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The Trichloromethide and Bromodichloromethide Carbanions

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ABSTRACT

$$:CCl_2 + Br^- \underset{k_{-1} = 2.1 \times 10^6\ M^{-1}s^{-1}}{\overset{k_1 = 2.1 \times 10^7\ M^{-1}s^{-1}}{\rightleftharpoons}} CCl_2Br^-$$

388 nm

Reactions of photochemically generated dichlorocarbene with chloride or bromide ions afford trichloromethide or bromodichloromethide carbanions, the central intermediates in the classical base-catalyzed generation of dichlorocarbene from haloforms.

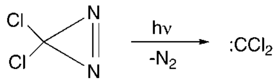
Sixty years ago, Hine established the intermediacy of “carbon dichloride” (dichlorocarbene, CCl_2) in the basic hydrolysis of chloroform.[1,2] His preferred mechanism, eqs 1−3, featured the rapid, reversible formation of trichloromethide carbanion (CCl_3^-), followed by rate-determining scission of CCl_3^- into CCl_2 and chloride ion.[1] Subsequently, Hine found that bromide and iodide ions could trap CCl_2 to form CCl_2Br^- and CCl_2I^- trihalomethide carbanions, which then gave the corresponding haloforms upon protonation.[3] Conversely, a variety of trihalomethide carbanions, $CXYZ^-$, was obtainable by the deprotonation of haloforms.[4]

$$CHCl_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CCl_3^- + H_2O \tag{1}$$

$$CCl_3^- \xrightarrow{\text{slow}} :CCl_2 + Cl^- \tag{2}$$

$$:CCl_2 \xrightarrow[H_2O]{OH^-\text{, fast}} CO + HCO_2^- \tag{3}$$

Our ability to photochemically generate CCl_2 from the spectroscopy-friendly precursor dichlorodiazirine [**1** in eq 4],[5] now allows us to conveniently study the *reverse* of eq 2, i.e., the reaction of CCl_2 with chloride (or other halides). Here we describe the reactions of CCl_2 with chloride and bromide ions as studied by laser flash photolysis (LFP), providing the first UV spectroscopic evidence for the generation of CCl_3^- and CCl_2Br^-.



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(4)

LFP of **1** at 351 nm in a solution of 0.9 M tetrabutylammonium chloride (TBACl) in 1:1 CH_2Cl_2−MeCN under nitrogen afforded a weak absorption at 328 nm (see Figure S-1 in the Supporting Information). The spectrum was reproducible, and the 328 nm signal was absent in a control experiment that omitted diazirine **1**. We assign the 328 nm absorption to the trichloromethide anion (CCl_3^-), which is computed to absorb at 344 nm in simulated MeCN, cf. Table 1.[6]

The stronger, more easily studied signal for bromodichloromethide carbanion (CCl_2Br^-) appears upon LFP of **1** in 0.6 M TBABr in 1:1 CH_2Cl_2−MeCN under nitrogen. The spectrum recorded 50 ns after the laser flash is shown in

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(1) Hine, J. *J. Am. Chem. Soc.* **1950**, *72*, 2438.
(2) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964; p 36f.
(3) Hine, J.; Dowell, A. M., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2688.
(4) (a) Hine, J.; Burske, N. W.; Hine, M.; Langford, P. B. *J. Am. Chem. Soc.* **1957**, *79*, 1406. (b) Hine, J.; Ehrenson, S. J. *J. Am. Chem. Soc.* **1958**, *80*, 824. (c) Hine, J.; Langford, P. B. *J. Am. Chem. Soc.* **1957**, *79*, 5497.
(5) Moss, R. A.; Tian, J.; Sauers, R. R.; Ess, D. H.; Houk, K. N.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2007**, *129*, 5167.

(6) Details of the calculations appear in the Supporting Information. The PBE/6-311+G(d) combination of exchange-correlation functionals and basis sets has shown excellent performance for the analysis of weak carbene−solute or carbene−solvent interactions, whereas the electronic transition spectra are modeled better with the B3LYP exchange-correlation functionals. The mixed computational scheme involving TD-B3LYP/6-311+G(d) excited state calculations on PBE/6-311+G(d) optimized ground state geometries combines advantages of both approaches. For examples of previous usage, see (e.g.) ref 5 and: Moss, R. A.; Wang, L.; Weintraub, E.; Krogh-Jespersen, K. *J. Phys. Chem. A* **2008**, *112*, 4651.

10.1021/ol902479x

Table 1. Computed Absorptions and Thermochemistry of Some Trihalomethide Carbanions[a]

process	λ[b,c]	f[d]	ΔH[e]	ΔG[e]
$CCl_2 + Cl^- \rightarrow CCl_3^-$	344	0.025	−8.4	−3.0
$CCl_2 + Br^- \rightarrow CCl_2Br^-$	376	0.036	−7.7	−2.5
$CCl_2Br^- + Br^- \rightarrow CClBr_2^- + Cl^-$	401[f]	0.026	0.6	0.5
$CFCl + Cl^- \rightarrow CFCl_2^-$	291	0.083	−5.4	0.2
$CFCl + Br^- \rightarrow CFClBr^-$	324	0.113	−4.9	0.5
$CF_2 + Cl^- \rightarrow CF_2Cl^-$	295	0.068	−0.7	3.6
$CF_2 + Br^- \rightarrow CF_2Br^-$	303	0.257	−1.0	3.5

[a] Complete details of the calculations appear in the Supporting Information. [b] TD-DFT calculations employed B3LYP/6-311+G(d) on PBE/6-311+G(d) optimized geometries and the CPCM continuum model with simulated acetonitrile solvent.[6] [c] Absorption wavelengths in nm. The transition involves electron excitation from the carbon lone pair into a delocalized antibonding carbon−halogen bond orbital ($n \rightarrow \sigma^*$). [d] Oscillator strength of electronic transition (dimensionless). [e] Reaction enthalpies and free energies (in kcal/mol) computed at the PBE/6-311+G(d) level with geometries optimized using the CPCM continuum model and simulated acetonitrile solvent. [f] Absorption by $CClBr_2^-$.

Figure 1. We assign the dominant absorption at 388 nm to CCl_2Br^-, which is calculated to absorb at 376 nm in MeCN (Table 1).[7] The shoulder visible at 404 nm could be dibromochloromethide carbanion ($CClBr_2^-$), computed to absorb at 401 nm, cf. Table 1. The absorptions at 388 and 404 nm persist over 1500 ns (see Figures S-2 and S-3 in the Supporting Information).

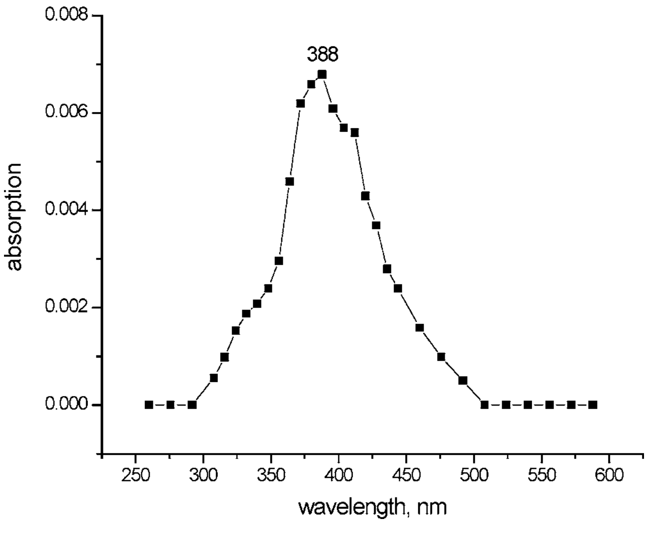

Figure 1. UV−vis spectrum acquired 50 ns after LFP of dichlorodiazirine ($A = 0.37$) with 0.6 M TBABr in 1:1 CH_2Cl_2−MeCN under N_2; absorption by CCl_2Br^- is at 388 nm.

A more tentative assignment for the weak shoulder visible at ∼330 nm in Figure 1 is CCl_3^- (328 nm, see above and Figure S-1 in the Supporting information), which could arise by reaction of CCl_2 with Cl^- released from CCl_2Br^- during the latter's conversion to $CClBr_2^-$.[8] However, the shoulder at 330 nm decays after 200 ns (see Figures S-2 and S-3 in the Supporting Information).

CCl_3^- and CCl_2Br^- are obtainable by thermodynamically favorable additions of Cl^- or Br^- to CCl_2 (cf. Table 1), whereas $CClBr_2^-$ can arise via a slightly endothermic exchange of CCl_2Br^- with excess Br^-.[8] On the other hand, we did not observe additions of Cl^- or Br^- to CClF[9] to afford $CFCl_2^-$ or $CFClBr^-$. These carbanions have been implicated in deuterium exchange reactions of the appropriate haloforms,[4a,10] but their formation from CClF is computed to be mildly uphill in terms of free energy (although enthalpically favorable), cf. Table 1. Given these negative results, we did not attempt the additions of Cl^- or Br^- to CF_2,[11] where the free energy of formation of CF_2Cl^- or CF_2Br^- is computed to be much more unfavorable (Table 1), and the carbanions are very unstable relative to reversion to CF_2.[4c]

The second order rate constant for the formation of CCl_2Br^- from CCl_2 and Br^- was determined as 2.08×10^7 M^{-1} s^{-1} from the slope of a correlation of the observed rate constants for the rise of CCl_2Br^- (measured at 380 nm) vs. the concentration of Br^- (as TBABr), cf. Figure S-4 in the Supporting Information. Carbanion CCl_2Br^- can be quenched by acrylonitrile (ACN), yielding the Michael addition carbanion **2**, which closes to 1-cyano-2,2-dichlorocyclopropane (**3**)[12] with the loss of bromide, cf. Scheme 1. We did not detect 1-cyano-2-bromo-2-chlorocyclopropane in the product mixture, but this material is somewhat unstable to the GC conditions.

The rate constant for the addition of CCl_2Br^- to ACN was determined from LFP experiments with diazirine **1** in the presence of 0.72 M TBABr and *variable* quantities of ACN in 1:1 CH_2Cl_2−MeCN. A correlation of k_{obs} for the *decay* of the CCl_2Br^- absorbance at 380 nm vs. the concentration of ACN appears in Figure 2, where the slope of the correlation line (4.07×10^6 M^{-1} s^{-1}) is taken as the rate constant k_4 in Scheme 1.[13]

Generally,[14] although not always,[15] CCl_2 behaves as an electrophile in additions to alkenes; for example, its addition to electron-poor ACN is much slower than that to cyclohexene. The absolute rate constants for these additions at 24 °C are 6.4×10^7 (for cyclohexene) and 4.9×10^5 M^{-1} s^{-1} (for ACN[15]), and the relative rate constant for ACN vs. cyclohexene is $k_{rel} = 4.9 \times 10^5/6.4 \times 10^7 = 7.7 \times 10^{-3} =$

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(7) The intensity of CCl_2Br^- ($f = 0.036$) is computed to be stronger than that of CCl_3^- ($f = 0.025$); cf. Table 1.

(8) This exchange could involve prior loss of Cl^- from CCl_2Br^- affording: CClBr, followed by reaction of the new carbene with Br^-.

(9) Moss, R. A.; Tian, J.; Sauers, R. R.; Skalit, C.; Krogh-Jespersen, K. *Org. Lett.* **2007**, *9*, 4053.

(10) Hine, J.; Butterworth, R.; Langford, P. B. *J. Am. Chem. Soc.* **1958**, *80*, 819.

(11) Moss, R. A.; Wang, L.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2009**, *131*, 2128.

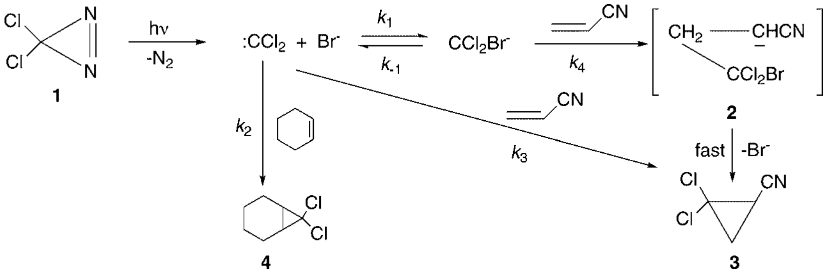
(12) Cyclopropane **3** was identified by capillary GC comparison with an authentic sample.

(13) The addition of CCl_2Br^- to acrylonitrile is assumed to be rate determining; the closure of Michael carbanion **2** is taken to be fast.

(14) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

(15) Moss, R. A.; Zhang, M.; Krogh-Jespersen, K. *Org. Lett.* **2009**, *11*, 1947.

Scheme 1. Reactions of Dichlorocarbene and Bromodichloromethide Carbanion



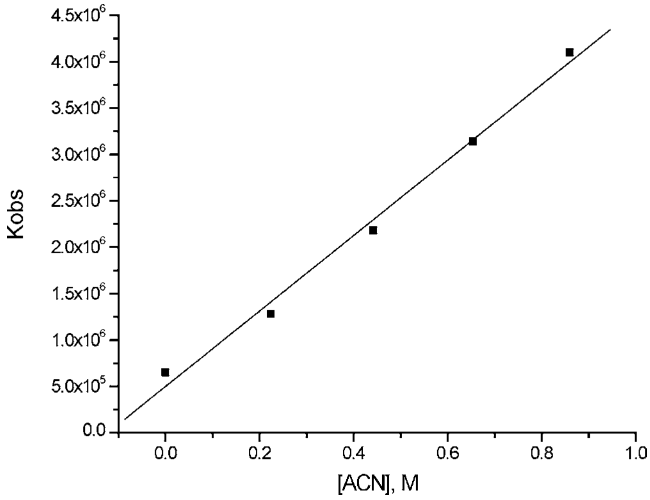


Figure 2. Observed rate constants (s^{-1}) for the quenching of CCl_2Br^- at 380 nm by acrylonitrile (M) in the LFP of diazirine **1** with 0.72 M TBABr in 1:1 CH_2Cl_2−MeCN; k_q ($=k_4$, see below) $= 4.07 \times 10^6$ M^{-1} s^{-1}; $r = 0.996$.

1/129.5.[15,16] However, the slow additions of electrophilic carbenes to electron-poor alkenes can be catalyzed by bromide ion: addition of Br^- to an electrophilic carbene affords a nucleophilic carbanion capable of rapid (though rate-determining) Michael addition to the electron-poor alkene. Ring closure with loss of Br^- then yields the same cyclopropane that would form in a direct addition of the carbene.

This catalytic process is illustrated in Scheme 1, and by analogous results in the bromide-assisted additions of phenylhalocarbenes to ACN.[17] In these latter examples, rate accelerations of 14−28 are observed for the bromide-catalyzed additions (of $PhCXBr^-$) to ACN, relative to direct carbenic additions of PhCX.[17] We find a comparable acceleration in the assisted addition of CCl_2 to ACN: k_{rel} for the competitive addition of CCl_2 to ACN vs. cyclohexene increases from 0.0077 in the direct addition[15] to 0.18 (±0.016 for two determinations) in the presence of 0.28 M TBABr, a 23-fold enhancement.

Scheme 1 depicts the competing pathways in unassisted and bromide-assisted additions of CCl_2 to cyclohexene and ACN. Here, LFP of diazirine **1** affords CCl_2, which either combines with Br^-, affording CCl_2Br^- ($k_1 = 2.1 \times 10^7$ M^{-1} s^{-1}), adds to cyclohexene, giving 7,7-dichloronorcarane **4** ($k_2 = 6.4 \times 10^7$ M^{-1} s^{-1}),[9] or adds to ACN, yielding cyclopropane **3** ($k_3 = 4.9 \times 10^5$ M^{-1} s^{-1}).[15] Carbanion CCl_2Br^- can either revert to CCl_2 (k_{-1}) or add to ACN affording carbanion **2** ($k_4 = 4.1 \times 10^6$ M^{-1} s^{-1}, see above), which rapidly closes to cyclopropane **3**.

With these absolute rate constants, and our observation that the apparent value of k_3/k_2 is 0.18 in the presence of 0.28 M bromide ion, we can estimate that $K = k_1/k_{-1} \approx 10$ M^{-1} in Scheme 1[18] This value for the equilibrium constant that governs the interconversion of CCl_2 and CCl_2Br^- leads to $k_{-1} \approx 2.1 \times 10^6$ s^{-1} for the reversion of CCl_2Br^- to CCl_2 and Br^-.[19] Another estimate of k_1/k_{-1} derives from the computed ΔG (−2.48 kcal/mol) for this equilibrium (Table 1), which leads to $K \approx 66$ M^{-1} and $k_{-1} \approx 3.0 \times 10^5$ s^{-1} at 25 °C.

In conclusion, reactions of photochemically generated CCl_2 with chloride or bromide ions afforded the trihalomethide carbanions CCl_3^- and CCl_2Br^-, the central intermediates in the classical base-catalyzed generation of dichlorocarbene from haloforms.[1−4] The kinetics of the reactions of CCl_2 with Br^-, and of CCl_2 and CCl_2Br^- with cyclohexene and acrylonitrile were analyzed and absolute rate constants were determined. The "slow" addition of electrophilic CCl_2 to electron-poor acrylonitrile could be catalyzed by bromide ion.

Acknowledgment. We are grateful to the National Science Foundation and the Petroleum Research Fund for financial support.

Supporting Information Available: Figures S-1−S-4, estimate of k_1/k_{-1}, NMR spectra of cyclopropanes **3** and **4**, and details of the computations that generated the data in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) See Table S-2 in the Supporting Information of ref 15.

(17) (a) Moss, R. A.; Tian, J. *J. Am. Chem. Soc.* **2005**, *127*, 8960. (b) Moss, R. A.; Tian, J. *Org. Lett.* **2006**, *8*, 1245. (c) Moss, R. A.; Tian, J. *Tetrahedron Lett.* **2006**, *47*, 3419.

(18) See the Supporting Information for details of this estimate.

(19) For a discussion of trihalomethide reversion reactions in water, see ref 4b. Loss of Br^- from CCl_2Br^- should be considerably faster than loss of Cl^-.