Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Formation of negative ions from cobalt tricarbonyl nitrosyl $Co(CO)_3NO$ clusters

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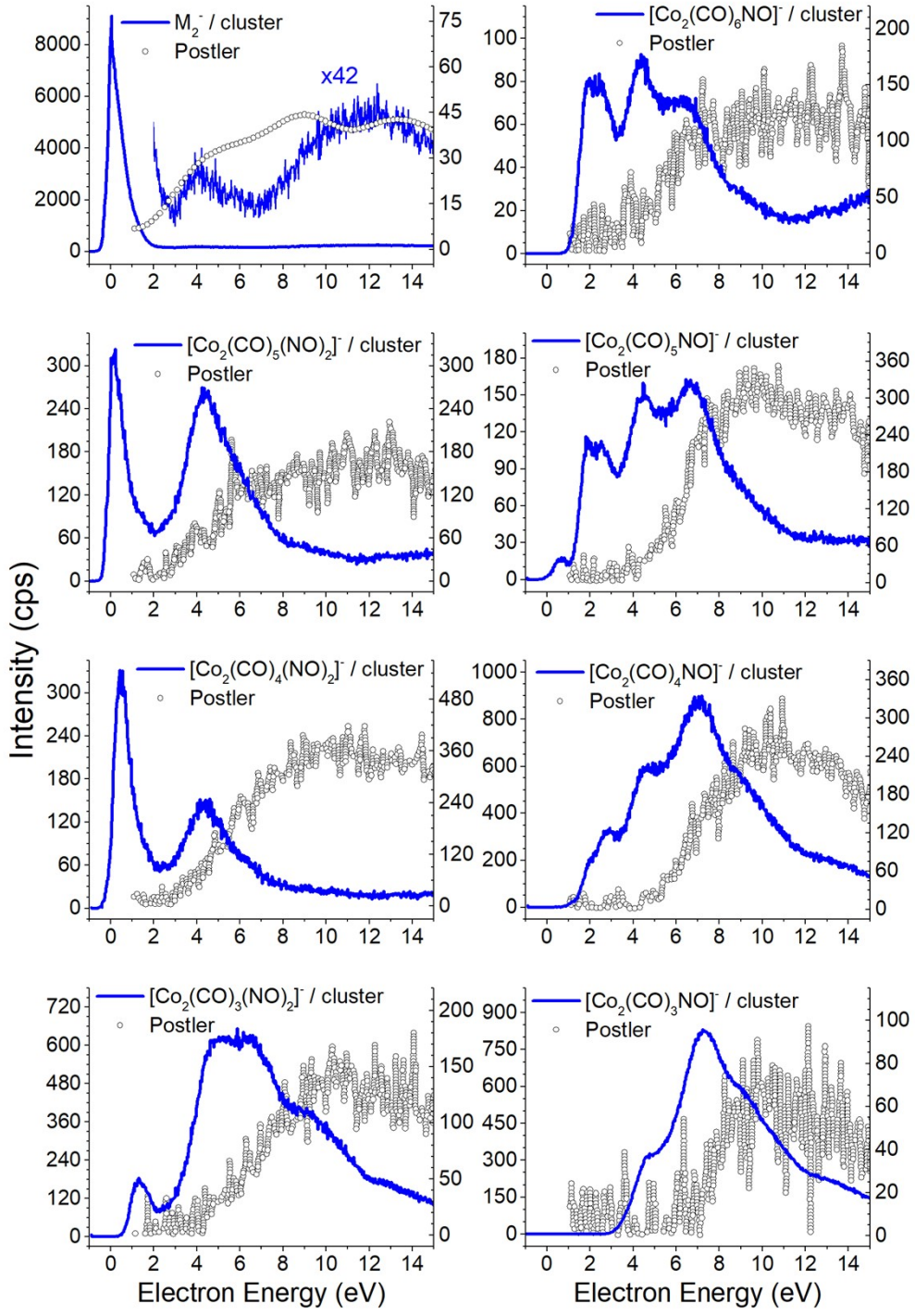


**Figure ESI 1** The molecular dimer $[Co(CO)_3NO_2]^-$ (labelled as $M_2^-$) and the associated clusters of one molecule (M) with the DEA products $[Co(CO)_2NO]^-$ … $Co^-$ obtained from CLUSTER-ILN measurements (blue lines, y-axes on left) compared with the He clusters data (grey, y-axis on right, taken from J. Postler, M. Renzler, A. Kaiser, S. E. Huber, M. Probst, P. Scheier and A. M. Ellis, J. Phys. Chem. C, 2015, **119**, 20917–20922).

**Table ESI 1** Reaction energies (**ΔH**) in eV evaluated from CBS-QB3 enthalpies for neutral dissociations as *ΔH = H([neutral fragment]) + Σ H(neutral products) – H(Co(CO)$_3$NO)* as well as for reactions leading to anionic products via DEA as *ΔH = H([anionic fragment]) + Σ H(neutral products) – H(Co(CO)$_3$NO)*. Last line corresponds to formation of neutral or ionic $Co(CO)_4$ via interaction of two $Co(CO)_3NO$ molecules.

| | | | ΔH/eV | | ΔH/eV |
|---|---|---|---|---|---|
| | | [neutral fragments] | | [anion fragments] | |
| $Co(CO)_3NO$ | | | | | |
| **1.1** | → CO | + $[Co(CO)_2NO]$ | 1.32 | + $[Co(CO)_2NO]^-$ | -0.01 |
| **1.2** | → NO | + $[Co(CO)_3]$ | 2.58 | + $[Co(CO)_3]^-$ | 0.85 |
| **1.3** | → CO + NO | + $[Co(CO)_2]$ | 4.17 | + $[Co(CO)_2]^-$ | 1.32 |
| **1.4** | → 2 CO | + [Co(CO)NO] | 3.26 | + $[Co(CO)NO]^-$ | 1.68 |
| **1.5** | → 2 CO + NO | + [CoCO] | 5.61 | + $[CoCO]^-$ | 4.82 |
| **1.6** | → 3 CO | + [CoNO] | 5.10 | + $[CoNO]^-$ | 4.14 |
| **1.7** | → 3 CO + NO | + [Co] | 6.63 | + $[Co]^-$ | 5.77 |
| **1.8** | → CO + O | + $[Co(CO)_2N]$ | 8.06 | + $[Co(CO)_2N]^-$ | 6.13 |
| **1.9** | → CO + O | + [Co(CO)(NO)C] | 10.73 | + $[Co(CO)(NO)C]^-$ | 8.87 |
| **1.10** | → CO + C | + [Co(CO)(NO)O] | 10.23 | + $[Co(CO)(NO)O]^-$ | 8.63 |
| 2 $Co(CO)_3NO$ | | | | | |
| **1.11** | → $Co(CO)_2NO$ + NO | + $[Co(CO)_4]$ | 2.30 | + $[Co(CO)_4]^-$ | -0.53 |

**Table ESI 2** Reaction energies (**ΔH**) in eV evaluated from CBS-QB3 enthalpies for dimer, where **ΔH** = Σ x H(CO) + Σ H$[Co_2(CO)_{6-x}(NO)_2]^-$ – 2 H$(Co(CO)_3NO)$, for x=0, 1, 2, 3, 4, 5.

| | | Ion+neutral pair considered in cluster | Neutral fragments | ΔH/eV |
|---|---|---|---|---|
| 2 $Co(CO)_3NO$ + e | | | | |
| **2.1** | → $[Co_2(CO)_6(NO)_2]^-$ | → $[2Co(CO)_3NO]^-$ + $Co(CO)_3NO$ | | -0.73 |
| **2.2** | → $[Co_2(CO)_5(NO)_2]^-$ + CO | → $[Co(CO)_2NO]^-$ + $Co(CO)_3NO$ | + CO | -0.11 |
| **2.3** | | → $[Co(CO)_3NO]^-$ + $Co(CO)_2NO$ | + CO | 0.59 |
| **2.4** | → $[Co_2(CO)_4(NO)_2]^-$ + 2 CO | → $[Co(CO)NO]^-$ + $Co(CO)_3NO$ | + 2 CO | 1.68 |
| **2.5** | | → $[Co(CO)_3NO]^-$ + Co(CO)NO | + 2 CO | 2.53 |
| **2.6** | | → $[Co(CO)_2NO]^-$ + $Co(CO)_2NO$ | + 2 CO | 1.31 |
| **2.7** | → $[Co_2(CO)_3(NO)_2]^-$ + 3 CO | → $[CoNO]^-$ + $Co(CO)_3NO$ | + 3 CO | 4.14 |
| **2.8** | | → $[Co(CO)_3NO]^-$ + CoNO | + 3 CO | 4.37 |
| **2.9** | | → $[Co(CO)_2NO]^-$ + Co(CO)NO | + 3 CO | 3.25 |
| **2.10** | | → $[Co(CO)NO]^-$ + $Co(CO)_2NO$ | + 3 CO | 3.00 |
| **2.11** | → $[Co_2(CO)_2(NO)_2]^-$ + 4 CO | → $[CoNO]^-$ + $Co(CO)_2NO$ | + 4 CO | 5.47 |
| **2.12** | | → $[Co(CO)_2NO]^-$ + CoNO | + 4 CO | 5.09 |
| **2.13** | | → $[Co(CO)NO]^-$ + Co(CO)NO | + 4 CO | 4.94 |
| **2.14** | | → $[Co(CO)_2]^-$ + $Co(NO)_2$ | + 4 CO | 3.74 |
| **2.15** | → $[Co_2(CO)(NO)_2]^-$ + 5 CO | → $[CoNO]^-$ + Co(CO)NO | + 5 CO | 7.40 |
| **2.16** | | → $[Co(CO)NO]^-$ + CoNO | + 5 CO | 6.79 |

**Table ESI 3** Reaction energies (ΔH) in eV evaluated from CBS-QB3 enthalpies for dimer, where ΔH = Σ x H(CO) + H(NO) + Σ H[$Co_2(CO)_{6-x}NO]^-$ – 2 H($Co(CO)_3NO$), for x=0, 1, 2, 3, 4, 5.

| | | Ion+neutral pair considered in cluster | Neutral fragments | ΔH/eV |
|---|---|---|---|---|
| 2 $Co(CO)_3NO$ + e | | | | |
| **3.1** | → $[Co_2(CO)_6NO]^-$ + NO | → $[Co(CO)_3]^-$ + $Co(CO)_3NO$ | + NO | 0.85 |
| **3.2** | | → $[Co(CO)_3NO]^-$ + $Co(CO)_3$ | + NO | 1.85 |
| **3.3** | | → $[Co(CO)_2NO]^-$ + $Co(CO)_4$ | + NO | 2.30 |
| **3.4** | | → $[Co(CO)_4]^-$ + $Co(CO)_2NO$ | + NO | -0.55 |
| **3.5** | → $[Co_2(CO)_5NO]^-$ + CO + NO | → $[Co(CO)_2]^-$ + $Co(CO)_3NO$ | + CO + NO | 1.32 |
| **3.6** | | → $[Co(CO)_3NO]^-$ + $Co(CO)_2$ | + CO + NO | 3.44 |
| **3.7** | | → $[Co(CO)_2NO]^-$ + $Co(CO)_3$ | + CO + NO | 2.57 |
| **3.8** | | → $[Co(CO)_3]^-$ + $Co(CO)_2NO$ | + CO + NO | 2.17 |
| **3.9** | | → $[Co(CO)_4]^-$ + Co(CO)NO | + CO + NO | 1.41 |
| **3.10** | | → $[Co(CO)NO]^-$ + $Co(CO)_4$ | + CO + NO | 2.66 |
| **3.11** | → $[Co_2(CO)_4NO]^-$ + 2 CO + NO | → $[CoCO]^-$ + $Co(CO)_3NO$ | + 2CO + NO | 4.82 |
| **3.12** | | → $[Co(CO)_3NO]^-$ + CoCO | + 2CO + NO | 4.88 |
| **3.13** | | → $[Co(CO)_2NO]^-$ + $Co(CO)_2$ | + 2CO + NO | 4.16 |
| **3.14** | | → $[Co(CO)_2]^-$ + $Co(CO)_2NO$ | + 2CO + NO | 2.64 |
| **3.15** | | → $[Co(CO)_3]^-$ + Co(CO)NO | + 2CO + NO | 4.11 |
| **3.16** | | → $[Co(CO)NO]^-$ + $Co(CO)_3$ | + 2CO + NO | 4.26 |
| **3.17** | | → $[CoNO]^-$ + $Co(CO)_4$ | + 2CO + NO | 5.13 |
| **3.18** | | → $[Co(CO)_4]^-$ + CoNO | + 2CO + NO | 3.25 |
| **3.19** | → $[Co_2(CO)_3NO]^-$ + 3 CO + NO | → $[Co]^-$ + $Co(CO)_3NO$ | + 3CO + NO | 5.77 |
| **3.20** | | → $[Co(CO)_3NO]^-$ + Co | + 3CO + NO | 5.91 |
| **3.21** | | → $[Co(CO)_2NO]^-$ + CoCO | + 3CO + NO | 5.60 |
| **3.22** | | → $[CoCO]^-$ + $Co(CO)_2NO$ | + 3CO + NO | 6.14 |
| **3.23** | | → $[Co(CO)_2]^-$ + Co(CO)NO | + 3CO + NO | 4.58 |
| **3.24** | | → $[Co(CO)NO]^-$ + $Co(CO)_2$ | + 3CO + NO | 5.85 |
| **3.25** | | → $[CoNO]^-$ + $Co(CO)_3$ | + 3CO + NO | 6.73 |
| **3.26** | | → $[Co(CO)_3]^-$ + CoNO | + 3CO + NO | 5.95 |
| **3.27** | → $[Co_2(CO)_2NO]^-$ + 4 CO + NO | → $[Co]^-$ + $Co(CO)_2NO$ | 4 CO + NO | 7.09 |
| **3.28** | | → $[Co(CO)_2NO]^-$ + Co | 4 CO + NO | 6.62 |
| **3.29** | | → $[Co(CO)NO]^-$ + CoCO | 4 CO + NO | 7.29 |
| **3.30** | | → $[CoCO]^-$ + Co(CO)NO | 4 CO + NO | 8.08 |
| **3.31** | | → $[Co(CO)_2]^-$ + CoNO | 4 CO + NO | 6.42 |
| **3.32** | | → $[CoNO]^-$ + $Co(CO)_2$ | 4 CO + NO | 8.31 |
| **3.33** | → $[Co_2(CO)NO]^-$ + 5 CO + NO | → $[Co]^-$ + Co(CO)NO | 5 CO + NO | 9.03 |
| **3.34** | | → $[Co(CO)NO]^-$ + Co | 5 CO + NO | 8.31 |
| **3.35** | | → $[CoCO]^-$ + CoNO | 5 CO + NO | 9.92 |
| **3.36** | | → $[CoNO]^-$ + CoCO | 5 CO + NO | 9.76 |

**Table ESI 4** Enthalpies of formation $\Delta_f H°(298.15\ K)$ in kJ/mol evaluated from CBS-QB3 Energy, Zero Point Energy, Thermal correction to Enthalpy and the $\Delta_f H°(0\ K)$ of elements taken from JANAF/NIST database [Chase Jr, M. W. (American Chemical Society, 1998, DOI: 10.18434/T42S31), https://srd.nist.gov/JPCRD/jpcrdM9.pdf]

| molecule, fragment | $\Delta_f H°(298.15\ K)$ neutral | JANAF/NIST | $\Delta_f H°(298.15\ K)$ anion | Electron Affinity [eV] |
|---|---|---|---|---|
| $Co(CO)_3NO$ | -411.93 | - | -488.06 | 0.79 |
| $Co(CO)_3$ | -267.26 | - | -435.55 | 1.74 |
| $Co(CO)_2NO$ | -185.46 | - | -316.95 | 1.36 |
| $Co(CO)_2$ | -14.00 | - | -289.39 | 2.85 |
| Co(CO)NO | 102.03 | - | -55.37 | 1.63 |
| CoCO | 226.56 | - | 147.06 | 0.82 |
| CoNO | 376.56 | | 282.84 | 0.97 |
| CO | -108.39 | -110.53 | | |
| NO | 93.13 | 90.29 | | |