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The gas-phase acidity of cyclopropene and simple alkyl derivatives: Can they be measured?

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Abstract

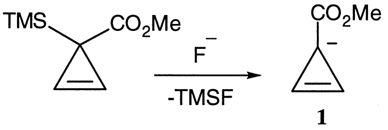
The gas-phase acidity of 3-methylcyclopropene (**5**) at the allylic position was explored computationally and experimentally. G2+ calculations indicate that $\Delta H^\circ_{\mathrm{acid}} = 415.5$ kcal/mol making 3-methyl-3-cyclopropenyl anion (**6**) an extremely strong base. This species is also predicted to be unstable with respect to electron loss (EA(3-methyl-3-cyclopropenyl radical) = -1.54 kcal/mol). A kinetic approach for determining the acidity of **5** using the hydroxide-induced desilylation of 3-methyl-3-trimethylsilylcyclopropene (the DePuy method) was employed but fails in this case because of an unanticipated rearrangement. This raises the question: Can the acidity of cyclopropene and its simple alkyl derivatives be measured? Positive and negative responses to this question are given and discussed. (Int J Mass Spectrom 201 (2000) 101–108) © 2000 Elsevier Science B.V.

Keywords: Antiaromaticity; Cyclopropenyl anions; G2 theory; Ion cyclotron resonance; Kinetic method

1. Introduction

Erich Hückel is often credited with the idea that fully conjugated monocyclic compounds with $4n + 2$ π electrons are stabilized by resonance, whereas those species with $4n$ π electrons are neither stabilized nor destabilized or are destabilized by conjugation (i.e. these substances are aromatic, nonaromatic or antiaromatic) [1–6]. Predictions based upon Huckel's rule have been amply demonstrated. Maybe the most dramatic success has been the synthesis of cyclopropenyl cation, the simplest aromatic molecule, and the observation of this ion in the tail of Halley's comet [7–9]. In contrast, relatively little is known about cyclopropenyl anion, the smallest antiaromatic compound.

In a series of seminal contributions Breslow and co-workers showed that the allylic position of cyclopropene and its derivatives is very weakly acidic [10–15]. We prepared the first stable cyclopropenyl anion (**1**) in the gas phase in 1994 by reacting fluoride ion with 3-carbomethoxy-3-trimethylsilylcyclopropene [Eq. (1)] [16]. Subsequently, we synthesized



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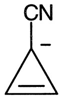
3-cyanocyclopropenyl anion (**2**) via the same route as **1** [17] and benzocyclopropenyl anion **3** [18] by deprotonating its conjugate acid. Even more recently, we prepared the first long-lived cyclopropenyl anion in the liquid phase [Eq. (2)] [19]. In nearly all of these studies one or more stabilizing substituents have been employed to increase the stability of the cyclopropenyl anion and facilitate its preparation. The gas-phase properties of the parent ion or a simple alkyl derivative of it also are of interest since the destabilizing antiaromatic interaction should be greatest in this case.



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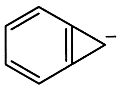

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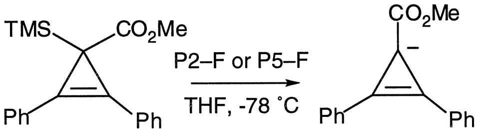
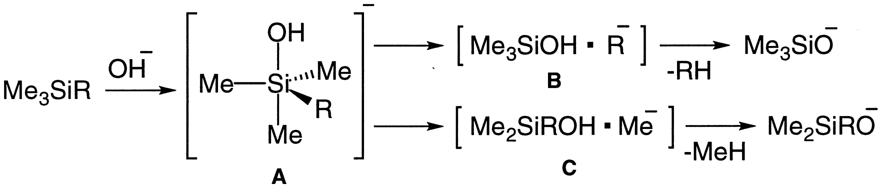


(2)

A variety of ab initio and density functional calculations have been carried out on cyclopropenyl anion [20–31]. While some of the finer points vary with the computational approach, all of the methods (second-order Møller–Plesset perturbation theory (MP2), Gaussian-2 (G2), multiconfiguration self-consistent field (MCSCF), and density functional theory (DFT)) unequivocally indicate that cyclopropenyl anion is a nonplanar ion, an extremely strong base, and unstable with respect to electron detachment (i.e. the anion is predicted to be unbound). This last point makes it highly unlikely that cyclopropenyl anion or its simple alkyl derivatives will be generated using conventional mass spectrometry techniques. An experimental determination of the acidity is not precluded a priori, however, because kinetic methods can be used. The DePuy approach is particularly attractive in this regard since it has been used to measure the acidity of very weak acids whose conjugate bases are unbound [32].

In the DePuy kinetic method, a trimethylsilane (Me_3SiR) is reacted with hydroxide ion to initially form a pentacoordinate siliconate ion (**A**, Scheme 1). This species can expel methyl anion or R^- to afford two different ion/molecule complexes (**B** and **C**) which subsequently decompose to afford trimethylsiloxide (Me_3SiO^-) and RH or Me_2SiRO^- and methane. A plot of the natural logarithm of the statistically corrected Me_3SiO^-/Me_2SiRO^- ratio versus the acidity of RH has been found to be linear and can be used to measure the acidities of unknown acids even in cases where the conjugate base is unbound; R^- can be unstable with respect to electron detachment because it is not formed as a free species.

3-Methyl-3-trimethylsilylcyclopropene (**4**) is an attractive substrate for measuring the acidity of a simple cyclopropene not only because it was available to us [33], but because the methyl group precludes decomposition of the substrate via an ene reaction; cyclopropene and its derivatives, which have an allylic hydrogen on the ring, often are unstable as neat liquids or at room temperature in solution [34]. It also should have little impact as a substituent on the thermodynamic stability of the anion. In this article we report G2+ calculations on methylcyclopropenyl anions and their conjugate acids as well as kinetic experiments aimed at measuring the acidity of the allylic position of 3-methylcyclopropene.



Scheme 1.

2. Experimental

2.1. Gas-phase experiments

All of the gas-phase experiments were carried out with a Finnigan FTMS 2001 mass spectrometer equipped with a 3 T superconducting magnet. Instrument operations such as ion generation, manipulation, and detection, control of the pulse valves, and data analysis were carried out using the ODYSSEY version 4.2 software package. Fluoride and hydroxide ions were generated by electron ionization (6 eV electron energy) of carbontetrafluoride and water, respectively. These ions were allowed to react with 3-methyl-3-trimethylsilylcyclopropene (prepared as described in [33]), 1-butyne or 2-butyne, and the resulting $C_4H_5^-$ ion at *m/z* 53 (calc 53.0397, found 53.0396) was isolated using a stored waveform inverse Fourier transform excitation [35,36]. Reactions of this ion were then followed for variable periods of time. For the DePuy kinetic acidity determination, hydroxide ion was cooled with a pulse of argon up to a nominal pressure of 2×10^{-5} Torr before undergoing reaction with 3-methyl-3-trimethylsilcyclopropene.

2.2. Computational methods

G2 theory and its variants are highly successful empirical additivity schemes in which several smaller calculations are carried out in order to approximate the results of a much larger and more expensive computation [37,38]. In this work we carried out a minor modification of the original G2 and G2+ procedures to afford a modified G2+ energy, which for simplicity sake we will also call G2+. These energies were obtained as follows: Full geometry optimizations were carried out at the MP2(fc)-6-31+G(d) level and then a series of single point energy calculations (MP4(SDTQ)/6-311+G(2df,p), QCISD(T)/6-311+G(d,p), and MP2/6-311+G(3df,2p)) were performed on these structures. The resulting correlation (ΔE(QCI)) and basis set (ΔE(3df,2p)) corrections were obtained [Eqs. (3) and (4)] and combined with a "higher level correction" (ΔE(HLC)) [Eq. (5)], where α and β represent the number of valence electrons in the species of interest. The final G2+ energy is then given by adding in the zero-point energy (ZPE) and thermal correction to 298 K [Eq. (6)], which were obtained from the MP2/6-31+G(d) vibrational frequencies using scaling factors of 0.9427 and 0.9646, respectively [39]; for the radicals that were examined, scaled (0.9135) Hartree–Fock frequencies were used for the ZPE and no thermal correction was made. This sequence of calculations results in an energy effectively corresponding to a QCISD(T)/6-311+G(3df,2p)//MP2(fc)/6-31+G(d) computation.

$$\Delta E(\text{QCI}) = \text{E[QCISD(T)/6-311+G(d,p)]} - E[\text{MP4(SDTQ)/6-311+G(d,p)}] \tag{3}$$

$$\Delta E(\text{3df,2p}) = E[\text{MP2/6-311+G(3df,2p)}] - E[\text{MP2/6-311+G(2df,p)}] \tag{4}$$

$$\Delta E(\text{HLC}) = -0.004891(\beta) + -0.00019(\alpha) \tag{5}$$

$$E(\text{G2+}) = E[\text{MP4(SDTQ)/6-311+G(2df,p)}] + \Delta E(\text{QCI}) + \Delta E(\text{3df,2p}) + \Delta E(\text{HLC}) + \text{ZPE} + \Delta H(298\ \text{K}) \tag{6}$$

All of the calculations reported in this article were carried out with GAUSSIAN94 [40]. They were performed on a series of UNIX-based IBM and SGI workstations at the University of Minnesota and the Minnesota Supercomputer Institute.

3. Results and discussion

3.1. Computations

Deprotonation of 3-methylcyclopropene (**5**) can afford two different cyclopropenyl anions: 3-methyl-3-cyclopropenyl anion (**6**) and 1-methyl-3-cyclopropenyl anion (**7**). Protonation of either of these ions can regenerate 3-methylcyclopropene but also might af-

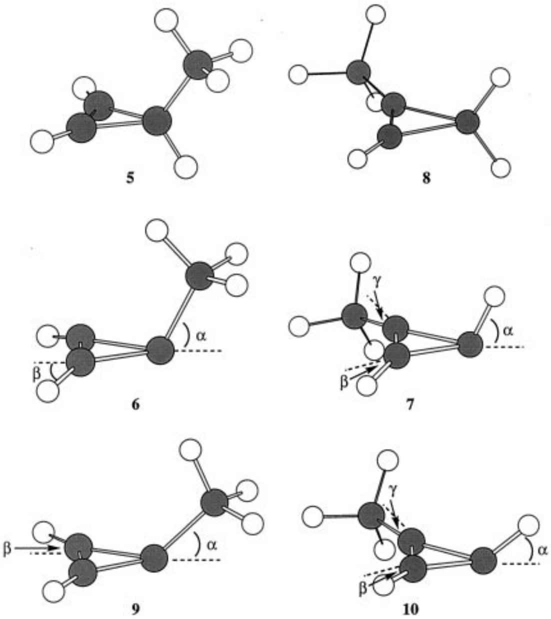


Fig. 1. MP2/6-31+G(d) optimized structures for **5**–**10**.

ford 1-methylcyclopropene (**8**). Loss of an electron from **6** and **7** can give 3-methyl-3-cyclopropenyl (**9**) and 1-methyl-3-cyclopropenyl (**10**) radicals. Therefore, full geometry optimizations and vibrational frequencies were carried out at the HF/6-31+G(d) level on **5**–**10** [41]. Those structures that correspond to energy minima were reoptimized and the Hessian matrixes were recomputed at the MP2(fc)/6-31+G(d) level (Fig. 1 and Table 1).

The ring portions of 3-methylcyclopropene and 1-methylcyclopropene are virtually identical and are in excellent accord with microwave data on cyclopropene (**11**), 3,3-dimethylcyclopropene and 1-methylcyclopropene [42–44]. No experimental results are available for the two radicals (**9** and **10**) or anionic (**6** and **7**) structures, but they are very similar to the computed geometries for 3-cyclopropenyl radical and anion (**12**) [45]. In the anions, all three are pyramidal at the charged center ($\alpha = 63.4$ (**6**), 68.2 (**7**), and 69.2 (**12**)), the vinyl substituents are bent out of the plane of the 3-membered ring in the opposite direction to the hydrogen or methyl group at the anionic site ($\beta =$ 13.0 (**6**), 15.0 and 12.3 (**7**), and 18.0 (**12**)) and the ring single bonds elongate relative to the conjugate acid ($\Delta r = 0.017$ (**6**–**5**), 0.013 and 0.056 (**7**–**8**), and 0.048 (**12**–**11**). These geometric changes minimize the formal interaction between the double bond and the carbon lone pair of electrons (i.e. the antiaromaticity). As for the radicals, they too are pyramidal but the

Table 1
MP2/6-31+G(d) structures for 3-methylcyclopropene (**5**), 1-methylcyclopropene (**8**), 3-methyl-3-cyclopropenyl anion (**6**), 1-methyl-3-cyclopropenyl anion (**7**), 3-methyl-3-cyclopropenyl radical (**9**), and 1-methyl-3-cyclopropenyl radical (**10**).

Parameter	**5** (C_s)[a]	**8** (C_1)[c]	**6** (C_s)[d]	**7** (C_1)	**9** (C_s)[e]	**10** (C_1)
C1–C2	1.308 [1.300]	1.306 [1.300]	1.319 [1.315]	1.287	1.326 [1.324]	1.324
C1–C3	1.509 [1.515]	1.510 [1.515]	1.526 [1.563]	1.523	1.463 [1.463]	1.479
C2–C3	1.509 [1.515]	1.514 [1.515]	1.526 [1.563]	1.570	1.463 [1.463]	1.450
C3(1)–C4	1.516 [1.521][b]	1.479 [1.476]	1.530	1.484	1.500	1.476
C1(2)–H	1.081 [1.070]	1.080 [1.070]	1.087 [1.088]	1.076	1.081 [1.080]	1.082
C3–H	1.095 [1.087]	1.093 [1.087]		1.107		1.093
C4–H_{syn}	1.095 [1.09][b]	1.094 [1.085]	1.122	1.092	1.102	1.093
C4–H	1.096 [1.09][b]	1.096 [1.098]	1.100	1.090, 1.089	1.094	1.096, 1.096
C1–C2–C3	64.3 [64.8]	64.6 [64.8]	64.4 [65.0]	67.3	63.0 [63.0]	64.3
C2–C3(1)–C4	121.5	151.7 [152.5]	113.9	146.7	130.5	151.5
α			63.4 [69.2]	68.2	43.2 [45.2]	45.2
β			13.0 [18.0]	15.0	1.2 [0.6]	4.0
γ				12.3		2.0

[a] Experimental values for cyclopropene are in brackets. See [44].

[b] Geometrical parameter from 3,3-dimethylcyclopropene. See [42].

[c] Experimental values for 1-methylcyclopropene are in brackets. See [43].

[d] MP2/6-31+G(d) geometrical parameters for 3-cyclopropenyl anion are in brackets.

[e] MP2/6-31+G(d) geometrical parameters for 3-cyclopropenyl radical are in brackets.

Table 2
Computed G2+ energies, acidities, and electron affinities for 1- and 3-methylcyclopropene and the corresponding radicals[a]

		ΔH°_{acid}		EA	
Compound	Energy (G2+)	5 →	8 →	9 →	10 →
5	−155.60301				
6	−154.94326	415.5	**418.5**	−1.54	**−4.08**
7	−154.94183	416.4	419.4	−2.38	−4.92
8	−155.60781				
9	−154.95157				
10	−154.95563				

[a] Energies are in hartrees (at 298 K except for **9** and **10** which are at 0 K) while acidities and electron affinities (EAs) are in kcal/mol. Bold values correspond to going from the lowest energy cyclopropene (**8**) or radical (**10**) to the most stable anion (**6**).

pyramidalization angles are smaller (α = 43.2 (**9**) and 45.2 (**10**)) and the carbon–carbon bond lengths are more typical of an allylic system (i.e. the double bonds elongate and the single bonds contract).

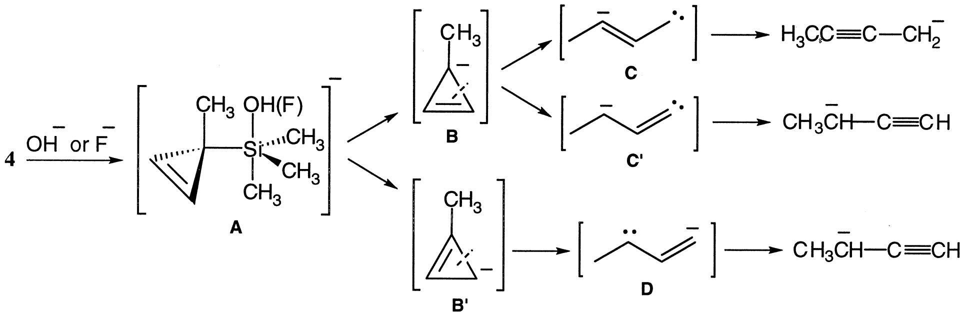
Energetically, 1-methylcyclopropene is predicted to be 3.01 kcal/mol more stable than 3-methylcyclopropene at the G2+ level. This difference is not surprising since the double bond is more substituted in the former compound. Likewise, 1-methyl-3-cyclopropenyl radical (**10**) is found to be 2.54 kcal/mol more stable than 3-methyl-3-cyclopropenyl radical (**9**). 3-Methyl-3-cyclopropenyl anion, on the other hand, is computed to be 0.90 kcal/mol more favorable than 1-methyl-3-cyclopropenyl anion. This reversal is presumably due to the greater polarizability of a methyl group compared to a hydrogen atom and favors having the former substituent at the charged site. Protonation of **6** at the vinyl position (C1) to afford **8** is energetically preferred over formation of **5** and the computed G2+ acidities are 418.5 and 415.5 kcal/mol, respectively (Table 2). These values, as expected, are similar to the calculated acidity of cyclopropene (418.9 (CCSD(T)/6-311+G(2df,2pd)//MCSCF(10(9),9)/6-31+G(d,p), 417.8 (G2), and 418.4 kcal/mol (B3LYP/6-311+G(2df,2pd)//B3LYP/6-31+G(d,p)) [20] and correspond to what should be measured via the DePuy method by using 3-methyl-3-trimethylsilylcyclopropene [46].

Our computational results lead to the prediction that 3-methyl-3-cyclopropenyl anion (**6**), like the parent ion, is among the very strongest bases in the gas phase. It also is predicted to be unstable with respect to electron detachment; the electron affinity of the radical corresponding to **6**(**9**) is −4.08 kcal/mol at the G2+ level, which is similar to the G2 result of −4.2 kcal/mol for the parent species. Computations on unbound anions can pose special challenges, but not typically for closed shell species represented by the restricted formalism as in this case [20,47]. Consequently, conventional mass spectrometry studies on cyclopropenyl anion and its simple alkyl derivatives appear to be precluded.

3.2. Experimental

3-Methyl-3-trimethylsilylcyclopropene reacts with hydroxide ion in a Fourier transform mass spectrometer to afford $C_4H_5^-$ (*m/z* 53, 15%), Me_3SiO^- (*m/z* 89, 69%) and an M −1 ion (*m/z* 125, 100%). To our surprise, after correcting for the double ^{13}C, ^{18}O, and ^{30}Si isotope contributions of the *m/z* 125 ion, little, if any, of the $C_4H_5Si(Me)_2O^-$ ion at *m/z* 127 is observed (≤1.1%). This implies that $\Delta H^\circ_{acid} \leq 393$ kcal/mol for 3-methylcyclopropene since the observed $Me_3SiO^-/C_4H_5Si(Me)_2O^-$ (*m/z* 89/127) ratio is ≥63; methane, benzene, and the α position of naphthalene have acidities of 416.6, 401.7, and 394.2 kcal/mol, respectively, and give statistically uncorrected $Me_3SiO^-/RSi(Me)_2O^-$ ratios of 1, 8, and 34 [48]. The formation of the $C_4H_5^-$ ion is consistent with an acidity of ≤400 since trimethylsilyl derivatives of less acidic compounds do not react with hydroxide ion to afford $(M–TMS)^-$ ions. These results strongly contrast with our G2+ calculations and the measured proton affinity of **1** (391 kcal/mol) [16] and suggest that a rearrangement to a more stable anion occurs *simultaneously* with the expulsion of the $C_4H_5^-$ ion from the pentacoordinate siliconate anion **A** shown in Scheme 1 [49]. If the isomerization took place after the formation of **B** it would not effect the $Me_3SiO^-/RSi(Me)_2O^-$ ratio and hence the acidity. As for the driving force of this rearrangement, strain relief and the elimination of an antiaromatic system must play a large role.

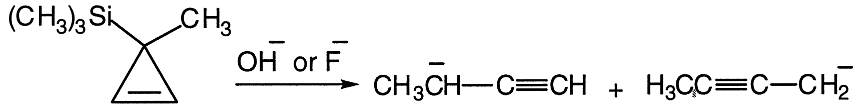
In order to explore the structure of the $C_4H_5^-$ ion it



Scheme 2.

was generated by desilylating 3-methyl-3-trimethylsilylcyclopropene with hydroxide or fluoride ion and its reactivity was examined. Both procedures lead to the same results, but the latter route gives more of the (M–TMS)$^-$ anion. In either case, deuterium oxide induces two hydrogen–deuterium exchanges, whereas methanol–OD reacts to afford methoxide ion. This behavior is inconsistent with a 3-cyclopropenyl anion (a more stable derivative **1** is capable of deprotonating water) [16] and the conjugate bases of a cyclopropene at the vinyl position, methylenecyclopropane, cyclobutene and 1,3-butadiene [50], but is in accord with the reported behavior of propargylic anions derived from 1- and 2-butyne (i.e., $\mathrm{CH_3^-CHC{\equiv}CH}$ (**13**) and $\mathrm{CH_3C{\equiv}CCH_2^-}$ (**14**)) [51]. DePuy et al. have shown that ions of this type undergo characteristic fragmentations upon reaction with carbon disulfide and that **13** and **14**, in particular, afford thioketene enolate ($\mathrm{HC{\equiv}C{-}S^-}$, *m/z* 57) and methylthioketene enolate ($\mathrm{CH_3C{\equiv}C{-}S^-}$, *m/z* 71), respectively [52–54]. Both of these products are formed in a 1 (**13**): 4 (**14**) ratio when the $\mathrm{C_4H_5^-}$ ion is reacted with carbon disulfide. These results indicate that 3-methyl-3-trimethylsilylcyclopropene reacts with hydroxide or fluoride ion to afford both **13** and **14** [Eq.(7)]. A reasonable pathway for their formation is illustrated in Scheme 2 where structures **B** and **B′** are provided for illustrative purposes only [55–58]; we do not mean to indicate that the cyclopropenyl anions are reaction intermediates, rather we believe that **A** rearranges directly to **C**, **C′** and/or **D**.

The predicted instability of cyclopropenyl anion with respect to electron detachment and the failure of our kinetic experiments to provide the acidity of 3-methylcyclopropene raises the question: Can the gas-phase acidity of cyclopropene or its simple alkyl derivatives be measured? Equilibrium, bracketing, and energy-resolved dissociation methods are precluded because of the instability of the anions with respect to electron loss. The failure of the DePuy kinetic method, which previously has been applied successfully to unbound species (e.g. ethyl, propyl and *tert*-butyl anions) [32], calls into question other kinetic approaches. Therefore, at this time, using conventional means, the answer to the question appears to be no. It is possible to measure electron affinities of unbound species, however, using electron transmission spectroscopy [59,60]. While this technique has not been used on radicals to the best of our knowledge, there is no inherent reason it could not be. By measuring the (negative) electron affinity of 3-cyclopropenyl radical and redetermining the radical's heat of formation (the experimental value reported by DeFrees et al. has been called into question. For



4 **13** **14** (7)

further details see [20] and references therein), one could derive the acidity of cyclopropene via the application of a thermodynamic cycle.

4. Conclusions

The G2+ acidity of 3-methylcyclopropene has been calculated. The corresponding anions (**6** and **7**) are predicted to be among the strongest bases in the gas phase and are computed to be unstable with respect to electron loss. A kinetic determination of the acidity of 3-methylcyclopropene using 3-methyl-3-trimethylsilylcyclopropene failed because of a surprising rearrangement which leads to the formation of the propargyl anions derived from 1- and 2-butyne (**13** and **14**, respectively). A reasonable mechanism based upon literature precedent on neutral cyclopropenes has been proposed. While this failure of a kinetic method suggests that conventional mass spectrometry will be unsuitable for measuring the acidity of cyclopropene or its simple alkyl derivatives, a thermodynamic cycle that includes the negative electron affinity of 3-cyclopropenyl radical could be employed to obtain this quantity.

Acknowledgements

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