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Electronic and Electron Spin Resonance Spectroscopic Study of the Sensitized Decomposition of Formaldehyde

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Abstract: The sensitized decomposition of formaldehyde to formyl radical was examined using triphenylamine (TPA) and primarily in dichloromethane, in 3-methylpentane, and on silica gel at 77°K. The formation of formyl radical is monophotonic in dichloromethane and primarily biphotonic in 3-methylpentane and on silica gel. We propose (1) the monophotonic process occurs *via* energy transfer from the first excited singlet state of TPA and an excimer or exciplex may be involved and (2), the biphotonic process occurs *via* energy transfer from an upper excited triplet state, T_2 or greater, of TPA and an excimer or exciplex may be involved. Another mechanism could also exist in these cases. The disappearance of formyl radical apparently occurs *via* both second- and first-order processes. A solvent radical of dichloromethane is produced in the presence of formaldehyde and a mechanism is proposed for its formation.

The absorption spectrum of formyl radical in the visible region has been detected by Herzberg and Ramsay[1] in the flash photolysis of acetaldehyde in the gas phase. Pimentel, *et al.*,[2] studied the infrared absorption spectrum of formyl radical, obtained by the photolysis of HI in CO at 20°K. From the same method of obtaining the formyl radical, Adrian and Cochran[3,4] studied the esr spectrum. Marx and Chachaty[5] obtained the formyl radical by γ, X, and uv irradiation of solid formaldehyde at 77°K. Other methods have been used as the irradiation of water–methanol solutions at 77°K[6] or crystals of formic acid.[7]

In a recent work, McQuigg and Calvert[8] studied the photodecomposition of formaldehyde by flash photolysis. Two distinct primary photodissociative processes have been found in the photolysis of formaldehyde. The authors found that the relative quantum efficiencies of the two processes show a marked dependence on the wavelength of absorbed light. From this work and others,[9] it is concluded that the upper limit of $D_{\mathrm{HCO-H}}$ is 81.5–85 kcal/mol.

Prior to the present work, the formyl radical has not been obtained *via* energy transfer from a donor to formaldehyde. In addition, the present work discusses the reactions in terms of (1) the monophotonic *vs.* the biphotonic dependence upon the nature of the solvent, (2) the concentration and temperature dependence, (3) the nature and role of donor and solvent radicals, and (4) the mechanisms.

Experimental Section

Purified paraformaldehyde from Fisher Scientific Co. that had been dryed 2 days in a vacuum desiccator over sulfuric acid was used. Formaldehyde was prepared in either of two ways. Formaldehyde gas formed from the decomposition of paraformaldehyde in mineral oil (at 120–140°) was passed through a $CaCl_2$ tube, together with nitrogen as carrier, directly into the appropriate solvent. The other method followed that described by Spence and Wild.[10]

Phillips Petroleum Co. pure grade 3-methylpentane (3-MP) was distilled of Na–Pb alloy and passed over dryed neutral silica gel and then over a silica gel–silver nitrate column. Fisher methylene chloride (reagent grade) and pure Eastman Organic Chemicals Co. triphenylamine (TPA) were used without further purification.

For photoreactions of TPA on silica gel, the experiment was conducted as follows: 12 mg of TPA in 5 ml of 3-MP was added to 1 g of silica gel; the mixture was evaporated and dried under vacuum for 1 day. From this was taken 0.4 g and formaldehyde was distilled onto the mixture as described in the literature.[11] Solutions of TPA and formaldehyde were obtained as follows: in an esr sample tube, 0.4 ml of a solution of TPA (2.5 mg in 1 cc of 3-MP) was added, the solvent vacuum evaporated, and formaldehyde distilled onto the TPA.

Solutions of formaldehyde in high concentrations ($>5 \times 10^{-2}$ *M*) in 3-MP are not stable at room temperature.[11] For this reason, cooling needs to be done very quickly for reproducible results.

Absorption spectra were taken on a Cary 15 recording spectrophotometer. The emission spectra were determined by the front-face method as described by Becker, *et al.*[12] Epr determinations were conducted in a Varian (E-3) epr spectrometer, and all irradiations were conducted with a 100-W high-pressure mercury lamp.

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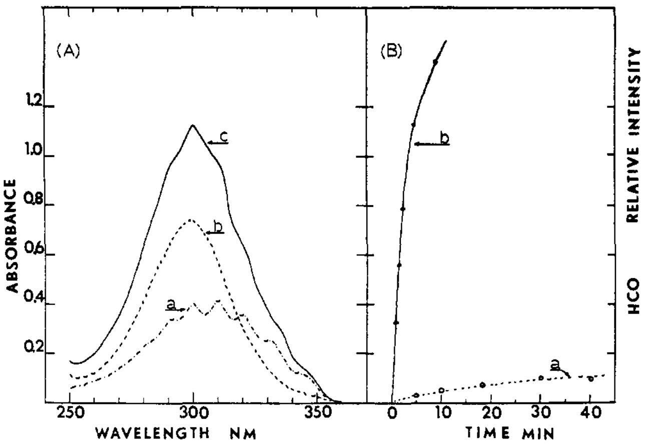

Figure 1. (A) Curve a, absorption spectra of formaldehyde in H_2CCl_2; curve b, absorption spectra of TPA in H_2CCl_2; curve c, 1:1 solution of a and b multiplied by 2. (B) Curve a, formation of formyl radical from formaldehyde adsorbed on silica gel (real intensity multiplied by 2); curve b, formation of formyl radical from formaldehyde in the presence of TPA.

A Corning filter 9863 with a Pyrex cutoff filter was used for the region 300–400 nm, a Corning filter 3486 for wavelengths >500 nm, and an Optics Technology interference filter for 405-nm irradiation (36-nm half-width). A calibrated transmission wire screen (50% T) was used for all light intensity dependence studies.

Results

No interaction in the ground state exists between TPA and formaldehyde in H_2CCl_2 at room temperature. As observed in (Figure 1A) the sum of the absorption spectra of TPA and formaldehyde is identical with the spectrum of a 1:1 solution of CH_2Cl_2 and CH_2O (multiplied by 2 to account for the dilution factor).

When formaldehyde adsorbed on silica gel[11] (20 mg on 0.4 g) is irradiated at 77°K with light between 300 and 400 nm, an esr signal characteristic of formyl radical is detected. The basis for the assignment of the radical as formyl in this and all succeeding cases will be discussed shortly. After 1 hr of irradiation, the intensity of formyl radical corresponds to a solution of 5×10^{-6} *M* DPPH. When triphenylamine (TPA) is added to an identical mixture of formaldehyde and silica gel, a signal corresponding to 10^{-4} *M* formyl radical is detected after only 5 min of irradiation, with the same wavelengths as described above (Figure 1B). In solution, the effect of the addition of TPA on the rate of formation of formyl radical is even more obvious. A solution of formaldehyde (5×10^{-1} *M*) and TPA (5×10^{-2} *M*) in 3-MP was irradiated at 77°K in the esr cavity using the same wavelengths as described above (TPA absorbs greater than 99.8% of the light). After 15 sec of irradiation, formyl radical is formed in a concentration of 10^{-5} *M* while after 5 min of irradiation 5×10^{-4} could be detected. Solutions of formaldehyde (5×10^{-1} *M*) only in 3-MP irradiated under the same conditions showed no formyl radical signal after several hours of irradiation. Similar results were obtained when CH_2Cl_2 was the solvent. More detailed results using this latter solvent will be discussed in a later section. The foregoing results on silica gel and in 3-MP and CH_2Cl_2 provide positive evidence that TPA plays an important role in the production of formyl radical by interaction with formaldehyde.

The same phenomenon as described above is observed by irradiating directly a solid solution of pure formaldehyde and TPA at 77°K for 5 min. Without TPA, irradiation of pure solid formaldehyde gives formyl radical only after 4 hr of irradiation (the latter observation has been noted by others[5]). No formyl radical could be detected by irradiation of a solution of formaldehyde and TPA in toluene at 77°K under the same concentrations and irradiation conditions as described above for 3-MP or CH_2Cl_2.

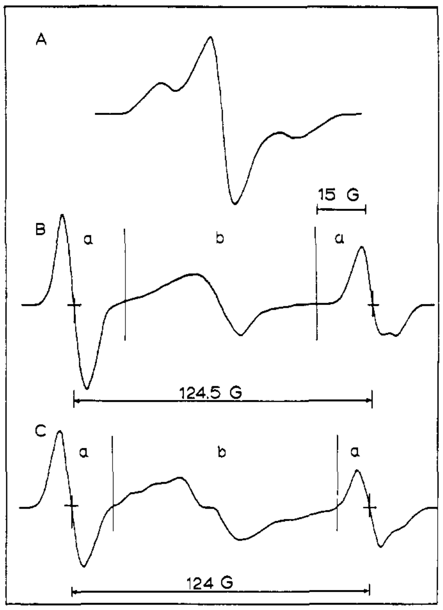

Figure 2. (A) Esr signal of $TPA\cdot^+$ obtained by uv irradiation of TPA adsorbed on silica gel. (B) Esr signal obtained by uv irradiation of a mixture of H_2CO and TPA adsorbed on silica gel at 77°K: (a) formyl radical, (b) formaldehyde polymer radical. (C) Esr signal obtained by uv irradiation of a solution of H_2CO and TPA in H_2CCl_2 at 77°K: (a) formyl radical, (b) solvent radical.

Formyl radical was identified from the splitting of 126 G observed in our signal as described in the literature[3,4] and shown in Figure 2. A signal corresponding to polymers of formaldehyde was also detected as has been previously described.[5]

Triphenylamine radical cation, $TPA\cdot^+$, was obtained in different ways. TPA adsorbed on silica gel was irradiated at room temperature with ultraviolet light (300–400 nm). A triplet-band signal with a splitting of 14.5 G was detected as shown in Figure 2 (this same signal on silica gel is still observable after 2 months in a desiccator). The same signal is also obtained from TPA when it is adsorbed on paraformaldehyde by ultraviolet irradiation and separately by heating to 60°. Also, it is possible to obtain the same $TPA\cdot^+$ signal in a plastic such as Lexan (a polycarbonate resin) by ultraviolet irradiation or by heating and in toluene solutions at 77°K by ultraviolet irradiation. Since the same signal with a splitting of 14.5 G occurs in all of the foregoing various media and the splitting is the same as that expected by ^{14}N (three-line spectrum),[13] we assign the signal as originating from $TPA\cdot^+$. No $TPA\cdot^+$ is observed in CH_2Cl_2 by irradiation of TPA.

As is observed from Figure 2C (for $TPA-CH_2O-CH_2Cl_2$), the b part of the signal is different from the

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[13] M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," W. A. Benjamin, New York, N. Y., 1966, p 35.

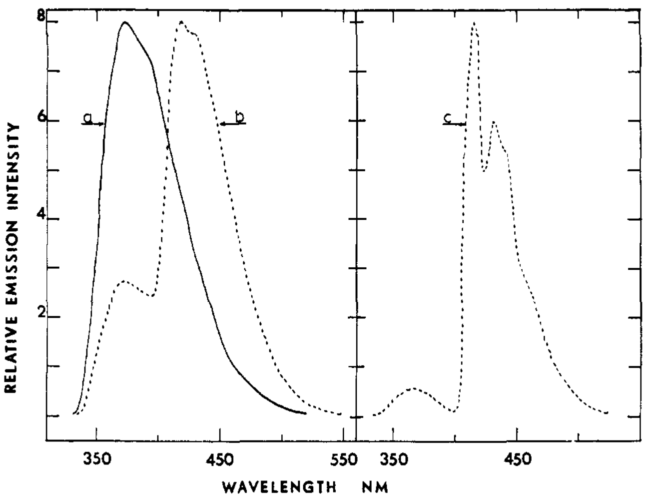

Figure 3. Curve a, emission of TPA adsorbed on silica gel at room temperature; curve b, emission of TPA adsorbed on silica gel at 77 °K; curve c, emission of TPA in 3-MP at 77 °K. All excitations at 310 nm.

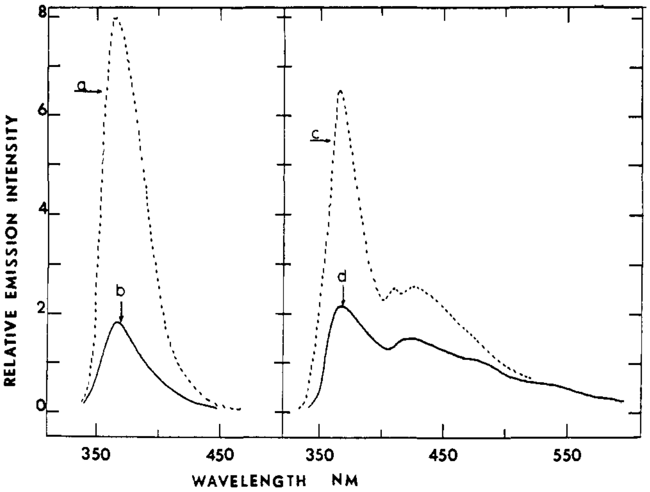

Figure 4. Curve a, emission of TPA (10^{-2} *M*) in H_2CCl_2 at room temperature; curve b, emission of TPA (10^{-2} *M*) and formaldehyde (10^{-1} *M*) in H_2CCl_2 at room temperature; curve c, emission of TPA (10^{-2} *M*) in H_2CCl_2 at 77 °K; curve d, emission of TPA (10^{-2} *M*) and formaldehyde (10^{-1} *M*) in H_2CCl_2 at 77 °K. All excitations at 310 nm.

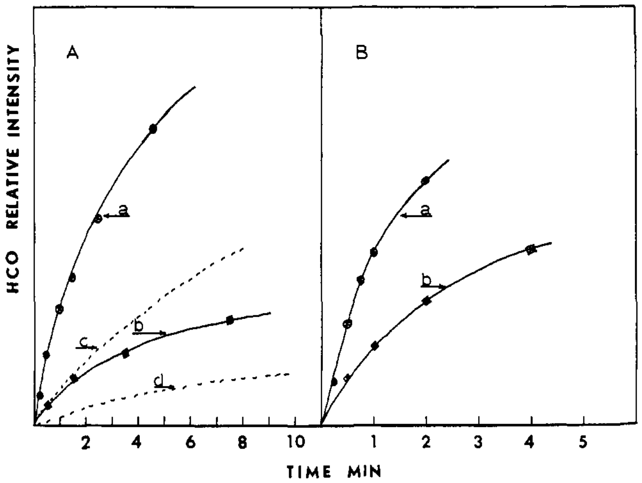

Figure 5. (A) Curve a, formation of formyl radical by irradiation of H_2CO and TPA adsorbed on silica gel; curve b, the same mixture as in a irradiated with 50% T screen wire; curve c, formation of formyl radical by irradiation of a solution of H_2CO and TPA in 3-MP; curve d, the same mixture irradiated with 50% T screen wire. (B) Curve a, formation of formyl radical by irradiation of a solution of H_2CO and TPA in H_2CCl_2; curve b, the same mixture irradiated with 50% T screen wire. All excitations at 300–400 nm and 77 °K.

signal obtained for TPA$\cdot^+$ and also different from part b of the signal obtained on silica gel which was assigned to radical(s) of formaldehyde polymers. It is concluded that it is the solvent radical $CH_2Cl\cdot$ or $CHCl_2\cdot$. The splitting observed is 10 G.

We wished to check if TPA$\cdot^+$ could either thermally or photochemically react with formaldehyde to produce formyl radical. TPA on silica gel was irradiated at 77 °K to produce TPA$\cdot^+$. The temperature was then raised to ~200 °K and formaldehyde (liquid) was distilled onto the silica gel–TPA–TPA$\cdot^+$ mixture and allowed to stand for 1 hr. After this, the temperature was lowered to 77 °K and the TPA$\cdot^+$ epr signal was monitored. There was no change in the shape or intensity of the TPA$\cdot^+$ signal nor was any formyl radical signal detected. This experiment clearly indicates that no thermal reaction occurs between TPA$\cdot^+$ and formaldehyde at temperatures up to 200 °K. In addition, irradiation with 405 nm at 77 °K produces no formyl radical. A reflectance spectrum on silica gel at room temperature shows that TPA$\cdot^+$ absorbs from 700 to 390 nm (cut-off). This result indicates no photochemical reaction occurs between CH_2O and TPA$\cdot^+$. Ultraviolet irradiation (300–400 nm) produces the formyl radical. Recall that irradiation of TPA and CH_2O does produce $CHO\cdot$ so that the lack of intimate contact is not the cause of the absence of a thermal or photoreaction between CH_2O and TPA$\cdot^+$.

TPA adsorbed on silica gel has a fluorescence emission at room temperature with a maximum at 372 nm. At 77 °K the emission consists of phosphorescence with a maximum at 420 nm and fluorescence with a maximum at 370 nm (Figure 3). The intensity ratio of phosphorescence to fluorescence at this temperature is 3 : 1. In 3-MP at 77 °K both fluorescence (max 367 nm) and phosphorescence (max 415 nm) exist (Figure 3) with an intensity ratio of phosphorescence to fluorescence of 18 : 1. TPA (10^{-2} *M*) in H_2CCl_2 at room temperature has a fluorescence maximum at 370 nm. At 77 °K in CH_2Cl_2, both fluorescence (max ~365 nm) and phosphorescence (max ~420 nm) can be observed. The ratio of the intensity of phosphorescence to fluorescence is 1 : 3, exactly the inverse of that observed on silica gel and inverse to that in 3-MP (Figure 4). Even more interesting is the fact that in the presence of formaldehyde (10^{-1} *M* in CH_2Cl_2), the fluorescence emission is quenched to one-third of its original value (absence of formaldehyde) both at room temperature and at 77 °K (Figure 4). Phosphorescence is quenched by approximately one-half in the presence of formaldehyde (at 77 °K).

In the case of formaldehyde and TPA adsorbed on silica gel at 77 °K, the concentration of formyl radical formed has a near-quadratic dependence upon the light intensity absorbed by TPA (Figure 5A). The ratio of the concentrations of formyl radical between 50% T and 100% T is 1 : 3.5. This result strongly indicates that on silica gel most of the formyl radical is formed *via* a biphotonic process involving the TPA. The same phenomenon is observed in solutions of 3-MP (Figure 5A). In solutions of CH_2Cl_2 the phenomenon is completely different. For example, for solutions of formaldehyde (5×10^{-1} *M*) and TPA (5×10^{-2} *M*) in CH_2Cl_2 at 77 °K, the concentration of formyl radical does not follow the quadratic low. The photoreaction is directly proportional to the intensity of light (Figure 5B) and therefore is monophotonic. The monophotonic nature of the reaction is independent of concentration (the same intensity dependence is observed when the concentration of formaldehyde is reduced tenfold and TPA fivefold). Also, oxygen does not affect the results.

In solutions of H_2CCl_2, we were concerned about the possibility of obtaining the formyl radical from the excited state of the solvent radical ($CH_2Cl\cdot$ or $CHCl_2\cdot$). Consequently, a mixture of TPA (10^{-2} *M*) and formaldehyde (5×10^{-1} *M*) was irradiated between 300 and 400 nm to obtain the formyl radical. At the same time, the solvent radical was also obtained (Figure 2). The formyl radical was completely erradicated with visible light (>500 nm) as has been described elsewhere.[14] No change was detected in the solvent radical signal. After erradication, the sample was irradiated at 405 nm resulting in the re-formation of the formyl radical. Irradiation at 405 nm prior to ultraviolet irradiation did not produce formyl radical or the solvent radical. Also recall that irradiation of $TPA\cdot^+$ at the same wavelength does not result in the formation of formyl radical. We believe that the foregoing results verify the fact that the excited state of the solvent radical is capable of inducing formation of formyl radical (although such a reaction is minor compared with the quantity produced *via* the TPA sensitized mechanism).

The concentration of formaldehyde strongly affects the concentration of formyl radical produced in CH_2Cl_2. For a 10^{-2} *M* concentration of the donor TPA, the concentration of formyl radical at the photostationary state has a direct dependence upon the concentration of formaldehyde (Figure 6). The rate of formation of the solvent radical also has a direct dependence upon the concentration of formaldehyde. In Table I, we show the irradiation time required to obtain the same concentration of solvent radical as a function of formaldehyde concentration. The concentration of the donor TPA was held constant at 10^{-2} *M*. Remember that the concentration increase of the formyl radical also follows a direct dependence upon the concentration of formaldehyde. The nature of the reactions giving the solvent radical will be discussed later.

Table I. Rate of Formation of Solvent Radical as a Function of Concentration Formaldehyde in CH_2Cl_2

H_2CO concn, *M*	5×10^{-1}	5×10^{-2}	5×10^{-3}	5×10^{-4}	0
Time, min	1	4	14	30[a]	32

[a] The data at this concentration of formaldehyde are unreliable for determining the nature of the dependence of solvent radical production upon formaldehyde concentration since it is almost the same as that with no formaldehyde present (see table) indicating another mechanism is operative.

In solutions of H_2CCl_2, it was possible to follow the kinetics of the disappearance of the formyl radical as a function of temperature. The experiment was conducted as follows: solutions of formaldehyde (5×10^{-1} *M*) and TPA (5×10^{-2} *M*) in H_2CCl_2 were irradiated in an esr sample tube with ultraviolet light at 77°K and the irradiated sample was quickly transferred into an esr variable-temperature dewar at the appropriate temperature. The esr was fixed at the maximum of the signal (in our case formyl radical) with no scanning of the magnetic field and the intensity of the signal monitored as a function of time. Plots of log concentration of $HCO\cdot$ *vs.* time were made. These were nearly linear over periods up to three to four times the $\tau_{1/2}$ for the reaction. In one case, −180°, the disappearance was followed to seven times the initial $\tau_{1/2}$ (~7.5 min) and in this case a second curve with about one-fifth the slope was apparent which was highly linear over two times the $t_{1/2}$ (~36 min). Our initial supposition was that the disappearance of $HCO\cdot$ was first order. However, the results of the latter experiment strongly indicate that there is an initial second-order reaction(s) mixed with a first-order reaction and the first-order one becomes dominant at relatively long times.

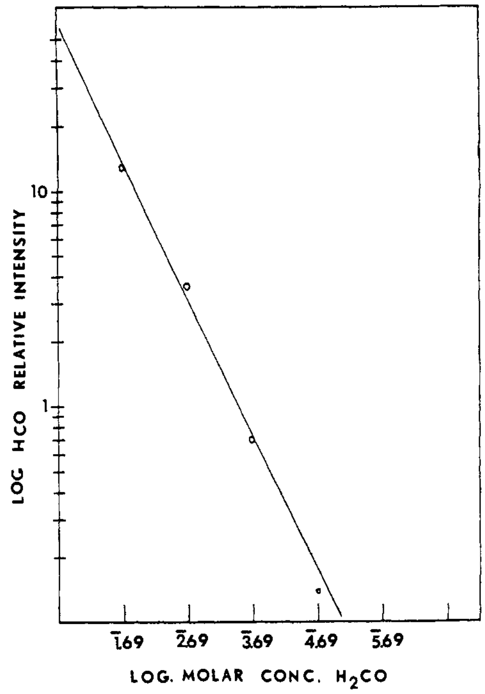

Figure 6. Formyl radical concentration as a function of the H_2CO concentration at a constant concentration of TPA (10^{-2} *M*) in CH_2Cl_2 at 77 °K.

Discussion

As is apparent from our results, there are two major processes by which the formyl radical can be obtained using TPA at 77°K: (1) monophotonic in solutions of H_2CCl_2 and (2) biphotonic on silica gel and in 3-MP solutions.

The upper limit of the energy required to break the C–H bond in formaldehyde is 81.5–85 kcal/mol.[8,9] The triplet state energy of TPA is ~70 kcal/mol which is too low to cause the foregoing bond breakage to occur. In CH_2Cl_2 the fluorescence of TPA is quenched both at room and low (77°K) temperatures in the presence of formaldehyde. The 0–0 band of fluorescence is at ~347 nm which corresponds to a lowest excited singlet state energy of ~82.5 kcal/mol. The latter energy is

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[14] Y. Michiyasu, H. Keiichiro, F. Yuzaburo, and K. Takao, *Kogyo Kagaku Zasshi*, 72, 123 (1969).

near that estimated for the C–H bond energy of CH_2O (to form formyl radical). Furthermore, the concentration of formyl radical is directly dependent upon the concentration of formaldehyde and the photoreaction is monophotonic in nature. No $TPA\cdot^+$ is observed in CH_2Cl_2–H_2CO solutions and furthermore, $TPA\cdot^+$ even if present does not thermally or photochemically react with formaldehyde to produce formyl radical (on silica gel). Finally no ground-state complex exists between formaldehyde and TPA. Based on these results we propose the mechanisms in eq 1 for the production of formyl radical in CH_2Cl_2 employing TPA,

$$\begin{aligned}
&(TPA)(S_0) \xrightleftharpoons[h\nu_F]{h\nu} (TPA)^*(S_1)\\
&(TPA)^*(S_1) + CH_2O(S_0) \rightleftharpoons (TPA\text{–}CH_2O)^*(S_1) \qquad (1)\\
&(TPA\text{–}CH_2O)^*(S_1) \longrightarrow TPA(S_0) + HCO\cdot + H\cdot
\end{aligned}$$

where $(TPA\text{–}CH_2O)^*(S_1)$ is a mixed excimer. Also an exciplex $(TPA\text{–}CH_2O\text{–}CH_2Cl_2)^*(S_1)$ could exist in place of the excimer. We cannot distinguish which of these is correct because of the lack of a distinguishable emission of the excimer or exciplex and of CH_2O (known to be weak even when directly excited at high concentrations[11]). It is also possible that the complex can be a semiionized charge-transfer state leading to electron capture by H_2CO and eventual dissociation.

In the case of formaldehyde and TPA in 3-MP and on silica gel, the mechanism of formyl radical formation appears to be different from that in CH_2Cl_2. As observed, the emission of TPA in these media has a phosphorescence to fluorescence intensity ratio of 18:1 and 3:1, respectively (compared with 1:3 in CH_2Cl_2). In these cases a biphotonic process exists *vs.* a monophotonic one in CH_2Cl_2.

There are two possible principal mechanisms that could occur *via* a biphotonic process, eq 2 and 3, where

$$\begin{aligned}
&(TPA)(S_0) \xrightarrow{h\nu_1} (TPA)^*(S_1) \rightsquigarrow (TPA)^*(T_1)\\
&(TPA)^*(T_1) \xrightarrow{h\nu_2} TPA\cdot^+ + e \qquad (2)\\
&TPA\cdot^+ + e + H_2CO \longrightarrow (TPA)(S_0) + H\cdot + HCO\cdot
\end{aligned}$$

$$\begin{aligned}
&(TPA)(S_1) \xrightarrow{h\nu_1} (TPA)^*(S_1) \rightsquigarrow (TPA)^*(T_1)\\
&(TPA)^*(T_1) \xrightarrow{h\nu_2} TPA^*(T_n) \qquad (3)\\
&(TPA)^*(T_n) + (H_2CO)(S_0) \longrightarrow (TPA)(S_0) + (CH_2O)^*(T_n)\\
&(CH_2O)(T_n) \longrightarrow HCO\cdot + H\cdot
\end{aligned}$$

$n = 2$ or greater. Also an excimer, $(TPA\text{–}CH_2O)^*(T_n)$ or exciplex $(TPA\text{–}CH_2O\text{–solvent})^*(T_n)$ could exist in place of $(CH_2O)^*(T_n)$. These latter complexes could be formed from an initial complex involving TPA in the T_1 state followed by absorption of a second photon.

The first mechanism (eq 2) involves photoionization of TPA to $TPA\cdot^+$. In the second mechanism (eq 3) an excited triplet state higher than the lowest one (T_1) is involved and a mixed excimer or exciplex intermediate is possible as indicated. It is unlikely that mechanism 2 involving reaction of $TPA\cdot^+$ and H_2CO is the correct one since one step involves a thermal (and possibly photochemical) reaction which we have shown does not occur (on silica gel). However, we cannot eliminate the possibility of electron capture by CH_2O followed by dissociation.

$T_1 \rightarrow T_n$ absorption of TPA has been determined[15,16] and one of the maxima[16] occurs at ~4060 Å (~70 kcal) which makes the absorption within our irradiation band width.

The lowest triplet of formaldehyde can be estimated to be at approximately 24,000 cm^{-1} (~69 kcal).[17] This is insufficient to break the C–H bond to produce $HCO\cdot$ and $H\cdot$. Therefore, we believe energy transfer occurs from T_n of TPA to T_n of CH_2O or an excited-state complex *via* which eventual dissociation occurs.

As is shown in Figure 5A, the phenomenon is not purely biphotonic. This fact could be explained if part of the photoreaction especially on silica gel remains monophotonic. In view of the fact that $TPA\cdot^+$ can be observed in addition to $HCO\cdot$, it is quite possible that the first two reactions in (2) are all that occur and these are competitive with the reactions in (3).

Recall that the concentration of the solvent radical $CH_2Cl\cdot$ or $CHCl_2\cdot$ is directly dependent upon the concentration of formaldehyde using TPA as a sensitizer. However in the absence of formaldehyde but in the presence of TPA, the amount of $CH_2Cl\cdot$ or $CHCl_2\cdot$ produced is very small (it is 32 times less compared to when 5×10^{-1} *M* formaldehyde is present). Therefore, based on the foregoing facts we propose the mechanism in eq 4 for the formation of $CH_2Cl\cdot$ or $CHCl_2\cdot$ in the presence of formaldehyde.

$$\begin{aligned}
&TPA(S_0) \xrightarrow{h\nu} TPA^*(S_1)\\
&TPA^*(S_1) + H_2CO \longrightarrow TPA(S_0) + H\cdot + HCO\cdot \qquad (4)\\
&H\cdot + H_2CCl_2 \longrightarrow H_2CCl\cdot \text{ or } HCCl_2\cdot + HCl \text{ or } H_2
\end{aligned}$$

Based on the fact that $CH_2Cl\cdot$ or $CHCl_2\cdot$ can be generated in the absence of formaldehyde (but in the presence of TPA), albeit small, there is a competing mechanism for formation of $CH_2Cl\cdot$ or $CHCl_2\cdot$ in the presence of TPA only.

As described in the results, it is possible to obtain the formyl radical *via* the excited state of the solvent radical. This latter path of formation of the formyl radical can be shown to be much less important than the TPA-sensitized process using ultraviolet radiation in CH_2Cl. This is proved by the facts (1) the photoreaction for formation of formyl radical is monophotonic, and (2) the rate of change in the concentration of formyl radical as a function of the time of irradiation (of $TPA\text{–}CH_2O\text{–}CH_2Cl_2$) does not increase with increasing concentration of the solvent radical.

Based on the kinetic analysis relative to the disappearance of $HCO\cdot$, we believe that one or more relatively fast second-order reactions can exist such as

$$\begin{aligned}
HCO\cdot + H\cdot &\longrightarrow H_2CO\\
&\longrightarrow H_2 + CO \qquad (5)
\end{aligned}$$

which are occurring along with a relatively slower first-order reaction

$$HCO\cdot \longrightarrow H\cdot + CO \qquad (6)$$

Acknowledgment. This investigation was supported by the Robert A. Welch Foundation.

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[15] B. R. Henry and M. Kasha, *J. Chem. Phys.*, 47, 3319 (1967).

[16] M. V. Alfinov, I. G. Batekha, Y. B. Sheck, and V. I. Gerko, *Spectrochim. Acta, Part A*, 329 (1971).

[17] J. J. Smith and B. Meyer, *J. Chem. Phys.*, **50**, 456 (1969).