VULCANISM, MERCURY-SENSITIZED PHOTO-REACTIONS AND ABIOGENETIC SYNTHESIS: A THEORETICAL TREATMENT

SANFORD M. SIEGEL

and

BARBARA Z. SIEGEL*

Department of Botany and Pacific Biomedical Research Center, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

Abstract. Attention is called to the photodynamic and thermodynamic properties of Periodic Group IIb elements, most notably Hg, as they relate to ultra-violet sensitization in organic chemical reactions. The energy levels of 6 $^1P_1$ and 6 $^3P_1$ resonance states and the high vapor pressure ($> 10^{-3}$ mm) of the metal at temperatures as low as 293 K bring Hg with the range of bond dissociation energies in most organic molecules and many inorganics.

These capabilities considered together with recent evidence for Hg emission as a regular part of volcanic and geothermal processes provide the basis for our proposal that Hg-sensitized ultraviolet photo-reactions may have played a significant part in abiogenetic organic synthesis on the primative earth.

1. Introduction

From the now classic investigation of Urey and Miller some 20 years ago to the most recent accounts of continuing research on abiogenesis of organic compounds (Urey, 1952; Miller, 1953; Urey and Miller, 1959) a wide array of presumed primitive atmospheres have been examined using heat (Harada and Fox, 1964) and an assortment of electromagnetic energy sources including arc discharges, ionizing radiation and ultraviolet. Simulation has been extended from the primitive earth to the outer planets (Ponnamperuma, 1975) and special considerations have included the probable role of heterogeneous (surface) catalysis in organic synthesis (Bernal, 1951).

The enhancement of specific amino acid photosynthesis in aqueous mixtures of carbohydrates and nitrates by Co(II), Ni(II) and Fe(II) has been described recently (Khenokh and Nikolayeva, 1975) and, more generally, sulfides and volatile organic compounds are presumed to serve as photosensitizers, as well as reactants.

Nevertheless, in spite of the frequent use of Hg-resonance radiation (Hg 6 $^3P_1$, at 253.7 nm) in most photochemical experiments, Hg° vapor has not been studied as a sensitizer in abiogenetic photosynthetic reactions.

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* Senior NATO fellow, Nordic Institute of Volcanology, University of Iceland, 1975.

2. Metal Photosensitizers

A. PROPERTIES AND ENERGY CHARACTERISTICS

Hg and certain other metals are well known to physical chemists as sensitizers of gas-phase ultraviolet photo-reactions (Steacie, 1954a). The number of such metals is virtually limited to four – Na, Hg, Cd and Zn – by the criteria put forth by Steacie:

i. Vapor pressures of ca 10^{-3} mm are needed at temperatures low enough for the stability of organic compounds.

ii. The spectrum must have a suitable resonance level corresponding to the order of magnitude of organic bond strengths.

iii. Energy sources must have suitable intensities at the resonance lines.

Even this small group of metals is subject to a further limitation, namely that Na° is unstable with respect to H_2O, hence is not compatible with experimental mixtures simulating an aqueous primitive atmosphere.

The triad of Periodic Group IIb thus remains for further consideration.

These elements differ less in their photodynamic than in their thermodynamic properties (Table I). They exhibit high energy excited singlets and lower energy excited triplets, most of which are capable of cleaving C—H and C—C bonds. Zn 4 ^3P, and Cd 5 ^3P, cannot dissociate H_2O (118 kcal), whereas their high energy states together with Hg 6 ^3P, and 6 ^1P, can do so (Tables II, III).

TABLE I

Selected thermodynamic and spectrochemical properties of metal sensitizers

Property	Metal		
	Zn	Cd	Hg
Boiling point (°K)	1180	1040	630
T at $P_{vapor} = 10^{-3}$ mm (°K)	565	493	291
P_{vapor} at 373 K (mm)	$<10^{-3}$	$<10^{-3}$	$>10^{-3}$
P_{vapor} at 273 K (mm)	ca 0	ca 0	10^{-3}
Resonance level			
singlet	$4\,^1P_1$	$5\,^1P_1$	$6\,^1P_1$
triplet	$4\,^3P_1$	$5\,^3P_1$	$6\,^3P_1$
$\lambda_{resonance\ line}$ (nm)			
singlet	213.9	228.8	184.9
triplet	307.6	326.1	253.7
$E_{excitation}$ (kcal)			
singlet	133.4	124.4	153.9
triplet	92.5	87.3	112.2
$E_{bond\ broken}$ (kcal)			
singlet	156.6	139.9	162.4
triplet	115.6	102.8	120.7
Abundance, igneous rocks			
matoms/kg	2.0	0.0014	0.0003

TABLE II

Representative dissociation energies for C—H and C—C bonds

Bond	D(A—B) kcal
Aliphatic C—H	
RCH$_2$—H	80–100
R=H, CH$_2$	
CH$_3$,....C$_4$H$_9$	
Aromatic C—H	
C$_6$H$_5$—H	102
C$_6$H$_5$CH$_2$=H	77
o, m, p—CH$_3$C$_6$H$_4$CH$_2$—H	75–77
C—to—C	
CH$_3$—CH$_3$	83
CH$_3$—CN	104
CH$_3$—CHO	75
C$_6$H$_5$—CH$_3$	89
NC—CN	112

TABLE III

Representative dissociation energies for bonds involving sulfur, oxygen and nitrogen

| Bonds containing	D(A—B) kcal
Sulfur	
CH$_3$—SH	74
CH$_3$—SCH$_3$	73
t—C$_4$H$_9$—SH	69
t—C$_4$H$_9$—SCH$_3$	65
H—SH	95
CH$_3$S—H	89
HS—SH	80
CH$_3$S—SCH$_3$	73
Oxygen	
HO—H	118
OC—O	127
HO—OH	54
Nitrogen	
NH$_2$—H	102
H$_2$N—NH$_2$	54

B. PHOTOSENSITIZED REACTIONS

Mercury is the most versatile of the IIb metals in sensitization, and can be used to illustrate representative primary mechanisms.

$$Hg(6\ ^1So) + h\nu(253.7\ nm) \rightarrow Hg(6\ ^3P_1) \tag{1}$$

$$Hg(6\ ^3P_1) + H_2 \rightarrow Hg(6\ ^1So) + 2H \tag{1a}$$

$$Hg(6\ ^3P_1) + R - H \rightarrow Hg(6\ ^1So) + R + H \tag{1b}$$
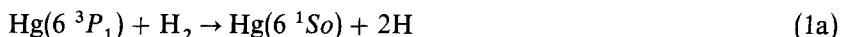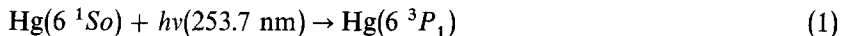
R = alkyl or aryl

Reaction (1) represents the excitation of a singlet ground state Hg atom to its excited triplet by absorption of a quantum of 253.7 nm radiation. The excited atom can then either reemit the energy within ca 0.1 μsec as fluoresence or transfers it by collision (quenching). Bond cleavage (reactions 1a, b) is the result of the collisional transfer process. Not shown is the intermediate step:

$$Hg(6\ ^3P_1) + RH \rightarrow Hg(6\ ^1So) + RH*$$
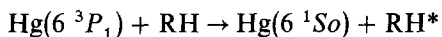
in which an excited organic molecule appears prior to dissociation. Such intermediates may always be formed, but their life times are often too brief for detection.

In general primary photolytic and pyrolytic products are the same. Hg and other photosensitizers which serve only to make use of electromagnetic energy not absorbed otherwise in the system, influence the extent of reactions under low temperature conditions.

Selectivity does exist sometimes in these reactions. For example, in the photo-reactions of ethylene. Thus:

Sensitizer	Reaction
Na (^2P)	None
Cd $(^3P_1)$	Slow
Zn $(^3P_1)$	Slow
Hg $(^3P_1)$	fast – acetylene a major product
Cd $(^1P_1)$	fast – acetylene a major product
Zn $(^1P_1)$	fast – no acetylene

The kinetic chain length initiated by the primary scission products depends upon the energetics of possible termination reactions. The high overall quantum yields of reactions such as ultraviolet-initiated formation of HCl from $H_2 + Cl_2$ are not typical of organic molecules.

Among the many hundreds of atomic and radical reactions reported to be photosensitized, some of particular relevance include:

  i. build-up of higher homologs from simpler alkanes (Paneth and Herzfeld, 1931; Paneth and Lautsch, 1931)
  ii. addition of alkenes and alkynes or their radicals to alkenes or alkyl radicals (Taylor and Smith, 1940; Trotman-Dickenson and Steacie, 1951; Gunning and Steacie, 1946)
  iii. polymerization of alkenes or alkynes (e.g. acetylene to cuprene and benzene) (Bates and Taylor, 1923; Lind and Livingston, 1930)

iv. coupling of aryl radicals with similar moieties or alkyls (Horn and Polanyi, 1934)

v. formyl and carbonyl group transformations – formation, disproportionation etc. (Barak and Taylor, 1932; Partingron, 1947; Rice and Herzfeld, 1934)

vi. HCN formation and CN – group transformation (Robertson and Pease, 1942; Greib and Hartack, 1933)

vii. transformation of amines to hydrazines (Patat, 1936; Wetmore and Taylor, 1944)

viii. thiolation of alkenes (Vaughan and Rust, 1942)

ix. formation of disulfides from thioalkyl groups (Meissner and Thompson, 1938)

x. formation of novel substituents e.g. RSO_2CL (Rice and Evering, 1934)

A unique role for metal photosensitization is seen in the hydrogenation of CO. The reaction

$$H_2 + CO \rightarrow CHO + (-CHO)_2 + HCHO$$
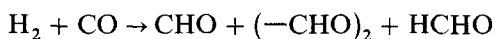
proceeds if Hg is present but not otherwise at ca 300 K even when supplied with atomic hydrogen (Steacie, 1954b).

Differential product formation is evident when ethylene oxide is pyrolyzed, or photolyzed with and without Hg as a sensitizer: at 700 K, CH_4 and CO are the main products; at 300 K exposure to UV above 200 nm yields C_2H_4 as well as the foregoing; but when Hg is present, CH_3CHO, H_2 and CO are formed with but little CH_4.

3. Vulcanism and Atmospheric Mercury

The foregoing discussion, although summary and general in character, demonstrates a role for Group IIb metals, especially Hg in experimental organic photochemistry.

It now remains for us to establish that the photodynamic properties of Hg are in fact, relevant to natural organic photochemistry hence to abiogenetic synthetic processes.

Hg is present in the Earth's atmosphere today. Its distribution appears closely related to current vulcanism and related geothermal phenomena as shown recently by comparative studies in Iceland and Hawaii (Siegel et al., 1973, a, b; Siegel and Siegel, 1975).

Air near fumarolic and magnetic sources yielded Hg levels of 6–17.6 μg m^{-3} averaging 12.7 $\pm$ 4.6 μg m^{-3} with individual readings in excess of 40 μg m^{-3}. Non-thermal areas on these two islands gave values of 0.8–1.7 μg m^{-3}. In contrast, the geochemical 'norm' over sea appears to be 0.01 μg m^{-3}, and even urban locations do not exceed 0.2 μg m^{-3}.

It appears that until the recent and still-increasing introduction of Hg into the atmosphere by fossil fuel burning, vulcanism was the major source of Hg. Reportedly, there are nearly 500 active volcanos on earth today, although not all have had recent eruption phases (Bullard, 1962). There are also countless low thermal areas (for example, local hot springs) which may emit Hg.

In addition to direct degassing or phreatic transport of the metal in mixed oxidation states, including Hg° (Siegel et al., 1973a), fine volcanic ash (Hekla, Iceland) has been found to contain large amounts (ca 375 ppb) of water soluble and volatile Hg. A further source, although perhaps minor, is the weathering of lavas and other igneous rocks. In only 2–10 years we have noted the Hg content of lava to fall from ca 750 ppb to 110 ppb or less (Siegel et al., 1973a).

Thus, there can be no question about natural sources of Hg and the means for its introduction into the environment, whether gradual and localized as in weathering or rapid, stratospheric and regional as in explosive eruptions.

Mercury is the least abundant of the IIb group, however its energetics and volatility (Table I) place it far above Zn and Cd in our consideration.

At present, the mercury content appears to be increasing in the biosphere. If, however the contribution of fossil fuels and industrial-agricultural sources is deducted then there is no longer a basis for any assumptions about pre-industrial long term increases in global mercury levels.

The present atmospheric level may represent part of a long term cycle or equilibrium modified by the activities of Hg – accumulating and volatilizing organisms. The absence of living matter will modify such cycling processes but it is not likely that the changes would be great.

At present, the lithosphere holds a total of about 10^{13} metric tons of Hg (Weast 1974). The more superficial igneous rocks – lavas, basalts, gabbros, granites contain ca 90 ppb on the average, whereas the deep ultramafic and igneous rocks are at least 5-fold richer (Fleischer, 1970), a difference that almost certainly relates to the degassing of magmatic materials as they are extruded on the surface.

Recently, Olafsson (1975) has estimated the amount of Hg injected into the atmosphere during the 5-month long Icelandic eruption at Heimaey in the Westmann Islands. His figure of 0.7 metric tons is small in itself but if this output is in fact representative of eruptions similar in quantities of steam and ejecta, then it must have been multiplied many million-fold during the earliest history of this planet.

Considering, therefore, the various photochemical, organic chemical, and geochemical aspects of the foregoing discussions, we propose that during the period some 3.5–4.5 aeons ago when conditions favored abiogenetic synthesis of organic compounds (moderately elevated temperatures; water in liquid and vapor phases; $CH_4 + NH_3$ atmosphere; unshielded solar radiation; intensive vulcanism and tectonic movements) the presence of gaseous Hg° and secondarily other Group IIb metals influenced significantly the course of atmospheric and surface photochemical synthesis of pre-biological molecules.

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