we find (8) to be exothermic by 36 kcal, much larger than the ²A'' → ²A' excitation energy of 9 to 20 kcal. Hence, even including errors due to the basis set inadequacy (mainly the lack of d-functions) and differential correlation energies, these results indicate that the HCO₃ radical is

surely formed with sufficient energy to be able to exothermically convert to the ${}^2A'$ excited state.

From fig. 1b we see that the radical orbital of the ${}^2A'$ state is in a good position for the H migration and hence for decomposition,



The HF results of table 1 indicate that (9) is exothermic by 76 kcal and consequently the exothermicity of

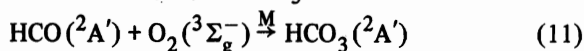


is 103 kcal.

Using standard heats of formation and bond strengths (see, for example, the tables in ref. [14]), reaction (8) is predicted to be 43 kcal exothermic [15][†] and reaction (10) is predicted to be 93 kcal exothermic. Combining this with the calculated excitation energy, the net energy released in (9) is 52–63 kcal. These thermochemical estimates and the calculated values are in reasonable agreement, differing by 7 kcal for the exothermicity of (8) and by 13 kcal for reaction (10).

4. Discussion

From the above considerations we see that the association (1) is sufficiently exothermic to lead to the excited state (${}^2A'$) of HCO_3

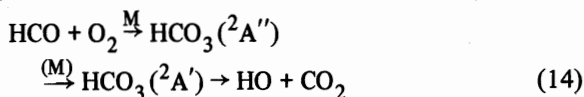


and that if formed the ${}^2A'$ state should lead to facile unimolecular decomposition to $\text{HO} + \text{CO}_2$. Of course the three-body reaction (11) must compete with the two-body reactions

[†] Based on bond energies [14] of 91, 70, and 107 kcal for $\text{HO}-\text{CH}_3$, HO_2-CH_3 , and $\text{HO}-\text{CHO}$, we estimate a bond energy of 86 kcal for HO_2-CHO leading to $\Delta H_f(\text{HO}_2\text{CHO}) = -74$ kcal. Assuming $D(\text{H}-\text{O}_2\text{CHO}) = 90$ kcal (as for H_2O_2) leads to $\Delta H_f(\text{O}_2\text{CHO}) = -36$ kcal and $D(\text{O}_2-\text{CHO}) = 43$ kcal (details of these calculations are in ref. [15]). In the above considerations we used $\Delta H_f(\text{CHO}) = 7.2$ kcal [14]. This value differs significantly from the value of -2.9 kcal quoted in the JANAF tables [16]. However, Golden and Benson [17] obtain $D(\text{H}-\text{HCO}) = 87.5 \pm 1.1$ kcal, which combined with the ΔH_f of H_2CO and H from JANAF yields $\Delta H_f(\text{HCO}) = 7.7$ kcal (298 K).

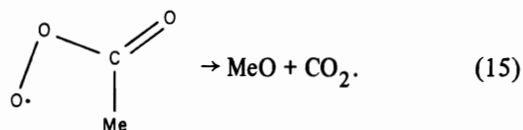


Initially we thought that the sequence



might play an important role in the early generation of OH radicals for the chain decomposition of hydrocarbons in polluted atmospheres. The energies worked out as expected; however, closer study of the experimental results for photooxidation of formaldehyde [18–20], does *not* support (14) as a dominant sequence. For example, the production of CO_2 is only 12–20% of the total $\text{CO} + \text{CO}_2$ [20]^{††}. Such results need *not* imply that $\text{HCO}_3({}^2A'')$ is not formed since as discussed in section 2 the ${}^2A''$ state should *not* decompose into $\text{HO} + \text{CO}_2$. Indeed, McMillan and Calvert [18, p. 109] argue that at lower temperatures (36°C) reaction (1) should be fast compared with (12). However, they noted that if this is so then the HCO_3 must not form CO_2 readily under those conditions (consistent with our considerations, assuming that HCO_3 is in the ${}^2A''$ state). A key step in (14) is the unimolecular (or bimolecular) conversion of ${}^2A''$ to ${}^2A'$, and it may be that this step is not sufficiently rapid to compete with the vibrational quenching of $\text{HCO}_3({}^2A'')$.

In the case of acetyl radical, MeCO , the role of the peroxyacetyl radical is more firmly established [18, p. 110] as playing a role in the photooxidation. In this case at low pressures the MeCO_3 decomposes as

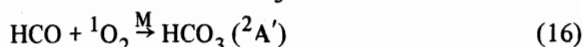


From our previous considerations we would expect this decomposition to involve the ${}^2A'$ excited state of MeCO_3 . Indeed the experimental evidence [18, p. 121] indicates an activation energy > 17 kcal which

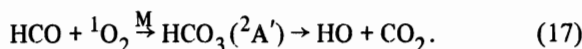
^{††} Even for the photooxidation of formaldehyde, which has been extensively studied, there are still significant uncertainties, for example, undetected carbon species are known to be formed [19].

is consistent with our estimates of the electronic excitation energy (9–20 kcal for HCO_3 ; there may also be a small barrier for the methyl migration in the excited state).

As mentioned in section 2, pulling the CHO from the $^2\text{A}'$ state of HCO_3 leads to the *singlet* state of O_2 (denoted hereafter as $^1\text{O}_2$). Thus association of $^1\text{O}_2$ with the ground state of HCO may lead directly to the excited state of HCO_3

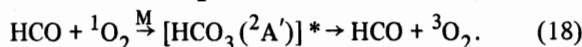


[of course (16) must compete with various quenching processes and other reactions, e.g., abstraction of H]. In this case the $^2\text{A}'$ state should decompose readily to $\text{HO} + \text{CO}_2$ as discussed earlier, leading then to the conversion of two reactive species HCO and $^1\text{O}_2$ to one, OH:



Note that the O in the OH comes from the $^1\text{O}_2$, hence with labelling experiments one could determine the role of (17).

A complication here is that the vibrationally excited $\text{HCO}_3(^2\text{A}')$ formed in (16) can dissociate to $\text{HCO} + ^3\text{O}_2$ leading to an overall process of merely quenching the $^1\text{O}_2$,



The relative rates of (17) and (18) will depend upon the pressure and temperature.

The calculations presented here have demonstrated (as was the case for HO_2) the existence of a low-lying excited state that could play an important role in oxidation processes. Using orbital plots and qualitative concepts of chemical bonding we have characterized the ground and excited states of HCO_3 in order to relate the ab initio results to the various possible reactions. Verification and extension of the conclusions drawn here requires further calculations including the electron correlation effects and polarization (d) basis functions. It would be especially interesting to determine the barrier for H-atom migration and the subsequent decomposition of the $\text{HCO}_3(^2\text{A}')$ state.

References

- [1] P.A. Leighton, Photochemistry of air pollution (Academic Press, New York, 1961).
- [2] H. Niki, E.E. Daby and B. Weinstock, *Advan. Chem.* 113 (1972) 16.
- [3] T.A. Hecht, J.H. Seinfeld and M.C. Dodge, *Environ. Sci. Technol.* 8 (1974) 327.
- [4] J.G. Calvert, J.A. Kerr, K.L. Demerjian and R.D. McQuigg, *Science* 175 (1972) 751.
- [5] M. Nicolet, in: Proceedings of Climatic Impact Assessment Program Conference, February 15–16, 1972, ed. P.E. Barrington (National Technical Information Service, Springfield, Virginia 22151), DOT-TSC-OST-72-13.
- [6] M.B. McElroy and J.C. McConnell, *J. Atmos. Sci.* 28 (1971) 879; T.M. Donahue, *J. Atmos. Sci.* 28 (1971) 895.
- [7] W.A. Goddard III, T.H. Dunning Jr., W.J. Hunt and P.J. Hay, *Accounts Chem. Res.* 6 (1973) 368.
- [8] W.A. Goddard III and T.H. Dunning Jr., to be published; Abstracts, Ohio State Symposium on Spectroscopy, June 1973.
- [9] J.J. Gole and E.F. Hayes, *J. Chem. Phys.* 57 (1972) 360.
- [10] R.B. Woodward and R. Hoffmann, *The conservation of orbital symmetry* (Academic Press, New York, 1970).
- [11] W.A. Goddard III, *J. Am. Chem. Soc.* 94 (1972) 793.
- [12] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [13] W.J. Hunt, P.J. Hay and W.A. Goddard III, *J. Chem. Phys.* 57 (1972) 738.
- [14] S.W. Benson, *Thermochemical kinetics* (Wiley, New York, 1968).
- [15] W.A. Goddard III, in: *Lecture Notes, School on the Fundamental Chemical Basis of Reactions in the Polluted Atmosphere*, ed. C.W. Kern (Battelle Memorial Institute, Columbus, Ohio, 1973).
- [16] D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, NSRDS-NBS 37.
- [17] D.M. Golden and S.W. Benson, *Chem. Rev.* 69 (1969) 125.
- [18] G.R. McMillan and J.G. Calvert, *Oxidation Combustion Rev.* 1 (1965) 83, see especially pp. 108 ff.
- [19] E.C.A. Horner, D.W.G. Style and D. Summers, *Trans. Faraday Soc.* 50 (1954) 1201.
- [20] J.J. Bufalini and K.L. Brubaker, in: *Chemical reactions in urban atmospheres*, ed. C.S. Tuesday (American Elsevier, New York, 1971) p. 225.