Solid-phase Reactivity of Pure Methyl Viologen upon Thermolysis and Photolysis: a Vibrational and Electronic Study

Olivier Poizat *
Laboratoire de Spectrochimie Infrarouge et Raman, CNRS, 2 rue Henri Dunant, 94320 Thiais, France
Charles Giannotti
Institut de Chimie des Substances Naturelles, CNRS, 91190 Gif-sur-Yvette, France
Claude Sourisseau
Laboratoire de Spectroscopie Infrarouge, Université de Bordeaux I, 33405 Talence, France

Two reactions are induced from pure solid methyl viologen dichloride, $MV^{2+}(Cl^-)_2$, upon heating under vacuum: warming over 50 °C yields $Cl^-MV^{+\bullet}Cl^\bullet$ *via* an intracomplex electron-transfer process; warming to 180 °C yields 4,4′-bipyridine and CH_3Cl, probably *via* a second intracomplex charge-transfer process. Both these reactions are also shown to occur upon visible excitation of dehydrated $MV^{2+}(Cl^-)_2$. In this case, the $MV^{2+} \longrightarrow MV^{+\bullet}$ reduction does not arise from direct photochemistry but rather results from thermal activation. Similar treatment of the bromide and iodide salts, $MV^{2+}(Br^-)_2$ and $MV^{2+}(I^-)_2$, lead only to the dealkylation products. These reactions have been investigated and followed using i.r., Raman, u.v.–visible, and e.s.r. spectroscopy and their mechanisms are discussed.

The chemistry of methyl viologen (1,1′-dimethyl-4,4′-dipyridinium; MV^{2+}) has been studied mostly in solution[1] and to a lesser extent in rigid media such as matrices or polymers.[2] However, the reactivity of pure methyl viologen salts in the solid state is not completely understood and we have chosen to develop this aspect. In a preliminary communication[3] we have shown that thermal excitation of the pure solid chloride salt, $MV^{2+}(Cl^-)_2$, leads to reduction of MV^{2+}. A mechanism for

$$MV^{2+} \longrightarrow MV^{+\bullet} \qquad (1)$$

intracomplex electron transfer involving the counter ion has been suggested.

Reaction (1) was also observed[3] upon visible light excitation even though the chloride salt does not absorb in the visible region. In both cases, simultaneous dealkylation leading to 4,4′-bipyridine and to methyl chloride has beeen observed.

$$Cl^-MV^{2+}Cl^- \longrightarrow \text{4,4'-bipyridine} + 2\,CH_3Cl \qquad (2)$$

However, it was noted that no reaction occurs upon irradiation if the sample is not dehydrated. In order to understand better the mechanisms governing the reactivity of pure methyl viologen in the solid state, we report here new experimental results obtained by vibrational (i.r., resonance Raman) and electronic (u.v.–visible, e.s.r.) techniques and present a comprehensive survey of spectroscopic data characterizing pure $MV^{+\bullet}$ species.

Experimental

Chloride, bromide, and iodide salts of the following methyl viologen derivatives: $CH_3\text{-}NC_5H_4\text{-}C_5H_4N\text{-}CH_3^{2+}$ ($[^1H_{14}]MV^{2+}$), $CH_3\text{-}NC_5D_4\text{-}C_5D_4N\text{-}CH_3^{2+}$ ($[^2H_8]MV^{2+}$), and $CD_3\text{-}NC_5H_4\text{-}C_5H_4N\text{-}CD_3^{2+}$ ($[^2H_6]MV^{2+}$) were synthesized as previously described.[4,5] All samples were highly purified by successive recrystallizations and their purity checked by microanalysis. Ether was excluded at all stages to avoid the formation of epoxide radicals.

Thermolyses were performed directly inside quartz tubes (for Raman and e.s.r. measurements) or inside special absorption cells (for u.v.–visible or i.r. measurements), according to procedures described in ref. 3. This absorption cell (Figure 1) was designed for simultaneous separation and spectroscopic characterization of the products of reactions (1) and (2). Samples for thermolysis are deposited in a glass bulb S formed in the reaction cell in the vicinity of one of the windows. Transport of products on the cell windows is achieved by

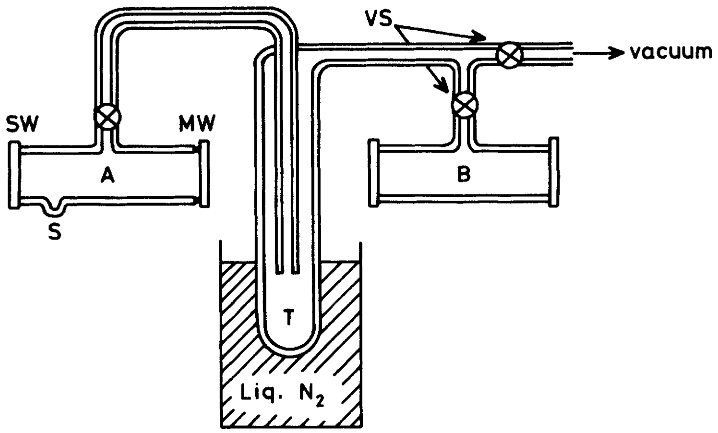

Figure 1. Experimental system used for methyl viologen thermolysis and photolysis. A, B, Absorption glass cells; T, trap; SW, MW, sealed and mobile (O-ring fixed) windows (CsI or CaF_2); VS, vacuum stopcock; S, sample bulb

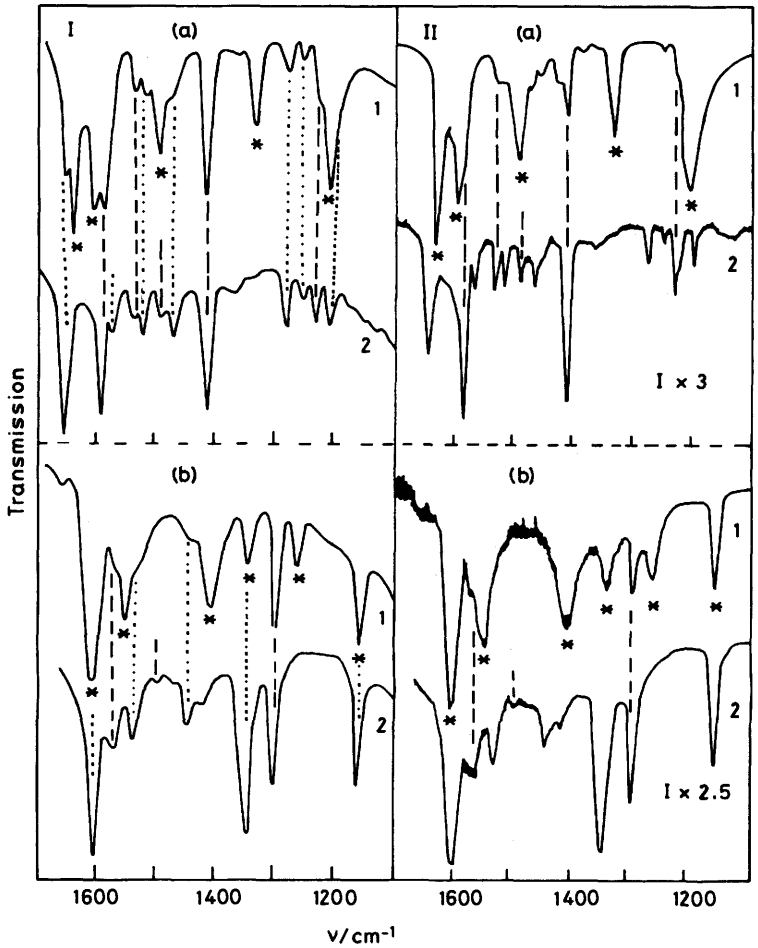

Figure 2. I.r. spectra (1 700—1 100 cm^{-1}) of the product of irradiation (I) and of thermal treatment (II) of the MV^{2+}(Cl$^-$)$_2$, ^{1}H$_{14}$ (a) and ^{2}H$_8$ (b) derivatives under vacuum (1) and after a few seconds air (2). Assignments are given in terms of MV^{2+} (· · · ·), MV$^{+\cdot}$ (*), and 4,4′-bipyridine (– – – –) absorption bands

sublimation and their separation is based on the difference of vapour pressure: the farthest window (MW) is slightly cooled by gaseous nitrogen flowing through liquid nitrogen in such a way that species with low vapour pressure, like MV$^{+\cdot}$, sublime around the heat source, *i.e.* on the closest window (SW), while species with higher vapour pressure like bipyridine sublime on the cooled window (MW). Finally the volatile methyl halides are trapped in a cold finger and can be transferred into a second absorption cell (B), placed in parallel between the trap and the vacuum pump, for further absorption measurements.

Photolysis was done with Spectra Physics 164 krypton (647.1 and 676.4 nm) and argon (454.5 and 514.5 nm) lasers (intensity 0.5—1.0 mW) using the cell in Figure 1. Samples were spread on a window by slow evaporation of water (CaF$_2$ windows) or alcohol solutions (CsI windows). The window was then set up, the cell evacuated, and the laser beam focused on the deposit through the window.

I.r. spectra were recorded on Perkin-Elmer 225 and 983 spectrometers. Nujol and Fluorolube were previously dried, deoxygenated, and stored in evacuated ampoules over sodium wire. U.V.–visible absorption spectra were obtained with a Cary 17 spectrometer in the transmission mode. Raman spectra were recorded on a Dilor RTI triple monochromator (visible range) and on a Jobin Yvon Ramanor HG2S double monochromator (using the 363.8 and 351.1 nm exciting lines from a Spectra Physics 171 argon laser).

E.s.r. spectra were carried out by using the ER 400 X RL cavity of a Bruker ER 420 spectrometer.

Results and Discussion

To extend the results obtained with the MV^{2+}(Cl$^-$)$_2$ salt in the solid state,[3] we have studied the reactivity of different MV^{2+}(X$^-$)$_2$ salts (X = Cl, Br, I) upon thermal and light excitation. For each complex the ^{1}H$_{14}$ (fully hydrogenated), ^{2}H$_8$ (ring deuteriated), and ^{2}H$_6$ (methyl deuteriated) MV^{2+} derivatives were investigated. The products were characterized by comparison of their i.r. spectra (1 800—200 cm^{-1}) with reference spectra for [^{1}H$_{14}$]-, [^{2}H$_8$]-, and [^{2}H$_6$]-MV$^{+\cdot}$,[4,5] 4,4′-bipyridine (^{1}H$_8$ and ^{2}H$_8$),* and methyl halides.[6]

Upon warming to 200 °C or exciting at 647.1 nm, under vacuum, dehydrated MV^{2+}(Cl$^-$)$_2$ samples yield the corresponding MV$^{+\cdot}$ and 4,4′-bipyridine derivatives and CH$_3$Cl (from [^{1}H$_{14}$] and [^{2}H$_8$]MV^{2+}) or CD$_3$Cl (from [^{2}H$_6$]-MV^{2+}). Figure 2 shows the i.r. spectra (1 700—1 100 cm^{-1}) of the products obtained by irradiation (I) and by thermal treatment (II) from [^{1}H$_{14}$]MV^{2+}(Cl$^-$)$_2$ (a), and [^{2}H$_8$]MV^{2+}(Cl$^-$)$_2$ (b); in each case the spectra of the products obtained under vacuum (spectrum 1) and after exposure to air (spectrum 2) are shown. The presence of bands due to residual

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* We have carried out the synthesis and vibrational analysis of the [^{1}H$_8$]- and [^{2}H$_8$]-4,4′-bipyridine. The following i.r. band wavenumbers have been observed in the range 1 700—350 cm^{-1}: NC$_5$H$_4$-C$_5$H$_4$N, 1 590s, 1 530w, 1 488w, 1 406w, 1 217m, 1 073w, 1 038vw, 988m, 977sh, 965vw, 850w, 811s, 733w, 672w, 607s, 570w, 498w, and 375vw cm^{-1}; NC$_5$D$_4$-C$_5$D$_4$N, 1 560s br, 1 502w, 1 310vw, 1 288s, 1 206vw, 958s, 903w, 834w, 646m, 637sh, 592s, 498m, 452m, 435sh, and 351w cm^{-1}.

Table. I.r. band wavenumbers (cm^{-1}) and assignments for the mixtures obtained by thermal treatment of the $^{1}H_{14}$ (fully hydrogenated) and $^{2}H_{8}$ (ring deuteriated) $MV^{2+}(Cl^{-})_2$ derivatives under vacuum and after air exposure

$^{1}H_{14}$		$^{2}H_{8}$		
Vacuum	Air	Vacuum	Air	[a]
1 636 $MV^{+\cdot}$	1 643 MV^{2+}	1 597 $MV^{+\cdot}$	1 602 MV^{2+}	8a
1 598 $MV^{+\cdot}$				
1 590 bipy	1 590	1 558 bipy	1 550	
	1 563 MV^{2+}	1 548 $MV^{+\cdot}$	1 530 MV^{2+}	19a
1 528 bipy	1 530			
1 493 $MV^{+\cdot}$	1 514 MV^{2+}			8b
bipy	1 488			
1 470 1 445 $MV^{+\cdot}$	1 465 MV^{2+}			
1 420 $MV^{+\cdot}$		1 413 $MV^{+\cdot}$	1 450 1 425 MV^{2+}	δ CH_3
1 408 bipy	1 405			
		1 336 $MV^{+\cdot}$	1 335 MV^{2+}	19b
1 332 $MV^{+\cdot}$	1 368 MV^{2+}			
		1 288 bipy	1 284	
		1 262 $MV^{+\cdot}$	1 284 MV^{2+}	14
	1 242 MV^{2+}			
1 212 bipy	1 217			
1 208 $MV^{+\cdot}$				
1 200 $MV^{+\cdot}$	1 189 MV^{2+}			
		1 142 $MV^{+\cdot}$	1 134 MV^{2+}	N–Me
1 070 bipy	1 073			
1 032 1 003 $MV^{+\cdot}$				1, 12
988 bipy	990	961 bipy		
		918 $MV^{+\cdot}$	917 MV^{2+}	9a
878 $MV^{+\cdot}$	884 MV^{2+}			
		868 822 $MV^{+\cdot}$	867 822 MV^{2+}	18a,b
809 $MV^{+\cdot}$ bipy	810			
		802 $MV^{+\cdot}$	806 MV^{2+}	5
		756 $MV^{+\cdot}$	755 MV^{2+}	17a
		676 $MV^{+\cdot}$	675 MV^{2+}	11

[a] Symbols characterizing the MV^{2+} and $MV^{+\cdot}$ normal modes in the notation used for MV^{2+} in ref. 5.

MV^{2+} in spectra 1 (Ia and Ib) is indicative of incomplete irradiation of the sample. The Table shows the corresponding i.r. band wavenumbers and assignments. These results confirm that $MV^{2+}(Cl^{-})_2$ undergoes both reactions (1) and (2) upon heating or upon visible irradiation. Interestingly, no reaction is observed in the presence of oxygen.

Similar treatment of the $MV^{2+}(Br^{-})_2$ and $MV^{2+}(I^{-})_2$ salts leads only to the related 4,4′-bipyridine and methyl halide derivatives, *i.e.* to the products of reaction (2). This reaction is also inhibited by the presence of oxygen.

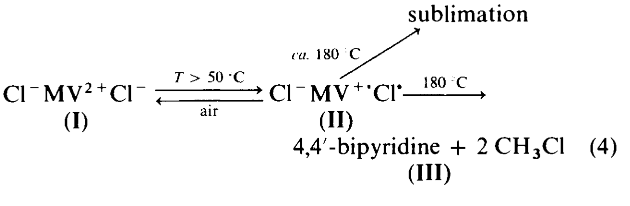
The fact that, as a general rule, similar behaviour is observed upon heating and upon visible light excitation indicates that in both cases the reactions are governed by similar thermally activated processes. To gain better insight into these processes, we first focused our attention on the reactivity of $MV^{2+}(Cl^{-})_2$ upon heating.

Reactivity of $MV^{2+}(Cl^{-})_2$ *upon Thermolysis.*—Pure solid $MV^{2+}(Cl^{-})_2$ is usually hydrated in air. We have established elsewhere[5] that dehydration of $MV^{2+}(Cl^{-})_2$ under vacuum occurs at *ca.* 50 °C and can be monitored by i.r. spectroscopy. From simultaneous i.r. and e.s.r. measurements we observed that an e.s.r. signal appears after complete dehydration and increases with increasing temperature. This signal is similar to that obtained with pure methyl viologen radical isolated after sublimation of $MV^{2+}(Cl^{-})_2$. When the temperature is lowered, this e.s.r. spectrum persists as long as the sample is maintained under vacuum. However, electronic and vibrational spectra are still characteristic of the starting complex, $MV^{2+}(Cl^{-})_2$. This indicates that the radical concentration is extremely low. The preceding results demonstrate that trace amounts of methyl viologen radical are present in the anhydrous salt; therefore reaction (1) occurs with very low efficiency over 50 °C. When the temperature reaches 180—200 °C, a heterogeneous mixture sublimes, composed of 4,4′-bipyridine and methyl viologen radical. This mixture has been characterized by the vibrational spectrum 1 (IIa Figure 2). This temperature range corresponds thus to the onset of sublimation for the radical species. However, 4,4′-bipyridine is much more volatile and usually sublimes at *ca.* 80 °C. Therefore its appearance at 180—200 °C characterizes the onset temperature for reaction (2). No intermediate products of monodealkylation nor degradation compounds were observed but 4,4′-bipyridine and methyl chloride were found. Moreover, the methyl viologen radical reverts to the dichloride complex, $MV^{2+}(Cl^{-})_2$, as soon as it is exposed to air. Spectroscopic and chemical analyses confirm that the solid mixture resulting from thermal treatment or irradiation, followed by oxidation in air, is composed exclusively of 4,4′-

bipyridine and $MV^{2+}(Cl^-)_2$. In the same way, pure radical samples lead quantitatively to the dichloride salt, $MV^{2+}(Cl^-)_2$, in air. Methyl viologen thus conserves a dichloride complexed form in its radical state. It turns out that, as suggested previously,[3] reaction (1) occurs *via* intracomplex electron transfer between the viologen entities and the counter ion [reaction (3)].

$$\underset{(I)}{Cl^-MV^{2+}Cl^-} \underset{air}{\overset{I}{\rightleftharpoons}} \underset{(II)}{Cl^-MV^{+\cdot}Cl^{\cdot}} \qquad (3)$$

In addition, we find that further thermal treatment of the pure radical salt, isolated by sublimation, again leads to the formation of 4,4′-bipyridine and methyl chloride. Therefore the dealkylation process is induced from the radical form of the complex *i.e.* reaction (2) follows (1) and is competitive with sublimation [reaction (4)].



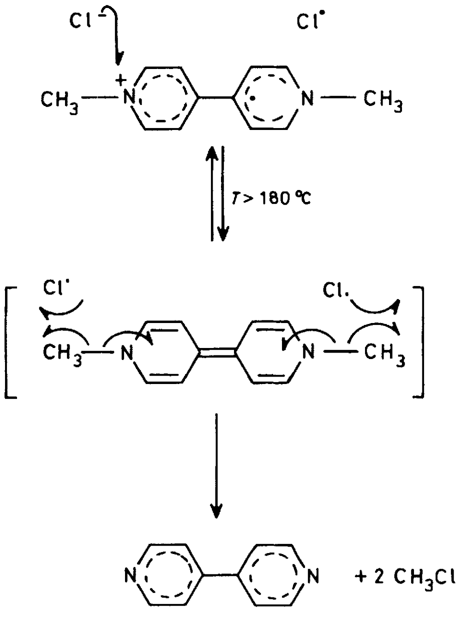
$$\underset{(I)}{Cl^-MV^{2+}Cl^-} \underset{air}{\overset{T > 50\ °C}{\rightleftharpoons}} \underset{(II)}{Cl^-MV^{+\cdot}Cl^{\cdot}} \xrightarrow{180\ °C} \underset{(III)}{4,4'\text{-bipyridine} + 2\,CH_3Cl} \qquad (4)$$

Similar schemes must govern the reactivities of the iodide and bromide salts. However in these cases the radical products of reaction (1) cannot be isolated under these conditions and probably exist only as transients of reaction (2).

$$X^-MV^{2+}X^- \overset{\Delta}{\rightleftharpoons} (X^-MV^{+\cdot}X^{\cdot}) \xrightarrow{\Delta} 4,4'\text{-bipyridine} + 2\,CH_3X \qquad (5)$$

(X = Br, I)

In both reactions (4) and (5), quenching by oxygen of the formation of the radical [reaction (1)] accounts for inhibition of dealkylation [reaction (2)] in air. A probable mechanism for this reaction would involve the formation of the unstable neutral intermediate $Cl^{\cdot}MV^0Cl^{\cdot}$ resulting from a second electron transfer, followed by spontaneous homolytic breaking of the N-CH_3 bonds (Scheme).



Scheme.

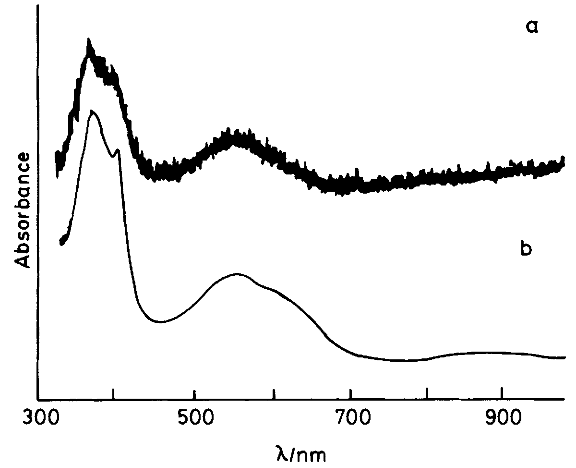


Figure 3. Electronic absorption spectra (300—1 000 nm) of the methyl viologen radical cation generated in the solid phase *via* light excitation (a) and *via* thermolysis (*b*)

In any case, reactions (4) and (5) definitely account for the reactivity of pure methyl viologen halides upon heating. As suggested above, similar thermally activated processes are also probably induced upon visible irradiation. We have thus attempted to confirm and to explain this behaviour.

Reactivity of $MV^{2+}(Cl^-)_2$ *upon Visible Irradiation*.—Pure $MV^{2+}(Cl^-)_2$ does not absorb in the visible range. However, this complex shows unexpected behaviour upon laser irradiation under vacuum: direct irradiation of moist $MV^{2+}(Cl^-)_2$ has no appreciable effect; in contrast, irradiations at 454.5, 514.5, 647.1, or 676.4 nm of dehydrated samples maintained under vacuum induce instantaneously reactions (1) and (2) and lead to a mixture of radical and 4,4′-bipyridine (see Figure 2, I). However, the amount of 4,4′-bipyridine increases quickly upon irradiation while the radical species disappears. This result is consistent with the existence of two consecutive reactions (6) and

$$Cl^-MV^{2+}Cl^- \underset{air}{\overset{\text{i, }-H_2O \atop \text{ii, }h\nu}{\rightleftharpoons}} Cl^-MV^{+\cdot}Cl^{\cdot} \xrightarrow{h\nu} 4,4'\text{-bipyridine} + 2\,CH_3Cl \qquad (6)$$

underlines the analogy of the $MV^{2+}(Cl^-)_2$ reactivities upon heating and upon irradiation. This analogy and the fact that $MV^{2+}(Cl^-)_2$ does not absorb in the visible range strongly confirm that reactions (6) do not involve photochemical effects but rather proceed *via* intramolecular heat transfers.

As shown above and as suggested in our preliminary communication,[3] dehydration of $MV^{2+}(Cl^-)_2$ leads to the formation of light-sensitive $MV^{+\cdot}$ which behaves as a heat source upon visible irradiation and gives rise to energy transfers *via* vibrational or collisional relaxation. In consequence, traces of $MV^{+\cdot}$ can be regarded as absorbing defects in the anhydrous $MV^{2+}(Cl^-)_2$ lattice which initiate, through energy transfer, chain processes which spread over the whole sample upon visible excitation.

Spectroscopic Analysis of Solid $MV^{+\cdot}$.—Figure 3 presents the u.v.–visible absorption spectra of $MV^{+\cdot}$ generated in the solid state *via* photolysis (a) and thermolysis (b) of pure $MV^{2+}(Cl^-)_2$ These spectra are characteristic of dimeric $(MV^{+\cdot})_2$ units[7] resulting from π-overlap. The related e.s.r. spectrum shows a single intense and unresolved isotropic line with g_{iso} 2.002 60 ± 0.000 08 and a peak to peak width of 3.23 ± 0.016 corres-

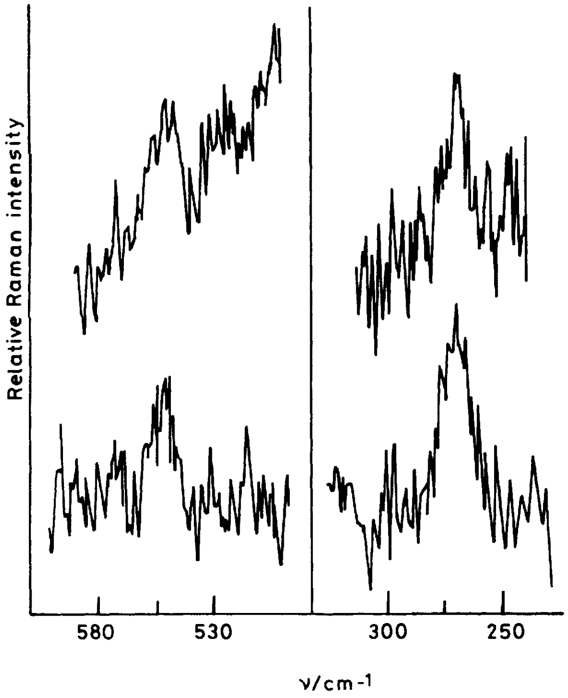


Figure 4. Details of the Raman spectra (610—500 and 330—230 cm^{-1}) of pure methyl viologen radical cation recorded by using the 363.8 (upper trace) and the 351.1 nm (lower trace) exciting laser lines

ponding probably to such molecular association.[8,9] The loss of hyperfine structure on going from dilute solutions[7] to solid samples is consistent with the formation of π-complexes and can be explained as a result of rapid charge exchanges in the radical dimer. However, the high intensity of this e.s.r. signal is indicative of the presence of unpaired electrons. We thus conclude that in the solid phase there exist paramagnetic diradical dimers ($MV^{+\cdot} \cdots MV^{+\cdot}$) with a large Coulomb repulsion and weak charge-transfer interaction between the π electrons in the two halves of the complex. The absence of strong π-interaction in the dimer is consistent with the facts that (i) no intense absorption is observed in the range 800—1 000 nm[10] (see Figure 3) and (ii) the vibrational data of the dimer and of the trapped $MV^{+\cdot}$ monomer are quite comparable.[4] Similar π-radical dimers stabilized by charge-transfer interaction have already been characterized[11] for most stable aromatic organic radicals like tetracyanoquinodimethane ($TCNQ^{-\cdot}$) or tetrathiafulvalene ($TTF^{+\cdot}$). The mechanism of charge exchange in the dimer has been studied;[12] it can be described as an oscillation of the unpaired electrons back and forth between the radicals induced by molecular vibrations.[12,13] This vibronic interaction is generally responsible of strong intensity perturbations in the i.r. spectra.[13] As a matter of fact, we have reported[3,4] the presence of such anomalies in the i.r. spectra of solid $MV^{+\cdot}$, which can be accounted for by vibronic effects.

The characteristic i.r. absorptions of pure $MV^{+\cdot}$ ([$^1H_{14}$] and [$^2H_8$] derivatives) are listed in the Table. The corresponding assignments in terms of normal modes of vibration have been given elsewhere.[3] The Raman spectra obtained using visible excitations have also been discussed previously.[5] However, we obtained new information from the Raman spectra recorded with u.v. excitation* (λ_0 351.1 and 363.8 nm). While bands due to $MV^{+\cdot}$ are very similar in frequency and relative intensity to those reported by Forster *et al.*[14] for $MV^{+\cdot}$ in aqueous solutions, new signals are observed at 268 and 540 cm^{-1} (±3 cm^{-1}) (Figure 4). We propose to assign these lines to the fundamental and the first overtone of the stretching vibration of the radical anion $(Cl_2)^{-\cdot}$. In fact $(Cl_2)^{-\cdot}$ is reported to absorb at *ca.* 340—390 nm[15] and to exhibit intense resonance Raman spectra upon u.v. excitation with a long progression of overtones[16,17] (fundamental at 225—265 cm^{-1} in rigid matrix[16] and at 271—279 cm^{-1} in aqueous solutions[17]). This indicates that part of the methyl viologen radical exists in the form $MV^{+\cdot}$-$(Cl_2)^{-\cdot}$. It is not easy to estimate the relative amounts of $Cl^{\cdot}$ and $(Cl_2)^{-\cdot}$ species from the Raman data only. Unfortunately we were unable to detect absorptions due to $(Cl_2)^{-\cdot}$ in the electronic spectra (Figure 3) because of the low signal-to-noise ratio at low wavelength and because dimeric $MV^{-\cdot}$ absorbs in the same region (maximum at 370 nm). In any case, absorption due to $Cl^{\cdot}$ in charge-transfer complexes also takes place in the 300—360 nm range[15] and it is probably difficult to discriminate between $Cl^{\cdot}$ and $(Cl_2)^{-\cdot}$ species from electronic data.

Conclusions.—From this spectroscopic study we have shown that an intracomplex electron-transfer process takes place in pure solid $MV^{2+}(Cl^-)_2$ over 50 °C in the absence of light, leading to the corresponding $Cl^-MV^{+\cdot}$ $Cl^{\cdot}$ radical. The formation of $MV^{+\cdot}(Cl_2)^{-\cdot}$ species has also been shown by resonance Raman spectroscopy. Upon further heating over 180 °C the radical undergoes dealkylation reaction leading to the formation of 4,4′-bipyridine and methyl chloride. This reaction is likely to result from an electron-transfer process in the second step yielding the unstable intermediate, $Cl^{\cdot}MV^0Cl^{\cdot}$, following by cleavage of the N–CH_3 bonds. Similar reactions are observed with the methyl viologen dibromide and di-iodide salts. However, in these cases, both electron-transfer products, $X^-MV^{+\cdot}X^{\cdot}$ and $X^{\cdot}MV^0X^{\cdot}$, are unstable and probably appear as intermediates in the dealkylation process.

Finally it appeared that both the methyl viologen radical complex and dealkylation products are generated upon visible excitation of pure dehydrated $MV^{2+}(Cl^-)_2$ in the solid state. In this case, the reactions do not result from a photochemical process but can once more be described in terms of thermally activated intracomplex electron transfers. They are initiated by the presence in anhydrous samples of traces of $MV^{+\cdot}$ which behave as absorbing centres and local heat sources for energy transfer. Thermal effect may thus provide a parallel reduction pathway to photosensitization and direct photochemistry of MV^{2+}.

Acknowledgements

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