TIME-RESOLVED RESONANCE RAMAN STUDIES OF TRANSIENT SPECIES IN THE PHOTOIONIZATION OF N,N,N',N'-TETRAMETHYL-p-PHENYLENEDIAMINE IN SOLUTION

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Summary

The time-resolved resonance Raman spectra of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in various solvents reveal that in polar solvents including acetone and in non-polar CCl_4 the ionization of TMPD takes place monophotonically, while in hydrocarbon solvents monophotonic ionization does not occur and only the lowest excited triplet state $^3TMPD^*$ is produced. The unusual monophotonic ionization of TMPD in CCl_4 solution is explained as being due to the large electron-attaching ability of CCl_4 leading to the formation of an ion pair consisting of the radical cation $TMPD^+$ and Cl^-. The existence of these ionic species is verified by the resonance Raman spectrum of an aqueous solution of the blue precipitate produced by prolonged UV irradiation of CCl_4 solution and by the results obtained on addition of $AgNO_3$ to the aqueous solution. Increasing the intensity of the irradiating UV light led to the detection of biphotonically produced $TMPD^+$ in hexane solution. The quantum yield of the biphotonic ionization is extremely small.

1. Introduction

Because of its relatively low ionization potential, N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) readily undergoes photoionization in solution on irradiation with UV light to produce the radical cation $TMPD^+$ (Wurster's blue) [1].

It is generally accepted that electron photoejection of TMPD in polar solvents proceeds monophotonically from the lowest excited singlet state $^1TMPD^*$ via a semi-ionized state [2 - 4], while in non-polar solvents monophotonic ionization is not induced by irradiation with UV light of wavelength longer than 300 nm [5, 6]. It has been demonstrated by means of photoconductivity measurements [7, 8] that the biphotonic ionization pro-

cess takes place in rigid and fluid 3-methylpentane or isopentane solutions, with ^{3}TMPD* or both ^{1}TMPD* and ^{3}TMPD* as the photoactive intermediates.

Recently, however, two experimental results have been reported which are not in accord with the operation of this accepted process. Time-resolved microwave conductivity measurements by Warman and Visser [9] revealed that monophotonic ionization of TMPD takes place even in non-polar CCl_4 solution. In contrast, the laser photolysis measurements of Tokumura et al. [10] seem to indicate that monophotonic ionization of TMPD did not occur in polar acetone solution.

In view of the fact that the photoionization mechanism of TMPD is closely related to the properties of the solvent, the interesting effect of the solvent on the nature of the photolytically produced transient species still needs to be investigated by various methods.

The purpose of this work was to obtain more information on the transient species of TMPD in various solvents, including CCl_4 and acetone, by time-resolved resonance Raman spectroscopy and to elucidate the photoionization mechanism of this compound.

2. Experimental details

The experimental system used for time-resolved Raman spectroscopy has been described previously [11]. A nitrogen laser (Molectron UV-24) or an excimer laser (Lambda Physik EMG 201E) was used as a UV source for photoexcitation, and a tunable flash-lamp pumped-dye laser (Phase-R DL-1400) was employed for Raman excitation. The Raman signals were detected on a multichannel analyser (Tracor Northern TN-1223-4GI), and the frequencies, which were calibrated using emission lines from a neon lamp, were believed to be accurate to ± 2 cm^{-1}.

TMPD was obtained from Aldrich Chemical Co. Inc. and was purified by sublimation in vacuo. Acetonitrile, methanol, 1-propanol and 2-propanol were GR grade from Kanto Chemical Co. Inc. and were used as received. Hexane, cyclohexane, 3-methylpentane and isopentane, which were also GR grade from Kanto Chemical Co. Inc., were dried by refluxing over sodium followed by distillation. Acetone and CCl_4 were Spectrograde from the same company and were distilled after refluxing over P_2O_5 for 2 h to remove traces of water.

3. Results

3.1. Hydrocarbon solutions

The time-resolved resonance Raman spectra of TMPD in deoxygenated hexane solution are shown in Fig. 1. At 200 ns after UV irradiation two bands were observed at 1530 and 1158 cm^{-1} which rapidly decreased in intensity and at 1 μs they had almost disappeared. When the solution was
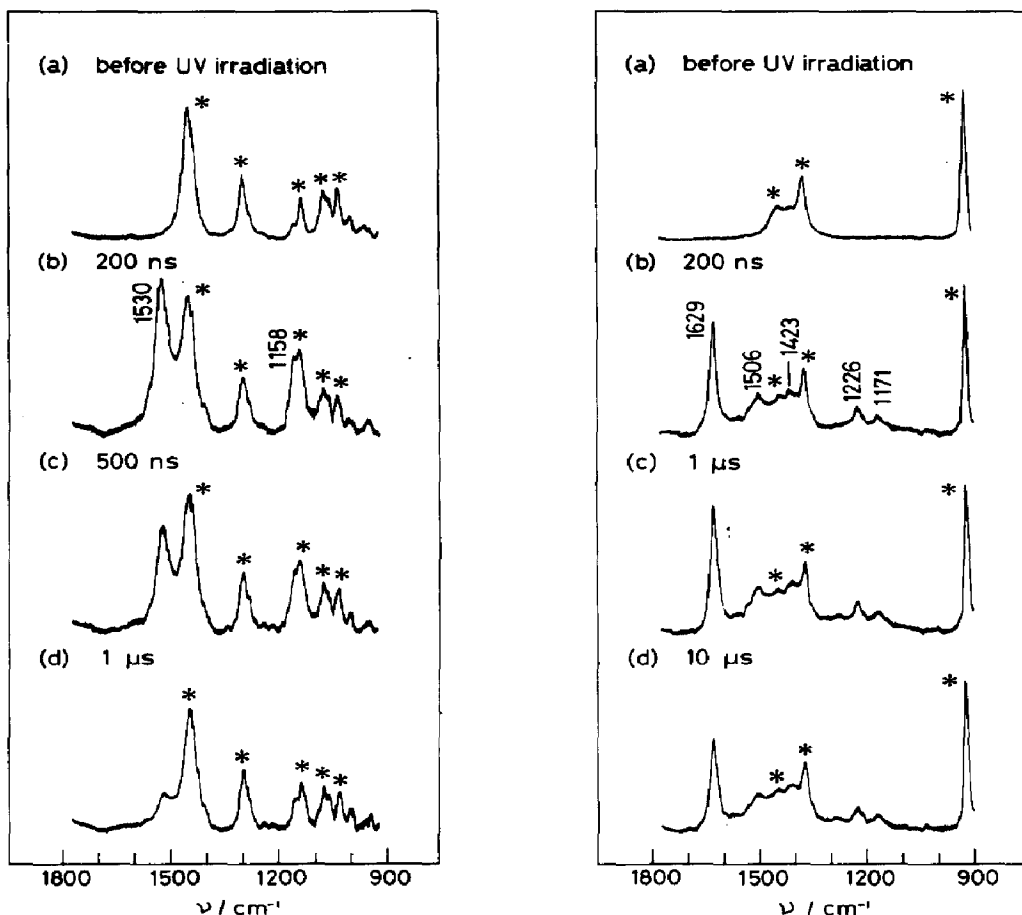
Fig. 1. Time-resolved resonance Raman spectra of TMPD in hexane solution (concentration, 10^{-2} mol 1^{-1}; excitation wavelength, 580 nm; UV source, N_2 laser with 10 mJ pulse^{-1} at the laser head): (a) before UV irradiation; (b) 200 ns after UV irradiation; (c) 500 ns after UV irradiation; (d) 1 μs after UV irradiation. (* indicates the bands of the solvent.)

Fig. 2. Time-resolved resonance Raman spectra of TMPD in acetonitrile solution (concentration, 10^{-3} mol 1^{-1}; excitation wavelength, 580 nm): (a) before UV irradiation; (b) 200 ns after UV irradiation; (c) 1 μs after UV irradiation; (d) 10 μs after UV irradiation. (* indicates the bands of the solvent.)

aerated, these bands weakened and their lifetime shortened drastically and they were only barely detectable at 200 ns.

Thus, these bands are attributable to ^{3}TMPD*. The band at 1530 cm^{-1} coincides with that reported by Yokoyama [12]. TMPD$^+$ was not detected. Similar results were obtained for cyclohexane, 3-methylpentane and isopentane solutions.

3.2. Solutions in polar solvents

Figure 2 shows the time-resolved resonance Raman spectra of TMPD in deoxygenated acetonitrile solution. At 200 ns after UV irradiation a

transient species characterized by the bands at 1629, 1506, 1423, 1226 and 1171 cm^{-1} was observed. The decay of the transient species was too slow to be measured using the present experimental set-up. The spectra were not affected by the presence of oxygen.

The frequencies coincide well with those of Wurster's blue [13] or the radical cation generated electrochemically [14]. Thus, the transient species is identified as TMPD$^+$. The triplet state was not detected. Since the decay time of ^{3}TMPD* in acetonitrile solution, which is about 500 ns [4], is within the detection limit of our set-up, the failure to observe ^{3}TMPD* is considered to be due to its very low quantum yield in this solvent [3]. A similar result was obtained in methanol solution.

Figure 3 shows the time-resolved resonance Raman spectra of TMPD in deaerated 2-propanol solution. In this solvent both ^{3}TMPD* and TMPD$^+$ were observed simultaneously. It is seen that the bands of ^{3}TMPD* rapidly decreased in intensity and had almost disappeared 1 μs after UV irradiation, while the intensity decrease of the bands of TMPD$^+$ was quite slow. Almost the same result was obtained in 1-propanol solution.
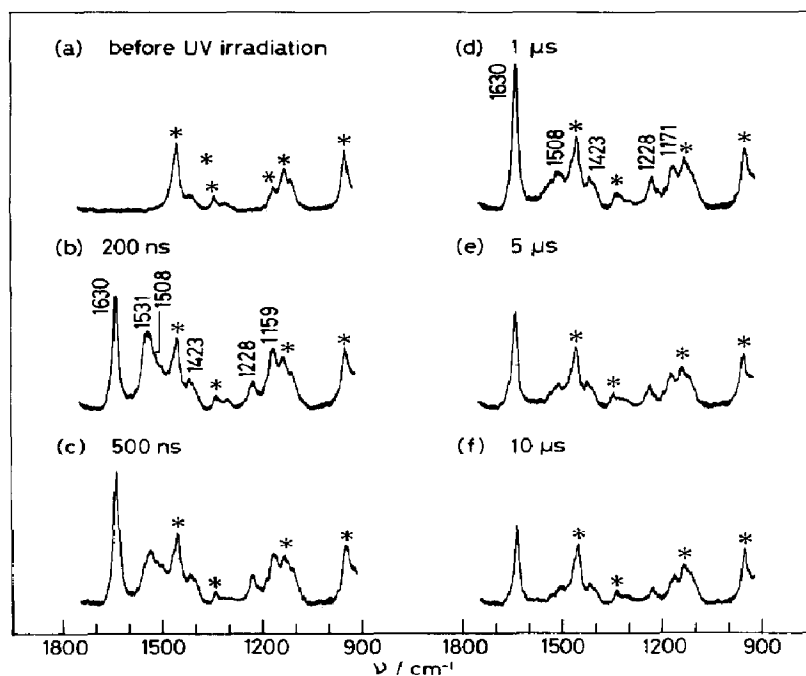

Fig. 3. Time-resolved resonance Raman spectra of TMPD in 2-propanol solution (concentration, 10^{-2} mol l^{-1}; excitation wavelength, 580 nm): (a) before UV irradiation; (b) 200 ns after UV irradiation; (c) 500 ns after UV irradiation; (d) 1 μs after UV irradiation; (e) 5 μs after UV irradiation; (f) 10 μs after UV irradiation. (* indicates the bands of the solvent.)

3.3. Comparison of the spectra of TMPD, ³TMPD* and TMPD⁺

Figure 4 compares the Raman spectra of the ground state, the triplet state and the radical cation of TMPD. Solvent bands were subtracted from each spectrum.

It is interesting to note that although it is sometimes quite difficult to discriminate between the absorption spectra of ³TMPD* and TMPD⁺ because of their strong similarity, the resonance Raman spectra of the two transients are distinctly different and readily distinguishable. In particular, the separation of almost 100 cm⁻¹ between the most prominent Raman bands of ³TMPD* and TMPD⁺ shows that resonance Raman spectroscopy is a more reliable means for the identification of these transient species than absorption spectroscopy.

The band at 1530 cm⁻¹ of ³TMPD* and the band at 1629 cm⁻¹ of TMPD⁺ are both assigned to the 8a mode (Wilson vibration number) of the benzene ring. Since this mode is 1621 cm⁻¹ for TMPD, the drop in frequency on going from the ground state to the triplet state is very large. This is to be expected since in the triplet state an electron is elevated to an antibonding orbital and thus the benzene ring is weakened.
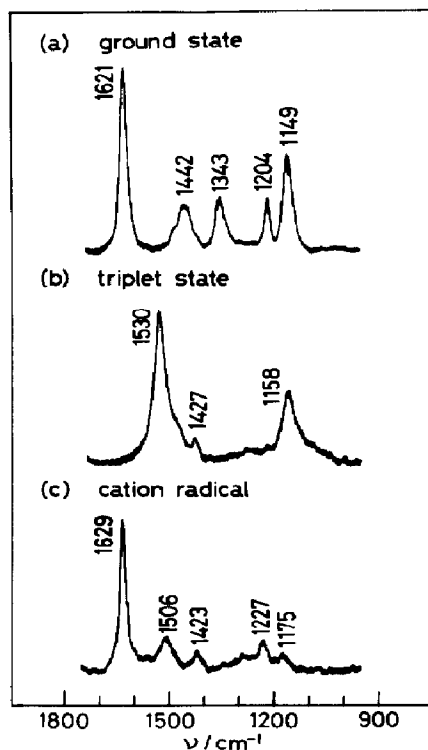

Fig. 4. Comparison of the Raman spectra of TMPD, ³TMPD* and TMPD⁺ (excitation wavelength, 580 nm): (a) Raman spectrum of TMPD; (b) resonance Raman spectrum of ³TMPD*; (c) resonance Raman spectrum of TMPD⁺. Solvent bands were subtracted.

3.4. Carbon tetrachloride solution

Warman and Visser [9] observed a large microwave conductivity change on laser flash photolysis of TMPD in CCl_4, which they ascribed to monophotonic ionization. They also suggested that the ion pair $TMPD^+Cl^-$ forms in this solvent on UV irradiation.

Our time-resolved resonance Raman spectra are in good agreement with their results. As shown in Fig. 5, weak Raman bands were observed at 1630, 1424, 1226 and 1174 cm^{-1} at 200 ns after UV irradiation. These bands may confidently be attributed to $TMPD^+$.

The quantum yield of $TMPD^+$ in CCl_4 is not so small as it appears. The intensities of these bands are weak because $TMPD^+$ is almost insoluble in this solvent. On prolonged irradiation with UV light a blue precipitate was formed, and this presumably originated from coagulation of $TMPD^+$ and counterions.

We found that the resonance Raman spectrum of an aqueous solution of the blue precipitate was identical with that of $TMPD^+$. In addition, the aqueous solution of the blue precipitate yielded a white precipitate of AgCl on addition of $AgNO_3$. Thus, the counterion is Cl^-, and the production of $TMPD^+$ and Cl^- in CCl_4 solution during UV irradiation is verified.

We believe that the unusual monophotonic ionization of TMPD in nonpolar CCl_4 solution should be ascribed to the formation of an ion pair consisting of $TMPD^+$ and Cl^- which stabilizes the radical cation.

3.5. Acetone solution

Tokumura et al. [10] reported that in acetone solution $TMPD^+$ was not detectable by laser photolysis measurement. They observed a very weak transient absorption in the region 500 - 650 nm with a decay time of 100 μs and attributed it to $^3TMPD^*$ on the grounds that the $S_1 \rightarrow T_1$ intersystem crossing probability of the solvent acetone, which is 0.90, is sufficiently high
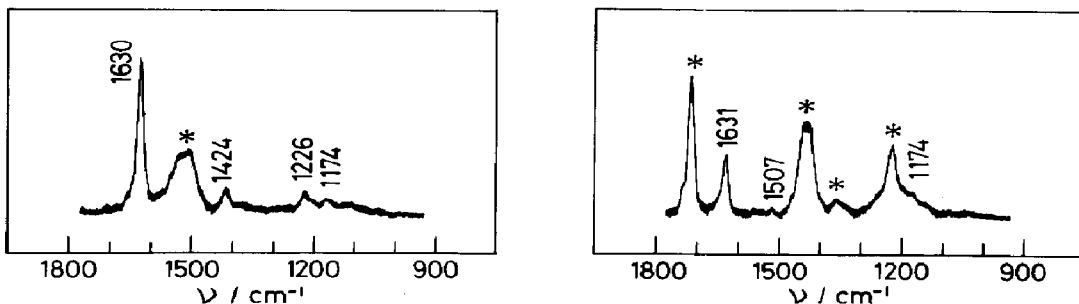

Fig. 5. Resonance Raman spectrum of TMPD in CCl_4 solution at 200 ns after UV irradiation (concentration, 10^{-2} mol l^{-1}; excitation wavelength, 580 nm). (* indicates the band of the solvent.)

Fig. 6. Resonance Raman spectrum of TMPD in acetone solution at 200 ns after UV irradiation (concentration, 10^{-2} mol l^{-1}; excitation wavelength, 580 nm). (* indicates the bands of the solvent.)

for the acetone triplet to excite TMPD to the triplet state through diffusion-controlled sensitization.

Our time-resolved resonance Raman spectra of TMPD in deaerated acetone solution did not agree with the above result. As shown in Fig. 6, weak Raman bands were observed at 1631, 1507 and 1174 cm^{-1} as soon as 200 ns after UV irradiation and these had disappeared after about 100 μs. The spectra were not affected by the presence of oxygen. These bands are confidently assigned to TMPD$^+$. No band attributable to ^{3}TMPD* was detected.

It is apparent, however, that despite the electron-attaching ability of acetone the quantum yield of TMPD$^+$ in this solvent is surprisingly small.

3.6. Biphotonic ionization

The biphotonic ionization of TMPD has not been demonstrated spectroscopically. We have tried to observe biphotonically produced TMPD$^+$ in hydrocarbon solutions by increasing the intensity of the irradiating UV light using an excimer laser operated at 308 nm with a pulse energy of 500 mJ at the laser head.

As shown in Fig. 7, when the UV light was sharply focused onto the sample, a very weak Raman band was observed at 1631 cm^{-1} for the hexane solution, in addition to the bands of ^{3}TMPD*. However, when the UV light was defocused, this band could no longer be detected despite the persistence of the bands of the triplet state. This weak band is undoubtedly the most prominent Raman band of TMPD$^+$. Thus, although the quantum yield is extremely low, it is obvious that TMPD$^+$ is produced.
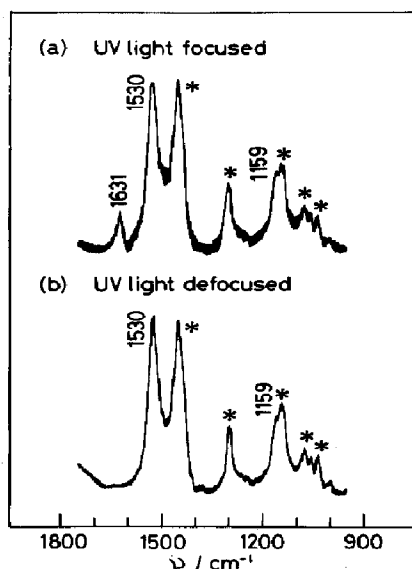

Fig. 7. Resonance Raman spectrum of TMPD in hexane solution at 200 ns after UV irradiation (concentration, 10^{-2} mol l^{-1}; excitation wavelength, 580 nm; UV source, excimer laser operated at 308 nm with 500 mJ pulse^{-1} at the laser head): (a) UV light sharply focused; (b) UV light defocused. (* indicates the bands of the solvent.)

It is tempting to associate the production of TMPD$^+$ in hexane solution with the biphotonic process. However, owing to the very weak intensity of the band at 1631 cm^{-1} and the fluctuation of the power of the excimer laser, it was not possible to obtain a correlation between the Raman band intensities and the UV light intensity with certainty.

The possibility that TMPD$^+$ was produced because of traces of water in the hexane can be ruled out because the hexane had been carefully dried with sodium followed by distillation. Although we do not have definite evidence at the moment, we are confident that the appearance of this weak Raman band can be ascribed to the biphotonic ionization.

4. Discussion

The ionization potential of TMPD is 6.6 eV in the gaseous state [15], and this corresponds to the energy of a photon of wavelength 188 nm. Although this value is remarkably low for an organic molecule, it is still sufficiently high to prevent TMPD undergoing monophotonic ionization on irradiation with UV light of wavelength longer than 300 nm.

In polar solvents having large dielectric constants, however, the ionization potential of TMPD is expected to be low owing to orientation of the solvent molecules around the TMPD molecules. The monophotonic ionization of TMPD in polar solvents may be explained in terms of this effect as well as the stabilization derived from solvation of photolytically produced TMPD$^+$.

In contrast, in non-polar solvents the ionization potential of TMPD is not reduced significantly because the dielectric constants of the solvents are small and thus two light quanta are needed for each one-electron photoionization.

Our time-resolved resonance Raman spectra of TMPD in various solvents show that the above interpretation is in general justified. However, they also reveal that there are exceptions where this interpretation fails. It is evident that the monophotonic ionization of TMPD in CCl$_4$ cannot be explained in terms of a lowering of the ionization potential resulting from the orientation of the solvent molecules, because the dielectric constant of CCl$_4$ is small ($\epsilon = 2.2$).

The unusual monophotonic ionization of TMPD in CCl$_4$ solution might be ascribable to the large electron-attaching ability of CCl$_4$, which could abstract an electron from TMPD in the lowest excited singlet state to form an ion pair consisting of TMPD$^+$ and Cl$^-$ and thus stabilize TMPD$^+$. Evidence for this process is provided by our observation that TMPD$^+$ and Cl$^-$ exist in CCl$_4$ solution after UV irradiation.

The behaviour in acetone solution is also anomalous. The dielectric constants of acetone and 2-propanol are almost the same ($\epsilon = 20.7$ and $\epsilon = 19.9$ respectively), but the quantum yield of TMPD$^+$ is much lower in acetone than in 2-propanol. Moreover, the electron-attaching ability of

acetone is larger than that of acetonitrile, but the quantum yield of $TMPD^+$ in acetone solution is much lower than that in acetonitrile solution.

Therefore the low quantum yield of $TMPD^+$ in acetone solution cannot be explained in terms of the dielectric constants or the electron-attaching abilities of the solvents. It seems probable that the stability of the semi-ionized state should be taken into account for a proper understanding of the photoionization of TMPD in solution.

For alcoholic solutions and acetonitrile solution, the semi-ionized states were identified by Hirata and Mataga [3] to be an ion pair consisting of $TMPD^+$ and a solvated electron and an ion pair consisting of $TMPD^+$ and $(CH_3CN)_n^-$ respectively. The quantum yield of $TMPD^+$ was dependent on the stability of these ion pairs. Although the semi-ionized state in acetone solution has not yet been identified, it is conceivable that the charge transfer state from TMPD to acetone is not very stable.

Our time-resolved resonance Raman spectra also demonstrate that monophotonic ionization of TMPD does not occur in hydrocarbon solutions on irradiation with UV light of wavelength 337.1 nm, but when the irradiating UV light is very intense biphotonic ionization does take place with an extremely low quantum yield. We could not determine, however, whether the photoactive intermediate was $^1TMPD^*$ or $^3TMPD^*$ or both, because the pulse width of the excimer laser (about 20 ns) used as the source of the UV light was longer than the lifetime of $^1TMPD^*$ (about 5 ns in hexane [4]).

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