

Associative Electron Attachment to 2-Aminopyridine-(CO₂)₁ Complex: Photoelectron Spectroscopic and Theoretical Approach

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Carbon dioxide is a very inert molecule whose reactivity is low at room temperature. It does not make a stable anion in the gas phase since it has a negative adiabatic electron affinity (AEA).¹ Instead, it becomes a metastable anion with quite a long lifetime ($< 100 \mu\text{s}$) when it adopts a bent geometry which differs greatly from the geometry of the neutral species.^{2,3} Clusters of carbon dioxide molecules have been extensively studied using photoelectron spectroscopy and theoretical calculations. DeLuca *et al.* and Tsukuda *et al.* found that core switching occurred in (CO₂)_n⁻.^{4,5} Clusters of CO₂ and H₂O, CO₂ and CH₃OH and CO₂ and atomic halide anions were also studied, and showed interesting properties.^{6,7} Furthermore, the existence of [O₂-CO₂]⁻ and [Au-CO₂]⁻ were indirectly observed from IR spectrum that showed a red shift in asymmetric stretch and combination bands of asymmetric stretch with other vibrational frequencies.^{8,9}

The most remarkable behavior observed, however, was the “associative electron attachment” to a neutral van der Waals complex, resulting in a new covalent bond being formed between the neutral molecule and CO₂ upon electron attachment. S. Y. Han *et al.* studied the associative electron attachment to [(pyridine)₁₋₆-(CO₂)₁₋₃]¹⁰ and S. H. Lee *et al.* extended this study to whole azabenzene-(CO₂)_n complexes.¹¹ Among the three diazine molecules (pyridazine, pyrimidine and pyrazine), pyridazine (Pd) formed only one covalent bond with two CO₂ molecules upon electron attachment due to the steric hindrance from the pre-existing CO₂ moiety while the other two diazine molecules formed two stepwise formations of a covalent bond with the large electron binding energy shift (~ 2 eV). Here, we studied the 2-aminopyridine (2AP), which is analogous to [Pd-(CO₂)₁]. We compared the behavior of the [2AP-(CO₂)₁] van der Waal complex upon electron attachment to [Pd-(CO₂)₂]⁻.

The details of our experimental scheme have been described elsewhere.¹² A [2AP-(CO₂)₁]⁻ complex anion was generated using a molecular beam apparatus with pulsed solenoid valve. The mixture of the evaporated 2AP and CO₂ (1.5 bar) gas was co-expanded with Ar carrier gas (4 bar) through the nozzle. The resulting van der Waals complex captured a low energy secondary electron which was generated by electron impact (400 eV, 200 μA). A Wiley-McLaren type time-of-flight mass spectrometer (TOF-MS) was used to separate the

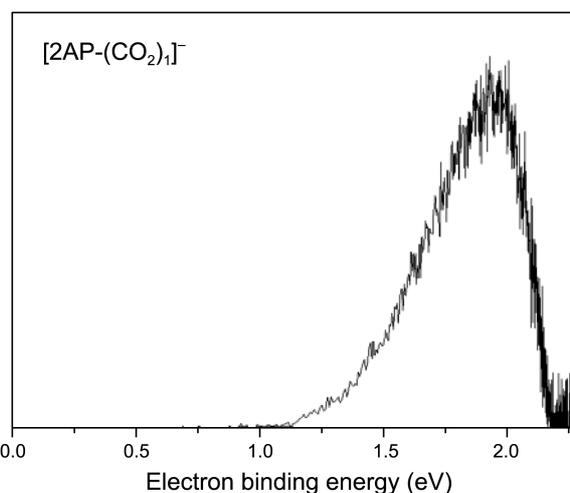


Figure 1. Photoelectron spectrum of [2AP-(CO₂)₁]⁻ obtained at 532 nm. Even 2AP molecule has negative VDE (~ -1 eV), associative electron attachment shifts VDE more than 2 eV due to the extending of π -conjugation over the entire complexes *via* covalent bond formation.

different anions by their masses. The mass-selected [2AP-(CO₂)₁]⁻ anions were then irradiated by second harmonic output (532 nm, 2.33 eV) of a pulsed Nd:YAG laser in order to eject photoelectrons. The photoelectrons were collected using a magnetic-bottle-type photoelectron spectrometer, and the electron kinetic energy was converted to electron binding energy by subtracting it from the photon energy.

Figure 1 shows the photoelectron spectrum of [2AP-(CO₂)₁]⁻ obtained at 532 nm with a single, broad featureless band which is evidence of the formation of a valence band anion. Surprisingly, [2AP-(CO₂)₁]⁻ shows an exceedingly high vertical detachment energy (VDE) value (1.95 eV) as opposed to 2AP⁻ which has a negative VDE according to our calculations (~ -1 eV, Table 1).¹³ This phenomenon is similar to that seen in azabenzene-(CO₂)_n complexes where the neutral van der Waal complexes underwent associative electron attachment resulting in a covalent bond formation.¹¹ In contrast to the [Pd-(CO₂)₂]⁻ complex, 2AP could form a covalent bond regardless of its structural similarity to [Pd-(CO₂)₁]⁻. This might be due to the reduced steric hindrance of the CO₂ molecule during the approach process. The O-O

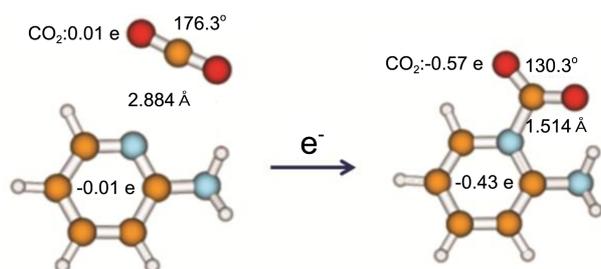


Figure 2. Optimized geometries of neutral (left) and anionic (right) $[2AP-(CO_2)_1]$ complex calculated at the B3LYP/6-311++G** level. A new covalent bond was formed between N in 2AP and C in CO_2 upon electron attachment. The distance between N and C decreased more than 1.3 Å. The O-C-O angle in CO_2 also decreased resulting in bent geometry. Note that the excess electron delocalized to the entire anion complex.

distance in the CO_2 in $[Pd-(CO_2)_1]^-$ is 2.26 Å while H-H distance in the NH_2 in 2AP is only 1.71 Å. The relatively small size of the NH_2 made the approaching CO_2 molecule feel much less repulsion due to the steric hindrance. In addition to this, the approaching CO_2 molecule was acted upon by an attractive force in the case of $[2AP-(CO_2)_1]^-$ since the H atom in the NH_2 has a partial positive charge whereas the approaching CO_2 molecule was acted upon by a repulsive force in the case of $[Pd-(CO_2)_2]^-$ since the O atom in the CO_2 has a partial negative charge. Both the B3LYP and MP2 methods underestimated the VDE values by more than 0.5 eV; however, ΔVDE (~ 2.2 eV) is consistent with that seen in azabenzene- $(CO_2)_n$ complex anions.

Theoretical calculations revealed the structural changes that occurred upon electron attachment (Figure 2). First of all, the distance between the N atom in 2AP and the C atom in the CO_2 decreased from 2.884 Å to 1.514 Å indicating the formation of the covalent bond. However, the C-O distance in the CO_2 increased from 1.164 Å to 1.254 Å indicating a decrease in the bond order due to the new covalent bond. Finally, the O-C-O angle decreased from 176.3° to 130.3° as was also seen in the $[(pyridine)_1-(CO_2)_1]$ complexes.¹⁰

To elucidate the origin of the large VDE shift, we analyzed the charge distribution in both the neutral and anionic complexes (Figure 2). In the neutral complex, both the 2AP and CO_2 molecules have a net charge of zero. However, the excess electron is totally delocalized to the entire anion complex to give $-0.43e$ in 2AP and $-0.57e$ in CO_2 . This means that the π -conjugation in 2AP extended over the entire complex through a newly formed covalent bond, greatly stabilizing the anionic complex (~ 2 eV).

In conclusion, we investigated the associative electron attachment to the $[2AP-(CO_2)_1]$ van der Waal complex using anion photoelectron spectroscopy and theoretical calcu-

Table 1. VDE of $[2AP-(CO_2)_n]^-$, $n=0$ and 1 calculated at the B3LYP/6-311++G** and MP2/6-311++G** level

| | B3LYP | MP2 | Experiment |
|--------------|----------|----------|------------|
| $n=0$ | -1.05 eV | -0.94 eV | N. A. |
| $n=1$ | 1.15 eV | 1.35 eV | 1.95 eV |
| ΔVDE | 2.2 eV | 2.29 eV | N. A. |

lations. We found a covalent bond formation between 2AP and CO_2 opposite to that seen in $[Pd-(CO_2)_2]^-$ which could not form an additional covalent bond due to the steric hindrance. Excess negative charge is totally delocalized to the entire complex to give extended π -conjugation.

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