$$\begin{array}{lr}
Al_4C_3 + 6O_2 = 2Al_2O_3 + 3CO_2 & \Delta H = -824{,}000 \\
4Al + 3O_2 = 2Al_2O_3 & -760{,}400 \\
C + O_2 = CO_2 & -\ 94{,}810 \\
2CO + O_2 = 2CO_2 & -136{,}400 \\
2Al_2O_3 + 9C = Al_4C_3 + 6CO & \Delta H = \ \ 379{,}910 \\
4Al + 3C = Al_4C_3 & -220{,}830
\end{array}$$

The first value is in disagreement with the results of the present work by 160,000 calories. However, the determination of the heat of reaction is not so accurate as those for the free energy, and the slope of the line in Fig. 3 could be reduced by one-third without very serious prejudice to the data; but Berthelot himself remarked that the heat of formation of the carbide seemed abnormally large. The presence of oxide in his carbide might account for the discrepancy.

Summary

Determinations have been made of the chemical equilibrium for the reaction

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO$$

The increases in free energy and heat content that would attend this reaction between 2000 and 2300°K. and one atmosphere pressure were found to be those given by the equations, $\Delta F^\circ = 507{,}760 - 225.6T$ and $\Delta H = 507{,}760$ calories. At 2251°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. III. BEHAVIOR OF AZIDO-CARBONDISULFIDE TOWARD CHLORINE, BROMINE AND IODINE[1]

BY WM. HOWLETT GARDNER AND A. W. BROWNE

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Azido-carbondisulfide may not inappropriately be designated as a *universal reagent* in the sense in which water has been termed a "universal solvent." Its reactivity toward acids and alkalies, toward oxidizing and reducing agents, toward certain metals and non-metals, toward water and ammonia, and apparently even toward certain organic solvents, together with its tendency to undergo an extremely regular autocatalytic decomposition at room temperature, seems to entitle this substance to characterization as an almost unique reagent.

In connection with the distinctly halogenoid character of azido-carbon-

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[1] For the earlier articles of this series see (a) Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923); (b) Wilcoxon, McKinney and Browne, *ibid.*, **47**, 1916 (1925). The current article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by William Howlett Gardner in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

disulfide the question has arisen as to whether this reagent may be caused to react with any of the other halogenoids, or with any of the halogens, forming inter-halogenoid or halogen-halogenoid compounds analogous to the inter-halogen compounds. The latter part of this question has been answered in the present investigation.

From the list of inter-halogen compounds theoretically capable of existence as definite chemical individuals, bromine trifluoride,[2] iodine pentafluoride,[3,2c] iodine monochloride and trichloride[4] and iodine monobromide[5] have been prepared. Among the halogen-halogenoid compounds are chlorazide,[6] bromazide[7] and iodazide;[8] cyanogen chloride,[9] bromide,[10] and iodide;[11] and thiocyanogen monochloride and trichloride.[12] The inter-halogenoids include cyanazide,[13] cyanogen thiocyanate,[14] and cyanogen selenocyanate.[15]

Behavior of Azido-carbondisulfide toward Chlorine

When dry azido-carbondisulfide is brought into contact at room temperature with chlorine, either in the gaseous form or in concentrated aqueous solution, a violent explosion occurs at once. It is very probable that the initial reaction consists in an exothermic union of chlorine with the halogenoid, resulting in the transitory, superficial formation of a chlorine azido-dithiocarbonate in accordance with the equation

$$Cl_2 + (SCSN_3)_2 = 2ClSCSN_3$$

Since a rise of temperature of but a few degrees suffices to initiate the explosion of azido-carbondisulfide, however, the reaction does not proceed

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[2] (a) Prideaux, *Proc. Chem. Soc.*, **21**, 240 (1905); (b) **22**, 19 (1906); (c) *J. Chem. Soc.*, **89**, 316 (1906); (d) Lebeau, *Compt. rend.*, **141**, 1018 (1905); (e) *Bull. soc. chim.*, [3] **35**, 148 (1906); (f) *Ann. chim. phys.*, [8] **9**, 241 (1906).

[3] (a) Gore, *Phil. Mag.*, (4) **41**, 309 (1871).

[4] (a) Stortenbecker, *Z. physik. Chem.*, **3**, 11 (1889); (b) *Rec. trav. chim.*, **7**, 152 (1888).

[5] Terwogt, *Z. anorg. Chem.*, **47**, 203 (1905).

[6] Raschig, *Ber.*, **41**, 4194 (1908). Qualitative evidence only has been adduced as yet in support of the existence of this compound.

[7] Spencer, *J. Chem. Soc.*, **127**, 216 (1925).

[8] (a) Hantzsch, *Ber.*, **33**, 522 (1900). See also Gutmann, *ibid.*, **57**, 1956 (1924).

[9] (a) Berthollet, *Ann. chim.*, [1] **1**, 30 (1789); (b) Gay Lussac, *ibid.*, [1] **95**, 156–231 (1815); (c) Serullas, *Ann. chim. phys.*, [2] **35**, 291 (1827).

[10] Serullas, *ibid.*, [2] **34**, 95 (1827).

[11] Serullas, *ibid.*, [2] **27**, 184 (1824).

[12] (a) Kaufmann and Liepe, *Ber.*, **57**, 923 (1924); (b) Lecher and Joseph, *ibid.*, **59**, 2603 (1926).

[13] Darzens, *Compt. rend.*, **154**, 1232 (1912).

[14] (a) Linnermann, *Ann.*, **120**, 36 (1861); (b) Söderbäck, *ibid.*, **419**, 217 (1919); (c) Schneider, *J. prakt. Chem.*, [2] **32**, 187 (1885).

[15] (a) Verneuil, *Ann. chim. phys.*, [6] **9**, 326 (1886); (b) Kaufmann and Kögler, *Ber.*, **59**, 178 (1926).

far before the reacting mass explodes, yielding the usual products of decomposition of the halogenoid.[1a]

By passing chlorine gas through an anhydrous solution of azido-carbondisulfide in chloroform at —15° no evidence of decomposition is obtained, unless the chlorine is introduced in large excess. After the unused chlorine has been removed by means of a current of dry air, the solution is found to have acquired a characteristic pungent odor and a white solid appears after vaporization of the greater part of the solvent. Even at temperatures below —20° this undergoes gradual transformation into a viscous, yellow oil, insoluble in water and in chloroform. The vapor of this oil affects the eyes and, if inhaled, appears to act as a heart depressant. It attacks rubber, causing it to swell. Contact of the oil with the skin causes blistering. At room temperature the oil undergoes rapid decomposition with evolution of gas.

Qualitative tests indicate that the unstable yellow oil may be a chlorine compound of azido-carbondisulfide of the formula $ClSCSN_3$. It has not yet been found possible to carry quantitative determinations of the compound to satisfactory completion.

Behavior of Azido-carbondisulfide toward Bromine

Attempts to prepare a bromine azido-dithiocarbonate by interaction of liquid bromine and solid azido-carbondisulfide at ordinary temperatures resulted in violent explosions. Even at temperatures slightly above the melting point of bromine, rapid decomposition was found to take place.

In organic solvents such as ethyl alcohol, acetone, ether, chloroform or carbon tetrachloride, however, the bromine color is immediately discharged by azido-carbondisulfide and no evolution of gas occurs if the solution is kept at a temperature below —5°, unless an excess of bromine is present. Evaporation of the resulting solutions at —10° by means of dry air yields a white, odorless, amorphous product which immediately turns yellow above —5°. The water extract of the white or of the yellow substance was found to contain bromides in considerable amount. The yellow solid, while not explosive, turns brownish in color slowly on standing, and rapidly when heated to 200°.

Because of the fact that solutions of azido-carbondisulfide in organic solvents after treatment with bromine solutions do not liberate iodine from potassium iodide until free bromine is present, it was found possible to titrate such solutions at —10°, using moist starch-potassium iodide paper as an outside indicator. The degree of accuracy obtainable by this method is somewhat lowered by the difficulty of judging the end-point and by the rather rapid deterioration of the bromine solutions.

With carbon tetrachloride and with ether as solvents, such titrations indicate that bromine reacts with the azido-carbondisulfide in equivalent

(1:1) ratio under the prevailing conditions. With other organic solvents varying results were obtained. In chloroform, for example, the results indicate that union takes place in a ratio smaller than 1:1. In ethyl bromide, on the other hand, no reaction at all was observed to occur.

When solutions of bromine in carbon tetrachloride, chloroform or ether were added to a suspension of silver azido-dithiocarbonate in the same liquid at —10°, the color of the bromine was at once discharged and silver bromide was formed. The colorless filtrate, like the solutions obtained by interaction of bromine and azido-carbondisulfide, showed no action upon aqueous solutions of potassium iodide, on treatment with iron filings gave no evidence of the presence of free thiocyanogen and underwent no decomposition with liberation of nitrogen below —5°. Evaporation at —10° yielded as before a white, amorphous solid apparently identical in properties and behavior with that just described.

Hydrolysis of non-aqueous solutions of bromine azido-dithiocarbonate by the action of aqueous alkalies yields solutions of the greenish-yellow color characteristic of similarly hydrolyzed azido-carbondisulfide.[1a] The presence of both bromine ion and azido-dithiocarbonate ion was readily established. Sulfites and thiosulfates were also demonstrated to be present. The following equations express the reactions believed to occur during hydrolysis of the compound in concentrated solutions of potassium hydroxide.

$$BrSCSN_3 + 2KOH = KBr + KOSCSN_3 + H_2O$$
$$2KOSCSN_3 + 2KOH = K_2S_2O_3 + 2KSCN + 2N_2 + H_2O$$
$$K_2S_2O_3 + 2KOH + 2KOSCSN_3 = 2K_2SO_3 + 2KSCSN_3 + H_2O$$

Determinations of the bromine-sulfur ratio were made upon samples of bromine azido-dithiocarbonate prepared by the interaction of bromine and the silver salt in ether, carbon tetrachloride and chloroform. The results indicate that in ether the formation of a tribromo-azido-dithiocarbonate takes place, while in the other solvents a mixture of a monobromo and a tribromo compound is obtained.

From these results it may be inferred that the reaction between bromine and silver azido-dithiocarbonate probably occurs in accordance with either or both of the equations

$$Br_2 + AgSCSN_3 = AgBr + BrSCSN_3$$
$$2Br_2 + AgSCSN_3 = AgBr + Br_3SCSN_3$$

Owing to the extreme instability of these compounds and their solutions, it has not yet been found possible to accomplish their complete isolation or more exact determinations of their composition.

Behavior of Azido-carbondisulfide toward Iodine

Treatment of solutions of azido-carbondisulfide in carbon tetrachloride, acetone or ethyl alcohol at temperatures between 0° and —10° with dilute solutions of iodine in these solvents does not result in a discharge of the iodine color. Unlike chlorine and bromine, therefore, iodine does not combine directly with the halogenoid under the specified conditions.

Addition of solid iodine to a concentrated aqueous solution of sodium azido-dithiocarbonate results in the immediate separation of a heavy, black oil.

Iodine reacts at once with silver azido-dithiocarbonate suspended in chloroform with formation of silver iodide. The filtrate is found to contain no iodine, however, unless this reagent has been used in excess. Therefore, no union of iodine with azido-carbondisulfide may be assumed to take place. The reaction of the substances in chloroform appears to follow a course similar to that of the reaction between iodine and sodium azido-dithiocarbonate in aqueous solution, and may be expressed by the equation

$$I_2 + 2AgSCSN_3 = 2AgI + (SCSN_3)_2$$

Summary

Solid azido-carbondisulfide reacts explosively with chlorine and bromine. In certain non-aqueous solvents more controllable reactions take place, with probable formation of the compounds $ClSCSN_3$ and $BrSCSN_3$. Bromine reacts with silver azido-dithiocarbonate in ether to form a tribromo-azido-dithiocarbonate, Br_3SCSN_3, and in chloroform and carbon tetrachloride to form a mixture of the monobromo and tribromo compounds.

The extreme instability of these compounds precludes their exact analysis and description.

Iodine forms no compound with azido-carbondisulfide under the conditions investigated.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

HYDROGEN PEROXIDE FORMATION PHOTOSENSITIZED BY MERCURY VAPOR

BY ABRAHAM LINCOLN MARSHALL

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This paper represents an effort to clear up some of the uncertain points in the photochemical combination of hydrogen and oxygen when sensitized to λ 2536.7 Å. from a cold mercury arc by means of mercury vapor. In a previous paper[1] this reaction was studied in a static system and the rates of reaction observed at that time were not at all reproducible. It was found, however, that for individual experiments the rate of reaction was best represented by the equation

$$\frac{d}{dt}(H_2O) = K\left(\frac{p_{H_2}}{p_{H_2} + p_{O_2}}\right)$$

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[1] Marshall, *J. Phys. Chem.*, **30**, 34 (1926).