Angewandte Chemie International Edition

DOI: 10.1002/anie.201302827

CO_2 Activation

Carboxylation of Methyl Acrylate by Carbon Dioxide Radical Anions in Gas-Phase Water Clusters**

Amou Akhgarnusch, Robert F. Höckendorf, Qiang Hao, K. Philip Jäger, Chi-Kit Siu, and Martin K. Beyer**

Dedicated to Professor Wolfgang Domcke on the occasion of his 65th birthday

With the growing interest in using carbon dioxide (CO_2) as a C_1 building block in chemical synthesis[1,2] and as a hydrogen-storage material,[3] the molecular principles of CO_2 activation have attracted considerable attention in gas-phase studies.[4] Of particular interest in applications is the addition of CO_2 to olefins.[2] Depending on the reaction conditions, the carboxylation of methyl acrylate ($CH_2{=}CHCOOCH_3$, MA) in electrochemical syntheses[5–7] may proceed by addition of CO_2 to the methyl acrylate radical anion $MA^{\bullet-}$ or by addition of the carbon dioxide radical anion $CO_2^{\bullet-}$ to neutral MA.[6] To better understand the mechanism of this reaction in aqueous media on a molecular level, we investigated the addition of $CO_2^{\bullet-}$ to MA in gas-phase water clusters by a combination of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and quantum chemical calculations.

$CO_2^{\bullet-}(H_2O)_n$ ($n \approx 50$–100) clusters were generated in a laser vaporization ion source[8–10] and transferred to the ICR cell, where they were allowed to collide with MA at a pressure of 7.5×10^{-9} mbar. The mass spectra in Figure 1 show clearly that $CO_2^{\bullet-}(H_2O)_n$ clusters quantitatively take up one MA molecule, which stays in the cluster. The reaction is accompanied by black-body radiation-induced dissociation (BIRD) of water molecules from the clusters.[11] After a reaction delay of 35 s, the clusters have "boiled down" to $[CO_2,MA,H_2O]^{\bullet-}$, which decays by evaporation of a neutral CO_2 to form $[MA,H_2O]^{\bullet-}$. This monohydrated methyl acrylate radical anion undergoes electron detachment. The final stage of the reaction can be quantitatively fitted with a kinetic model consisting of first-order reaction steps (for details see the Supporting Information).

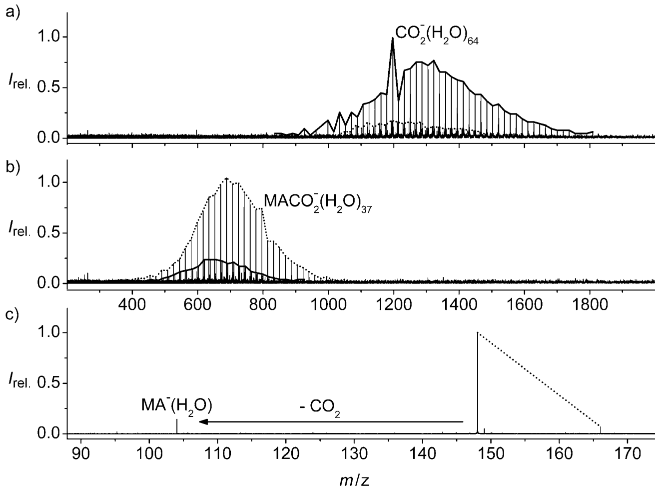


Figure 1. Mass spectra of the reaction of $CO_2^{\bullet-}(H_2O)_n$ ($n \approx 50$–100) with $CH_2{=}CHCOOCH_3$ (MA) at a pressure of 7.5×10^{-9} mbar, after reaction delays of a) 0 s, b) 7 s and c) 35 s.

In order to quantitatively fit the reaction kinetics and to extract thermochemical information from the data, the intensities of reactant and product clusters were summed over all cluster sizes, and their average sizes were calculated as a function of time. Figure 2a shows that the kinetics exhibits pseudo-first-order behavior, with a rate constant of $k_{abs} = 1.6 \times 10^{-9}\ cm^3 s^{-1}$. This compares well with theoretical estimates of the collision rate;[12] hard-sphere average dipole orientation theory (HSA) yields $k_{HSA} = 1.4 \times 10^{-9}\ cm^3 s^{-1}$, while the surface charge capture model (SCC) results in $k_{SCC} = 2.7 \times 10^{-9}\ cm^3 s^{-1}$, equivalent with efficiencies of $\Phi_{HSA} = 114\,\%$ and $\Phi_{SCC} = 60\,\%$.

A nanocalorimetric fit[10,13] (Figure 2b,c) reveals that during the uptake of MA, on average (2.2 ± 0.5) water molecules evaporate from the cluster, equivalent to a reaction enthalpy of (-95 ± 22) kJ mol^{-1}.[14] The uptake of one and only one MA molecule together with the high exothermicity of the reaction strongly indicate that a covalent bond is formed between $CO_2^{\bullet-}$ and MA. The $[CO_2,MA]^{\bullet-}$ radical anion is stabilized by hydration. When the hydration shell is "boiled down" to only one water molecule, the newly formed C–C bond is broken again, and a neutral CO_2 molecule evaporates from the cluster.

---

[*] M. Sc. A. Akhgarnusch, Dr. R. F. Höckendorf, K. P. Jäger, Prof. Dr. M. K. Beyer
Institut für Physikalische Chemie
Christian-Albrechts-Universität zu Kiel
Olshausenstrasse 40, 24098 Kiel (Germany)
E-mail: beyer@phc.uni-kiel.de

Dr. Q. Hao, Dr. C.-K. Siu
Department of Biology and Chemistry
City University of Hong Kong
83 Tat Chee Avenue, Kowloon Tong, Hong Kong (China)
E-mail: chiksiu@cityu.edu.hk

[**] Financial support from the Deutsche Forschungsgemeinschaft (grant no. BE2505/4-2), the German Academic Exchange Service (DAAD), PPP Hongkong (project ID 50750748), Research Grants Council, Hong Kong SAR (grant no. G_HK006/10 and CityU 102911), and City University of Hong Kong (grant no. 7002817) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302827.

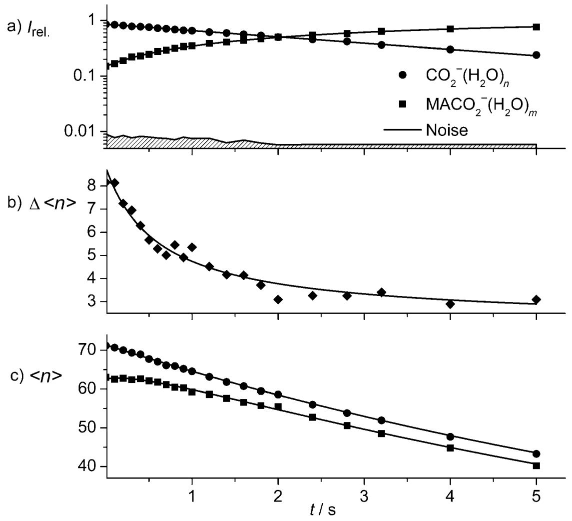
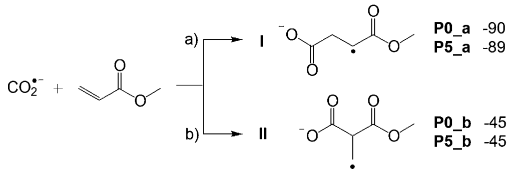


Figure 2. a) Kinetic fit of the reaction of $CO_2^{\bullet-}(H_2O)_n$ ($n \approx 50$–100) with $CH_2{=}CHCOOCH_3$, summed over reactant and product intensities. b) Nanocalorimetric fit to the difference of the average cluster size of reactant and products Δ< n > and c) to the average cluster size < n > as a function of time.

Reaction of $CO_2^{\bullet-}$ with MA involves a radical addition to the unsaturated C=C bond, giving two possible carboxylated isomers either by reaction (a) to form the monomethyl succinate radical anion (**I**) or by reaction (b) to form the monomethyl methylmalonate radical anion (**II**) (Scheme 1).



Scheme 1. Reactions between MA and $CO_2^{\bullet-}$. Reaction energies (ΔH°_0/kJ mol^{-1}) for the formation of products **Pn_a** and **Pn_b**, where *n* denotes the number of water molecules presented, were evaluated at the B3LYP/6-311++G(d,p) level of theory.

Isomer **I** is predicted to be the preferred product because the radical is secondary and stabilized by π-conjugation with the ester group. In addition, the radical addition to the terminal carbon is less sterically hindered.[15] This is supported by density functional theory (DFT) calculations; reaction (a) and reaction (b) for bare $CO_2^{\bullet-}$ are exothermic, respectively, by −90 kJ mol^{-1} and −45 kJ mol^{-1}, as evaluated at the B3LYP/6-311++G(d,p) level of theory, forming products **P0_a** and **P0_b**. Solvation does not significantly change the reaction energies; reaction (a) and reaction (b) for $CO_2^{\bullet-}(H_2O)_5$ are exothermic by −89 kJmol^{-1} (**P5_a**) and −45 kJ mol^{-1} (**P5_b**), respectively. The theoretical exothermicity for the formation of the thermodynamically more favorable **P5_a** agrees within error limit with the experimental nanocalorimetric value of (−95 ± 22) kJ mol^{-1}.

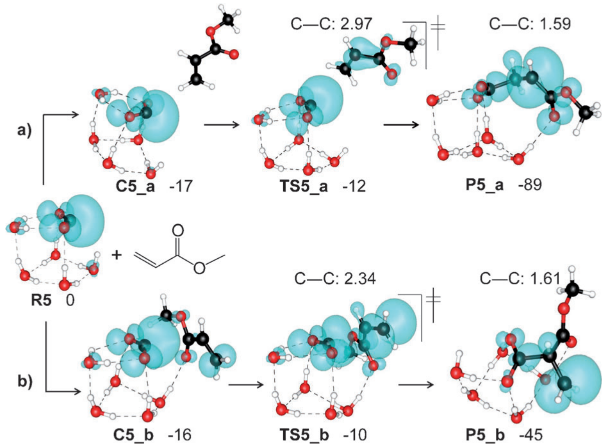


Figure 3. Mechanisms for the reaction between MA and $CO_2^{\bullet-}(H_2O)_5$. Geometries and spin-density distributions were calculated at the B3LYP/6-311++G(d,p) level of theory. All energies (in kJ mol^{-1}) are relative to that of the reactants (i.e. MA + $CO_2^{\bullet-}(H_2O)_5$). The lengths of the C—C bond being formed are given in Ångstrom.

The reaction mechanisms are straightforward as illustrated with the $n = 5$ cluster as shown in Figure 3. For reaction (a), the MA is solvated on the cluster to form the complex **C5_a** with a binding energy of only −17 kJ mol^{-1}, around half the value of the binding energy of one water molecule to the cluster. This weakly bound complex undergoes a radical attack of $CO_2^{\bullet-}$ on the terminal olefin carbon, against a barrier of only 5 kJ mol^{-1}, via the transition structure **TS5_a** which has a long C—C distance of 2.97 Å. The reaction is driven thermodynamically by the formation of the strong C—C bond (1.59 Å) and the radical in the resulting product **P5_a** is stabilized by π-conjugation. The theoretical calculations are consistent with the experimental observations that only one MA can be taken up by the cluster, while binding of a second MA will be very weak and inefficient.

The alternative reaction (b) also involves an intermediate complex **C5_b** with the MA binding energy of −16 kJ mol^{-1}, similar to that for **C5_a**. The transition structure **TS5_b** associated with the formation of the product **P5_b**, in which the radical is mainly located on the primary carbon, is 2 kJ mol^{-1} above **TS5_a** in energy. Reaction (b) is less likely to occur because the barrier is slightly higher and the resulting product **P5_b** is thermodynamically less stable. The reverse reaction with a barrier of 35 kJ mol^{-1} (which is less than the energy required to evaporate a water molecule) is still accessible in the cluster, while the product **P5_a**, once it is formed, is more likely to be stabilized by water evaporation rather than undergo C—C bond rupture with a barrier of 77 kJ mol^{-1}.

The experimentally observed elimination of CO_2 from $[CO_2,MA,H_2O]^{\bullet-}$ indicates that the newly formed C—C bond is more stable against homolytic than heterolytic bond cleavage. To learn more about this decay channel, we calculated the potential energy surface (PES) for the final reaction steps, that is, CO_2 elimination followed by electron detachment for the $n = 1$ product cluster. The results are shown in Figure 4. In the structure **P1_a** located at the global minimum on the PES, H_2O forms two hydrogen bonds with the carboxylate group. Before CO_2 can be eliminated from this position, H_2O has to move to a different binding site to

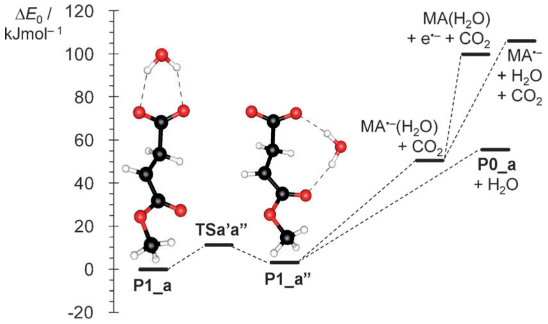


Figure 4. Potential energy surface for the decay channels of $[CO_2,MA,H_2O]^{\bullet-}$ (**P1_a**) calculated at the B3LYP/6-311++G(d,p) level of theory. The experimentally observed CO_2 elimination lies 5 kJ mol^{-1} lower in energy than the potentially competing loss of H_2O. Similarly, electron detachment from $MA^{\bullet-}(H_2O)$ is 6 kJ mol^{-1} lower in energy than loss of H_2O.

form **P1_a″**, which is only 3 kJ mol^{-1} higher in energy than **P1_a**. CO_2 elimination from **P1_a″** is endothermic by 47 kJ mol^{-1}, resulting in a total binding energy of 50 kJ mol^{-1} for neutral CO_2 to the monohydrated methyl acrylate radical anion, 5 kJ mol^{-1} lower than the binding energy of water to **P0_a**. Adiabatic electron detachment from $MA^{\bullet-}(H_2O)$ requires another 50 kJ mol^{-1}, which is 6 kJ mol^{-1} lower than the potentially competing loss of water to form the unsolvated $MA^{\bullet-}$.

Experiment and theory in the gas phase provide a mechanistic understanding of the observations from electrochemistry in the condensed phase.[5–7] The carboxylated radical anion can be formed in two ways, by addition of $CO_2^{\bullet-}$ to neutral methyl acrylate, or by addition of neutral CO_2 to the methyl acrylate radical anion. The decay of the product will preferentially occur as the reverse reaction of the latter pathway. The results show that the chemistry of CO_2 in the presence of an extra electron is very subtle. The good news is that C–C bond formation between $CO_2^{\bullet-}$ and olefins readily occurs, with significant bond strengths and moderate barriers. To proceed to intact products, they need to be stabilized before elimination of neutral CO_2 takes place.

Experimental Section

The experiments were performed on a modified Bruker/Spectrospin CMS47X FT-ICR mass spectrometer described in detail previously.[9,10] $CO_2^{\bullet-}(H_2O)_n$ ions were generated by laser vaporization of a solid zinc target and supersonic expansion in helium seeded with traces of water vapor and carbon dioxide.[10] To minimize changes in the initial cluster size distribution, the vaporization laser and frequency doubling crystal were heated by 20 laser shots, followed by 20 laser shots at 10 Hz and 5 mJ pulse energy to generate the ions. The reaction delay is measured relative to the end of the fill cycle, at nominal $t = 0$ s. Reaction products are observed at nominal 0 s, since the clusters have been exposed to the reaction gas for up to 2 s. Methyl acrylate (Fluka, > 99.5 %) was introduced into the cell region of the mass spectrometer through a needle valve at a constant pressure of 7.5×10^{-9} mbar, calibrated as described previously.[16] The reaction was monitored by recording mass spectra at different reaction delays. The Gaussian 09 program package[17] was employed for quantum chemical calculations. All calculations were performed using density functional theory at the B3LYP/6-311++G(d,p) level.

Received: April 5, 2013

Keywords: alkenes · calorimetry · carbon dioxide · carboxylation · electrochemistry

---

[1] a) W. Leitner, *Angew. Chem.* **1995**, *107*, 2391–2405; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207–2221; b) M. Aresta, A. Dibenedetto, *Dalton Trans.* **2007**, 2975–2992; c) K. M. K. Yu, I. Curcic, J. Gabriel, S. C. E. Tsang, *ChemSusChem* **2008**, *1*, 893–899.

[2] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662–8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537.

[3] a) B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026–4029; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962–3965; b) B. Loges, A. Boddien, H. Junge, J. R. Noyes, W. Baumann, M. Beller, *Chem. Commun.* **2009**, 4185–4187.

[4] a) R. N. Compton, P. W. Reinhardt, C. D. Cooper, *J. Chem. Phys.* **1975**, *63*, 3821–3827; b) C. E. Klots, *J. Chem. Phys.* **1979**, *71*, 4172–4172; c) M. Knapp, O. Echt, D. Kreisle, T. D. Märk, E. Recknagel, *Chem. Phys. Lett.* **1986**, *126*, 225–231; d) D. Schröder, C. A. Schalley, J. N. Harvey, H. Schwarz, *Int. J. Mass Spectrom.* **1999**, *187*, 25–35; e) T. Tsukuda, T. Nagata, *J. Phys. Chem. A* **2003**, *107*, 8476–8483; f) K. Sudoh, Y. Matsuyama, A. Muraoka, R. Nakanishi, T. Nagata, *Chem. Phys. Lett.* **2006**, *433*, 10–14; g) M. Z. Kamrath, R. A. Relph, M. A. Johnson, *J. Am. Chem. Soc.* **2010**, *132*, 15508–15511; h) R. F. Höckendorf, C.-K. Siu, C. van der Linde, O. P. Balaj, M. K. Beyer, *Angew. Chem.* **2010**, *122*, 8433–8435; *Angew. Chem. Int. Ed.* **2010**, *49*, 8257–8259; i) R. F. Höckendorf, Q. Hao, Z. Sun, B. S. Fox-Beyer, Y. Cao, O. P. Balaj, V. E. Bondybey, C.-K. Siu, M. K. Beyer, *J. Phys. Chem. A* **2012**, *116*, 3824–3835; j) H. Dossmann(Soldi-Lose), C. Afonso, D. Lesage, J.-C. Tabet, E. Uggerud, *Angew. Chem.* **2012**, *124*, 7044–7047; *Angew. Chem. Int. Ed.* **2012**, *51*, 6938–6941; k) K. J. Breen, A. F. DeBlase, T. L. Guasco, V. K. Voora, K. D. Jordan, T. Nagata, M. A. Johnson, *J. Phys. Chem. A* **2012**, *116*, 903–912; l) B. J. Knurr, J. M. Weber, *J. Am. Chem. Soc.* **2012**, *134*, 18804–18808; m) E. Surber, R. Mabbs, T. Habteyes, A. Sanov, *J. Phys. Chem. A* **2005**, *109*, 4452–4458; n) L. Velarde, T. Habteyes, A. Sanov, *J. Chem. Phys.* **2006**, *125*, 114303; o) T. Habteyes, L. Velarde, A. Sanov, *Chem. Phys. Lett.* **2006**, *424*, 268–272; p) T. Habteyes, L. Velarde, A. Sanov, *J. Chem. Phys.* **2007**, *126*, 154301; q) R. F. Höckendorf, K. Fischmann, Q. Hao, C. van der Linde, O. P. Balaj, C.-K. Siu, M. K. Beyer, *Int. J. Mass Spectrom.* in print, http://dx.doi.org/10.1016/j.ijms.2013.05.027.

[5] D. A. Tyssee, J. H. Wagenknecht, M. M. Baizer, J. L. Chruma, *Tetrahedron Lett.* **1972**, *13*, 4809–4812.

[6] D. A. Tyssee, M. M. Baizer, *J. Org. Chem.* **1974**, *39*, 2819–2823.

[7] D. A. Tyssee, M. M. Baizer, *J. Org. Chem.* **1974**, *39*, 2823–2828.

[8] a) V. E. Bondybey, J. H. English, *J. Chem. Phys.* **1981**, *74*, 6978–6979; b) T. G. Dietz, M. A. Duncan, D. E. Powers, R. E. Smalley, *J. Chem. Phys.* **1981**, *74*, 6511–6512; c) S. Maruyama, L. R. Anderson, R. E. Smalley, *Rev. Sci. Instrum.* **1990**, *61*, 3686–3693.

[9] C. Berg, T. Schindler, G. Niedner-Schatteburg, V. E. Bondybey, *J. Chem. Phys.* **1995**, *102*, 4870–4884.

[10] R. F. Höckendorf, O. P. Balaj, C. van der Linde, M. K. Beyer, *Phys. Chem. Chem. Phys.* **2010**, *12*, 3772–3779.

[11] a) D. Thölmann, D. S. Tonner, T. B. McMahon, *J. Phys. Chem.* **1994**, *98*, 2002–2004; b) M. Sena, J. M. Riveros, *Rapid Commun. Mass Spectrom.* **1994**, *8*, 1031–1034; c) P. D. Schnier, W. D. Price, R. A. Jockusch, E. R. Williams, *J. Am. Chem. Soc.* **1996**, *118*, 7178–7189; d) T. Schindler, C. Berg, G. Niedner-Schatteburg, V. E. Bondybey, *Chem. Phys. Lett.* **1996**, *250*, 301–308; e) B. S. Fox, M. K. Beyer, V. E. Bondybey, *J. Phys. Chem. A* **2001**, *105*, 6386–6392; f) R. C. Dunbar, *Mass Spectrom. Rev.*

2004, *23*, 127–158; g) O. P. Balaj, C. B. Berg, S. J. Reitmeier, V. E. Bondybey, M. K. Beyer, *Int. J. Mass Spectrom.* **2009**, *279*, 5–9.

[12] G. Kummerlöwe, M. K. Beyer, *Int. J. Mass Spectrom.* **2005**, *244*, 84–90.

[13] W. A. Donald, R. D. Leib, J. T. O'Brien, M. F. Bush, E. R. Williams, *J. Am. Chem. Soc.* **2008**, *130*, 3371–3381.

[14] a) C. Hock, M. Schmidt, R. Kuhnen, C. Bartels, L. Ma, H. Haberland, B. von Issendorff, *Phys. Rev. Lett.* **2009**, *103*, 073401; b) W. A. Donald, R. D. Leib, M. Demireva, B. Negru, D. M. Neumark, E. R. Williams, *J. Phys. Chem. A* **2011**, *115*, 2–12.

[15] B. Giese, *Angew. Chem.* **1983**, *95*, 771–782; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 753–764.

[16] a) J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149–153; b) T. Schindler, C. Berg, G. Niedner-Schatteburg, V. E. Bondybey, *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1114–1120; c) C. van der Linde, R. F. Höckendorf, O. P. Balaj, M. K. Beyer, *Low Temp. Phys.* **2010**, *36*, 411–416; d) R. F. Höckendorf, C. van der Linde, O. P. Balaj, I. Herber, M. K. Beyer, *Int. J. Mass Spectrom.* **2011**, *300*, 44–49.

[17] Gaussian 09 (Revision B.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., Gaussian, Inc., Wallingford CT, **2010**.