

Alternative Mechanism for 'Plasma Reduction'

Masayuki Kuzuya,^{*a} Seiko Mizutani,^a Takachiyo Okuda,^a Kaoru Kamiya,^b and Yasukichi Yanagihara^b

^a Gifu Pharmaceutical University, 6-1, Mitahora-Higashi 5-Chome, Gifu 502, Japan

^b Tomei Sangyo Co. Ltd., Noritake-shinmachi, Nishi-Ku, Nagoya 461, Japan

'Plasma reduction' of various types of compounds, including non-electron-accepting ones, by plasma electrons can be rationalized in terms of base-catalysed reactions with nitrogen-derived basic ultrathin films which are rapidly formed by a brief plasmolysis of various nitrogen-containing organic vapours.

We report here the evidence that a nitrogen-derived basic moiety is readily leached out of a novel ultrathin film, formed by a brief plasmolysis of various nitrogen-containing organic vapours, into either polar or nonpolar solvents so that it can induce a base-catalysed auto-reduction of viologen homologues, and the electronic spectral changes of iodine and organic dye compounds.

Recently, we reported that a plasma-exposed glass prepared from several hydrocarbons and/or oxygen-containing organic compounds under brief plasma exposure in a closed system exhibited a catalytic effect, initiating not only the radical chain polymerization of vinyl monomers,^{1,2} but also the spin adduct formation of phenyl t-butyl nitron (PBN) in benzene over a long period of time.^{3,4} Subsequently it was found that a novel invisible ultrathin film was deposited on the glass surface,^{3,5,6} and a mechanistic insight into the immobilization and release of active radical species on such a plasma-driven ultrathin film was also reported.⁷

Plasma-exposed glass prepared from nitrogen-containing organic compounds, however, was found to induce neither the polymerization of vinyl monomers nor the spin adduct formation of PBN, unlike glasses from non-nitrogen-containing organic compounds.^{3,7}

Thus, we decided to use X-ray photoelectron spectra (X.P.S.) for the surface analysis of such a plasma-exposed glass. The X.P.S. studies showed that nitrogen-containing ultrathin films were indeed formed in all the cases examined. The elemental ratios determined from the spectra of several films are summarized in Table 1. As can be seen from Table 1, the nitrogen/carbon ratio varies with the compounds used for plasmolysis, but does not follow a systematic trend, whereas the oxygen/carbon ratio reveals that all the films contain oxygen atoms, even from non-oxygen-containing compounds, owing to a reaction between atmospheric oxygen and dangling bond sites on the film surface.⁹ The ratio for the film from

dimethylformamide (DMF) plasmolysis is more or less the same as those from non-oxygen-containing compounds, indicating that the aldehyde moiety of DMF is not incorporated into the resulting ultrathin film, and the film is mainly composed of the residual nitrogen basic moieties. The elemental ratios from the X.P.S. data obtained after agitation

Table 1. Elemental ratios from X.P.S. data^a and molecular formulae.

Organic vapour for plasmolysis ^b	N(1s)/C(1s)		O(1s)/C(1s)	
	X.P.S. ^c	Formula	X.P.S. ^c	Formula
<i>N,N</i> -Dimethylhydrazine	0.418 (0.254)	1.000	0.418 (3.460) ^d	0
Piperidine	0.167	0.200	0.036	0
<i>N</i> -Methylbutylamine	0.174	0.200	0.040	0
Dimethylaniline	0.098	0.125	0.164	0
Pyridine	0.098	0.200	0.115	0
Acetonitrile	0.337 (0.124)	0.500	0.168 (1.912) ^d	0
Isobutyronitrile	0.182	0.250	0.090	0
Dimethylformamide (DMF)	0.328 (0.095)	0.333	0.107 (2.725) ^d	0.333
<i>N</i> -Vinylpyrrolidone (NVP)	0.087	0.167	0.183	0.167
Acrylamide (AAm)	0.086	0.333	0.317	0.333

^a The relative atomic sensitivity was considered to be 2.93 for O(1s), 1.80 for N(1s), and 1.00 for C(1s).⁸ ^b Cover glasses (18 × 18 mm) were used for preparation of plasma-exposed glass samples. The plasma states were generated by radio-frequency (r.f.) discharges operating at 13.56 MHz and 50 W in a closed system with a plasma duration of 60 s. The apparatus used in the present investigation is the same as that reported previously.⁵ ^c The values in parentheses are for the glass after agitation in DMF for 2 h at 25 °C. ^d The increase in value is due to oxygen of the glass substrate.

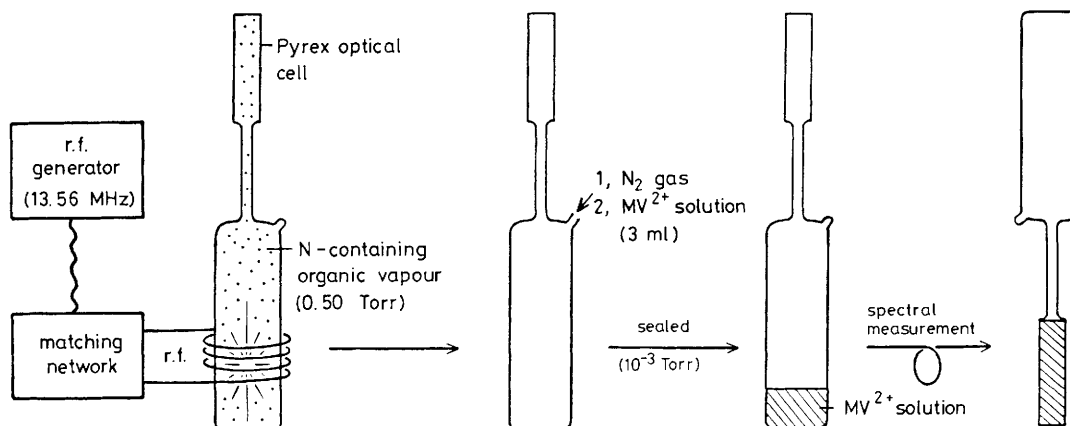


Figure 1. Schematic representation of the measurement of the electronic spectra.

of several plasma-exposed glasses in DMF are also shown in Table 1. It can be seen that the N/C ratio decreased considerably after such agitation, indicating that most of the nitrogen-containing moieties had been leached out of the film into the solvent.

The above-mentioned features are of special interest in connection with the mechanism of 'plasma reduction' recently reported, by which not only electron-accepting compounds, such as solvated and solid viologen homologues, iodine, and organic dye compounds but also some other non-electron-accepting compounds have been shown to undergo an apparent 'one-electron reduction' under plasma conditions similar to those in the present case, but almost exclusively in DMF.¹⁰⁻¹² The mechanism by which these reductions proceeded was ascribed to energetic electrons produced in a plasma state or trapped electrons in DMF.

It is known, however, that some nitrogen bases, like pyrrolidine and piperidine, cause an apparent auto-reduction of the viologens (disproportionation) even at the low concentrations used in biochemical work.¹³ We have also observed, without plasma-exposure, that a variety of nitrogen bases induced not only rapid auto-reductions of viologen homologues under anaerobic conditions, but also instant colour-discharges of iodine and the above-mentioned dye compounds in aprotic solvents such as DMF and acetonitrile.

In this connection, we have examined the catalytic effect of such ultrathin films prepared from several nitrogen-containing organic vapours on the reduction of methyl viologen (MV^{2+}), iodine, and Methylene Blue in DMF solutions, according to the method shown in Figure 1, and the progressive spectral changes for the formation of the monocation radical of MV^{2+} in a DMF plasma-exposed ampoule are shown in Figure 2 as a representative example. It can be seen that an apparent auto-reduction of MV^{2+} was indeed induced by the ultrathin film prepared by a brief plasmolysis of DMF. Similar progressive spectral changes of MV^{2+} were also observed in plasma-exposed ampoules from various nitrogen-containing organic vapours such as *N,N*-dimethylhydrazine, piperidine, *N*-methylbutylamine, dimethylaniline, isobutyronitrile, and acetonitrile. Likewise, the progressive spectral changes of iodine and Methylene Blue in DMF were also observed in a similar procedure. These spectral changes can be ascribed to the formation of a well-known $n-\sigma$ type charge-transfer complex and leuco dye compound, respectively.

Our results strongly suggest that 'plasma reduction' in DMF could be caused by nitrogen-derived basic ultrathin films which are rapidly formed during a brief plasmolysis of DMF on the glass surface and/or on the frozen DMF.† Likewise, a rapid 'plasma reduction' of non-volatile solid (BV^{2+}) benzyl viologen could be ascribed to the instant and direct contact of nitrogen-derived basic plasma-fragmented species and/or an

† A referee claimed that the reaction rate in the present case is much too slow to account for the results reported previously. The numerical data shown for the spectral changes of the reported 'plasma reduction', however, represent the total time for the plasma-generation, not the reaction time,¹⁰⁻¹² which is equivalent to the repeated formation of similar fresh ultrathin film several times in one reaction. Thus, one cannot compare the reaction rates of the present case with those reported previously simply based on comparison of the numerical data shown in both Figures.

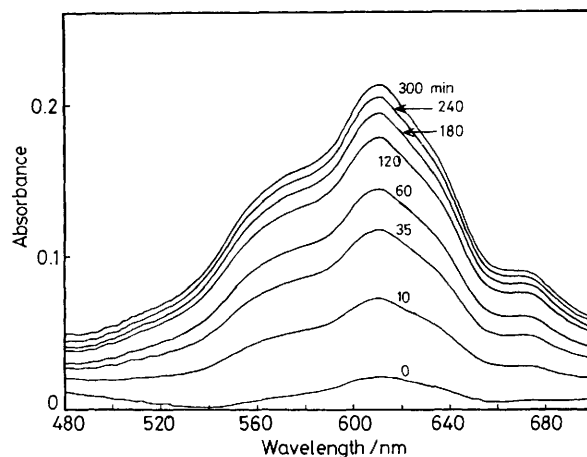


Figure 2. Progressive spectral changes of DMF solution containing MV^{2+} ($1.56 \times 10^{-4} M$) in a DMF plasma-exposed ampoule.

ultrathin film formed from the BV^{2+} itself on the surface of the solid BV^{2+} , induced by brief plasma generation of some residual gaseous compounds, since BV^{2+} is a basic pyridine-based compound.

Furthermore, our suggestion can also account not only for the reported specific solvent effect of DMF, but also for the occurrence of the postreduction of BV^{2+} viologen by plasma-treated DMF solution,¹⁰⁻¹² which otherwise seem difficult to interpret.

We thank Professor Y. Osada (Ibaraki University, Japan) for stimulating discussions.

Received, 10th July 1986; Com. 951

References

- M. Kuzuya, T. Kawaguchi, T. Daikyo, and T. Okuda, *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21**, 515.
- M. Kuzuya, T. Kawaguchi, S. Mizutani, and T. Okuda, *J. Polym. Sci., Polym. Lett. Ed.*, 1985, **23**, 69.
- M. Kuzuya, T. Kawaguchi, Y. Yanagihara, and T. Okuda, *Nippon Kagaku Kaishi (Special Articles on Functional Surface and Interface)*, 1985, 1007.
- M. Kuzuya, S. Nakai, T. Okuda, T. Kawaguchi, and Y. Yanagihara, *J. Chem. Soc., Faraday Trans. 1*, in the press.
- M. Kuzuya, T. Kawaguchi, M. Nakanishi, and T. Okuda, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 1441.
- M. Kuzuya, T. Kawaguchi, Y. Yanagihara, and T. Okuda, *J. Polym. Sci., Polym. Chem. Ed.*, 1986, **24**, 707.
- M. Kuzuya, M. Nakanishi, and S. Nakai, *Chem. Lett.*, 1986, 1985.
- C. D. Wagner, *Anal. Chem.*, 1972, **44**, 1050.
- M. Millard, 'Techniques and Applications of Plasma Chemistry,' eds. J. R. Hollahan and A. T. Bell, Wiley, New York, 1974, pp. 177-213.
- Y. Osada and Y. Iriyama, *J. Am. Chem. Soc.*, 1982, **104**, 2925.
- Y. Osada and Y. Iriyama, *J. Phys. Chem.*, 1984, **88**, 5951.
- Y. Osada, K. Honda, and M. Takase, *Nippon Kagaku Kaishi*, 1984, 1693.
- A. H. Corwin, R. R. Arellano, and A. B. Chivvis, *Biochim. Biophys. Acta*, 1968, **162**, 533.