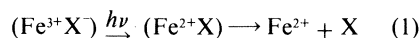


Reports

Fuel Formation from Aqueous Ferric Bromide by Photolysis in the Visible

Abstract. *Illumination of acid aqueous ferric bromide containing excess bromide yields free Br₂ and ferrous ions. The quantum yield is independent of wavelength up to about 600 nanometers, and increases with temperature; quantum yields of up to about 5 percent 1/2 Br₂ were observed at 42°C and further improvement should be possible. Some aspects of this system for the quantum utilization of solar energy are discussed.*

On the absorption of a light quantum, charge transfer within an ion pair complex in solution from a negative to a positive ion may occur and result in photochemical reactions. The spectroscopy and related energetics of such processes, particularly for complexes of ferric ion of the type (Fe³⁺X⁻), has been a subject of interest (1-3), especially when X is a halide (F, Cl, Br, or I) or halide-like (OH or CNS) ligand.

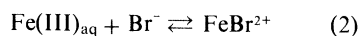


From Eq. 1, photochemistry of the radical X or of the ferrous ion will be due to those entities escaping geminate recombination into the homogeneous bulk of the solution. Of such photochemical processes, radical reaction of X—for example, the initiation of polymerization by addition or radical abstraction from substrates—has been much investigated (2, 4), while formation of products such as X₂ has been investigated hardly at all.

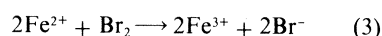
In this report we describe our work on the photochemistry of the (Fe³⁺Br⁻) ion pair complex in acid aqueous solution, leading to the formation of Fe²⁺ ions and free Br₂. In this endoergic photochemical process some of the quantum energy is stored in the products, which may be used as fuels. We shall consider the potential of

this system in the utilization of solar energy, for which the quantum processes of photochemistry constitute one of the important options (5).

The absorption spectrum of aqueous acidic ferric bromide, Fig. 1, is well matched to the insolation spectrum. Absorption in the visible by such solutions is almost entirely due to FeBr²⁺ (1)



with an association constant at 25°C of 4 and a standard enthalpy of association of + 6.1 kcal/mole. If the excitation process, as in Eq. 1, is followed by dissociation of (Fe²⁺Br⁻), generation of a potentially useful fuel is possible



where the standard free energy change is -14.6 kcal/mole. The photochemical characteristics of the photoproduction of Br₂ from aqueous acidic ferric bromide offer some attractive specific features because of the volatility of Br₂, the relatively high potential of the resulting fuel system, and the specific properties of the Br atom and its radical ions, such as Br₂⁻. In our apparatus, bromine was swept out of the photolysis solution with N₂ and collected in a trap cooled with liquid N₂. It was determined by the absorbance of solutions produced by its reaction with Hg(SCN)₂ in the presence of ferric alum (6). Results of a typical experiment are shown in Table 1. The apparent initial increase in quantum yield of Br₂ is presumably due to an increase in the efficiency of its removal as its concentration increased. The subsequent decrease in the quantum yield of Br₂ is presumably due to increase in the rate of "dark" reversal as Fe(II) accumulated. The latter presumption is supported by the observation that the initial quantum yields of Br₂ are reduced by the addition of Fe(ClO₄)₂, for example, 5 × 10⁻⁴M Fe(II) reduced the initial yield to one-half its value in the absence of added Fe(II). The ini-

tial quantum yield of Br₂ was not affected significantly by a tenfold variation in the intensity of the incident light. As shown in Fig. 1, the initial quantum yield was essentially independent of wavelength from 366 to 578 nm.

The quantum yield (φ) of isolated bromine is greater at higher temperatures; at ~ 42°C the initial value of φ(1/2 Br₂) was 4.8 moles per 100 einsteins under conditions similar to those of Table 1.

Data presented above establish that photolysis of acidic aqueous ferric bromide in the visible generates potentially useful fuel. Absorbed photons are utilized with equal efficiency over a wide wavelength region. The increase in φ(1/2 Br₂) with increasing temperature is promising for conditions of solar illumination. Whether efficient separation of Fe(II) during illumination will be necessary, or even desirable, will depend on the approach that is taken to convert chemical potential energy into a useful form; for example, separation would not be necessary in a photogalvanic cell employing reaction 3 (standard potential = 0.317 volt).

One of the advantages of the (Fe³⁺Br⁻) system for solar energy utilization is its homogeneous nature, which obviates the necessity for expensive light-sensitive electrodes or membrane structures. Of other homogeneous systems, those utilizing water decomposition with H₂ evolution were recently critically examined (7, 8). When one-quantum processes are utilized the useful wavelength region is severely limited to one having relatively high quantum energies, because of the thermodynamic requirements for covalent bond splitting in water plus the nonequilibrium strain energy of the spectroscopic process (7). Cumulative two-photon processes which

Table 1. Quantum yields of isolated bromine from successive irradiations of aqueous acidic ferric bromide at 436 nm and room temperature. The composition of the solution was 0.045M HClO₄, 0.10M Fe(ClO₄)₃, and 1.0M FeBr₃. In each case, 5 minutes irradiation under N₂ purging was followed by N₂ purging for 20 minutes.

Irradiation number	φ(1/2 Br ₂) (moles per 100 einsteins absorbed)
1	1.3
2	2.0
3	1.5
4	1.3
5	1.0
6	1.0

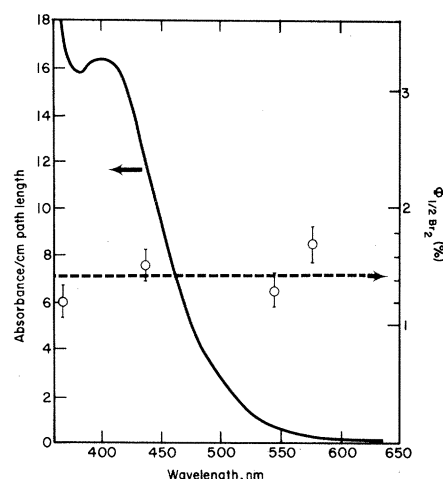


Fig. 1. The curve shows the absorption spectrum of (Fe³⁺Br⁻) and the data points with error bars the dependence of quantum yield of Br₂ formation on wavelength. The composition of the solution was 0.1M Fe(ClO₄)₃, 1.0M NaBr, and 0.045M HClO₄.

could extend the spectral range have not yet been experimentally elaborated. In comparison, charge transfer processes within ion pairs produce radical intermediates without the necessity of covalent bond breakage. The energetic limitations are much lower, the utilizable spectral range broader. Of such systems, those with Br^- have some advantages in spectrum, electric potential, or quantum yield over systems with other halides or other ligands.

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Shanidar IV, a Neanderthal Flower Burial in Northern Iraq

Abstract. *The discovery of pollen clusters of different kinds of flowers in the grave of one of the Neanderthals, No. IV, at Shanidar cave, Iraq, furthers our acceptance of the Neanderthals in our line of evolution. It suggests that, although the body was archaic, the spirit was modern.*

What was originally thought to be a simple Neanderthal burial at Shanidar cave (number IV in the series of skeletons) has proved of singular importance. The death had occurred approximately 60,000 years ago (1), yet the evidence of flowers in the grave brings Neanderthals closer to us in spirit than we have ever before suspected. The flower pollens discovered by Leroi-Gourhan, a palynologist (2), in the soil samples that I had taken from around the skeleton emphasize the rich dividends of interdisciplinary research in studies of prehistory.

The Neanderthal finds made at Shanidar cave in 1960 were initially described by Stewart (3) and, at about the same time, by me (4). At that time, the palynological analysis of the soils was still to be made.

Shanidar IV and associated remains from three other individuals were found about 15 m from the cave mouth at a depth of about 7.5 m below the cave floor. The skeletons were crammed in a niche of stones measuring about 90 cm north to south by 150 cm east to west and covered by a widespread rockfall.

The discovery of Shanidar IV was made in the course of trimming a dangerous-looking bulge in the east wall of the excavation. Included in the bulge zone was a relatively small remnant of unexcavated soil left over from an earlier season. It was during this trimming operation that we encountered the first bones, heavily encrusted with a coating of limestone deposit. After

identifying the bones as human, Stewart assumed supervision of the exhumation of the find, which proved to be an adult male. While he was engaged in this operation, another Neanderthal, Shanidar V, was brought to light only yards away.

By cleaning away the loose soil in front of Shanidar IV, Stewart found the crushed parts of a new individual, Shanidar VI, an adult female. Rather than trying to take up Shanidar IV bone by bone in order to expose the new find, it was thought best to box the extremely fragile remains en bloc for removal to the laboratory in Baghdad.

In his laboratory examination 2 years later, Stewart (3) discovered that among the bones which had been identified in the field as Shanidar VI were the bones of yet another individual, a second adult female, which should technically be given the find designation of Shanidar VII. He could not be sure which of the female bones belonged to which individual, and thus provisionally lumped them both together as a unit which we call Shanidar VI-VII. The bones of a baby, which were found below Shanidar IV and VI-VII, are designated as Shanidar VIII. The remains of these three individuals (Shanidar VI-VII and VIII) seem to have been only partially complete, according to Stewart's findings. From the position of the skeletal remains, it would appear that the baby had been laid in first, followed by the two females. Finally, room was made for the male, who was evidently an important man.

I took a number of soil samples from around Shanidar IV, with a special note that samples 313, 314, and 315 were specifically for pollen analysis. These were sent for examination by Leroi-Gourhan in Paris. She processed the six soil samples that were taken from around Shanidar IV and the immediately adjacent area, and much to her surprise found that among others, samples 313 and 314 were especially rich in flower pollen (2). The humid condition of the soil undoubtedly contributed to the good preservation of the pollen grains, although it had a bad effect on the skeletons.

The recovery of pollen grains around the Neanderthal burial was in itself unusual and without precedent to our knowledge, but to find flower pollen, and in quantity, was an added extraordinary dividend. The association of flowers with Neanderthals adds a whole new dimension to our knowledge of his humanness, indicating that he had "soul."

The flowers identified by Leroi-Gourhan can still be found in Iraq (5). Even more importantly, by coincidence, seven of the eight flower species are cited by Al-Rawi and Chakravarty (6) for their herbal and medicinal properties, which raises some fine points for speculation with regard to their associations in Neanderthal burial.

When reviewing the list of flowers, we start with the Compositae, the family of flowers collectively and commonly known as the daisies. In this family at least six species of the *Achillea* genus are found in the Shanidar area today (5, 7). The common name of *Achillea* is yarrow, or milfoil. Yarrow is an Anglo-Saxon derivation meaning healer. In addition to its specific use in the past for wounds, it has been widely used in herbal medicine. In Iraq, Al-Rawi and Chakravarty (6) inform us that the herb of *Achilles santolina* Linn. possesses insect repellent properties, and its leaves are useful against dysentery, intestinal colic, "expulsion of gases," and as a general tonic and carminative. Leroi-Gourhan also found pollens of the *Centaurea* genus, also of the Compositae family, among the burial soils. Al-Rawi and Chakravarty (6) note that the *Centaurea cyanus* Linn. (commonly known as the cornflower, blue bottle, or blue bonnet), which is found farther south in Iraq today, has uses as a diuretic, emmenagogue, tonic, pectoral, stimulant, astringent, febrifuge, and collyrium.

Centaurea solstitialis, commonly known as St. Barnaby's thistle, is a conspicuous plant that I have observed in great numbers at Shanidar. It is mentioned as one of the wild plants of Iraq by Al-Rawi (5), and of the eastern Mediterranean in general by Polunin and Huxley (8). It has white cot-