

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### The Photochemical Reactions of Carbamates III. The Solution Photochemistry of Metacrate, 3-methylphenyl-N-methyl carbamate

J. B. Addison<sup>a</sup>; P. J. Silk<sup>a</sup>; I. Unger<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of New Brunswick, New Brunswick, Canada

**To cite this Article** Addison, J. B. , Silk, P. J. and Unger, I.(1973) 'The Photochemical Reactions of Carbamates III. The Solution Photochemistry of Metacrate, 3-methylphenyl-N-methyl carbamate', *International Journal of Environmental Analytical Chemistry*, 3: 1, 73 – 79

**To link to this Article:** DOI: 10.1080/03067317308071069

**URL:** <http://dx.doi.org/10.1080/03067317308071069>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# The Photochemical Reactions of Carbamates

## III. The Solution Photochemistry of Metacrate, 3-methylphenyl-N-methyl carbamate

J. B. ADDISON, P. J. SILK, and I. UNGER

*Department of Chemistry, University of New Brunswick,  
Fredericton, New Brunswick, Canada*

(Received February 1, 1973)

**KEY WORDS:** carbamates; Metacrate; photodecomposition; 3-methylphenyl-N-methyl Carbamate.

The photodecomposition of Metacrate ( $\lambda > 265$  nm) has been carried out in aerated and degassed solutions. The major products observed are *m*-cresol, 2-hydroxy-4-methyl-N-methylbenzamide and 4-hydroxy-2-methyl-N-methylbenzamide. These products indicate that the photo-Fries reaction is operative in the photo-degradation of Metacrate.

## INTRODUCTION

The O-phenyl-N-methyl carbamates form an important class of pesticides. The absorption spectra of most of these molecules extend into the solar region ( $\lambda > 300$  nm). Casida and collaborators have shown that some of the carbamates undergo photo-oxidation when deposited on bean foliage<sup>1,2</sup> and that a variety of organic molecules can sensitize the decomposition of certain carbamates.<sup>3,4</sup> This work, however, does not allow one to differentiate between products arising solely from photochemical reaction and those due to either a combination of photo and enzymatic action or sensitization of the carbamate by natural products present in the bean foliage. The carbamates are also of interest in organic photochemistry since they are expected to

undergo a photo-Fries<sup>5,6</sup> reaction, the mechanism of which is still under discussion in the literature.<sup>7,8</sup> We have been examining the solution photochemistry of carbamates<sup>9,10</sup> with a view to determining the nature of products due purely to photodegradation, thus enabling analytical chemists to develop techniques for their detection, and to the elucidation of the photo-Fries reaction in carbamates. This paper presents the results of such a study on the solution photochemistry of Metacrate, 3-methylphenyl-N-methyl carbamate.

## EXPERIMENTAL

### Chemicals

Metacrate was obtained from Sumitomo Shoji Kaisha Limited, Osaka, Japan. This material was dried under vacuum and TLC showed it to be pure to the limits of detection; its spectral properties determined by us are listed below:

ms,  $M^+$  165; n.m.r. ( $CDCl_3$ )  $\tau$  7.65 (s, 3H, tolyl methyl), 7.10 (d, 3H, 5Hz, N-methyl), 3.00–2.80 (multiplet, 4H, aromatic H's); infrared ( $CHCl_3$ )  $\nu_{Max}$  3462  $cm^{-1}$ , 1736  $cm^{-1}$ ; u.v. (ethanol)  $\lambda_{Max}$  = 264.0 nm,  $\epsilon \approx 345$  liters/mole-cm;  $\lambda_{Max}$  = 270.5 nm,  $\epsilon \approx 300$  liters/mole-cm.

Absolute ethanol, for solution photolyses, was obtained from Consolidated Alcohols Limited, Toronto, Ontario. Cyclohexane was obtained from Harleco, Philadelphia, Pa., as fluorometric grade; both solvents were used without further purification. Carbon tetrachloride was obtained from Fisher Scientific Co. as reagent grade. Chloroform, used as a general solvent for TLC, was distilled and stored over molecular sieve.

### Instrumentation

Infrared spectra were recorded on a Perkin-Elmer grating spectrophotometer, Model 457; u.v. spectra were determined on either a Perkin Elmer 402 u.v.—visible spectrophotometer or a Hitachi EPS-3T spectrophotometer. N.m.r. spectra were recorded on a Varian T-60 n.m.r. spectrometer; tetramethylsilane was used as an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

### Photochemical procedures

For aerated ethanol solutions the photochemical set-up used was similar to that described by Calvert and Pitts.<sup>11</sup> The source was a Hanovia medium-

pressure Hg arc, contained in a quartz water jacket and equipped with a Hanovia cylindrical Vycor filter (512/27/114), encasing the entire lamp. The cell housing had an approximate volume of 250 ml. For all other photolyses, 1 × 4 cm fluorometric quartz cuvettes were used. They were placed 20 cm from the centre of the lamp housing, the water jacket being removed in these circumstances. Solution concentrations were typically 4 g/l except with aerated ethanol where it was 8 g/l.

### Analytical techniques

Analytical and preparative TLC was performed on microscope slides or 20 × 20 cm glass plates. Silica gel G (Merck) was used throughout at a layer thickness of 0.5 mm for the preparative plates. The plates were activated by heating in an air-oven at 140°C for 6 hr. Elution was achieved by the ascending technique using chloroform/ether (6 : 4) at tank saturation. Samples, scraped from the plates, were eluted from the silica gel with methanol, filtered and the solvent evaporated. The residue was then dissolved in chloroform, filtered to remove traces of silica gel, followed by drying with magnesium sulphate and solvent evaporation prior to spectral analysis. Phenolic products were also extracted from photolysed solutions using 1N sodium hydroxide solution followed by neutralization with hydrochloric acid and extraction into chloroform. Ninhydrin was used as a visualization reagent along with potassium permanganate/sodium carbonate solution. U.v. detection was also used aided by "phosphor Green" (Sylvania) incorporation into the silica gel layers.

VPC was performed on a Perkin-Elmer 990 gas chromatograph equipped with a flame-ionization detector. Helium was used as a carrier gas throughout. The column was 6' long  $\frac{1}{8}$ " o.d. stainless steel packed with 10% w/w UCW-98 on Chromosorb Q. Column temperature was 150°C. Samples were dissolved in chloroform prior to injection.

### RESULTS AND DISCUSSION

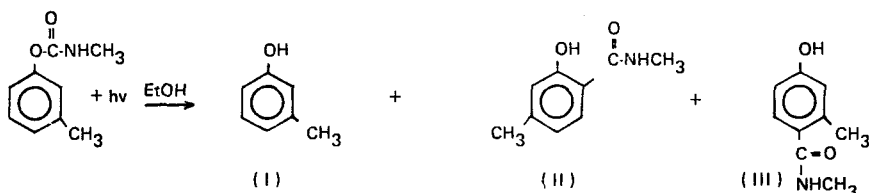
The photodecomposition of Metacrate was examined in both aerated and degassed ethanol and cyclohexane solutions and also in aerated carbon tetrachloride solution. The results are summarized in Table I. In ethanol for both the aerated and degassed cases, four major photo-products were isolated and identified to be: *m*-cresol (I), 2-hydroxy-4-methyl-N-methylbenzamide (II), 4-hydroxy-2-methyl-N-methylbenzamide (III) and a product arising out of the secondary photolysis of III, IV. Small quantities of oxidation products

TABLE I  
Typical photolysis results

Solvent	Aerated or degassed	Photolysis time (hr)	Decomposition* (%)	Products (%)				Comments
				I	II	III	IV	
Ethanol (0.05 M)	Degassed	2	~ 2	19	39	32	~ 3	
Ethanol	Aerated	4	6	18	34	30	~ 6	
Ethanol	Aerated	8	10	16	31	26	~ 10	
Ethanol	Aerated	22	23	19	28	15	> 20	
Ethanol	Aerated	30	26	18	27	8	> 28	
Ethanol	Degassed	22	20	—	—	—	—	No $R_f$ = 0.0 products
Cyclohexane	Aerated	22	15	> 95	—	—	—	$R_f$ = 0.0 products evident [photo-oxidation and/or polymeric product(s)].
Cyclohexane	Degassed	22	17	> 95	—	—	—	
Carbon tetrachloride	Aerated	22	18	> 90	—	—	—	

\* Determined by VPC.

were also observed in aerated solutions. The reaction scheme can be represented as:



Preparative TLC always showed seven distinct bands, under u.v. light (with "phosphor" incorporated in the plates), with unique colours. The description of each band is given in Table II.

TABLE II  
 $R_f$  values for photolysis products of Metacrate

Band No.	Assignment	Band colour	$R_f$
1	—	trace only	0.94
2a	I	light brown	0.86
2b	Metacrate	light brown	0.79
3	II	blue	0.66
4	III	light brown	0.41
5	IV	dark brown	0.26
6	oxidation products and polymer	yellow	0.00

The spectral properties of the isolated and purified products are given below:

*m-cresol (I)*. oil; ms,  $M^+$  108; n.m.r. ( $\text{CDCl}_3$ )  $\tau$  7.68 (s, 3H, tolyl-Me), 2.87–3.32 (multiplet, 4H, aromatic H's); infrared ( $\text{CHCl}_3$ )  $\nu_{\text{Max}}$   $3600\text{ cm}^{-1}$ ,  $1590\text{ cm}^{-1}$ .

This compound was identical, spectroscopically, to an authentic sample of *m-cresol* and also to the product produced in the alkaline hydrolysis of Metacrate.

*2-hydroxy-4-methyl-N-methylbenzamide (II)*. white crystals; ms,  $M^+$  165; n.m.r. ( $\text{CDCl}_3$ )  $\tau$  7.69 (s, 3H, tolyl-Me), 7.00 (d, 3H, 5 Hz, N-Me), 2.84–3.42 (multiplet, 3H, aromatic H's); infrared ( $\text{CHCl}_3$ )  $\nu_{\text{Max}}$   $3600\text{ cm}^{-1}$ ,  $3480\text{ cm}^{-1}$ ,  $1645\text{ cm}^{-1}$ ,  $1605\text{ cm}^{-1}$ ; u.v. (ethanol)  $\lambda_{\text{Max}}$  303 nm, 245 nm (cf. ref. 12).

4-hydroxy-2-methyl-N-methylbenzamide (III). white crystals; ms,  $M^+$  165; n.m.r. ( $CDCl_3$ )  $\tau$  7.49 (s, 3H, tolyl-Me), 6.97 (broad-s, 3H, N-Me), 2.65–3.36 (multiplet, 3H, aromatic H's); infrared ( $CHCl_3$ )  $\nu_{Max}$  3630  $cm^{-1}$ , 1636  $cm^{-1}$ , 1602  $cm^{-1}$ ; u.v. (ethanol)  $\lambda_{Max}$  283 nm (*cf.* ref. 12).

(IV). Spectra not clearly defined; infrared ( $CHCl_3$ ) indicates  $\nu(C=O) \sim 1640$   $cm^{-1}$ , (O—H)  $\sim 3630$   $cm^{-1}$ , broad H-bonding band  $\nu_{Max} \sim 3400$   $cm^{-1}$ ; n.m.r. ( $CD_3COCD_3$ ) indicates N-Me moiety ( $\tau$  7.05—broad singlet).

The photo-products of Metacrate, under the conditions of this study, are those expected from a photo-Fries rearrangement of this molecule.<sup>5</sup> This rearrangement has been demonstrated to occur, in part, in the insecticidal carbamate, Zectran.<sup>9</sup> The photolysis of Metacrate follows a similar pattern to that described for the isomeric *p*-tolyl-N-methyl carbamate,<sup>6</sup> where *p*-cresol and 2-hydroxy-5-methyl-N-methylbenzamide are the major photolysis products. In the case of the *p*-tolyl compound, the *para* position is effectively blocked, since alkyl elimination is not known to occur in photo-Fries rearrangements,<sup>5,10</sup> and hence *para*-product formation is not possible. In the case of Metacrate, the *para* position is open and in addition to the cresol and *ortho*-benzamide the *para*-benzamide (III) is produced, although not in high yield due to its secondary photolysis.† Steric factors play an important role in *ortho*-product formation (II) in Metacrate where it appears quite clear, from spectral evidence in the present and from previous work,<sup>9,10</sup> that the acylamino group migrates to the *ortho* position in the ring away from the ring-methyl group.

In degassed ethanol solutions, products I, II, III and IV were also obtained but no oxidation products were observed (at  $R_f = 0.0$ ). In aerated and degassed cyclohexane solutions, photo-Fries rearrangement products were not observed under these conditions except for *m*-cresol (I) which was the major product. In aerated carbon tetrachloride solutions, again photo-Fries rearrangement is not observed; *m*-cresol is the major product. It seems logical to suggest, then, that photo-Fries rearrangement for Metacrate solutions is solvent dependent. That solvent polarity plays an important role in rearrangements of this type has been known for some time. The yield of phenol, for example, is favoured by non-polar solvents whereas *ortho*/*para* rearrangement products are favoured in polar solvents.<sup>5</sup> This argument lends an explanation to product formation in this work; photo-Fries rearrangement seems only to occur in the polar solvent, ethanol, whereas in cyclohexane and carbon tetrachloride, it does not and phenol formation is evident. Photolyses

† This was confirmed by separate photolyses of the isolated *ortho*- and *para*-benzamides in ethanol solution. The *ortho*-benzamide showed little or no decomposition whereas the *para*-benzamide disappeared rapidly, giving a compound whose  $R_f$  was identical to band IV, Table II.

carried out on the *ortho*- and *para*-benzamides, under identical conditions to that of Metacrate, indicate that the *ortho* compound is far more photostable than the *para* compound. The photostability of the *ortho* compound is probably due to rapid enolisation in the excited state.<sup>13</sup> The *para* compound, likely, photo-pinacolizes and evidence from the literature bears this out.<sup>5</sup> The photolysis of Metacrate is self-terminating; the maximum conversion possible is of the order of 30%. This is a common feature of photo-Fries rearrangement.<sup>6</sup>

An attempt to synthesize products II and III by the acid catalysed Fries rearrangement using aluminium chloride was unsuccessful. Only *m*-cresol was produced in fair yield. From this work and from previous studies<sup>9,10</sup> it appears unlikely that the acid-catalysed Fries rearrangement can be induced in these carbamates. Instead, considerable decomposition occurs.

*Late Note*—Toluene was also observed as a product in ethanol solutions. The mechanistic implications of this product will be discussed in forthcoming publications in this series.

### Acknowledgments

The authors wish to thank the Sumitomo Chemical Co., Osaka, Japan for the gift of Metacrate. We are also grateful for financial aid for this project from the University of New Brunswick research fund, and from the National Research Council of Canada. Finally, we wish to acknowledge many helpful discussions with Professor G. P. Semeluk.

### References

1. A. M. Abdel-Wahab, R. J. Kuhr, and J. E. Casida, *J. Agr. Food Chem.* **14**, 290 (1966)
2. A. M. Abdel-Wahab and J. E. Casida, *J. Agr. Food Chem.* **15**, 479 (1967).
3. G. W. Ivie and J. E. Casida, *J. Agr. Food Chem.* **19**, 405 (1971).
4. G. W. Ivie and J. E. Casida, *J. Agr. Food Chem.* **19**, 410 (1971).
5. D. Bellus, *Advan. Photochem.* **8**, 109 (1971).
6. D. J. Trecker, R. S. Foote, and C. L. Osborn, *Chem. Commun.* 1034 (1968).
7. J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.* **94**, 2219 (1972).
8. F. A. Carroll and G. S. Hammond, *Isr. J. Chem.* **10**, 613 (1972).
9. P. J. Silk and I. Unger, *Intern. J. Environ. Anal. Chem.*, **2**, 213 (1973).
10. J. B. Addison, P. J. Silk, and I. Unger, *Bull. Environ. Contam. Toxicol.*, in press.
11. J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (John Wiley and Sons, Inc., New York, 1967), p. 752.
12. L. Lang (Ed.), *Absorption Spectra in the UV and IR*, Vol. 5 (Academic Press, New York, 1961).
13. A. A. Lamola and L. J. Sharp, *J. Phys. Chem.* **70**, 2634 (1966).