

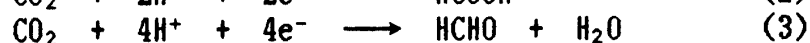
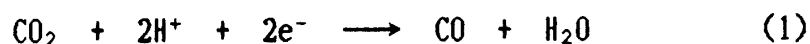
Molecular Orbital Studies on the Two-Electron Reduction of Carbon Dioxide to Give Formate Anion

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Abstract : Molecular orbital calculations by the MNDO method have been performed for all the possible reaction intermediates in the two-electron reduction of CO_2 to give HCOO^- ; $\text{CO}_2^{\cdot-}$, CO_2^{2-} , OCOH^+ , HCOO^+ , OCOH^\bullet , HCOO^\bullet , and OCOH^- , as well as CO_2 , and HCOO^- . Comparison of the heats of formation obtained by the calculations indicates that the reaction may proceed *via* $\text{CO}_2^{\cdot-}$, OCOH^\bullet , and OCOH^- successively, followed by proton (or H atom) transfer to the carbon atom affording HCOO^- , while the preferential formation of CO is suggested in the liquid phase. Moreover, *ab initio* calculations at the STO-3G level for those three intermediates together with CO_2 , HCOO^- , and HCOOH have been achieved; the resulting molecular and electronic structures are discussed in comparing with those calculated by the MNDO method.

INTRODUCTION

Much attention has been paid for the reduction or the fixation of carbon dioxide in recent one or two decades, because effective utilization of CO_2 as carbon resources is one of the most important subjects in the field of chemistry to cope with a predictable oil shortage in near future. Thus, electrochemical, photochemical, photoelectrochemical, and thermal reductions of CO_2 have widely been studied in the presence of proton donors,¹⁾ where as the reduction products have been obtained CO, HCOOH , HCHO , CH_3OH , CH_4 , and other organic compounds.²⁾ Of these reductions of CO_2 , the formation of CO and HCOOH (or HCOO^-) may be the most fundamental reactions, since they require only two electrons (eqs. 1 and 2), while much more electrons are demanded in other reactions (see eqs. 3-5).



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From such a point of view, the present work was undertaken to perform MNDO calculations for possible reaction intermediates in the two-electron reduction of CO_2 giving HCOO^- to elucidate the reaction pathways. In addition, *ab initio* calculations at the STO-3G level for the reaction intermediates, *i.e.*, carbon dioxide radical anion $\text{CO}_2^{\cdot-}$, hydroxycarbonyl radical OCOH^\bullet , and hydroxycarbonyl anion OCOH^- , as well as CO_2 , HCOO^- , and HCOOH were conducted; the results are discussed in comparing with those obtained by the MNDO method.

MOLECULAR ORBITAL CALCULATIONS

MNDO calculations were carried out by using an MNDOH package transplanted by Dr. H. Tanaka, Mitsui Petrochemical Co. Ltd., from Program No. 353 supplied from QCPE, Indiana University. *ab initio* Calculations at the STO-3G level were performed on an IMSPACK package transplanted from IMS372 program³⁾ developed in Institute for Molecular Science, Okazaki.

RELIABILITY OF MNDO CALCULATIONS

For examining the reliability of the MNDO method for the chemical species studied here, the heats of formation and related physical properties of CO_2 , OCOH^\bullet , and HCOOH were calculated by this method to compare with the observed values. The results are shown in Table 1, which confirms satisfactory agreement between the observed and calculated values, except the heat of formation of CO_2 , whose calculated value is around 20% smaller than the observed one. This discrepancy may be due to the MNDO method developed mainly for the calculation of organic species.

Table 1. Calculated and observed heats of formation (ΔH_f), ionization potentials (IP), and dipole moments (μ) of CO_2 , OCOH^\bullet , and HCOOH .

| Species | ΔH_f / kJ mol^{-1} | | IP / eV | | μ / Debye | |
|-----------------------|-------------------------------------|----------------------|---------|----------------------|---------------|---------------------|
| | Calcd. | Obsd. | Calcd. | Obsd. | Calcd. | Obsd. |
| CO_2 | -309.2 | -393.5 ^{a)} | 12.88 | 13.769 ^{b)} | 0.00 | 0.00 |
| OCOH^\bullet | -228.9 | -224 ^{c)} | — | — | 2.69 | — |
| HCOOH | -370.3 | -378.6 ^{d)} | 11.77 | 11.33 ^{e)} | 1.34 | 1.415 ^{f)} |

^{a)} Ref. 4. ^{b)} Ref. 5. ^{c)} Ref. 6. ^{d)} Gaseous state; Ref. 7. ^{e)} Ref. 8.

^{f)} Gaseous phase; Ref. 9.

POSSIBLE REACTION INTERMEDIATES

There may be several pathways in the reduction of CO_2 giving HCOO^- ; such as hydride (H^-) transfer, H atom transfer followed by electron transfer, separated transfer of electrons and protons, *e.g.*, successive electron-proton-electron

transfer, and so on. If the third one is assumed to take place in the present reaction, there may be seven possible reaction intermediates other than the substrate CO_2 and the reduction product HCOO^- , as shown in Scheme 1. Heats of formation of those possible intermediates calculated by the MNDO/RHF method are listed in Table 2, which clearly indicates that the CO_2^{2-} dianion as well as both OCOH^+ and HCOO^+ cations are unlikely as intermediates, because of their positively large heats of formation. The HCOO^\bullet radical may also be no probable intermediate owing to its instability compared with the OCOH^\bullet radical (Table 2). Thus, the reaction may proceed *via* $\text{CO}_2^{\cdot-}$ radical anion, OCOH^\bullet radical, and OCOH^- anion as intermediates, the last of which may be transformed to HCOO^- anion.

Scheme 1 : Possible reaction pathways.

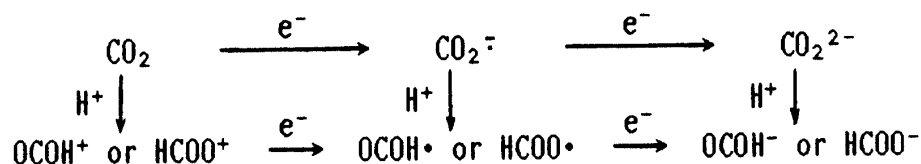
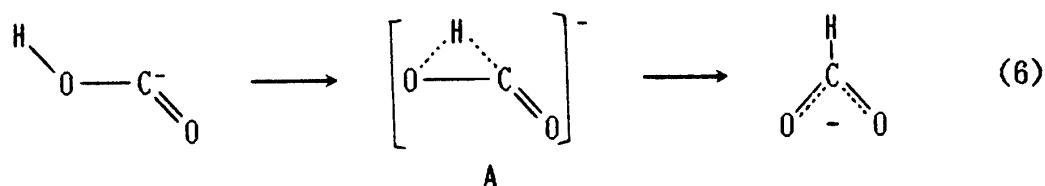


Table 2. Calculated heats of formation of possible reaction intermediates.

| Intermediate | $\Delta H_f^\circ/\text{kJ mol}^{-1}$ | Intermediate | $\Delta H_f^\circ/\text{kJ mol}^{-1}$ |
|-----------------------------|---------------------------------------|-----------------------|---------------------------------------|
| $\text{CO}_2^{\cdot-}$ | -332.1 | OCOH^\bullet | -238.1 |
| CO_2^{2-} [singlet | +376.4 | HCOO^\bullet | -75.10 |
| triplet | +496.8 | OCOH^- | -333.0 |
| OCOH^+ | +597.3 | HCOO^- | -425.6 |
| HCOO^+ | +1096 | | |

It has been reported that the deprotonation reaction of HCOOH with HO^- produces the OCOH^- anion as a minor product together with the HCOO^- anion as a major one.¹⁰⁾ This result has been compatible with the *ab initio* calculation of these anions, which indicated that HCOO^- is more stable by some 160 kJ mol^{-1} than OCOH^- ,¹¹⁾ while the present MNDO calculation exhibits HCOO^- being more stable by about 93 kJ mol^{-1} than OCOH^- . In addition, a potential surface map of the H^-/CO_2 system calculated by Gaussian 86 at the RHF/6-31+G* level has suggested that OCOH^- may convert to HCOO^- *via* an intermediate (A in eq. 6) with a



barrier 122 kJ mol^{-1} in the gaseous phase.¹²⁾ These results are in consistent with the present reaction pathways involving OCOH^- anion. Reaction coordinate of the two-electron reduction of CO_2 giving HCOO^- is illustrated in Fig. 1.

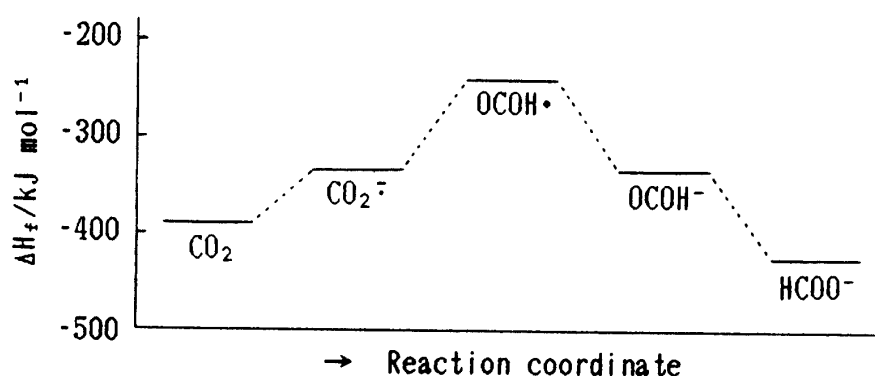
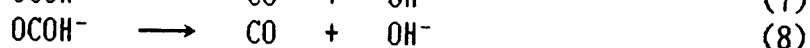
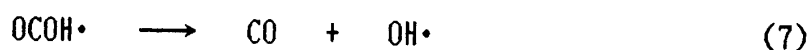


Fig. 1. Reaction coordinate for the two-electron reduction of CO_2 to afford HCOO^- ; ΔH_f° for CO_2 is observed value.

FORMATION OF CARBON MONOXIDE IN THE TWO-ELECTRON REDUCTION OF CO_2

The electrochemical technique has most extensively been applied for the reduction of CO_2 in solution, where transition metal complexes have been used as catalysts. Most of those studies, however, have resulted in the formation of a mixture of HCOO^- and CO ¹⁾ or only CO ;¹⁴⁾ selective formation of HCOO^- has scarcely been reported.¹⁵⁾

Carbon monoxide may be generated by degradation of either OCOH^\bullet or OCOH^- formed in the course of two-electron reduction of CO_2 (eq. 7 or 8). The heats



of formation of CO and OH^\bullet in the gaseous phase are reported as $-110.54^4)$ and $+38.99^4)$ kJ mol^{-1} , respectively.¹⁶⁾ The sum of these values ($-72.1 \text{ kJ mol}^{-1}$) is higher energy than the heat of formation of OCOH^\bullet ($-238.1 \text{ kJ mol}^{-1}$), indicating that the OCOH^\bullet radical is unlikely to undergo degradation to CO and OH^\bullet . On the other hand, there is no reliable datum for the heat of formation of OH^- in the gaseous phase. Thus, the MNDO calculation for this anion was conducted to give the heat of formation as $-24.16 \text{ kJ mol}^{-1}$. The sum of this value and the observed heat of formation of CO ($-134.7 \text{ kJ mol}^{-1}$) is still higher energy than the heat of formation of OCOH^- , suggesting that the OCOH^- anion may not be decomposed into CO and OH^- in the gaseous phase. In solution, however, the OH^- anion is expected to receive significant stabilization by the solvation; e.g., the heat of formation of OH^- in aqueous solutions has been reported as $-230.0 \text{ kJ mol}^{-1}$.⁴⁾ Such stabilization of the OH^- anion in solution may assist the destruction of

OCOH⁻ producing CO, before the OCOH⁻ anion is transformed to HCOO⁻.

MOLECULAR AND ELECTRONIC STRUCTURES OF CO₂, HCOO⁻, AND HCOOH

Structure parameters and electron populations calculated by the MNDO and *ab initio* (STO-3G) methods for the substrate CO₂ and the reduction product HCOO⁻ together with HCOOH are listed in Table 3, which shows experimentally determined bond lengths and bond angles for those molecules as well. The calculated bond lengths shown in Table 3 agree with the observed values within ± 3 pm, except the C-O² bond of HCOOH, for which the *ab initio* calculation has given the length of about 4 pm longer than the observed one. On the other hand, both the MNDO and the *ab initio* calculations displayed 180° for all the dihedral angles not only in HCOO⁻ but also in HCOOH, confirming their planar structures. The calculated bond angles, however, sometimes exhibit discrepancies by some degrees or more

Table 3. Calculated and observed structure parameters and electron populations of CO₂, HCOO⁻, and HCOOH.

| Molecule or anion | Structure parameter ^{a)} or atom | Calculated value | | Observed value ^{b)} |
|-------------------|---|------------------|------------------|------------------------------|
| | | MNDO | <i>ab initio</i> | |
| O=C=O | R(C-O) | 118.60 | 118.79 | 116.32 |
| | A(OCO) | 180.0 | 180.0 | 180.0 |
| | C | 5.552 | 5.556 | |
| | O | 8.224 | 8.222 | |
| | R(C-O) | 126.0 | 126.6 | 127 |
| | A(OCO) | 125.6 | 130.0 | 124 |
| | D(HCOO) | 180.0 | 180.0 | 180 |
| | C | 5.627 | 5.842 | |
| | H | 1.117 | 1.128 | |
| | O | 8.628 | 8.515 | |
| | R(C=O ¹) | 122.7 | 121.4 | 120.2 |
| | R(C-O ²) | 135.4 | 138.6 | 134.3 |
| | R(C-H) | 110.4 | 110.4 | 109.7 |
| | R(O ² -H) | 94.9 | 99.0 | 97.2 |
| | A(O ¹ CH) | 126.8 | 126.0 | 124.1 |
| | A(O ¹ CO ²) | 120.6 | 123.6 | 124.9 |
| | A(CO ² H) | 116.2 | 104.7 | 106.3 |
| | D(HCO ¹ H) | 180.0 | 180.0 | 180 |
| | D(O ¹ CHO ²) | 180.0 | 180.0 | 180 |
| | C | 5.640 | 5.745 | |
| | (C-)H | 0.894 | 0.926 | |
| | (O-)H | 0.784 | 0.793 | |
| | O ¹ | 8.369 | 8.285 | |
| | O ² | 8.313 | 8.251 | |

^{a)} R: Bond length/pm, A: Bond angle/deg., D: Dihedral angle/deg.

^{b)} Obtained from vibrational spectra for CO₂,¹³⁾ X-ray crystal analysis for HCOONa,¹⁷⁾ and microwave spectroscopy for HCOOH.⁸⁾

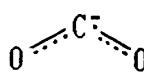
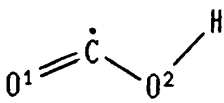
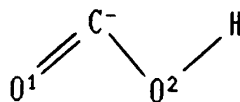
from the observed values.

It should be noted that there is seen satisfactory agreement of electron populations on each atom of CO_2 , HCOO^- , and HCOOH between the MNDO and *ab initio* methods; those calculated values fall within ± 0.1 , except the carbon and oxygen atoms of HCOO^- , and the carbon atom of HCOOH , whose discrepancies between the two methods are 0.215, 0.113, and 0.105, respectively (Table 3).

MOLECULAR AND ELECTRONIC STRUCTURES OF REACTION INTERMEDIATES

Table 4 summarizes the bond lengths and bond angles as well as the electron populations obtained by the MNDO and *ab initio* calculations for the reaction intermediates of two-electron reduction of CO_2 ; $\text{CO}_2^{\cdot -}$ radical anion, OCOH^\bullet radical, and OCOH^- anion; for the former two species the UHF method was adopted in the *ab initio* calculation, and the RHF method was used in the MNDO calculation.

Table 4. Calculated structure parameters and electron populations of $\text{CO}_2^{\cdot -}$, OCOH^\bullet , and OCOH^- .

| Intermediate | Structure parameter ^{a)} or atom | MNDO | <i>ab initio</i> |
|---|--|-------|------------------|
|  | R(C-O) | 123.8 | 126.3 |
| | A(OCO) | 135.3 | 131.0 |
| | C | 5.960 | 6.004 |
| | O | 8.520 | 8.498 |
|  | R(C-O ¹) | 119.7 | 119.8 |
| | R(C-O ²) | 132.6 | 139.3 |
| | R(O ² -H) | 95.1 | 99.0 |
| | A(O ¹ CO ²) | 131.6 | 124.7 |
| | A(CO ² H) | 111.8 | 105.4 |
| | D(O ¹ CO ² H) | 180.0 | 180.0 |
| | C | 5.833 | 5.748 |
| | O ¹ | 8.195 | 8.214 |
| | O ² | 8.202 | 8.260 |
|  | R(C-O ¹) | 123.9 | 123.2 |
| | R(C-O ²) | 140.6 | 153.4 |
| | R(O ² -H) | 94.4 | 100.2 |
| | A(O ¹ CO ²) | 110.8 | 105.2 |
| | A(CO ² H) | 107.2 | 103.3 |
| | D(O ¹ CO ² H) | 180.0 | 180.0 |
| | C | 6.140 | 6.119 |
| | O ¹ | 8.564 | 8.486 |
| | O ² | 8.420 | 8.425 |
| | H | 0.876 | 0.970 |

^{a)} R: Bond length/pm, A: Bond angle/deg., D: Dihedral angle/deg.

Of those reaction intermediates, the CO_2^- radical anion has received spectroscopic studies for the species trapped in alkali halide matrices or adsorbed on inorganic salts, from which the OCO bond angle has been estimated, as listed in Table 5, where is found some scatter ranging from 124° to 144° . It should be mentioned, however, that the bond angle may be changed by the conditions to generate the CO_2^- species.²⁵⁾ Thus, the OCO bond angle of CO_2^- may reasonably be assumed to fall in the 125° - 130° range, which agrees with the result by *ab initio* calculation better than MNDO.

Table 5. Experimentally derived OCO bond angle of CO_2^- /deg.

| Method | Sample | Bond angle | Ref. |
|--------|--|-------------|------|
| esr | Adsorbed on HCOONa | 128.4 | 18) |
| esr | Adsorbed on HCOONa | 134 | 19) |
| esr | Adsorbed on CaCO_3 | 130.4 | 20) |
| esr | Adsorbed on MgO | 124.4 | 21) |
| ir | Trapped in NaBr, KCl, KBr, KI | 127 ± 8 | 22) |
| esr | Adsorbed on HCOONa | 129.1 | 23) |
| esr | Formed by the reaction of CO_2 with F^+ center ^{a)} | 124.9 | 24) |
| esr | Formed by the reaction of O^{2-} ^{b)} with CO on F^+ center | 125.5 | 24) |
| esr | Formed by the reaction of CO_2 with F^+ center at rt ^{c)} | 125 | 25) |
| esr | Formed by the reaction of CO_2 with F^+ center at 88K | 144 | 25) |

^{a)} Produced by uv irradiation of a low pressure Hg lamp to activated MgO in the presence of H_2 . ^{b)} Generated by the reaction of F^+ center with N_2O . ^{c)} rt: Room temperature.

It is noticed that for the three chemical species shown in Table 4 all the bond lengths obtained by the *ab initio* calculation are more or less larger than those derived by the MNDO method. On the contrary, all the bond angles calculated by the *ab initio* method are smaller than those by the MNDO method, while dihedral angles of the OCOH^\bullet radical and its anion agree well between the *ab initio* and MNDO methods. Both methods have yielded satisfactory agreement in the electron populations of those three species with each other, except the H atom of OCOH^- .

CONCLUSION

The MNDO calculation for reaction intermediates in the two-electron reduction of CO_2 (in the gaseous phase) indicates that the reaction proceeds *via* CO_2^- , OCOH^\bullet , and OCOH^- successively, the last of which may be transformed to the final product HCOO^- . In solution, however, the OCOH^- anion may readily undergo degradation to afford CO and OH^- , probably because of negatively large solvation energy of OH^- . In general, both the MNDO and the *ab initio* calculations can

provide the structure parameters to be satisfied for CO_2 , CO_2^- , HCOO^- , and HCOOH , whose molecular structures have been reported, while the *ab initio* method seems to be superior to MNDO in detailed structure.

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