optimization of all geometrical parameters (within any restrictions desired).

References and Notes

(1) Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111. Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.
(2) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552.
(3) Böhm, M. C.; Gleiter, R. *Tetrahedron Lett.* **1978**, 1179.
(4) Bingham, R. C.; Carrion, F.; Dewar, M. J. S.; Kollmar, H., to be published.
(5) Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 4342.
(6) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.
(7) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.
(8) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.
(9) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(10) Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157.
(11) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89.
(12) Kollmar, H., unpublished.
(13) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(14) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017.
(15) Ahlrichs, R.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.*

1975, *62*, 1225.
(16) Kollmar, H. Habilitationsschrift, Bochum, 1978.
(17) Ahlrichs, R.; Driessler, F. *Theor. Chim. Acta* **1975**, *36*, 275.
(18) Hinze, J.; Roothaan, C. C. J. *Prog. Theor. Phys., Suppl.* **1967**, *40*, 37. Veillard, A.; Clementi, E. *Theor. Chim. Acta* **1967**, *7*, 133.
(19) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317.
(20) Das, G.; Wahl, A. C. *J. Chem. Phys.* **1966**, *44*, 87.
(21) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583; **1978**, *100*, 4304.
(22) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.
(23) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.
(24) Kollmar, H. *Theor. Chim. Acta* **1978**, *50*, 235.
(25) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.
(26) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404. Flitcroft, T. L.; Skinner, H. A. *Ibid.* **1958**, *54*, 47.
(27) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.
(28) Duff, R. E.; Bauer, S. H. *J. Chem. Phys.* **1962**, *36*, 1754. Cowperthwaite, M.; Bauer, S. H. *Ibid.* **1962**, *36*, 1745.
(29) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.
(30) Kollmar, H. *J. Am. Chem. Soc.*, in press.
(31) Bauld, N. L.; Welsher, T. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920.
(32) Dewar, M. J. S. *Pure Appl. Chem.* **1975**, *44*, 767.
(33) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
(34) Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976; **1970**, *53*, 858.
(35) Horsley, J. A.; Lean, Y.; Moser, C.; Salem, L.; Stevens, T. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.
(36) Ahlrichs, R.; Lischka, H.; Zurawski, B.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *63*, 4685.
(37) Ahlrichs, R.; Driessler, F.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *62*, 1235.

Ab Initio Study of $(NO_2)_2^+$ and $(CO_2)_2^-$

Y. Yoshioka and K. D. Jordan*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received October 1, 1979

Abstract: Ab initio calculations are employed to investigate the structure and stability of the $(NO_2)_2^+$ ion and these results are compared with those obtained earlier for the isoelectronic $(CO_2)_2^-$ ion. For both species, the lowest energy structure is well described as a monomeric ion "solvated" by a neutral molecule. The $NO_2^+ \cdot NO_2$ structure, with the electron essentially localized on one of the monomers, is 1.56 eV more stable than the D_{2h} structure with the odd electron equally shared between the two NO_2 monomers. The ion-molecule complex form of $(CO_2)_2^-$ is only 0.31 eV more stable than the lowest energy symmetric structure. The bonding in the $CO_2^- \cdot CO_2$ and $NO_2^+ \cdot NO_2$ ions is interpreted in terms of electrostatic interactions between the ionic and neutral monomers.

I. Introduction

During the past few years a wide variety of techniques have been applied to the study of molecular clusters. The ion cyclotron resonance (ICR), flowing-afterglow, and nozzle expansion methods have yielded much information on ion clustering in the gas phase. ESR and Raman spectroscopy of cluster ions formed in matrices have also provided new information on the ions of dimers and larger aggregates.

One of the most interesting questions concerning clusters containing unpaired electrons is whether these electrons are delocalized over the cluster or localized on one of the monomer units. Even for the ions of most molecular dimers, it is not known whether the odd electron is localized. For this reason we have undertaken a study of the structure of the $(NO_2)_2^+$ and $(CO_2)_2^-$ ions and the energetics of the $NO_2 + NO_2^+ \rightarrow (NO_2)_2^+$ and $CO_2 + CO_2^- \rightarrow (CO_2)_2^-$ reactions.

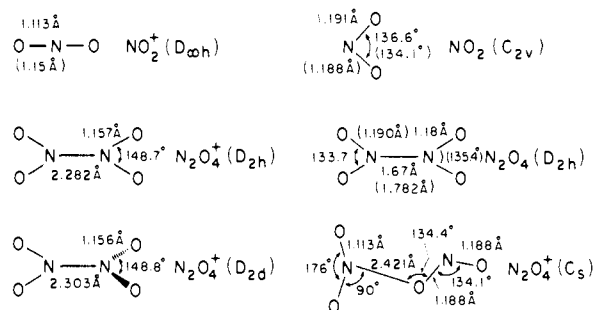Results of ab initio calculations on the properties of $(CO_2)_2^-$ were reported in a recent communication[1] by Rossi and Jordan. In this study it was found that the structure consisting of a bent

* Alfred P. Sloan Foundation Fellow, Camille and Henry Dreyfus Teacher-Scholar.

CO_2^- "solvated" by a nearly linear CO_2 was the most stable form of the complex. The stability of this structure was attributed to charge-induced dipole and charge-quadrupole interactions. In the present paper we carry out similar calculations on the isoelectronic $(NO_2)_2^+$ ion and then compare the bonding in these two ions.

Neutral $(NO_2)_2$, which has a planar symmetric (D_{2h}) equilibrium structure, has been the subject of several theoretical and experimental studies.[2-13] Much of this interest is due to the fact that the N–N bond in this molecule is unusually long and weak. Ab initio self-consistent-field (SCF) calculations[3] suggest that the stability of the D_{2h} structure is due to a σ-type 1,4 interaction[14,15] between the oxygen atoms. Recent calculations of Cederbaum et al.[12] and Harcourt[13] have apparently resolved the controversy concerning the assignments of the vertical ionization potentials (IP) of $(NO_2)_2$ as measured by the He(I) photoelectron spectrum.[7-10] However, we are not aware of any theoretical studies addressing the adiabatic ionization processes of $(NO_2)_2$.

In the present article, we employ ab initio SCF calculations to investigate the D_{2h} and D_{2d} forms of $(NO_2)_2^+$ as well as the planar nonsymmetric $NO_2^+ \cdot NO_2$ complex. The bonding in

1.113 Å
O—N—O NO_2^+ ($D_{\infty h}$)
(1.15 Å)

1.191 Å O
N 136.6° (134.1°) NO_2 (C_{2v})
(1.188 Å) O

O   1.157 Å O
N——N 148.7° $N_2O_4^+$ (D_{2h})
O   2.282 Å O

O (1.190 Å) 1.18 Å O
133.7 N——N (135.4) N_2O_4 (D_{2h})
O   1.67 Å O
(1.782 Å)

O   1.156 Å O
N——N 148.8° $N_2O_4^+$ (D_{2d})
O   2.303 Å O

O   134.4°
176° N 1.113 Å 2.421 Å N—O 1.188 Å $N_2O_4^+$ (C_s)
O   90° O 134.1° 1.188 Å

Figure 1. Optimized and experimental geometries of NO_2, NO_2^+, $(NO_2)_2^+$, and $(NO_2)_2$. In the case of $(NO_2)_2$ the "optimized" geometry is from Howell and Van Wazer (ref 3), who actually optimized only the N–N bond length. The experimental bond lengths and angles, when known, have been indicated in parentheses.

1.161 Å
(1.159 Å)
O——C——O CO_2 ($D_{\infty h}$)

(a)

1.249 Å O
C 134.9° (134°) CO_2^- (C_{2v})
O

(b)

O   1.212 Å O
143.1° C——C $C_2O_4^-$ (D_{2h})
O   2.132 Å O

(c)

O   1.261 Å
(1.25 Å) O
125.3° C——C $C_2O_4^-$ (D_{2h})
(126.3) 1.582 Å O
(1.57 Å)

(d)

O   1.219 Å O
142.8° C——C $C_2O_4^-$ (D_{2d})
O   1.940 Å O

(e)

O   1.248 Å
1.166 Å C——O
131.8° 135.5°
169.5° C 2.494 Å C 1.262 Å $C_2O_4^-$ (C_s)
95.2° O
1.166 Å O

(f)

Figure 2. Optimized and experimental geometries of CO_2, CO_2^-, $(CO_2)_2^-$, and $(CO_2)_2^{2-}$. This figure is from the paper of Rossi and Jordan (ref 1).

each of these structures is compared with that for the corresponding structures of $(CO_2)_2^-$. The relative stabilities of the various forms of these two ions are discussed in detail. We report estimates of both the vertical and adiabatic ionization potentials of $(NO_2)_2$.

II. Computational Details

The spin-restricted Hartree–Fock and spin-unrestricted Hartree–Fock methods were used for the calculations on the closed-shell and open-shell species, respectively. The MOLECULE program[16] was employed to generate the electron integrals over symmetry-adapted basis functions, expressed in terms of contracted Gaussian-type functions, and the GRNFNC program[17] was utilized to solve the self-consistent-field (SCF) equations.

Even in the Hartree–Fock approximation complete potential energy searches of a molecules as complex as $(NO_2)_2^+$ require a prohibitive amount of computer time. Therefore, we limit our study to the optimization of the planar symmetric D_{2h}, staggered symmetric D_{2d}, and nonsymmetric C_s ion–molecule complex structures. There is a danger in employing the symmetry-restricted Hartree–Fock method in comparing structures of different symmetry. Therefore, after optimization of the D_{2h} and D_{2d} forms of $(NO_2)_2^+$, we then repeated the calculations with the symmetry lowered to C_s and employing initial-guess vectors with the odd electron localized. These results converged back to the same energies and vectors obtained using the symmetry-restricted Hartree–Fock method.

The split-valence shell 6-31G basis sets,[18] modified by splitting off the most diffuse component of three-component inner valence 2s functions, are employed. This uncontraction, which leads to a slight lowering of the energies, is necessary because the MOLECULE program requires positive coefficients. In the case of $(CO_2)_2^-$, after optimization of the structures of interest, the energies were then recalculated using an augmented basis set to allow for the more diffuse nature of the anionic species. The augmented basis set was formed by adding diffuse s and p GTOs with exponents of 0.05 to the carbon basis set.[1]

Owing to the high symmetry of the D_{2h} and D_{2d} structures, the geometry optimizations require determination of only two bond lengths and one angle. The complete optimization of the C_s structure, is however, a nine-variable problem. Moreover, since the C_s structure has only one reflection plane, the integral generation and SCF calculations are rather expensive (about 90 min CPU time per point on a DEC 10/99). Examination of the C_s structure of $(CO_2)_2^-$, for which all nine variables were optimized,[1] shows that this species is well described as a $CO_2^-·CO_2$ complex with the CO bond lengths on one monomer unit being nearly equal to those of CO_2 and those on
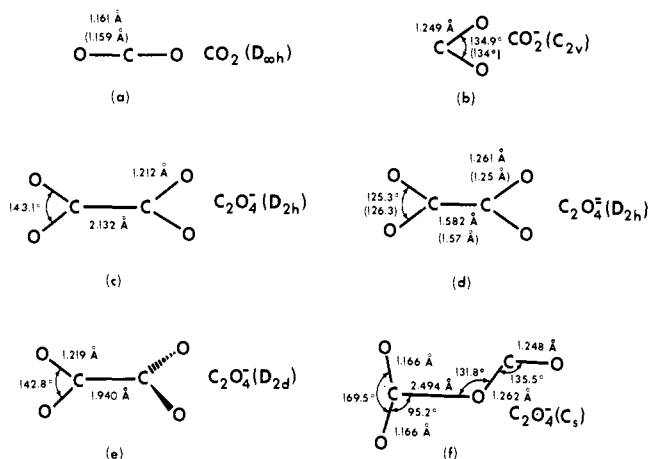
the other being nearly equal to those of CO_2^-. Furthermore, the OCO angle on the monomer unit on which the extra electron is localized is nearly the same as that in CO_2^-. Therefore, in the optimization of the geometry of C_s $NO_2^+·NO_2$, in one monomer we retain the experimental[19] bond length and bond angle of NO_2, while in the other we retain the bond length of NO_2^+. This latter bond length (1.113 Å) was obtained from SCF calculations on NO_2^+ using the 6-31G basis set. Since relaxing the OCO angle of the CO_2 portion of $CO_2^-·CO_2$ had a small but important effect (~0.06 eV) on the energy, we have varied the ONO angle of the NO_2^+ portion of $NO_2^+·NO_2$. With the above restrictions, we are left with the optimization of four coordinates.

III. Results and Discussion

A. Optimized Structures of $(NO_2)_2^+$. The geometries obtained for NO_2, NO_2^+, and the various forms of $(NO_2)_2^+$ are summarized in Figure 1. For purposes of comparison we reproduce in Figure 2 the geometries of CO_2^-, CO_2, and $(CO_2)_2^-$ obtained by Rossi and Jordan.[1] For each of the three structures considered, the geometry of $(NO_2)_2^+$ is close to that of the corresponding structure for $(CO_2)_2^-$.

For both $(NO_2)_2^+$ and $(CO_2)_2^-$ the ion–molecule complex is predicted to be the most stable form. The SCF calculations yield a value of 0.54 eV for the dissociation energy of planar $NO_2^+·NO_2$ ($E = 407.4394$ au) to NO_2 ($E = 203.9077$ au) + NO_2^+ ($E = -203.5121$ au). The value calculated[1] for the process $CO_2^-·CO_2 \rightarrow CO_2^- + CO_2$ was only 0.03 eV larger than this.

We have also carried out a calculation on $NO_2^+·NO_2$ with the NO_2^+ group rotated 90° with respect to the NO_2 group keeping the bond lengths and angles of the monomer units fixed. This perpendicular structure is 0.13 eV less stable than the C_s species. This suggests but it does not prove that the equilibrium structure is planar. In section IIIC, we show that the bonding in $NO_2^+·NO_2$ is dominated by charge–quadrupole and charge–induced dipole interactions. In terms of this picture the planar structure is energetically favored.

For $(NO_2)_2^+$, the D_{2h} structure ($E = -407.3822$ au) lies 1.56 eV above the ion–molecule complex, and the staggered D_{2d} structure ($E = -407.3768$ au) is 0.15 eV above the D_{2h} species. The bond lengths and ONO angles of the D_{2h} structure are very close to those of the D_{2d} structure. For $(CO_2)_2^-$, on the other hand, the D_{2d} and D_{2h} species lie only a few tenths of an electronvolt above the $CO_2^-·CO_2$ complex and the D_{2d} is more stable than the D_{2h} structure. Also the C–C bond length of the D_{2h} structure of $(CO_2)_2^-$ is 0.363 au larger than that of the D_{2d} form. The symmetric structures of $(NO_2)_2^+$
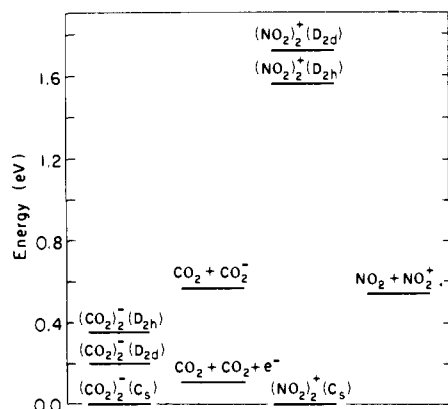
Figure 3. Energy correlation diagram for $(NO_2)_2^+$ and $(CO_2)_2^-$.

Figure 4. Charge densities of the highest occupied molecular orbitals of the D_{2h} and D_{2d} structures of $(NO_2)_2^+$ and $(CO_2)_2^-$: (a) D_{2d} $(CO_2)_2^-$; (b) D_{2d} $(NO_2)_2^+$; (c) D_{2h} $(CO_2)_2^-$; (d) D_{2h} $(NO_2)_2^+$. Contour lines corresponding to charge densities of 0.0001, 0.0002, 0.0004, 0.0008, 0.0016, 0.0035, 0.0070, 0.014 and 0.028 e/a_0^3 are presented for both species. Two additional contour lines, 2.5×10^{-5} and 5×10^{-5}, are included for $(CO_2)_2^-$.

and $(CO_2)_2^-$ have larger bond lengths and OMO angles (M = N, C) than those of the neutral dimers. This is consistent with the observation that the highest occupied molecular orbitals (HOMOs) of $(NO_2)_2$ and $(CO_2)_2^{2-}$ are M–M bonding and MO antibonding. An energy correlation diagram for $(NO_2)_2^+$ and $(CO_2)_2^-$ is presented in Figure 3.
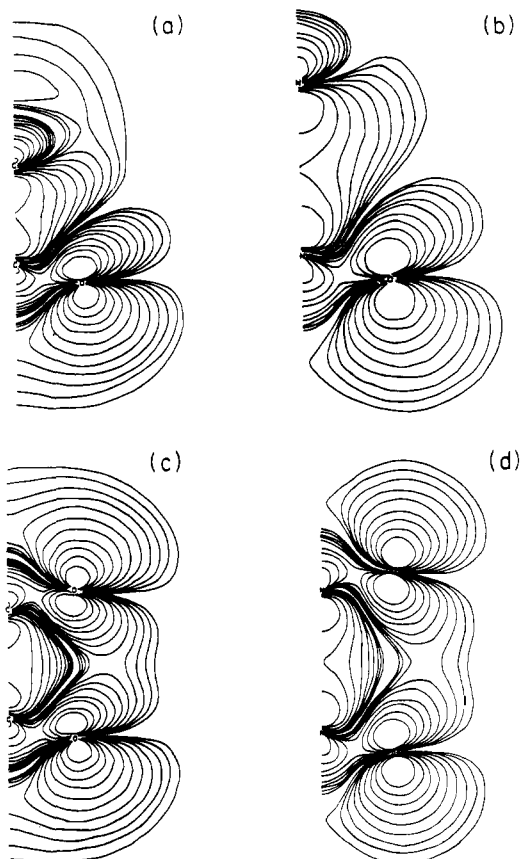
The 11.79-eV vertical ionization potential obtained in the present study for $(NO_2)_2$ at its experimental geometry is in good agreement with the experimental value of 11.4 eV.[9,10] On the other hand, the energy difference between $(NO_2)_2$ at its equilibrium configuration and $(NO_2)_2^+$ in its optimized D_{2h} structure is 10.65 eV. The adiabatic IP, which is given by the energy difference between the minimum energy structures of $(NO_2)_2$ and $NO_2^+ \cdot NO_2$, is 9.1 eV.

Calculations of the gradient of the energy using the GAUSSIAN-78 program[20] were carried out in order to examine the stability of the D_{2h} and D_{2d} species. For reasons of cost we did not treat all possible distortions and also utilized the minimal, STO-3G basis sets rather than the 6-31G basis. The distortions considered are indicated below.
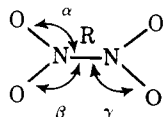
The D_{2d} structure is a saddle point on the potential-energy surface of $(NO_2)_2^+$ since there exists a monotonically decreasing path to the D_{2h} structure. The D_{2h} structure of $(NO_2)_2^+$, however, appears to be a true local minimum with barriers both to dissociation to $NO_2 + NO_2^+$ and to interconversion to the C_s structure.

Another interesting question concerns the rearrangement process:
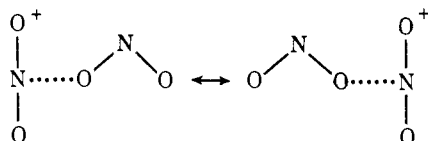
for the C_s structure. If the barrier to this interconversion is sufficiently small, then one could study the process by ESR. If, however, the D_{2h} (or D_{2d}) structure is encountered in the interconversion, the barrier will be over 1.6 eV for $NO_2^+ \cdot NO_2$ but only about 0.3 eV for $CO_2^- \cdot CO_2$. The height of the barrier and the reaction path for interconversion of the D_{2h} species to $NO_2 + NO_2^+$ and to the C_s structure are not known at present.

B. Bonding in the D_{2h} and D_{2d} Forms of $(NO_2)_2^+$ and $(CO_2)_2^-$. The results for the symmetric forms of these ions pose two interesting problems. First, why is the most stable symmetric structure for $(CO_2)_2^-$ D_{2d} while that of $(NO_2)_2^+$, $(NO_2)_2$, $(CO_2)_2^{2-}$ is D_{2h} symmetry? Secondly, why is the

calculated D_e of $(NO_2)_2^+$ (0.54 eV) nearly the same as the experimental D_e^{21} of $(NO_2)_2$ (0.06 eV)? Since $(NO_2)_2$ and $(CO_2)_2^{2-}$ have bond orders of one and $(NO_2)_2^+$ and $(CO_2)_2^-$ have bond orders of $\frac{1}{2}$, a simple orbital picture would lead us to expect a much smaller dissociation energy (D_e) for the latter two species. The calculated dissociation energy of $(CO_2)_2^-$ is 0.57 eV. The dissociation energy of $(CO_2)_2^{2-}$ is not known but is expected to be comparable.

The similar dissociation energies for $(NO_2)_2^+$ and $(NO_2)_2$ may have a simple origin: the importance of the long-range charge–induced dipole interaction between NO_2 and NO_2^+. We note that an analogous situation occurs for Li_2^+ and Li_2: the dissociation energy of Li_2^+ is greater than that of Li_2 even though the bond orders of the ion and neutral molecule are $\frac{1}{2}$ and 1, respectively. Dixon et al.[22] have proposed that the surprisingly strong bonding in Li_2^+ (and Li_2^-) is due to the importance of the charge–induced dipole interaction.

The charge distributions of the highest occupied molecular orbitals for the D_{2h} ($6a_g$) and D_{2d} ($6a_1$) structures are shown in Figure 4. The D_{2h} structures of $(NO_2)_2^+$ and $(CO_2)_2^-$ have similar charge densities as do the D_{2d} structures. However, the 1,4 bonding interaction[14,15] between the oxygens on the two monomer units is more important in D_{2h} $(NO_2)_2^+$ than in $(CO_2)_2^-$, although the O_1–O_4 separations agree to 0.01 Å for these two species. This is consistent with the observation that the D_{2h} species is the more stable structure for $(NO_2)_2^+$ and the D_{2d} for $(CO_2)_2^-$. The 1,4 O–O interactions are unimportant in the D_{2d} structures and as a result the HOMOs of the D_{2d} ions have charge densities quite similar to those obtained from the sum of the HOMO charge density functions (divided
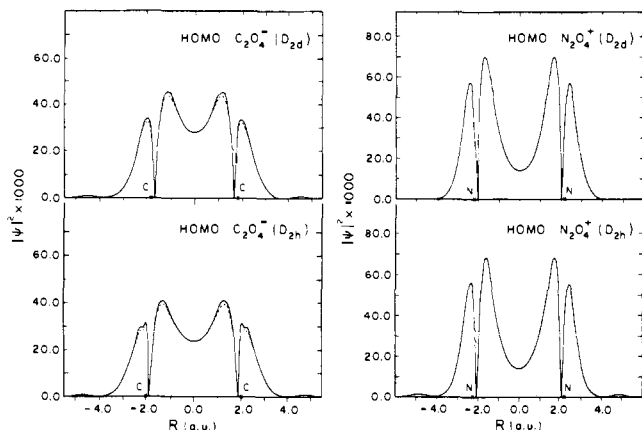
Figure 5. The charge densities along the N–N and C–C bond axes. For $(CO_2)_2^-$ the solid lines represent the charge densities calculated using the 6-31G and the dashed line the densities from the augmented basis set.

by two) of two isolated NO_2 or CO_2^- molecules, respectively.

The HOMO charge density plots along the N–N and C–C bond for the D_{2h} and D_{2d} ions are presented in Figure 5. For $(CO_2)_2^-$ two sets of results are given: solid curves presenting the densities obtained from the 6-31G basis and dotted curves obtained from the basis, augumented with diffuse s and p functions on the carbon atoms. The addition of the diffuse functions does not significantly affect the amount of charge density between the carbon atoms.

The D_{2h} and D_{2d} structures of $(NO_2)_2^+$ possess very similar charge densities along the N–N axis. This suggests that the contribution of the N–N bonding component of the HOMO is nearly the same for the D_{2d} and D_{2h} forms of the ion, and that the σ-type 1,4 interaction is largely responsible for the additional stabilization of the D_{2h} structure. This consideration is confirmed by the fact that the $6a_g$ orbital of the D_{2h} structure possesses a slightly lower energy than the $6a_1$ orbital of the D_{2d} structure (-0.663 vs. -0.654 au). The shifts in the energies of the other occupied molecular orbitals upon going from the D_{2h} to D_{2d} structure are smaller.

The charge density along the C–C bond of the D_{2d} structure of $(CO_2)_2^-$ is considerably greater than that of the D_{2h} species. This fact, combined with the relative unimportance of the 1,4 O–O interaction for $(CO_2)_2^-$, is consistent with the greater stability of the D_{2d} species.

In order to explain the differences in the relative importance of the 1,4 O–O and N–N/C–C σ contributions to the bonding in symmetric $(NO_2)_2^+$ and $(CO_2)_2^-$, it is instructive to examine the bonding in the isolated NO_2 and CO_2^- molecules. The N–O bond of NO_2 is 0.058 Å shorter than the CO bond of CO_2^-, suggesting that there is a significant difference in the hybridization of the 2s and 2p orbitals in the C of CO_2^- as compared to the N of NO_2. This difference in hybridization reflects itself in the charge density of the HOMO of these two species as may be seen from Figure 5. A comparison of the charge density plots along the C_2 axes of CO_2^- and NO_2 indicates that the HOMO of CO_2^- is much more spatially extended in the direction pointed away from the oxygens than that of NO_2. For example, the charge density of the HOMO of NO_2 is 8 e/a_0^3 at a distance of 2.15 au behind the nitrogen atom while the charge denisty of the HOMO of CO_2^- is 18 e/a_0^3 at a distance of 2.0 au behind the carbon. These two distances were chosen because they represent one-half the N–N and C–C bond lengths of $(NO_2)_2^+$ and $(CO_2)_2^-$, respectively. Hence just from consideration of the charge densities of the monomers one is led to expect that the C–C bond in symmetric $(CO_2)_2^-$ should be much more strongly bonding than the N–N bond of $(NO_2)_2^+$. We also note that the HOMO

of NO_2 localizes more charge density in the vicinity of the oxygens than does that of CO_2^-, consistent with the greater importance of the 1,4 O–O interactions in $(NO_2)_2^+$.

Both the D_{2h} and D_{2d} forms of $(CO_2)_2^-$ have appreciably more charge density between the carbons than the D_{2h} and D_{2d} forms of $(NO_2)_2^+$ have between the nitrogen atoms. It is for this reason that the symmetric forms of $(CO_2)_2^-$ lie only a few tenths of an electronvolt above the $CO_2^-\cdot CO_2$ complex while the symmetric forms of $(NO_2)_2^+$ lie considerably above the $NO_2^+\cdot NO_2$ complex.

Earlier, we indicated that $(CO_2)_2^{2-}$ is generally believed to have D_{2h} structure. This is not necessarily in disagreement with the prediction that for $(CO_2)_2^-$ the D_{2d} structure is slightly more stable than the D_{2h} structure. In particular we note that the distance between the cis oxygens in D_{2h} $(CO_2)_2^{2-}$ (2.74 Å) is much less than that for D_{2h} $(CO_2)_2^-$ (2.90 Å). The shorter O–O separation for the doubly charged anion should enhance the stabilizing σ-type 1–4 interaction between the oxygens and hence should favor the D_{2h} structure.

There is also the possibility that the equilibrium structure of an *isolated* $(CO_2)_2^{2-}$ ion is D_{2d} rather than D_{2h}. The structural data available for the oxalate ion has been obtained from salts or from matrix isolation work. It is possible that the structure of the gas-phase species could differ considerably from that of the condensed-phase ion. This is a difficult question to resolve since $(CO_2)_2^{2-}$, owing to autodetachment of an electron, is not a stable species in the gas phase.

C. Bonding in the C_s Structures of $(NO_2)_2^+$ and $(CO_2)_2^-$. The C_s forms of $(NO_2)_2^+$ and $(CO_2)_2^-$ are well described as ion-molecule complexes. It is apparent from Figure 6, showing the charge densities of the HOMOs of the two ions, that the "odd" electron is essentially localized on the bent NO_2 or CO_2^-. The charge density associated with the CO_2^- portion of $CO_2^-\cdot CO_2$ is similar to that of an isolated CO_2^-. Similarly, the charge density on the NO_2 portion of $NO_2^+\cdot NO_2$ is similar to that of an isolated NO_2 molecule, the major difference being that the charge density of the complex is shifted slightly toward the oxygen atoms.

The localization of the odd electron is reflected in the Mulliken population analysis. The nitrogen atom of the NO_2^+ portion of $NO_2^+\cdot NO_2$ has a net charge of 0.56 and the two oxygen atoms on this group have charges of 0.20 and 0.22. For the CO_2^- portion of $CO_2^-\cdot CO_2$, charges of -0.04, -0.44, and -0.42 are calculated for the carbon and the two oxygen atoms, respectively.

The above results suggest that the stability of the C_s structures can be explained in terms of the electrostatic interaction between the ionic and neutral molecules. To verify this we have performed a series of calculations on various models. In the simplest model, the NO_2^+ and CO_2^- portions of the dimers are replaced by single point charges ($+1$ and -1) located at the N and C atoms, respectively. We also consider a more realistic model in which the charges are distributed over the three atoms of the ion according to the results of the population analysis described above.[23] For each of these two models two estimations of the stabilization energy are obtained: (1) by carrying out Hartree–Fock calculations on the NO_2 and CO_2 molecules in the presence of the charges, and (2) by considering separately the contributions of the charge–permanent dipole, charge–induced dipole, and charge–quadrupole interactions. In the distributed charge model these interactions are calculated for each of the three charges. The results obtained from these two models are compared in Table I with those from the fully ab initio calculations. In the SCF approximation the single-point charge model overestimates the stability of $NO_2^+\cdot NO_2$ by 0.1 eV and underestimates that of $CO_2^-\cdot CO_2$ by 0.2 eV. On the other hand, the model employing the distributed charge distributions correctly predicts (to within 0.04 eV) the stability of the complexes. It is concluded, therefore,

Table I. Comparison of the Dissociation Energies of $NO_2{}^+\cdot NO_2$ and $CO_2{}^-\cdot CO_2$ with the Stabilization Energies of NO_2 and CO_2 by Plus and Negative Charges, Respectively (Energies in eV)

model		$NO_2{}^+\cdot NO_2$	$CO_2{}^-\cdot CO_2$
Hartree–Fock calculations on the dimer ion		0.54	0.57
point charge model	long-range interactions[a]	0.81	0.49
	Hartree–Fock[b]	0.63	0.34
distributed charge model	long-range interactions[a]	0.56	0.64
	Hartree–Fock[b]	0.54	0.53

[a] Model employing point charge approximation of $NO_2{}^+$ and $CO_2{}^-$ and considering the charge–dipole, charge–quadrupole, and charge–induced dipole interactions. [b] Hartree–Fock calculation on $[NO_2, +]$ and $[CO_2, -]$.

Table II. Calculated Orbital Energies (eV) of NO_2, $NO_2{}^+\cdot NO_2$, and $[NO_2, +]$[a]

NO_2		$NO_2{}^+\cdot NO_2$		$[NO_2, +]$	
α	β	α	β	α	β
15.05 (5b$_2$)	16.38	10.75	11.67	10.76	12.07
11.23 (7a$_1$)	11.79	6.62	7.16	6.75	7.57
1.37 (2b$_1$)	2.27	−2.89	−2.06	−2.10	−1.26
−13.89 (6a$_1$)	0.65	−18.24	−6.10	−18.06	−3.27
−14.43 (1a$_2$)	−14.35	−19.40	−19.02	−18.60	−19.26
−16.53 (4b$_2$)	−13.72	−21.58	−18.26	−20.91	−18.63
−21.48 (1b$_1$)	−20.86	−26.07	−25.49	−26.43	−25.26
−21.94 (3b$_2$)	−20.46	−26.68	−24.60	−26.07	−23.94
−23.25 (5a$_1$)	−19.85	−27.85	−25.26	−27.61	−25.02

[a] $[NO_2, +]$ represents NO_2 in the field of a + charge, distributed according to the population analysis to represent the $NO_2{}^+$ portion of $NO_2{}^+\cdot NO_2$.

(a)

(b)

Figure 6. Charge densities of the highest occupied molecular orbitals of the C_s structure of $(CO_2)_2{}^-$ (a) and $(NO_2)_2{}^+$ (b). The contour lines are the same as utilized in Figure 4.

that the bonding in $NO_2{}^+\cdot NO_2$ and $CO_2{}^-\cdot CO_2$ is due to electrostatic (permanent and induced) interactions between the ions and the neutral molecules.

In the model in which the $NO_2{}^+$ in $NO_2{}^+\cdot NO_2$ is replaced by a single point charge located at the N the charge–permanent dipole, charge–induced dipole, and charge–quadrupole interactions with NO_2 are 0.02, −0.48, and −0.35 eV, respectively. As expected from the geometry of $NO_2{}^+\cdot NO_2$ and the charge distribution obtained from the Mulliken analysis this simple model overestimates considerably (0.3 eV) the stabilization of the NO_2. If the charge on the $NO_2{}^+$ is distributed according to the results of the population analysis, then the contributions due to these three interactions are +0.02, −0.27, and −0.31 eV, respectively, giving a total stabilization of 0.56 eV, in excellent agreement with the ab initio result.

Table II lists the orbital energies of NO_2, NO_2 in the field of the distributed charges, and $NO_2{}^+\cdot NO_2$. For $NO_2{}^+\cdot NO_2$ we report only the energies of those orbitals localized on the NO_2 group. The energies of both the α and β orbitals of $[NO_2, +]$ are in good agreement with those of $NO_2{}^+\cdot NO_2$ with the exception of the lowest unoccupied β molecular orbital (the unpaired electron is in an α orbital). The average difference between the energies of occupied orbitals of the $[NO_2, +]$ model and those of the orbitals localized on the NO_2 portion of $NO_2{}^+\cdot NO_2$ is only 0.42 eV. This agreement lends additional support to the picture that the stability of $NO_2{}^+\cdot NO_2$ is the result of the electrostatic interaction between the $NO_2{}^+$ and NO_2 and not the result of chemical bonding. The stabilization of the orbitals of a molecule due to the interaction with a positive charge has been discussed by Imamura and Hirano[24] and by Bigelow.[25] We find that the positive charge induces shifts ranging from 4.1 to 5.2 eV for the energies of the occupied
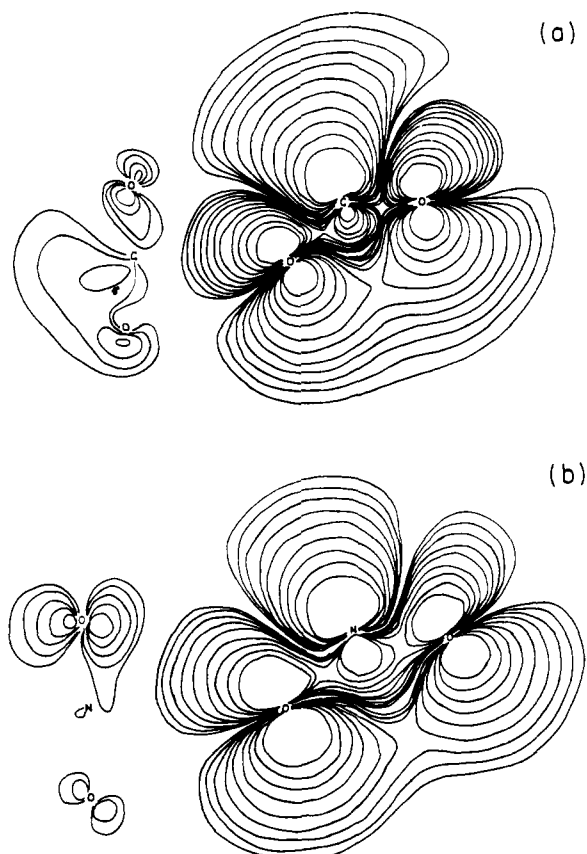
orbitals of NO_2. The variation in the shifts in the orbital energies is due partly to the overlaps of the molecular orbitals with the point charges, and partly due to the r^{-1} dependence of the Coulomb interaction combined with the fact that not all atoms are equidistant from the point charges.

The stability of the $CO_2{}^-\cdot CO_2$ ion is correctly predicted (to within 0.04 eV) by the model in which the $CO_2{}^-$ is replaced by the charge distribution determined from the population analysis. The orbital energies of the CO_2 portion of $CO_2{}^-\cdot CO_2$ are close to those of the $[CO_2, -]$ model. In this case the orbitals of CO_2 are destabilized by the presence of the negative charges, and the spread in the shifts in the energies due to the varying overlap of the orbitals with the charge distribution is again above 1 eV. Whereas the electrostatic picture appears to be equally valid for $CO_2{}^-\cdot CO_2$ and $NO_2{}^+\cdot NO_2$, there are some important differences in the magnitudes of the various interaction terms. In the case that $CO_2{}^-$ is replaced by a single charge at the carbon position, values of −0.09, −0.19, and −0.21 eV are found for the charge–permanent dipole, charge–induced dipole, and charge–quadrupole interactions, respectively. The corresponding values in the distributed charge model are −0.12, −0.13, and −0.39 eV, respectively. Unlike the NO_2 case, the charge–permanent dipole interaction is now *negative* and *relatively important*, contributing 0.12 eV to the stabilization energy. Apparently, it is the charge–permanent dipole interaction which causes the OCO angle of the CO_2 portion of $CO_2{}^-\cdot CO_2$ to close to 170°. The angle of 170° represents the optimal compromise between the increasing charge–dipole stabilization and the increasing energies of the CO_2 moiety as the angle is decreased. The $NO_2{}^+$ portion of $NO_2{}^+\cdot NO_2$ is more nearly linear ($\alpha = 176°$). The energy of CO_2, bent by 170°, is 0.08 eV above that of the linear species.

IV. Summary and Suggestions for Future Studies

In the case of $(CO_2)_2^-$, all three structures investigated are stable with respect to dissociation to $CO_2 + CO_2^-$. However, in the case of $(NO_2)_2^+$ only the C_s species is stable; the D_{2h} and D_{2d} forms of $(NO_2)_2^+$ are unstable with respect to $NO_2^+ + NO_2$. Calculations using the gradient method indicate that the optimized D_{2h} structure for $(NO_2)_2^+$ possesses a barrier both to dissociation and to rearrangement to the C_s form of the ion. However, D_{2h} $(NO_2)_2^+$ produced by vertical ionization of N_2O_4 may have a much smaller barrier to dissociation than does the optimized D_{2h} species. Further theoretical work on the minimum-energy paths for these rearrangements would be especially valuable.

The two major limitations of the present study are the neglect of d polarization functions and the neglect of electron correlation. We do not expect these to be serious limitations for the determination of the structures and dissociation energies of the C_s ion-molecule complexes, since it is well known that the Hartree–Fock method with double-ζ basis sets gives good descriptions of ion-molecule complexes such as $F^-\cdot H_2O$. We believe that the dissociation energies of the C_s complexes are good to 0.1–0.2 eV, with most of the uncertainty being due to basis-set effects. On the other hand, the relative energies of the D_{2h}, D_{2d}, and C_s structures are subject to greater uncertainties, since species with different types of bonding are being compared. D_{2h} and perhaps D_{2d} $(CO_2)_2^-$ could perhaps lie below C_s $CO_2^-\cdot CO_2$ in energy, but it is very unlikely that D_{2h} or D_{2d} $(NO_2)_2^+$ could be energetically below C_s $NO_2^+\cdot NO_2$. Additional studies including d polarization functions and including electron correlation are certainly called for for the species examined here.

There are several experiments that could provide information on the structure and stabilities of the C_s forms of the ions. Raman and ESR studies of the ions in rare-gas matrices could provide important information on the bonding of the complexes. The authors of a recent ESR study[11] of $(NO_2)_2^+$ interpreted the observed spectrum in terms of a D_{2h} structure for the ion and concluded that the odd electron cannot occupy a $6a_g$ orbital as would be expected for this structure. It is possible that the ESR spectrum originated from the C_s form of the cation. The HOMO of C_s $NO_2^+\cdot NO_2$ localizes most of its charge density in an sp hybrid orbital on the NO_2 portion of the monomer. Such a charge distribution for the odd electron appears to be consistent with the ESR results.

The complexes $(CO_2)_n^-$, for $n = 1$–6, have been detected mass spectroscopically. Based on the results of the present study we speculate that the equilibrium structures of these clusters may all be of the form of a monomeric ion solvated by $(n - 1)$ neutral monomers. For the $(NO_2)_n^+$ clusters the situation is more complicated since the dimerization energy of

NO_2 is nearly the same as energy of the $NO_2^+\cdot NO_2 \rightarrow NO_2^+ + NO_2$ reaction. Moreover, for reactions of the type

$$AB_{n-1}^{\pm} + B \rightarrow AB_n^{\pm}, \, n = 1, 2, \ldots$$

the second and subsequent solvent molecules generally have a smaller enthalpy of reactions than does the first ($n = 0$). Therefore, the larger $(NO_2)_n^+$ complexes may actually be of the form $NO_2^+\cdot N_2O_4$, $NO_2^+(NO_2)(N_2O_4)$, etc.

References and Notes

(1) A. R. Rossi and K. D. Jordan, *J. Chem. Phys.*, **70**, 4422 (1979).
(2) R. Ahlrichs and F. Keil, *J. Am. Chem. Soc.*, **96**, 7615 (1974).
(3) J. M. Howell and J. R. Van Wazer, *J. Am. Chem. Soc.*, **96**, 7902 (1974).
(4) L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties", Wiley, New York, 1972.
(5) B. W. McClelland, G. Gunderson, and K. Hedberg, *J. Chem. Phys.*, **56**, 4541 (1972).
(6) C. H. Bibart and G. E. Ewing, *J. Chem. Phys.*, **61**, 1284 (1974).
(7) D. L. Ames and D. W. Turner, *Proc. R. Soc. London, Ser. A*, **348**, 175 (1976).
(8) T. Yamazaki and K. Kimura, *Chem. Phys. Lett.*, **43**, 502 (1976); K. Nomoto, Y. Achiba, and K. Kimura, *ibid.*, **63**, 277 (1979).
(9) D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, **10**, 293 (1977).
(10) T. H. Gan, J. B. Peal, and G. D. Willett, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1459 (1977).
(11) R. D. Brown and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1389 (1977).
(12) W. Von Niessen, W. Domcke, L. S. Cederbaum, and J. Schirmer, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1550 (1978).
(13) R. D. Harcourt, *Chem. Phys. Lett.* **61**, 25 (1979).
(14) W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 779 (1972).
(15) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973); N. D. Epiotis, D. Bjorkquist, and S. Sarkenon, *ibid.*, **95**, 7558 (1973).
(16) J. Amlös, University of Stockholm, Institute of Physics, Report 74-29, Dec 1974.
(17) The GRNFNC program was developed by G. Purvis III at the University of Florida's Quantum Theory Project and at Battelle Memorial Institute.
(18) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975), and references cited therein.
(19) In the calculations on NO_2 a bond length of 1.188 Å was employed. This value was from R. C. Weast and S. M. Selbey, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland. This value differs slightly from that given in ref 21 (1.1934 Å).
(20) The gradient calculations were performed with the GAUSSIAN-78 developed by J. A. Pople and his co-workers at Carnegie-Mellon University.
(21) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1966.
(22) D. A. Dixon, J. L. Gole, and K. D. Jordan, *J. Chem. Phys.*, **66**, 567 (1977).
(23) The population analysis on $NO_2^+\cdot NO_2$ indicates a charge of 0.98 on the NO_2 portion of the dimer. In our model calculations we employ a charge of 1.00, with the extra 0.02 being distributed over the three centers proportionally according to the results of the population analysis on $NO_2^+\cdot NO_2$.
(24) A. Imamura and T. Hirano, *J. Am. Chem. Soc.*, **97**, 4192 (1975).
(25) R. W. Bigelow, *J. Chem. Phys.*, **70**, 3139 (1979).