Ishikawa, S.; Sakuragi, H.; Yoshida, M.; Inamoto, N.; Tokumaru, K. *Chem. Lett.* 1975, 819.

Johnson, P. Y.; Berchtold, G. A. *J. Am. Chem. Soc.* 1967, 89, 2761.

Johnson, P. Y.; Berchtold, G. A. *J. Org. Chem.* 1970, 35, 584.

Kosower, E. M.; Clossen, W. D.; Goering, H. L.; Gross, J. C. *J. Am. Chem. Soc.* 1961, 83, 2013.

Leermakers, P. A.; Thomas, H. T.; Weis, L. D.; James, F. C. *J. Am. Chem. Soc.* 1966, 88, 5075.

Leonard, N. J.; Johnson, C. R. *J. Am. Chem. Soc.* 1962, 84, 3701.

Magee, T. A.; Limpel, L. E. *J. Agric. Food Chem.* 1977, 25, 1376.

Ohta, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* 1975, 48, 2393.

Padwa, A. *Chem. Rev.* 1977, 77, 37.

Payne, L. K., Jr.; Stansbury, H. A., Jr.; Weiden, M. H. J. *J. Agric. Food Chem.* 1966, 14, 356.

Pfoertner, K.; Foricher, J. *Helv. Chim. Acta* 1982, 65, 798.

Readio, P. D.; Skell, P. S. *J. Org. Chem.* 1966, 31, 759.

Sato, T.; Inoue, T.; Yamamato, K. *Bull. Chem. Soc. Jpn.* 1972, 45, 1176.

Skell, P. S.; Shea, K. J. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 809.

Stenhagen, E.; Abrahamsson, S.; McLafferty, F. W. "Atlas of Mass Spectral Data"; Wiley: New York, 1969; p 6.

Vermes, J.-P.; Beugelmans, R. *Tetrahedron Lett.* 1969, 25, 2091.

Yoshida, H.; Sakuragi, H.; Nichimura, T.; Ishikawa, S.; Tokumura, K. *Chem. Lett.* 1975, 1125.
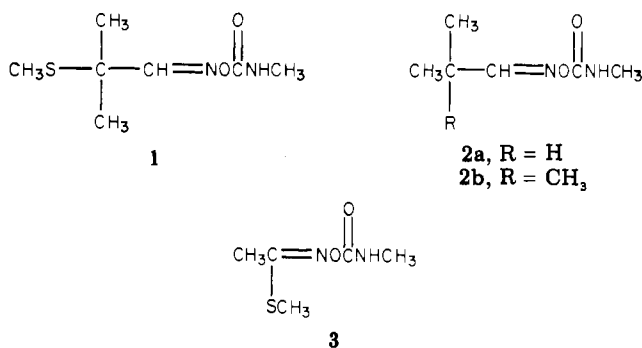
Photochemistry of Oxime Carbamates. 2. Phototransformations of Methomyl

Peter K. Freeman* and Edmund M. N. Ndip

The irradiation of methomyl in dilute aqueous solution at 254 nm formed acetonitrile, dimethyl disulfide, acetone, N-ethylidenemethylamine, and carbon dioxide. Irradiation in tetrahydrofuran produced carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4) as major products, with acetone, dimethylamine, N,N'-dimethylurea, dimethyl sulfoxide, methyl thioacetate (5), and methomyl oxime (6) as minor products. Irradiation of methomyl in the presence of benzophenone sensitizer in THF at 254 nm results in the formation of carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4). Irradiation in THF in the presence of acetophenone generated carbon dioxide, methylamine, acetonitrile, and dimethyl disulfide, while irradiation in THF in the presence of benzonitrile produced methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4). The quenching effects on the quantum yields of photoproducts using isoprene as the triplet-state quencher were measured, providing a linear Stern–Volmer plot. The mechanistic implications of these results are discussed.

Our earlier study on the photochemistry of aldicarb (1)

$$CH_3S—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH=NO\overset{O}{\overset{||}{C}}NHCH_3$$

1

$$CH_3\underset{\underset{R}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH=NO\overset{O}{\overset{||}{C}}NHCH_3$$

2a, R = H
2b, R = CH₃

$$CH_3C=NO\overset{O}{\overset{||}{C}}NHCH_3$$
$$\underset{SCH_3}{|}$$

3

and related model oxime carbamates (2a,b) (Freeman and McCarthy, 1984) led us to a consideration of the phototransformations of the closely related methomyl, methyl N-[[(methylamino)carbonyl]oxy]ethanimidothioate (3). To the best of our knowledge there have been no reports in the literature on the photochemistry of methomyl other than the very recent study of Koshy et al. (1983), which focused principally on the photodecomposition of a thiophosphoramide derivative of methomyl.

EXPERIMENTAL SECTION

In initial analytical work, a programmable Varian Aerograph Series 1200 gas chromatograph equipped with a flame ionization detector was employed. Nitrogen was used as the carrier gas. In subsequent analyses a programmable Varian Chromatograph Model 3700 equipped with both flame ionization and thermal conductivity detectors was used. Helium was used as the eluent gas. The following columns were used during analysis: (A) 10 ft × 1/4 in. o.d. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60–80 mesh; (B) 20 ft × 1/8 in. o.d. 5% Carbowax 20 M aluminum column on Chromosorb W AW, 60–80 mesh; (C) 15 ft × 1/8 in. o.d. 10% Carbowax 20 M-2% KOH copper column on Anakrom ABS, 70–80 mesh; (D) 5 ft × 1/8 in. o.d. 10% Carbowax 1500 aluminum column on Chromosorb W, 60–80 mesh; (E) 19 ft × 1/8 in. o.d. 20% Carbowax 20 M aluminum column on Anakrom ABS, 70–80 mesh; (F) 2 m × 1/8 in. o.d. 10% Dinonyl phthalate aluminum column on Chromosorb W AW DMCS, 80–100 mesh, for Varian Series 1200 chromatograph; (H) 10 ft × 1/8 in. o.d. 10% Dinonyl phthalate aluminum column on Chromosorb W AW DMCS, 80–100 mesh, for Varian Model 3700 Series chromatograph.

High-pressure liquid chromatography (HPLC) analyses were effected by using a liquid chromatograph from Water Associates fitted with a Model 660 solvent programmer and an ultraviolet model 440 absorbance detector. In direct-phase HPLC analysis, the following conditions were used: column material, Spherisorb (SS); column length, 25 cm, 4.6-mm i.d.; column packing, Lichrosorb silica; particle size and frit, 5 and 0.5 µm, respectively; flow rate 1 mL/min; solvent system, dichloromethylene (DCM)–methanol–isooctane (TMP). For reversed-phase HPLC analysis a 50:50

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331.

acetonitrile–water mixture was used as the eluent system.

Columns A, E, and G were used for GC–MS analyses. Direct mass spectral and GC–MS data were obtained by using a CH7 mass spectrometer fitted with a Varian Aerograph Series 1200 gas chromatograph. Infrared spectra were obtained on a Perkin-Elmer 727B infrared spectrophotometer, while ultraviolet–visible spectra were obtained on a Cary 118 spectrophotometer and also on a Beckman DB spectrophotometer. The proton NMR spectra were obtained by using a Varian HA-100 unit, while carbon-13 NMR spectra were obtained on a Varian FT-80A instrument. Elemental analyses were performed by Dr. Johnson of MICANAL, Inc., of Tempe, AZ.

Solvent Purification. Acetonitrile was purified according to a standard procedure (Gordon and Ford, 1972). Phototrex methanol for UV spectrophotometry and absolute ethanol, USP quality, were used without purification. 2-Propanol (technical grade) was used without purification.

Reagent-grade THF was treated with metallic sodium and a suitable amount of benzophenone. The resulting mixture was then heated slowly in a nitrogen atmosphere until the mixture turned to a blue color. The mixture was then refluxed for an additional hour and the distillate collected thereafter.

Photolyses and Quantum Yields. Sample irradiations were carried out in a Rayonet Type RS preparative photochemical reactor from the Southern New England Ultraviolet Co. using 2537- and 3000-Å mercury lamps or in a reactor using a Hanovia 450-W high-pressure mercury lamp. Samples were contained in 13-mm Pyrex or quartz resealable tubes or in appropriate photochemical quartz containers.

Quantum yields were run in a merry-go-round apparatus using a suitable choice of radiant energy source. Typically four 5-mL portions of methomyl (0.38 M) in the solvent of choice and four 5-mL portions of the actinometer (cyclopentanone) in the same solvent were placed in resealable quartz tubes, degassed by at least five freeze–thaw cycles, and irradiated. Analyses were carried out by comparison of peak areas of the products relative to that of a standard on an FID-GC with an integrator. All products were analyzed with column H at 55 °C with isoamyl alcohol as the internal standard. The actinometer was analyzed under the same conditions. Cyclopentanone forms 4-pentenal as the major product with a quantum yield of 0.37 at 313 nm or 0.38 at 254 nm (Dunion and Trumbore, 1965). Calculations done were based on the method of Calvert and Pitts (1966).

Quantum yields in the sensitized runs were carried out as in the following typical experiment with benzophenone–THF. A 250-mL solution of methomyl (1.25 g, 7.72 mmol) and benzophenone (3.01 g, 16.5 mmol) in tetrahydrofuran was prepared. Portions of 5 mL were placed in resealable quartz tubes, degassed, and irradiated in the Rayonet reactor with 254-nm lamps. Analyses were performed by using column H at 40–100 °C and peak areas obtained by using a digital integrator.

Photolysis of Methomyl in Water (λ = 254 nm). A solution of methomyl (0.70 g, 0.0043 mol) was prepared in 100 mL of water. Portions of 6 mL each were introduced into eight resealable quartz tubes, which were than degassed by four freeze–thaw cycles. The samples were irradiated for 10 h with Rayonet 254-nm lamps. At the end of irradiation, the samples were refrigerated, and the contents were transferred into a 100-mL round-bottom flask and extracted continuously with ether for 96 h. The extract was then concentrated to 25 mL and the final

solution chromatographed with column B at 70 °C, which provided evidence of seven components. The seven components were analyzed by GC–MS using column B at 70 °C: A, m/e 44, carbon dioxide; B, m/e 57 N-ethylidenemethylamine; C, m/e 58, acetone; D (not identified); E, m/e 74, diethyl ether; F, m/e 41, acetonitrile; G, m/e 94, dimethyl disulfide. Peaks obtained with less than 5% intensity were not identified.

Photolysis of Methomyl in Acetonitrile (λ = 254 nm). A 100-mL solution of methomyl (3.24 g, 0.0200 mol) in acetonitrile was prepared. Approximately 6-mL portions of the sample solution were placed in four resealable quartz tubes and degassed by a series of freeze–thaw cycles. The samples were irradiated with Rayonet 254-nm lamps for 6 h. Gas chromatographic and GC–MS analyses on column B at 60–250 °C gave evidence for six components. GC–Mass spectral analysis revealed that peak 1 was carbon dioxide, peak 2 methylamine, peak 3 too small to be identified, peak 4 acetonitrile (solvent), and peak 5 dimethyl disulfide. Smaller peaks were not identified.

The photolysis of methomyl was carried out in acetonitrile solution (3.24 g, 0.0200 mol, in 40 mL of acetonitrile) with a Hanovia 450-W high-pressure lamp. The same general procedure as above was used. The samples were irradiated for a period of 6 h. Gas chromatographic analyses with columns G and H at 50–110 °C gave evidence of at least six components. By comparison of retention times with those of the different components in a standard solution and with mass spectra of authentic samples, the products were identified as methylamine (m/e 31), acetonitrile (solvent), dimethyl disulfide (m/e 94), the methylhydrazone of biacetyl (m/e 142), and the oxime of methomyl (m/e 105).

Photolysis of Methomyl in Tetrahydrofuran (λ = 254 nm). A solution of methomyl (3.24 g, 0.0200 mol) in 100 mL of tetrahydrofuran was prepared, and the general procedure described above was followed. Irradiation with Rayonet 254-nm lamps for varying times (50 min to 3.5 h) gave the same peak sequence on analysis with column A at 60 °C, column B at 70–180 °C, and columns G and H at 55–90 °C. Analysis on column B at 70 °C gave 8–10 peaks. When column F at 70 °C was used, peak 1 was identified as carbon dioxide and peak 2 as methylamine, a result reinforced by using column G at 35 °C; peak 3 was identified as solvent; peak 4 was identified as acetonitrile (m/e 41). Peak 5 with m/e 58 was acetone, while peak 6 with m/e 94 proved to be dimethyl disulfide; peaks 7–9 were not completely characterized. Peaks 10 and 11, with m/e 142, were identified as the methylhydrazone of biacetyl, $C_6H_{14}N_2$, and a dimer of tetrahydrofuranyl radical.

Photolysis of Methomyl in Tetrahydrofuran (Hanovia 450-W Lamp). A 50-mL solution of methomyl (0.138 g, 0.852 mmol) in tetrahydrofuran was prepared. The sample was treated following the general procedure described above. Analysis using column E at 35–100 °C gave at least 12 peaks. In addition to peaks corresponding to methylamine, acetonitrile, dimethyl disulfide, and biacetyl methylhydrazone, additional peaks proved to be due to dimethylamine (m/e 45), N,N'-dimethylurea, dimethyl sulfoxide, methyl thioacetate (m/e 90), and the oxime of methomyl (m/e 105).

Photolysis of Methomyl in Tetrahydrofuran with Benzonitrile Sensitizer. A solution of methomyl (0.50 g, 0.0031 mol) and benzonitrile (4.02 g, 0.039 mol) in 100 mL of tetrahydrofuran was prepared and irradiated with Rayonet 254-nm lamps by using the general procedure described above. When analyzed by using column B at 60 °C and column G at 55 °C, the products obtained were the
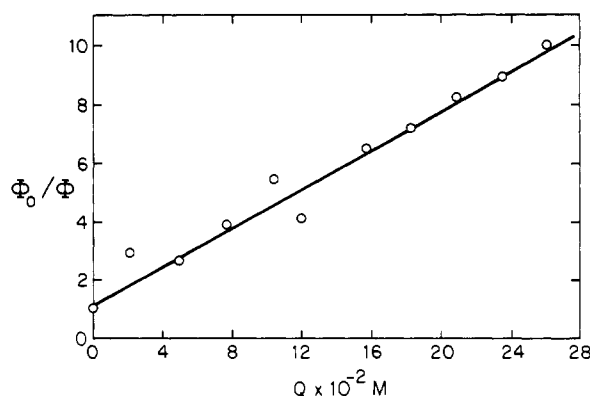
Phototransformations of Methomyl

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Figure 1. Stern–Volmer plot of Φ_0/Φ vs. concentration of isoprene (Q).

same as those in the direct irradiation. The products were identified as methylamine (16%), acetonitrile (45%), dimethyl disulfide (29%), and biacetyl methylhydrazone (5%).

Photolysis of Methomyl in Tetrahydrofuran with Benzophenone Sensitizer. A solution of methomyl (0.499 g, 0.0031 mol) and benzophenone (5.47 g, 0.0300 mol) was prepared in 100 mL of tetrahydrofuran. Sample solutions in resealable quartz tubes were degassed and irradiated with Rayonet 300-nm lamps. Analysis using column B at 60 °C and column H showed that methylamine (32%), acetonitrile (30%), dimethyl disulfide (30%), and biacetyl methylhydrazone (7%) are the major products. The same array of products was obtained with Rayonet 254-nm lamps.

Photolysis of Methomyl in Acetonitrile with Benzophenone Sensitizer. A solution of methomyl (1.369 g, 8.45 mmol) and benzophenone (1.7230 g, 9.46 mmol) in 25 mL of acetonitrile was prepared, degassed, and irradiated for 15 h by using Rayonet 254-nm lamps. Analysis on column H at 55 °C gave seven peaks. The main products obtained were methylamine, dimethylamine, acetonitrile (solvent), and dimethyl disulfide. Products were observed in slightly higher yields when compared to those from direct irradiation experiments. Reactions in acetonitrile were observed to be less efficient than reactions in tetrahydrofuran.

Quenching Effects on Methomyl Photoproduct Quantum Yields. A 0.50 M standard solution of methomyl (16.2 g, 0.10 mol) and isoamyl alcohol (3.04 g, 0.035 mol) in 200 mL of tetrahydrofuran was prepared. A 2.60 M standard solution of isoprene (17.7 g, 0.260 mol) in tetrahydrofuran was prepared. Samples of 10 mL of the methomyl standard solution were introduced into 10 different 100-mL volumetric flasks. Varying amounts of the isoprene solution were then added to each of the volumetric flasks, and the volume of solution made up to 100 mL. Samples of the final solutions (5-mL portions) ranging in concentration from 2.6×10^{-2} to 26.0×10^{-2} M were placed in sample tubes, degassed, and irradiated within the Rayonet apparatus at 300 nm for 31 h. This is approximately equivalent to a 90% conversion of methomyl in the absence of a quencher. The final solutions were 0.05 M in methomyl. An actinometer solution in tetrahydrofuran was prepared and photolyzed accordingly. Quenching quantum yields were determined by disappearance of starting material relative to isoamyl alcohol (internal standard). The quantum yields of photoproducts in absence of quencher were determined based on product formation in the sample that contained no quencher. The corresponding Stern–Volmer plot of the ratio of quantum yields in the absence and presence of quencher against

Scheme I
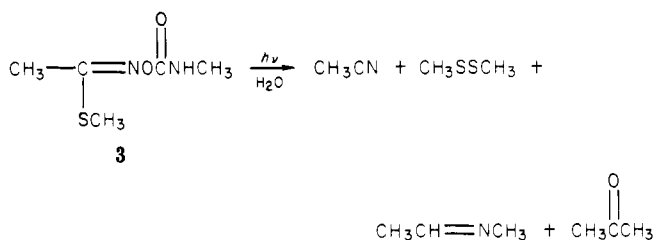
quencher concentration is presented in Figure 1.

Synthesis of Biacetyl Bis(methylhydrazone) (4). Methylhydrazine (25 g, 0.544 mol) was dissolved in 130 mL of phototrex methanol contained in a 250-mL three-necked round-bottom flask equipped with a dropping funnel, a magnetic stirrer, and a thermometer. The solution was maintained at 45–50 °C while a freshly distilled solution of biacetyl (5.0 g, 0.058 mol) in 100 mL of phototrex methanol was added with stirring over a period of 2.5 h. After addition was complete, stirring was continued at the same temperature for at least 5 h. Excess solvent was removed by fractional distillation, and the resulting solid was removed by filtration, washed with methanol and water, and then air-dried.

The yield of biacetyl bis(methylhydrazone) was 6.2 g (75%): mp 44 °C; the infrared spectrum neat showed absorptions at 3325 (N–H), 2850, and 1685 cm^{-1} (C=N–); NMR (CDCl$_3$, 100 MHz) δ 1.9 (s, 6 H), 3.0 (s, 6 H), 4.6 (2 H); ^{13}C NMR δ 9.00 (CH$_3$–C=N), 38 (N–CH$_3$), 144.8 (–C=N); MS m/e 142, comparable to that obtained in photolysis experiments. Anal. Calcd for C$_6$H$_{14}$N$_2$: C, 50.68; H, 9.92; N, 39.40. Found: C, 50.01; H, 9.81; N, 39.46. This compound is somewhat volatile and evaporates at room temperature. In addition, it loses weight easily and apparently undergoes air oxidation.

RESULTS AND DISCUSSION

Initially we investigated the photolysis of methomyl in dilute aqueous solutions. Irradiation at 254 nm for a period of 10 h generated a reaction mixture containing acetonitrile (40%), dimethyl disulfide (30%), acetone (15%), and N-ethylidenemethylamine (5%) (Scheme I). Additional minor contributors to the product mixture (<5%) were not identified. It seems likely that methylamine, an expected photolysis product, was lost in the workup procedure.

In order to simplify our analytical procedures and broaden the scope of our study, we considered next the phototransformations of 3 in organic solvents. Irradiation of methomyl in tetrahydrofuran produced carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4) as major products, with acetone, dimethylamine, N,N'-dimethylurea, dimethyl sulfoxide, methyl thioacetate (5), and methomyl oxime (6) as minor products (Scheme II). The quantum yields for these photolyses in tetrahydrofuran are provided in Table I. Irradiation of dilute solutions of methomyl in acetonitrile gave the same array of major products: carbon dioxide, methylamine, dimethyl disulfide, biacetyl bis(methylhydrazone) (4), and methomyl oxime (6) (Table II). For the most part, the identification of these products was a matter of routine GC–MS; however, in the case of biacetyl bis(methylhydrazone), we found it necessary to synthesize this product component from biacetyl in order to provide firm identification.

In order to characterize the spin state of the product determining intermediate, irradiations were carried out in the presence of sensitizers. With benzophenone in THF, irradiation at 254 nm results in the formation of carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and
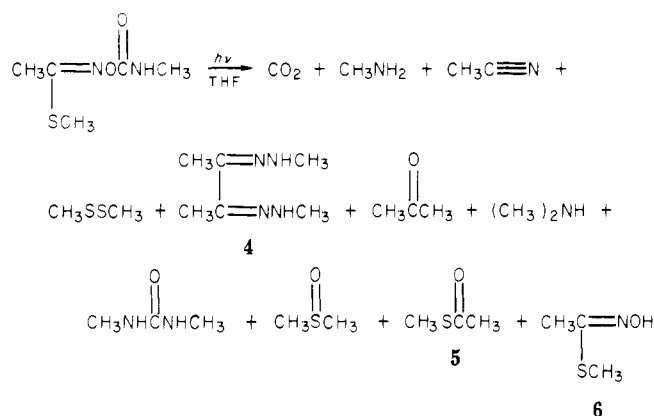
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Freeman and Ndip

Scheme II

Scheme III

Table I. Quantum Yields of Photoproducts in Tetrahydrofuran

product	run A[a]		run B[b]	
	Φ[c]	% yield[d]	Φ[c]	% yield
CH_3NH_2	0.930 ± 0.09[e]	38	0.0903	3.9
$(CH_3)_2NH$			0.111	4.8
CH_3CN	0.681 ± 0.09	28	0.965	41.9
CH_3SSCH_3	0.732 ± 0.069	30	0.801	34.8
4	0.126 ± 0.0002	5.1	0.338	14.6

[a] Photolysis at 254 nm. [b] Photolysis with medium-pressure mercury lamp. [c] Quantum yields were determined by using cyclopentanone actinometry. [d] Percent yields are calculated according to the relationship percent yield = $100[\phi_x/(\phi_x + \sum \phi_i)]$ where ϕ_x = quantum yield of interest and $\sum \phi_i$ = the summation of the quantum yields of all other competing reactions. Thus, this is not the percent of starting material converted to product, which would be given by $100(\Phi_x I/C_0)$ where I = the radiation absorbed and C_0 = moles of starting material. [e] Standard deviation.

**Table II. Quantum Yields of Photoproducts in Acetonitrile (λ = 254 nm)**

product	Φ[a]	% yield[b]
CH_3NH_2	0.036 ± 0.001[c]	4.2
CH_3SSCH_3	0.706 ± 0.024	82.4
$CH_3SC(CH_3)NOH$	0.049 ± 0.016	5.7
4	0.066 ± 0.022	7.7

[a] Quantum yields determined by using cyclopentanone actinometry. [b] See footnote c, Table I. [c] Standard deviation.

biacetyl bis(methylhydrazone) (4). Irradiation in THF in the presence of acetophenone generated carbon dioxide, methylamine, acetonitrile, and dimethyl disulfide, while similar treatment using benzonitrile in THF produced methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4). The quantum yields in the presence of benzophenone are listed in Table III.

A comparison of the quantum yields in the direct irradiations (Tables I and II) with those for the sensitized reactions (Table III) suggests that the triplet state is the key product determining intermediate in this photofragmentation process. In order to reinforce this view, we
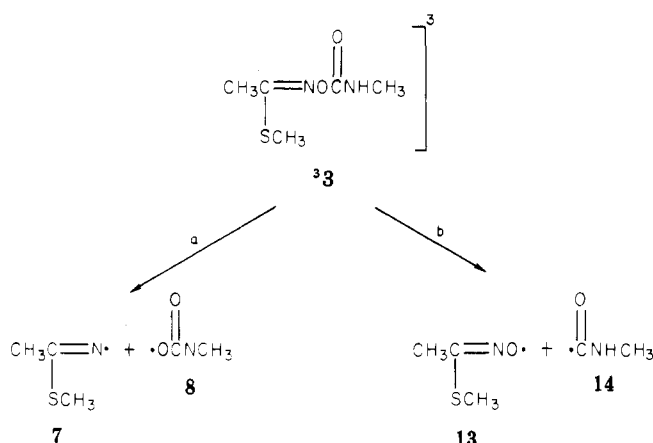
Scheme IV
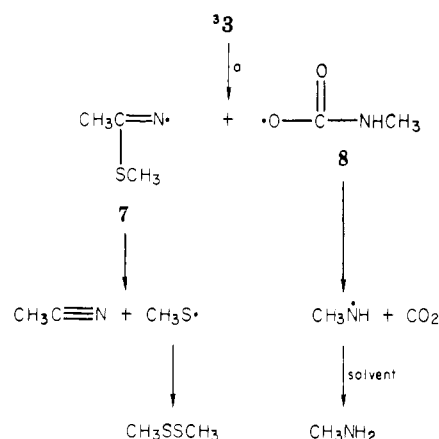
studied quenching effects on the quantum yields of the photoproducts using isoprene as the triplet-state quencher. The resulting Stern–Volmer plot of Φ_0/Φ vs. quencher concentration, given in Figure 1 (correlation coefficient r = 0.981), is consistent with expectations.

The products obtained in these photofragmentation reactions of methomyl (3) can be understood in terms of fission of the triplet state (³3) at the nitrogen–oxygen bond (route a, Scheme III) as the major process with a minor contribution of fission at the oxygen–carbamoyl bond (route b). Cleavage of ³3 at the nitrogen–carbamoyloxy bond has precedence in the photochemical nitrogen–oxygen cleavage of oxime esters and ethers (Ishikawa et al., 1975; Ohta and Tokumaru, 1975; Padwa, 1977; Pfoertner and Foricher, 1982; Sato et al., 1972; Vermes and Beugelmans, 1969; Yoshida et al., 1975), while O-carbamoyl cleavage is similar to the O–acyl cleavage observed in the photolysis of O–acyl oximes of steroidal ketones (Beugelmans and Vermes, 1971; Vermes and Beugelmans, 1969).
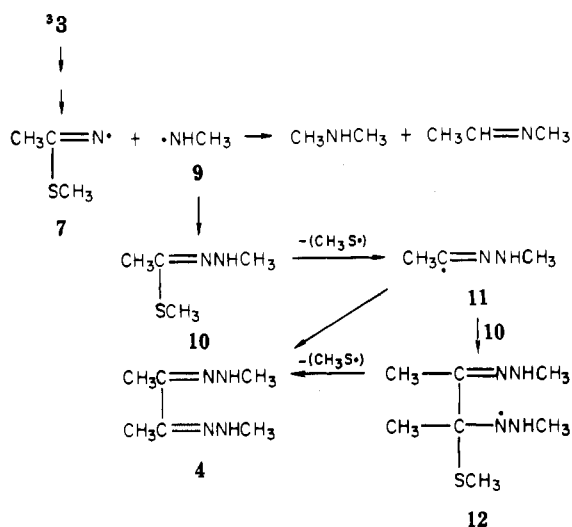
Subsequent to the initial fission at the nitrogen–oxygen bond, route a, and formation of radical pair 7/8, loss of the methylthio radical from 7 generates acetonitrile [thiyl

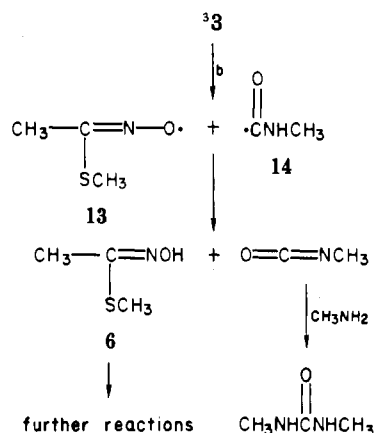**Table III. Quantum Yields of Photoproducts Formed in Reactions Sensitized with Benzophenone[a]**

product	Φ[b] (THF)	% yield[c]	Φ[b] (CH_3CN)	% yield[c]	Φ[b] (CH_3OH)	% yield[c]
CH_3NH_2	0.91 ± 0.11[d]	32	0.017 ± 0.002[d]	2	0.12 ± 0.03[d]	12
CH_3CN	0.88 ± 0.02	31			0.84 ± 0.30	85
CH_3SSCH_3	0.87 ± 0.01	30	0.66	68	e	
4	0.20 ± 0.01	7	0.29 ± 0.001	30	0.026 ± 0.006	3

[a] All runs carried out with 254-nm lamps. [b] Cyclopentanone actinometry was used to determine quantum yields. [c] See footnote c, Table I. [d] Standard deviations. [e] Could not be determined under the analytical conditions employed.

Phototransformations of Methomyl

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Scheme V

$$^3 3$$

$$\downarrow$$

$$CH_3C{=}N\cdot\ +\ \cdot NHCH_3\ \longrightarrow\ CH_3NHCH_3\ +\ CH_3CH{=}NCH_3$$

under first structure: SCH_3 ; labels **7**, **9**

$$CH_3C{=}NNHCH_3\ \xrightarrow{-(CH_3S\cdot)}\ CH_3C{=}NNHCH_3$$

with SCH_3 below left (**10**) and **11** at right

$$CH_3C{=}NNHCH_3\ \xleftarrow{-(CH_3S\cdot)}\ CH_3{-}C{=}NNHCH_3$$

$$CH_3C{=}NNHCH_3 \qquad\qquad CH_3{-}C{-}\dot{N}NHCH_3$$

$$\mathbf{4} \qquad\qquad\qquad SCH_3$$

$$\qquad\qquad\qquad\qquad \mathbf{12}$$

with $\downarrow 10$ between **11** and **12**

Scheme VI

$$^3 3$$

$$\downarrow b$$

$$CH_3{-}C{=}N{-}O\cdot\ +\ \overset{O}{\overset{\|}{\cdot CNHCH_3}}$$

$$SCH_3 \qquad\qquad \mathbf{14}$$

$$\mathbf{13}$$

$$CH_3{-}C{=}NOH\ +\ O{=}C{=}NCH_3$$

$$SCH_3 \qquad\qquad\qquad \downarrow CH_3NH_2$$

$$\mathbf{6}$$

$$\downarrow \qquad\qquad\qquad \overset{O}{\overset{\|}{CH_3NHCNHCH_3}}$$

further reactions

radical addition to π bonds is reversible (Abell, 1973)] and forms dimethyl disulfide through dimerization. The carbamoyloxy radical undergoes decarboxylation, forming a methylamino radical, which abstracts hydrogen from the solvent to form methylamine (Scheme IV).

The radical pair 7/8 subsequent to decarboxylation generates radical pair 7/9, which, after intersystem crossing, might well combine to form hydrazone 10 (Scheme V). Carbon–sulfur bond fission forming radical 11 might be followed by addition to 10 producing species 12, which upon extrusion of the methylthio radical would yield biacetyl bis(methylhydrazone) (4). The methylamino radical of radical pair 7/9 should abstract hydrogen from

the solvent, forming methylamine, which would be expected to lead to some dimethylamine and N-ethylidene-methylamine (Michael and Noyes, 1963).

Returning to pathway b of Scheme III, the minor amounts of N,N'-dimethylurea and methomyl oxime (6) observed provide the evidence for oxygen–carbamoyl cleavage (route b, Scheme III) elaborated in Scheme VI. In a process analogous to that suggested for aldicarb (Freeman and McCarthy, 1984), the initially formed radical pair 13/14 might undergo intersystem crossing and then hydrogen atom transfer within a solvent cage to produce methomyl oxime (6) and methyl isocyanate, which then reacts with methylamine to generate N,N'-dimethylurea.

ACKNOWLEDGMENT

LITERATURE CITED

Abell, P. I. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 63.
Beugelmans, R.; Vermes, J.-P. *Bull. Soc. Chim. Fr.* 1971, 343.
Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 798.
Dunion, P.; Trumbore, C. N. *J. Am. Chem. Soc.* 1965, 87, 4211.
Freeman, P. K.; McCarthy, K. C. *J. Agric. Food Chem.* 1984, preceding paper in this issue.
Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972; p 431.
Ishikawa, S.; Sakuragi, H.; Yoshida, M.; Inamoto, N.; Tokumaru, K. *Chem. Lett.* 1975, 819.
Koshy, K. T.; Burdick, M. D.; Knuth, D. W. *J. Agric. Food Chem.* 1983, 31, 625.
Michael, J. V.; Noyes, W. A. *J. Am. Chem. Soc.* 1963, 85, 1228.
Ohta, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* 1975, 48, 2393.
Padwa, A. *Chem. Rev.* 1977, 77, 37.
Pfoertner, K.; Foricher, J. *Helv. Chim. Acta* 1982, 65, 798.
Sato, T.; Inoue, T.; Yamamato, K. *Bull. Chem. Soc. Jpn.* 1972, 45, 1176.
Vermes, J.-P.; Beugelmans, R. *Tetrahedron Lett.* 1969, 25, 2091.
Yoshida, H.; Sakuragi, H.; Nichimura, T.; Ishikawa, S.; Tokumaru, K. *Chem. Lett.* 1975, 1125.