

Original Articles

Photodecomposition of 3,3'-Dimethyl-4-Methoxybenzophenone (Methoxyphenone, NK-049) and Its Photosensitizing Activity

Yasuo FUJII, Akira KUROZUMI and Tomomasa MISATO*

*Ageo Research Laboratory, Agrochemicals Division, Nippon Kayaku Co., Ltd.,
Ageo, Saitama 362, Japan*

**The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan*

(Received April 28, 1979)

Exposure of ^{14}C -NK-049 labeled at the carbonyl carbon to UV light in water solution resulted in rapid decomposition. NK-049 was decomposed predominantly by ways of cleavage at the carbonyl group to produce *m*-toluic acid and 4-methoxy-3-methylbenzoic acid followed by the liberation of ^{14}C -carbon dioxide. Other photodecomposition reactions observed were stepwise oxidation of 3 or 3'-CH₃ group, reduction of the carbonyl group and desmethylation of 4-OCH₃ group. When exposed to sunlight, NK-049 was rapidly decomposed both on glass and silica gel plates and in water in the same ways as that when exposed to UV light. More than 16 photodecomposed products from NK-049 were detected on *tlc* and 10 of them were identified. Practically, no difference was observed between the photodecomposed products obtained by sunlight and those by UV light.

NK-049 acts as an effective photosensitizer similar to benzophenone. Dieldrin was rapidly photoconverted to intramolecular bridged photodieldrin by sunlight exposure in the presence of NK-049.

INTRODUCTION

3,3'-Dimethyl-4-methoxybenzophenone (methoxyphenone, NK-049) is a herbicide having a high selectivity to rice and barnyardgrass both in paddy and upland fields.¹⁻⁴⁾ It has been demonstrated that NK-049 was readily metabolized in rats,⁵⁾ plants,^{6,7)} and soils,^{8,9)} in which evolution of carbon dioxide was observed. Further, photodecomposition of NK-049 on glass plates using non-labeled NK-049 was studied by Yamada *et al.*,¹⁰⁾ and 11 photoproducts were identified. The present study deals in more details with the photodecomposition of ^{14}C -NK-049 when it was irradiated with sunlight and UV light in solution and on silica gel or glass plate for the elucidation of its fates in the environment. Furthermore, photosensitizing activity of NK-049 was evaluated.

MATERIALS AND METHODS

1. Chemicals

^{14}C -NK-049 (5.52 mCi/mmol) labeled at the carbonyl carbon was synthesized in our laboratory.⁵⁾ The radioactive purity was more than 99% based on *tlc* analysis. Non-labeled authentic NK-049, 3,3'-dimethyl-4-hydroxybenzophenone, 3-carboxy-4-methoxy-3'-methylbenzophenone, 3'-carboxy-4-methoxy-3-methylbenzophenone, 3-hydroxymethyl-4-methoxy-3'-methylbenzophenone, 3'-hydroxymethyl-4-methoxy-3-methylbenzophenone, 3-formyl-4-methoxy-3'-methylbenzophenone, 3'-formyl-4-methoxy-3-methylbenzophenone, 3,3'-dimethyl-4-methoxybenzhydrol and 4-methoxy-3-methylbenzoic acid were kindly supplied by Mr. O. Yamada of Ageo Research Lab. *m*-Toluic acid was purchased from Tokyo Kasei Co., Ltd. (Tokyo, Japan).

Methyl and trimethylsilyl derivatives of all these compounds were prepared by the reaction with diazomethane and a mixture of trimethylchlorosilane and hexamethyldisilazane, respectively, for identification of decomposed products on GC-MS.

2. Radioanalysis and Product Characterization

The procedures employed were the same as those described previously.^{3,11)} Photodecomposed products were identified with *tlc* co-chromatography, GC-MS, *ir* and *nmr*. The operational conditions for them were described in our previous papers.^{3,5)}

3. Irradiation with Ultraviolet Light

¹⁴C-NK-049 in 350 ml of distilled water (1 ppm, 1.028×10^6 dpm) in 400 ml cylindrical glass flask was irradiated with either of two types of ultraviolet lamps. One was a low pressure mercury lamp with a maximum intensity at 254 nm (Nikko Sekiei Co., Ltd., NY-1, 10 W) which was immersed directly into the solution. The other was a high pressure mercury lamp with a maximum intensity at 365 nm (Nikko Sekiei, NY, 100 W) covered with a quartz glass for cooling by water and was also immersed into the solution. ¹⁴C-Carbon dioxide evolved was trapped in a mixture of methyl cellosolve and mono-ethanolamine (2 : 1) through the toluene layer for the absorption of other volatile radioactive compounds. After the designated irradiation time the sample solution was acidified to pH2 with 1 N HCl and extracted with 200 ml of ethyl acetate twice. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. An aliquot of the aqueous and ethyl acetate solution was radioassayed. Another aliquot of the organic solvent was analyzed for the detection of photodecomposed products by *tlc*.

4. Exposure to Sunlight

Four μ g of ¹⁴C-NK-049 (2.06×10^5 dpm) in 20 μ l of ethanol was spotted on a silica gel chromatoplates and exposed to sunlight after evaporation of ethanol (January to March, 1978). After the serial exposure time the *tlc* plates were developed and autoradiograms were

taken.

For decomposition on glass plates, 20 μ g of ¹⁴C-NK-049 (1.028×10^6 dpm) dissolved in 0.1 ml of ethanol was spread in a Petri-dish (5 cm in diameter) to make thin film of the chemical. After the plates were exposed to sunlight for up to 24 hr, radioactive compounds on the plate were collected by washing with acetone and then with water, and each radioactivity was measured. Photodecomposed products in the acetone solution were analyzed by *tlc*.

¹⁴C-NK-049 dissolved in 150 ml of distilled water (2 ppm, 1.52×10^6 dpm) was put into each of two Petri-dishes (15 cm in diameter). One dish was covered with a quartz glass (1 mm in thickness), and the other was left uncovered, and both were exposed to sunlight. Determinations of radioactivity and extraction of photodecomposed products were carried out according to the method described by Ishikawa *et al.*¹²⁾ In all cases samples were exposed to sunlight ranging from 5 to 7 hours daily from January to March.

5. Assay for Photosensitizing Activity

Pesticide chemicals used for this study, such as aldrin, dieldrin, endrin, DDT, and α , β and γ -BHC, were commercial goods. The compounds for the internal standard of *glc* were kindly supplied by Mr. O. Yamada. Two ml each of acetone solution of chemicals (2 mg/ml) was put into Petri-dishes (9 cm in diameter) or spread over the surface of 30 g of dry soil in the same dishes, and the same amount of NK-049 was added immediately. After the solvent had evaporated, the dishes were exposed to sunlight directly. Pesticide chemicals and their photodecomposed products were then collected by washing with acetone from Petri-dishes or extracted with iso-propanol : *n*-hexane (1 : 1) from soils, respectively. Each extract was concentrated and analyzed by *glc* with FID after the addition of the internal standard solution. The conditions for *glc* were listed in Table 1. Photoproduct of dieldrin was separated by silica gel *tlc* (Merck 60F254, developing solvent=*n*-hexane : ethyl acetate=4 : 1) and identified by *ir*, *nmr* and elemental analysis.

Table 1 Operating conditions of FID-gas liquid chromatography.

Pesticide	Column (2 mm × 1 m glass column)	Column temp. °C	IS*
α -BHC	5% SE30, 3% FFAP on Celite 545 (60–80 mesh)	215–235 (10°C/min)	A
β -BHC	5% SE30, 3% FFAP on Celite 545 (60–80 mesh)	215–235 (10°C/min)	A
γ -BHC	5% SE30, 3% FFAP on Celite 545 (60–80 mesh)	220–235 (10°C/min)	A
DDT	0.3% Polyester FF on Glass beads (60–80 mesh)	170	B
Aldrin	5% SE30, 3% FFAP on Gaschrom P (60–80 mesh)	180	A
Dieldrin	3% Carbowax 20M on Neosorb NCS (60–80 mesh)	205	B
Endrin	3% Carbowax 20M on Neosorb NCS (60–80 mesh)	205	B

*IS: internal standard.

A: 4-methoxybenzophenone, B: 3'-bromo-4-methoxybenzophenone.

RESULTS

1. Photodecomposition of NK-049 in Water Solution Irradiated with UV Light

When ^{14}C -NK-049 in water solution was irradiated with UV light with air bubbling (10 ml/min), its decomposition proceeded rapidly. The half-life was about 1.5 hr and 50 hr for UV light of long (maximum intensity at 365 nm, 100 W) and short (254 nm, 10 W) wave length, respectively. ^{14}C -Carbon dioxide was the main photodecomposed product, accounting for 76.0% and 30.8% of the original radiocarbon for NK-049, after 12 hr and 120 hr irradiation with 100 W and 10 W, respectively (Table 2). In addition, more than 16 photodecomposed products were detected on *tlc*.

Among them, photoproducts P1, P5, P7, P8 and P9 were identified as 3,3'-dimethyl-4-hydroxybenzophenone, 3-carboxy-4-methoxy-3'-methylbenzophenone, 3'-formyl-4-methoxy-3-methylbenzophenone, 3'-carboxy-4-methoxy-3-methylbenzophenone and *m*-toluic acid, respectively. The amount of these compounds was fairly small (Table 2).

P2 was not completely characterized, but it was assumed to be 3,3'-dimethyl-4-methoxybenzhydrol, as it cochromatographed well with the authentic compound on *tlc*.

2. Photodecomposition of NK-049 by Sunlight

2.1 Decomposition on glass plates

When exposed to sunlight on glass plates,

Table 2 Photodecomposition of ^{14}C -NK-049 in water solution irradiated with UV light in the presence of air.

	% of recovered radiocarbon as indicated compounds						
	Irradiation time (hr)						
	100 W				10 W		
	3/4	2	6	12	24	48	120
Solvent soluble							
P0 NK-049	79.2	33.7	3.5	0.1	66.8	46.9	14.5
P1 NK-049-OH	2.9	6.8	7.4	0.1	5.4	5.7	5.5
P2	0.6	1.0	0.3	—	—	—	—
P5	4.3	4.7	1.3	0.1	2.1	4.1	5.8
P7	0.9	0.3	—	—	0.2	0.1	0.1
P8	1.0	2.5	3.2	0.3	0.7	1.1	0.8
P9	—	—	1.0	0.1	2.2	2.0	1.5
Others	8.1	27.9	21.2	2.7	12.4	11.4	14.8
Subtotal	97.0	76.9	37.9	3.4	89.8	71.3	43.0
Water soluble	2.3	6.6	11.1	10.8	3.4	5.0	5.1
^{14}C -CO ₂	0.6	5.9	38.4	76.0	5.6	14.7	30.8
Volatile	0.1	0.1	0.1	0.1	—	—	0.1
Total	100.0	89.5	87.5	90.3	98.8	91.0	79.0

Table 3 Photodecomposition of ^{14}C -NK-049 on glass plates exposed to sunlight.

	% of recovered radiocarbon as indicated compounds						
	Exposure time (hr)						
	1/4	1/2	1	3	6	12	24
Acetone soluble							
P0 NK-049	83.9	36.4	10.2	1.3	0.6	0.4	0.4
P1 NK-049-OH	0.3	0.9	0.4	0.3	0.3	0.2	—
P2	0.1	0.4	0.4	0.1	0.2	0.2	—
P3	0.4	0.7	0.4	0.3	—	—	—
P4	0.5	0.5	0.1	0.1	0.1	—	—
P5	0.4	0.8	0.5	—	—	—	—
P6	0.2	0.3	0.4	0.1	—	—	—
P7	0.7	0.5	0.3	0.2	0.2	0.2	0.2
P8	0.5	1.0	1.2	1.4	0.9	1.0	0.2
P9	0.2	0.9	0.9	0.4	0.5	0.4	0.3
P10	0.1	1.0	1.4	1.3	1.2	0.8	0.5
Origins	7.4	37.6	48.6	45.6	45.8	38.1	25.4
Unknown	0.2	7.3	7.2	4.2	4.2	2.3	3.3
Subtotal	94.9	88.3	72.0	55.3	54.0	43.6	30.3
Water soluble	1.0	1.5	2.1	4.2	3.4	11.6	22.0
Total	95.9	89.8	74.1	59.5	57.4	55.2	52.3

NK-049 was rapidly decomposed with concomitant increase of photoproducts together with loss of radioactivity by volatilization. The half-life of NK-049 was about 20 min. Ten of the photoproducts in acetone soluble fraction were identified, though their amounts were very small. The percentages of them are listed in Table 3. Under these test conditions, most of the photoproducts were unidentified polar materials which retained at the origin of *tlc* and water soluble ones. After 24-hour exposure, the recovery of the total radiocarbon was 52.3%.

Photoproducts P4 and P10 were identified as 3-formyl-4-methoxy-3'-methylbenzophenone and 4-methoxy-3-methylbenzoic acid, respectively, as reported previously.¹⁰⁾

P3 was identified as 3-hydroxymethyl-4-methoxy-3'-methylbenzophenone by *tlc* co-chromatography. Also the mass spectra of P3 and TP3 (trimethylsilylated with trimethylchlorosilane and hexamethyldisilazane) gave identical spectra of *m/e* at 256(M^+), 225, 165, 119 and 91, and 328(M^+), 313, 297, 210, 119, 91 and 73, respectively, with the authentic compounds.

P6 was identified as 3'-hydroxymethyl-4-methoxy-3-methylbenzophenone, as it co-

chromatographed well with the authentic compound on *tlc* and the mass spectra of P6 and TP6 showed the following ions; *m/e* 256(M^+), 225, 149, 135, 121 and 91, and 328(M^+), 297, 210, 207, 179, 149, 121 and 91, respectively. These values were identical with those of au-

Table 4 Photodecomposition of ^{14}C -NK-049 on silica gel chromatoplates exposed to sunlight.

	% of recovered radiocarbon as indicated compounds				
	Exposure time (hr)				
	3	12	24	72	120
P0 NK-049	88.2	75.4	67.7	44.4	29.4
P1 NK-049-OH	0.4	0.1	0.1	—	—
P2	0.2	0.2	0.2	0.4	0.3
P3	0.6	1.0	1.0	0.9	1.3
P4	1.0	1.1	1.3	1.1	0.8
P5	0.4	0.9	1.1	1.4	2.7
P6	0.2	0.6	0.4	0.7	0.7
P7	1.0	1.0	1.0	1.0	1.5
P8	0.5	0.6	0.8	0.9	1.6
P9	1.4	3.8	5.6	12.3	18.7
P10	0.2	0.4	0.6	2.0	1.9
Origins	3.2	5.8	8.6	18.6	18.3
Unknowns	2.7	4.4	5.8	5.2	4.4
Total	100.0	95.3	94.2	88.9	81.6

thetic compounds.

2.2 Decomposition on silica gel plates

NK-049 underwent slow photodecomposition on silica gel *tlc* plates having a 70-hour of half-life time when compared with the case on glass plates (Table 4). During 120-hour exposure, the recovery of the radiocarbon was more than 81% and 29% of the original radioactivity was found to be intact NK-049. The photoproducts obtained were common with

those on glass plates. The major photoproduct was *m*-toluic acid (P9) accounting 18.7% of the original radiocarbon, and the polar materials which retained at the origin of *tlc* accumulated as much as P9.

2.3 Decomposition in water solution

Table 5 shows the changes in the amount of radioactivity and water in Petri-dishes which were exposed to sunlight with and without a cover of quartz glass. After 36-hour exposure,

Table 5 Changes in the level of radioactivity and in the volume of water under exposure to sunlight.

Exposure time (hr)	Uncovered				Covered			
	Radioactivity (%)		Water (%)		Radioactivity (%)		Water (%)	
	sunlight	dark*	sunlight	dark*	sunlight	dark	sunlight	dark
0	100.0	100.0	100.0	100.0	100.0		100.0	
2	90.9	93.6	93.3	88.0	98.3		100.0	
4	88.0	91.8	88.8	82.0	96.4		96.8	
6	86.1	89.7	84.5	77.7	93.4		93.2	
10	83.3	84.7	74.8	70.3	77.2		86.2	
16	74.0	78.1	60.8	62.2	72.4		81.2	
28	57.0	65.3	41.1	42.0	68.2		76.4	
36	41.8	44.5	26.5	23.7	65.7	100.0	73.4	100.0

* Blown with cold wind.

Table 6 Photodecomposition of ^{14}C -NK-049 in water solution exposed to sunlight without cover.

	% of recovered radiocarbon as indicated compounds					
	Exposure time (hr)					
	2	6	16	28	36	36 (Dark)*
Exposed solution solvent soluble						
P0 NK-049	84.9	78.2	59.2	39.1	15.9	41.3
P1 NK-049-OH	0.6	0.3	0.7	0.7	1.2	0.1
P2	—	0.1	0.7	0.7	0.8	—
P3	0.4	0.4	0.7	1.2	1.3	0.3
P5	0.7	1.1	1.8	1.7	1.6	—
P6	—	—	0.7	1.0	0.9	0.1
P7	0.6	0.5	0.6	0.1	0.1	0.3
P8	0.4	0.6	1.2	2.2	2.4	0.1
P9	—	0.1	0.1	0.1	0.1	—
P10	0.7	0.7	1.4	1.1	1.0	—
Others	1.3	2.6	3.0	2.4	3.0	0.2
Water soluble	1.3	1.5	3.9	6.7	13.5	2.1
Subtotal	90.9	86.1	74.0	57.0	41.8	44.5
Residue**					19.2	55.5
Total					61.0	100.0

* Blown with cold wind.

** Radiocarbon deposited on Petri-dish.

Table 7 Photodecomposition of ^{14}C -NK-049 in water solution exposed to sunlight with cover.

	% of recovered radiocarbon as indicated compounds					
	Exposure time (hr)					
	2	6	16	28	36	36 (Dark)
Exposed solution						
solvent soluble						
P0 NK-049	90.4	78.0	52.7	35.2	24.1	97.9
P1 NK-049-OH	1.3	1.5	1.7	1.9	1.5	—
P2	—	0.3	0.4	0.5	0.5	0.1
P3	0.6	0.7	1.1	1.3	1.5	0.2
P5	0.5	2.6	4.1	8.6	11.3	0.5
P6	0.3	0.5	0.6	0.9	0.8	—
P7	—	0.8	0.5	1.7	1.3	—
P8	1.0	1.4	2.3	3.5	4.1	0.5
P9	0.3	1.4	2.4	4.4	6.2	—
P10	0.2	0.7	0.6	1.5	1.5	—
Others	3.3	4.7	4.6	5.9	7.5	0.4
Water soluble	0.4	0.8	1.4	2.8	5.4	0.4
Subtotal	98.3	93.4	72.4	68.2	65.7	100.0
Residue*					20.7	0
Total					86.4	100.0

* Radiocarbon deposited on Petri-dish.

65.7% and 41.8% of the original radioactivity were recovered from the water solution with and without a cover, respectively. The cover greatly suppressed the loss of water and radioactivity. As shown in Table 6 and 7, NK-049 in water solution decomposed rapidly but negligible amount of photoproducts were detected except formation of P5 in covered solution. In the case of uncovered solution, water soluble materials were the dominant photoproducts, but their chemical structures were not identified as yet.

3. Photosensitizing Activity of NK-049

When α , β and γ -BHC were exposed to sunlight on glass plates, α and γ -BHC were gradually decomposed by themselves, but β -BHC was fairly stable. NK-049 accelerated partially the photodecomposition of α and γ -BHC, but not that of β -BHC (Fig. 1). Anthraquinone was less effective than NK-049. With cyclodiene pesticides such as aldrin, dieldrin and endrin, NK-049 was as effective as benzophenone in sensitizing photodecomposition, while it was completely ineffective with DDT (Table 8). In the case of soil surface, NK-049

Table 8 Photosensitizing activity of NK-049 in degradation of cyclodiene pesticides and DDT exposed to sunlight.

Conditions	Recovered pesticide (%)																
	Aldrin				Dieldrin				Endrin				DDT				
	Irradiation time (min)																
	10	30	120	dark*	10	30	120	dark*	10	30	120	dark*	10	30	120	240	dark**
Control	75.6	50.0	7.0	100.0	100.0	97.9	93.0	100.0	96.2	99.0	85.2	100.0	100.0	100.0	96.5	96.0	100.0
NK-049	13.0	0	0	97.0	32.0	4.3	0	97.1	52.6	30.8	5.2	100.0	99.0	95.0	93.2	92.3	100.0
Benzophenone	15.3	0	0	93.0	44.6	7.3	0	94.4	73.0	55.4	—	100.0	100.0	95.0	94.1	89.0	100.0

* 120 min, ** 240 min

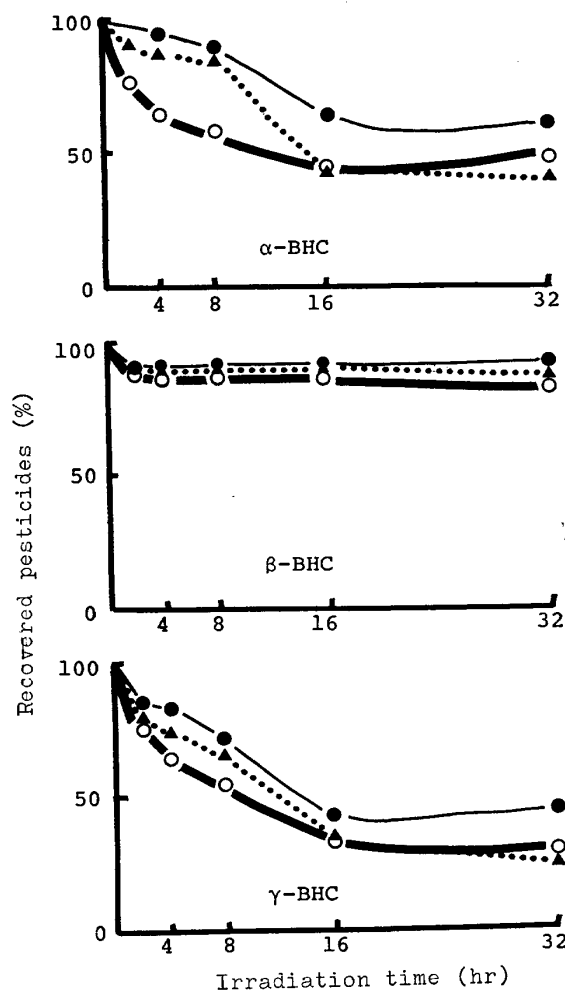


Fig. 1 Effect of NK-049 on the photodecomposition of α , β and γ -BHC.

● without sensitizer, ○ with NK-049,
▲ with anthraquinone

did not act as sensitizer at all (Table 9).

The chemical structure of photoproduct of dieldrin decomposed by sunlight with NK-049 was identified as photodieldrin¹³⁾ [3,4,5,6,6,7-hexachloro-12-oxahexacyclo-(6.5.0.0.2,10.0^{3,7}.0^{5,9}.0^{11,13}) tridecane] based on the following evidences. The product recrystallized from ethanol resulted in white crystals and exhibited a melting point¹⁴⁾ of 194–196.5°C, and its *ir* spectrum¹⁴⁾ in KBr tablet and *nmr* spectrum¹⁵⁾ in CDCl_3 [δ =4.84(1H.s), 3.48, 3.27, 3.18, 3.06, 3.02, 2.66, 2.54(1H.m)] were identical with the published spectra. Elemental analysis calculated for $\text{C}_{12}\text{H}_8\text{Cl}_6\text{O}$ (C: 37.84%, H: 2.12%) coincided well with the found data (C: 37.61%, H: 1.67%).

Table 9 Effect of NK-049 on the photodecomposition of dieldrin on soil surface.

	Recovered dieldrin (%)			
	Irradiation time (hr)			
	2	4	8	16
Dieldrin	89.0	73.7	71.8	70.2
Dieldrin + NK-049	82.2	70.3	72.2	64.6

DISCUSSION

Photodecomposition is one of the most typical process in dissipation of pesticides in environment, as well as a microbial degradation in soil. When irradiated with UV light or sunlight NK-049 underwent rapid photodecomposition. Most of the photoproducts were identified and significant evolution of ^{14}C -carbon dioxide from ^{14}C -NK-049 labeled at carbonyl carbon was observed. The primary photochemical reaction was supposed to be cleavage of the either side of phenyl-CO linkage to produce *m*-toluic acid or 4-methoxy-3-methylbenzoic acid, and carbon dioxide would be liberated partly from them or during the cleavage reaction of the mother compound.

Interrelations between the photochemistry and mass spectrometry of organic molecules were investigated especially with carbonyl compounds, and the similarity between the electronic structures of the molecular ions and the n, π^* states of carbonyl compounds was indicated.^{16–18)} Mass spectra of NK-049 gave parent ion at m/e of 240 (62%) and fragment ions at m/e of 225 (6%), 149 (100%), 119 (8%) and 91 (2%). The fragments of m/e 149 and 119 are considered to be 4-methoxy-3-methylphenyl carbonyl ion and 3-methylphenyl carbonyl ion or 4-methoxy-3-methylphenyl ion, respectively. The cleavage at phenyl-CO linkage of NK-049 in the mass spectrometer at an ionization voltage of 70eV was the dominant process as in the case of photodecomposition.

Other photochemical reactions observed were stepwise oxidation of 3 or 3'- CH_3 group to CH_2OH , CHO and COOH , and desmethylation of 4- OCH_3 group and reduction of CO group to CHOH . Desmethylation and oxidation

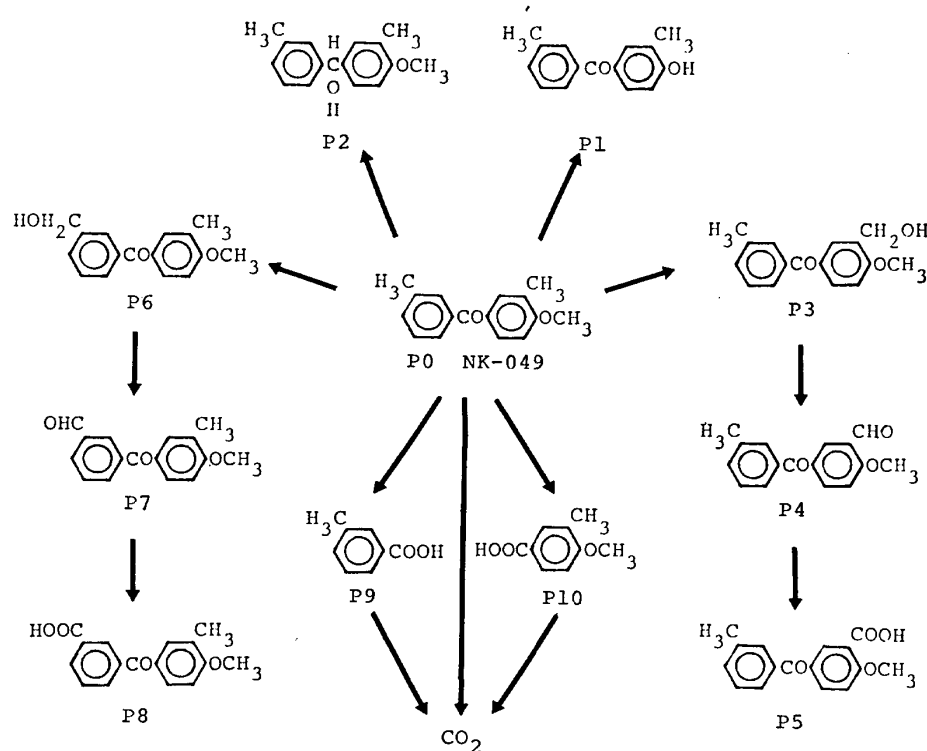


Fig. 2 Possible photodecomposition pathways of NK-049.

reaction of NK-049, the major metabolic reactions in rats⁵⁾ and rice plants,^{6,7)} were slightly observed under the tested conditions.

A possibility of manipulating the persistence of pesticide residues by pesticide-photosensitizer interactions was shown by Ivie and Casida.^{19,20)} Rotenone^{20,21)} and benzophenone^{19,22,23)} sensitize the photodecomposition of cyclodienes, aromatic amines^{19,24)} act on DDT and cyclodienes, and anthraquinone¹⁹⁾ shows the broad spectrum of activity in many pesticides. In our study, NK-049 acted as an effective sensitizer as benzophenone and accelerated the photodecomposition of cyclodienes on glass plates, but it was ineffective to DDT and β -BHC as shown in case of benzophenone by Casida.¹⁹⁾ The formation of photodiieldrin will increase rather than reduce the level and persistence of the resulting toxic residues, because the toxicity of photodiieldrin is rather greater than that of diieldrin itself,^{25,26)} and it is more persistent on plant leaves due to its lower volatility.^{20,27)} Although there may be some possibility of the contact between NK-049 and other pesticides in practical application in the field, still it may be safe to conclude that a photosensitizing pesticide dose

not alter the persistence of other pesticide residues because no accelerating action of NK-049 was observed on soil surface.

The studies reported here indicate that NK-049 is readily susceptible to sunlight photodecomposition as surface deposits and in water solution and will be of short persistence in environment. Possible decomposition pathways for NK-049 are tentatively proposed in Fig. 2.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. I. Yamaguchi, The Institute of Physical and Chemical Research, and Dr. S. Ishida and Mr. O. Yamada of Nippon Kayaku Co., Ltd., for helpful discussions.

REFERENCES

- 1) K. Ito, F. Futatsuya, K. Hibi, S. Ishida, O. Yamada & K. Munakata: *Weed Res. (Japan)* **18**, 10 (1974)
- 2) K. Ito, F. Futatsuya, K. Hibi, S. Ishida, O. Yamada & K. Munakata: *Weed Res. (Japan)* **18**, 16 (1974)
- 3) Y. Fujii, T. Kurokawa, I. Yamaguchi & T. Misato: *J. Pesticide Sci.* **3**, 291 (1978)
- 4) K. Ito, F. Futatsuya, K. Hibi, S. Ishida, O. Yamada & K. Munakata: *Proc. of the*

- 5th APWSS Conference, p. 159 (1975)
- 5) Y. Fujii, T. Kurokawa, S. Ishida, I. Yamaguchi & T. Misato: *J. Pesticide Sci.* **1**, 313 (1976)
- 6) A. Kurozumi, Y. Fujii, T. Kurokawa, S. Ishida, I. Yamaguchi & T. Misato: The Abstract of the 1st Ann. Meeting of Pesticide Science Society of Japan (in Japanese). p. 211 (1976)
- 7) Y. Fujii, A. Kurozumi, T. Kurokawa, I. Yamaguchi & T. Misato: *J. Pesticide Sci.* **4**, 511 (1979)
- 8) A. Kurozumi, T. Kurokawa, I. Yamaguchi & T. Misato: The Abstract of the 3rd Ann. Meeting of Pesticide Science Society of Japan (in Japanese) p. 121 (1978)
- 9) A. Kurozumi, T. Kurokawa, I. Yamaguchi & T. Misato: *J. Pesticide Sci.* **3**, 59 (1978)
- 10) O. Yamada, K. Hirose, S. Asaka, S. Ishida & K. Munakata: The Abstract of the 12th Ann. Meeting of the Weed Science Society of Japan (in Japanese) p. 7 (1973)
- 11) Y. Fujii, S. Asaka & T. Misato: *J. Pesticide Sci.* **3**, 361 (1979)
- 12) K. Ishikawa, Y. Nakamura & S. Kuwatsuka: *J. Pesticide Sci.* **2**, 17 (1977)
- 13) J. Robinson, A. Richardson, B. Bush & K. E. Elgar: *Bull. Environ. Contam. Toxicol.* **1**, 127 (1966)
- 14) W. R. Benson: *J. Agric. Food Chem.* **19**, 66 (1971)
- 15) A. M. Parsons & D. J. Moore: *J. Chem. Soc. (C)*, 2026 (1966)
- 16) T. W. Martin & N. J. Pitts: *J. Am. Chem. Soc.* **77**, 5465 (1955)
- 17) F. W. McLafferty: *Anal. Chem.* **31**, 821 (1959)
- 18) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner & P. D'Angelo: *J. Am. Chem. Soc.* **87**, 4097 (1965)
- 19) G. W. Ivie & J. E. Casida: *J. Agric. Food Chem.* **19**, 405 (1971)
- 20) G. W. Ivie & J. E. Casida: *J. Agric. Food Chem.* **19**, 410 (1971)
- 21) G. W. Ivie & J. E. Casida: *Science* **167**, 1620 (1970)
- 22) J. D. Rosen & W. F. Carey: *J. Agric. Food Chem.* **16**, 536 (1968)
- 23) J. D. Rosen & M. Siewierski: *J. Agric. Food Chem.* **18**, 943 (1970)
- 24) L. L. Miller & R. S. Narang: *Science* **169**, 368 (1970)
- 25) J. D. Rosen & D. J. Sutherland: *Bull. Environ. Contam. Toxicol.* **1**, 133 (1966)
- 26) J. D. Rosen & D. J. Sutherland: *Bull. Environ. Contam. Toxicol.* **2**, 1 (1967)
- 27) B. C. Turner, D. E. Glotfelty & A. W. Taylor: *J. Agric. Food Chem.* **25**, 249 (1977)

要 約

3,3'-Dimethyl-4-methoxybenzophenone (メトキシフェノン, NK-049) の光分解とその光増感作用

藤井保男, 黒 濟 晃, 見里朝正

NK-049 の光による分解性とその光増感作用を検討した。¹⁴C-NK-049 (カルボニル・ラベル) は太陽光線ならびに紫外線照射によって速やかに分解し, *tlc* 上で 16 種類以上の分解物が検出されたがその内の 10 種類が同定された。これらの分解物は 3 位または 3' 位のメチル基の酸化, 4-メトキシ基の脱メチル化, カルボニル基の還元とその切断反応によって生じたものであるが, いずれもごく少量しか生成されなかった。水溶液中の ¹⁴C-NK-049 を紫外線照射した場合顕著な炭酸ガスの生成が認められ, カルボニル位での切断が主な光分解反応と考えられた。NK-049 はドリン剤の光分解に対しベンゾフェノンと同程度の光増感作用を持っており, デイルドリンの光分解物は分子内で架橋されたフォトデイルドリンと同定された。