81389-49-3; $PhSCH_2Li$, 13307-75-0; H_2C=CMeCHO, 78-85-3; H_2C=CMeCH(OH)CH_2SPh, 81306-15-2; $PhSCH_2COCMe$=CH_2, 77004-05-8; maleic anhyride, 108-31-6; *N*-phenylmaleimide, 941-69-5; *p*-benzoquinone, 106-51-4; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; acrolein, 107-02-8.

Plasma-Exposed Reduction of Solid and Solvated Viologens†

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Considerable attention has been focused on the study of organic radicals prepared by one-electron reduction of the parent molecules, among which viologens (4,4′-bipyridinium salts) have special interests in terms of the photochemical production of hydrogen gas from water.[1-4] We report here that solid and solvated samples of viologens can be reduced exclusively and quickly and can form cation radicals when exposed to a radio-frequency plasma.

The technique of most interest to plasma chemistry is the glow discharge, in which free electrons gain energy from an imposed electrical field and subsequently lose it through collisions with neutral molecules in the gas. The transfer of energy to the gas molecule leads to the formation of a host of chemically active species such as electrons and ions, some of which become precursors to the chemical reactions[5-7] and polymerizations[8,9] as well. It was, therefore, of interest as to whether the energetic electrons in the gaseous plasma could directly induce the reduction of viologens.

The plasma exposure was carried out in an optical quartz cell of 10-mm path length, in which 3 mL of DMF solution of viologen was placed (Figure 1). The cell was inserted between a pair of parallel-plate electrodes connected to an RFG-200 radio-frequency generator, operating at 13.56 MHz and delivering up to 200 W. The solution was frozen, followed by degassing several times at 10^{-4} torr. A glow discharge was then generated in the gas space above the solution for a prescribed period of time according to the method described previously.[10-13]

The transparent DMF solution of benzylviologen (1,1′-dibenzyl-4,4′-bipyridinium dichloride, BV^{2+}) changed to deep blue color as soon as the plasma was exposed. Figure 2 shows the absorption spectra of plasma-exposed BV^{2+} in DMF at various plasma durations measured in vacuo. The spectra were in good agreement with the reported spectra of photochemically reduced viologens,[3,4] showing the monotonous increase of the intensity with the plasma duration. The characteristic absorptions at 402 and 607 nm clearly show the formation of the cation radical, $BV^{+}\cdot$.

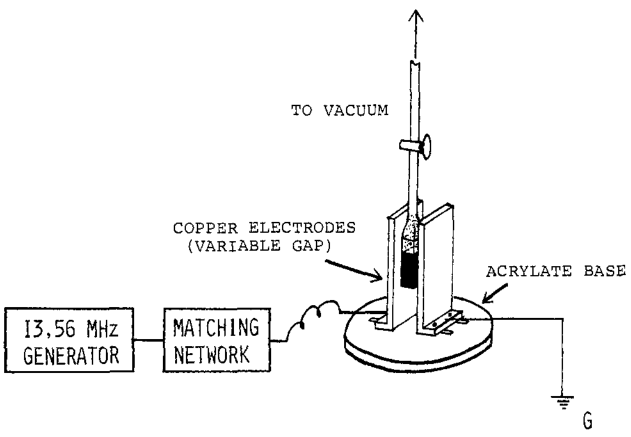


Figure 1. Apparatus for plasma exposure of the viologen solution.

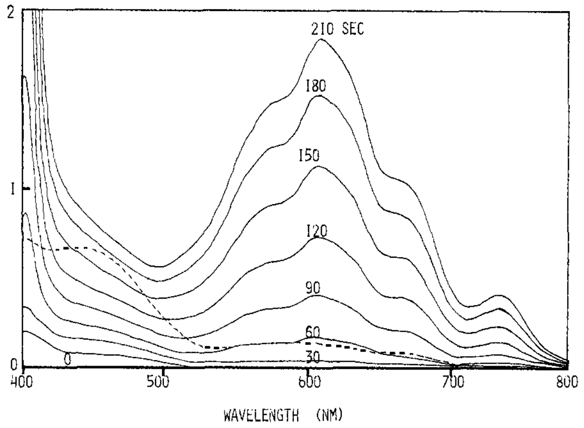
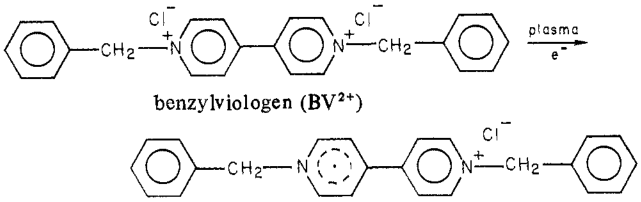


Figure 2. Progressive spectral changes of benzylviologen with plasma duration (spectra were measured after 5 min of plasma exposure). Figures denote plasma duration: after air quenching (---); benzylviologen, 4.88×10^{-4} M in DMF (plasma, 100 W).

The spectrum disappeared on exposure to air but reappeared with repeated plasma exposure. This fact suggests that the reduction occurred via a one-electron process:



benzylviologen (BV^{2+})

cation radical of benzylviologen ($BV^{+}\cdot$)

$BV^{+}\cdot$ is the major product, since no spectral absorption other than by BV^{2+} and $BV^{+}\cdot$ appeared in the UV and visible wavelength range. Also, no insoluble product was formed. Furthermore, the efficiency of the reduction was almost the same when BV^{2+} was present during the plasma exposure as when it was added later. The yield of $BV^{+}\cdot$ based on the amount of BV^{2+} was determined from the ESR spectrum by using 2,2-diphenyl-1-picrylhydrazyl and was calculated as 66% for 4.9×10^{-4} mol/L of DMF solution by the plasma exposure for 180 s at 100 W. These facts indicate that the reduction of BV^{2+} is the main pathway.

From experiments at different concentrations of BV^{2+} and different plasma powers, the rate of reduction of BV^{2+} can be expressed as follows (Figure 3):

$$d[BV^{+}\cdot]/dt = K[BV^{2+}]^{0.5}[\text{power}]^{1.0}$$

where K is a constant depending on the plasma reactor.

In addition to the DMF solution of BV^{2+}, a solid sample of BV^{2+} and poly(xylylviologen dichloride) were reduced successfully by the plasma, but no reduction occurred for dichlorides and di-

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† Study of Plasma-Initiated Polymerization. 6.

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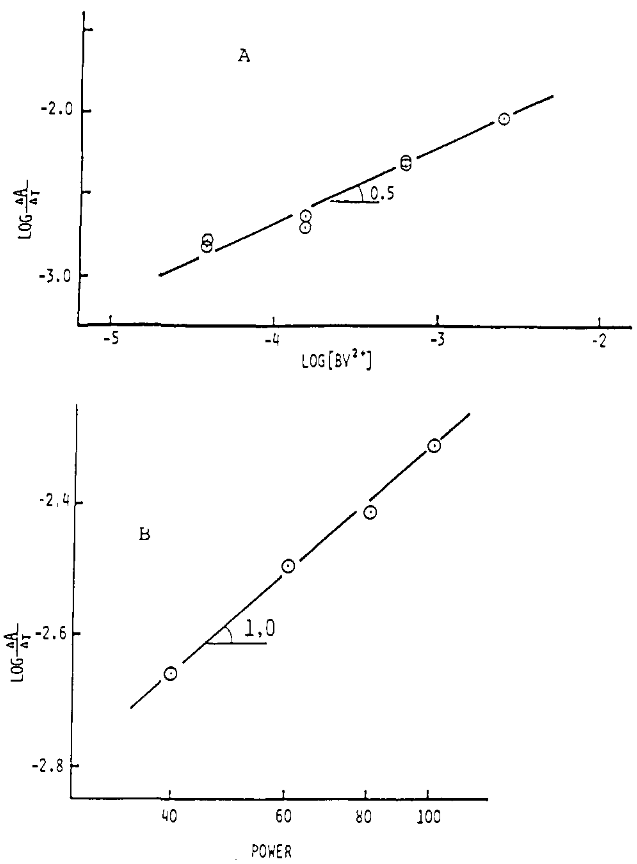

Figure 3. Logarithmic dependences of the rate of reduction on BV^{2+} concentration (A) and plasma power (B).

bromides of methyl-, *n*-propyl-, *n*-hexyl-, and *n*-laurylviologens both as solid or solvated samples even with 10 min of exposure to the plasma at 100 W.

The interesting feature here is that the spontaneous reduction occurs in the plasma-exposed DMF solution of BV^{2+} after the plasma is quenched. Thus, the absorbance of BV^{2+} in DMF (2.4 × 10^{-3} M), exposed to the plasma for 60 s at 100 W, increased ca. 8 times when the solution was held for 60 min at room temperature in vacuo. The reduction also took place when BV^{2+} was mixed with DMF that had been exposed to the plasma a few days prior to mixing. It was also found that plasma-exposed DMF is capable of initiating polymerization when vinyl monomers such as acrylamide, 2-hydroxyethyl methacrylate, or methacrylic acid are mixed instead of BV^{2+}. Gas chromatograms of plasma-exposed DMF showed no evidence of reaction product. These experimental facts imply that the reaction species generated by the act of the plasma are sufficiently long lived so as to induce "postreduction" and "postpolymerization" in DMF.

At present DMF and hexamethylphosphoramide are the only solvents in which the formation of the cation radical has been observed. No reduction of BV^{2+} occurs in Me_2SO, dioxane, acetonitrile, or water. Only frozen water exhibited the pale blue color of the cation radical at the surface when exposed to the plasma. The color, however, paled rapidly upon melting, presumably due to reoxidation via a back-electron transfer reaction.

The mechanism of the reduction under the effects of a low-pressure plasma has not been determined. However, the reduction is considered to occur by reaction with energetic electrons in the plasma directly at the gas–liquid interface, since the plasma penetrates only a few microns below most surfaces. It may also be possible that the reduction proceeds via solvated electrons which then transfer to BV^{2+} in DMF.

The results suggest not only a new method for quantitative studies of complicated elementary processes in plasma reactions but also provide a novel reducing intermediate for a variety of chemical reactions, including the production of hydrogen gas from water.

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Registry No. $BV^{2+}\cdot 2Cl^-$, 1102-19-8; $BV^{+}\cdot Cl^-$, 77938-64-8; poly(xylylviologen dichloride), 81534-71-6; acrylamide, 79-06-1; 2-hydroxyethyl methacrylate, 868-77-9; methacrylic acid, 79-41-4; 4,4′-bipyridinebis(chloromethyl)benzene copolymer, 81388-55-8.

Thermal Rearrangements of Encumbered Methylenecyclobutanes. 1. 6-Methylenebicyclo[3.2.0]heptane

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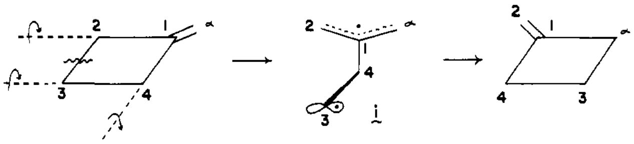
Upon being heated, methylenecyclobutanes undergo [1,3] sigmatropic rearrangements,[2-5] one-center epimerizations,[3-5] [2 + 2] cycloreversions,[6] and perhaps other reactions. This rich chemistry has been reviewed by Gajewski,[7] who earlier proposed[8] meshed conrotatory-bevel motions for the preferred manner of ring opening (eq 1). If these motions lead directly to [1,3] rearrangement as shown, C_3 will have migrated over the C_2–C_1–C_α allylic framework suprafacially (S) and with configurational inversion (I). Even though this SI combination constitutes one allowed[9,10] pathway, the measured activation parameters[2] and MINDO/2 calculations[13] for the degenerate rearrangement of the parent implicate a diradical intermediate or transition state such as i.



(1)

We report the thermal behavior of some encumbered bicyclic methylenecyclobutanes **1** which incorporate three useful structural features: the two allylic bonds (C_1–C_5, C_1–C_7) are distinct; [1,3] migration may only occur from cleavage of one of these (C_1–C_7), and in that event, the migrating C_1 can only move from C_7 to C_α with retention of configuration.

Compound **1a** is prepared[14] by Wittig methylenation of ketone

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