# Kinetic and Theoretical Studies of the Hydration of Carbon Suboxide

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Hydration rates in H_2O of carbon suboxide are substantial but less than those of ketene, by factors of 2.5 × 10^3 and 5.2 × 10^4 for the neutral and acid-catalysed reactions, respectively, in qualitative agreement with ab initio calculated stabilities of probable intermediates.

Carbon suboxide 1 was first reported by Diels and Wolf in 1906,[1a] and it has been widely studied since that time.[1b–g,2,3] There have, however, been few quantitative mechanistic studies of this unique polyfunctional molecule.

We and others have been pursuing the study of 1,2-bis(ketenes),[4] and the hydration of ketenes,[1g,5] and therefore were attracted to the study of the reaction of carbon suboxide with H_2O. A recent proposal,[6a] that C_3O_2 is present on comet Halley, which is largely composed of water ice,[6a] increased our interest in this subject. Carbon suboxide is known to react with water to form $CH_2(CO_2H)_2$, with alcohols ROH to form esters $CH_2(CO_2R)_2$, and with HCl to form $CH_2(COCl)_2$.[2c] As shown in eqn. (1) for alcohol addition acylketenes 2 have been implicated as reactive intermediates in these reactions.[1d,e,2d]

$$O=C=C=C=O \xrightarrow{ROH} RO_2CCH=C=O \xrightarrow{ROH} CH_2(CO_2R)_2$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

(1)
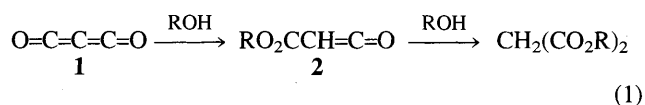
Rate constants were measured for reaction of 1 in H_2O by monitoring the decrease of the UV absorption maximum at 260 nm ($\varepsilon = 90$ dm^3 mol^{-1} cm^{-1})[3b] (Table 1). Only a single rate process was observed in each case, and this is assigned to the initial reaction of carbon suboxide.

To interpret the mechanisms involved the structures and energies of some of the possible intermediates were calculated by ab initio methods using Gaussian 92[7] at the MP2/6-31G* + ZPVE//MP2/6-31G* level, as we have done previously for other ketenes.[4b,c] The geometries of the possible species involved were fully optimized at the level specified without geometrical constraints. Energies for a number of different possible transformations are given in Table 2.

The rate constant of C_3O_2 in 55.6 mol dm^{-3} neutral water (Table 1) is less by a factor of 2.5 × 10^3 than that reported[8a] for of $CH_2=C=O$. In H_2O–MeCN (1:9) this factor drops to 60.3, reflecting a greater decrease in the reactivity of $CH_2=C=O$ on dilution with MeCN.[5b,8b] The isotope effects k_{H_2O}/k_{D_2O} for the neutral reaction are similar, 2.20 and 1.59[8a] for C_3O_2 and ketene, respectively. These results may suggest similar mechanisms for the neutral hydrations of ketene and C_3O_2, and in our

previous studies of ketene reactivity[1g,5a–c] the mechanism of ketene hydration has been interpreted as involving an initial nucleophilic attack by H_2O at the carbonyl carbon to give a rather polar transition state resembling 3, that is also solvated by additional water molecules. This forms an intermediate enediol 4, or the corresponding enolate, and then is rapidly converted to acetic acid (Scheme 1).

The addition of H_2O to C_3O_2 could occur by 1,2-addition to the C=O or C=C bonds to produce as the first intermediate the geminal diol $(HO)_2C=C=C=O$ 5 or the ketenyl carboxylic acid $HO_2CCH=C=O$ 6, and a 1,4-addition would yield hydroxypropynoic acid $HO_2CC≡COH$ 7. These species would be at least partly ionized under the reaction conditions.

From Table 2 the gas-phase hydration of C_3O_2 and ketene on the C=O bond to form enediols is calculated to have ΔE of 41.4 and −25.1 kJ mol^{-1}, respectively, while addition to the C=C bond to form $HO_2CCH=C=O$ and $MeCO_2H$ have ΔE of −98.3

Table 2 MP2/6-31G* + XPVE//MP2/6-31G* calculated energies (kJ mol^{-1}) for reactions of carbon suboxide and ketene

Reaction	ΔE/kJ mol^{-1}
$O=C=C=C=O + H^+ \rightarrow O=C=C=C=OH^+$	−627.6
$O=C=C=C=O + H^+ \rightarrow O=C=CH-\overset{+}{C}=O$ 8	−765.3
$CH_2=C=O + H^+ \rightarrow CH_2=C=OH^+$	−620.1
$CH_2=C=O + H^+ \rightarrow Me\overset{+}{C}=O$	−833.5
$O=C=C=C=O + H_2O \rightarrow (HO)_2C=C=C=O$ 5	41.4
$O=C=C=C=O + H_2O \rightarrow HO-C≡C-CO_2H$ 7	82.0
$O=C=C=C=O + H_2O \rightarrow HO_2CCH=C=O$ 6	−98.3
$(HO)_2C=C=C=O$ 5 $\rightarrow HO_2CCH=C=O$ 6	−139.7
$HO-C≡C-CO_2H$ 7 $\rightarrow HO_2CCH=C=O$ 6	−179.9
$HO_2CCH=C=O$ 6 + $H_2O \rightarrow HO_2CCH=C(OH)_2$	−84.5
$CH_2=C=O + H_2O \rightarrow CH_2=C(OH)_2$	−25.1
$CH_2=C(OH)_2 \rightarrow MeCO_2H$	−148.1
$HO_2CCH=C(OH)_2 \rightarrow CH_2(CO_2H)_2$	−51.5
$O=C=C=C=O + OH^- \rightarrow {}^-O-C≡C-CO_2H$	−260.2
${}^-O-C≡C-CO_2H \rightarrow HO-C≡C-CO_2{}^-$	132.8
${}^-O-C≡C-CO_2H \rightarrow O=C=CH-CO_2{}^-$	−46.9
$CH_2=C=O + OH^- \rightarrow CH_2=C(OH)O^-$	−316.3
$CH_2=C(OH)O^- \rightarrow CH_3CO_2{}^-$	−128.4

Table 1 Hydration rates of C_3O_2 in H_2O–MeCN, and acid catalysis, 25 °C

% H_2O[a]	[H_2O]/mol dm^{-3}	k_{obs}[b]/s^{-1}	[HCl][c]/mol dm^{-3}	k_{obs}/s^{-1}	[DCl][d]/mol dm^{-3}	k_{obs}
100	55.6	1.45 × 10^{-2e}	0.989	2.00 × 10^{-1}	0.968	1.63 × 10^{-1}
100f		6.59 × 10^{-3}	0.791	1.77 × 10^{-1}	0.774	1.28 × 10^{-1}
90	50.0	1.81 × 10^{-1}	0.593	1.32 × 10^{-1}	0.581	1.12 × 10^{-1}
80	44.4	1.77 × 10^{-2}	0.395	9.80 × 10^{-2}	0.194	3.88 × 10^{-2}
70	38.9	2.26 × 10^{-2}	0.198	6.14 × 10^{-2}	0.0	6.76 × 10^{-3}
60	33.3	2.47 × 10^{-2}	0.0988	2.14 × 10^{-2}		
50	27.8	2.22 × 10^{-2}	0.0	1.20 × 10^{-2}		
40	22.2	1.86 × 10^{-2}				
30	16.7	1.44 × 10^{-2}				
20	11.1	1.12 × 10^{-2}				
10	5.56	4.48 × 10^{-3}				
2	1.11	1.91 × 10^{-4}				

[a] The noted volume of H_2O (ml) was diluted to 100 ml with MeCN. [b] Monitored by observing the decrease in the absorption at 260 nm. [c] In H_2O at $I = 1.00$ (NaCl); $k_{obs} = 0.195$ dm^3 mol^{-1} s^{-1} [HCl] + (1.61 × 10^{-2}) s^{-1}, $r = 0.996$. [d] In D_2O at $I = 1.00$ (NaCl); $k_{obs} = 0.161$ dm^3 mol^{-1} s^{-1} [DCl] + (8.78 × 10^{-3}) s^{-1}, $r = 0.996$; $k_{H^+}/k_{D^+} = 1.21$. [e] k_{obs} 3.55 × 10^{-2} s^{-1} (36.8 °C), 2.28 × 10^{-3} (4.9 °C), $\Delta H^‡ = 59.4$ kJ mol^{-1}, $\Delta S^‡$ −80.8 J K^{-1} mol^{-1}. [f] D_2O, $k_{H_2O}/k_{D_2O} = 2.20 \pm 0.30$.

and -173.2 kJ mol^{-1}, respectively. The reversible hydration of $CH_2=C=O$ to acetic acid has been repeatedly examined by theoretical[9a–e] and experimental methods,[9f] and our results agree with recent results for comparable levels.[9d,e] For both C_3O_2 and $CH_2=C=O$ addition of H_2O to the $C=C$ bond is calculated to give more stable products than addition to the $C=O$ bond, by similar factors of 139.7 and 148.1 kJ mol^{-1}, respectively (Table 2). However for $CH_2=C=O$ addition of H_2O to the $C=O$ bond is nevertheless predicted to have a lower barrier,[9] and this has also been found experimentally in solution.[1g,5,8a] Even though the transition states for hydration of C_3O_2 have not yet been successfully calculated for the gas phase and especially not for solution, it appears plausible that just as for ketene the initial step involves addition to the $C=O$ bond to form the enediol 5, even though addition to the $C=C$ bond, which involves simultaneous rehybridization of both carbons, leads to a more stable product.

The reaction of OH^- with C_3O_2 in the gas phase has been studied using a flowing afterglow apparatus,[3d] and has been interpreted as involving formation of $-O(HO)C=C=C=O$, which then rearranges to $-O_2CCH=C=O$, which cleaves to CO_2 and $HC\equiv C-O-$. The first two steps of this process are analogous to those suggested here for the successive formation of $(HO)_2C=C=C=O$ 5 and $HO_2CCH=C=O$ 6. We calculate (Table 2) that these steps are exothermic by 260.2 and 46.9 kJ mol^{-1}, respectively.

For the reaction of C_3O_2 in dilute HCl, the linear dependence on $[H^+]$ of the rate, and the isotope effect $k_{H^+}/k_{D^+} = 1.21$, are both consistent with a mechanism involving rate-limiting proton transfer to $C\beta$ (Scheme 2), as has been proposed for other ketenes.[5a–d] The value of k_{H^+} for C_3O_2 is less by a factor of 5.2 $\times$ 10^4 than that reported[8a] for $CH_2=C=O$, in agreement with the theoretical results (Table 2). Protonation at $C\beta$ in C_3O_2 would be favoured by the high negative charge density at this carbon, as indicated by the ^{13}C NMR chemical shift of δ -14.6,[3a] and by the favourable bisacylium type resonance expected for this species, as shown in 8. Whether or not 8 would have a sufficient lifetime to exist as a genuine intermediate under the conditions is a question that cannot be answered by the current experiments.

These results are relevant to a recent proposal[6a] that photolysis of C_3O_2 is the source of atomic carbon in the coma and nucleus material of comet Halley. Our results establish the

temperature dependence of the reactivity of C_3O_2 with liquid water, but do not yet address the call for 'experiments to assess the chemical stability of C_3O_2 in a H_2O ice matrix'.[6a]

In summary C_3O_2 shows appreciable neutral and acid-catalysed reaction rates with H_2O, although $CH_2=C=O$ is significantly more reactive. *Ab initio* molecular orbital calculations are in agreement with these results. This reactivity is relevant to a proposal that C_3O_2 is present in the water ice of comet Halley. Further studies, including examination of the reaction of C_3O_2 with bases, are underway.

Scheme 1

Scheme 2

References

1 (a) O. Diels and B. Wolf, *Chem. Ber.*, 1906, **39**, 689, (b) H. Staudinger and S. Bereza, *Chem. Ber.*, 1908, **41**, 4462; (c) H. Ulrich, *Cycloaddition Reactions of Heterocumulenes*, Academic, New York, 1967, ch. 3, pp. 110–121; (d) T. Kappe and E. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 491; (e) T. Kappe, in *Methoden der Organischen Chemie*, Thieme, Stuttgart, 1993, vol. 15E; (f) D. Borrmann, in *Methoden der Organischen Chemie*, Thieme, Stuttgart, 1968, vol. 7/4; (g) T. T. Tidwell, *Ketenes*, Wiley, New York, 1995.

2 (a) L. Birkofer and P. Sommer, *Chem. Ber.*, 1976, **109**, 1701; (b) U. Schmidt and M. Schwochau, *Monatsh. Chem.*, 1967, **98**, 1492; (c) G. Hagelloch and E. Feess, *Chem. Ber.*, 1951, **84**, 730; (d) H. Binder and W. Lindner, *J. Chromatogr.*, 1973, **77**, 323.

3 (a) E. A. Williams, J. D. Cargioli and A. Ewo, *J. Chem. Soc., Chem. Commun.* 1975, 366; (b) K. D. Bayes, *J. Am. Chem. Soc.*, 1962, **84**, 4077; (c) K. Conrow and D. L. Morris, *J. Chem. Soc., Chem. Commun.*, 1973, 5; (d) C. R. Roberts and C. H. DePuy, *Zh. Obshch. Chem.*, 1989, **59**, 2153; *Engl. Transl.*, 1989, **59**, 1931.

4 (a) D.-c. Zhao, A. D. Allen and T. T. Tidwell, *J. Am. Chem. Soc.*, 1993, **115**, 10097; (b) A. D. Allen, J. Ma, M. A. McAllister, T. T. Tidwell and D.-c. Zhao, *Acc. Chem. Res.*, 1995, **28**, 265; (c) M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc.*, 1994, **116**, 7233; (d) A. D. Allen, J. Ma, M. A. McAllister, T. T. Tidwell and D.-c. Zhao, *J. Chem. Soc., Perkin Trans. 2*, 1995, 847.

5 (a) T. T. Tidwell, *Acc. Chem. Res.*, 1990, **23**, 273; (b) A. D. Allen and T. T. Tidwell, *J. Am. Chem. Soc.*, 1987, **109**, 2774; (c) A. D. Allen, M. A. McAllister and T. T. Tidwell, *Tetrahedron Lett.*, 1993, **34**, 1095; (d) J. Andraos, A. J. Kresge and N. P. Schepp, *Can. J. Chem.*, 1995, **73**, 539; (e) M. Birney and P. E. Wagenseller, *J. Am. Chem. Soc.*, 1994, **116**, 6262.

6 (a) W. T. Huntress, Jr., M. Allen and M. Delitsky, *Nature*, 1991, **352**, 316; (b) C. E. M. Strauss, S. H. Kable, G. K. Chawla, P. L. Houston and I. R. Burak, *J. Chem. Phys.*, 1991, **94**, 1837.

7 Gaussian 92, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.

8 (a) J. Andraos and A. J. Kresge, *J. Photochem. Photobiol. A: Chem.*, 1991, **57**, 165; (b) E. Bothe, A. M. Dessouki and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1980, **84**, 3270.

9 (a) M. T. Nguyen and A. F. Hegarty, *J. Am. Chem Soc.*, 1984, **106**, 1552; (b) J. Andraos, A. J. Kresge, M. R. Peterson and I. G. Csizmadia, *J. Mol. Struct. (Theochem)* 1991, **232**, 155; (c) P. N. Skancke, *J. Phys. Chem.*, 1992, **96**, 8065; (d) X. Duan and M. Page, *J. Am. Chem. Soc.*, 1995, **117**, 5114; (e) M. T. Nguyen, D. Sengupta, G. Raspoet and L. C. Vanquickenborne, *J. Phys. Chem.*, 1995, **99**, 11883; (f) N. I. Butkovskaya, G. Manke, II and D. W. Setser, *J. Phys. Chem.*, 1995, **99**, 11115.