Effects of pH, Light and Temperature on Carbaryl in Aqueous Media[1]

by R. D. WAUCHOPE[2] and R. HAQUE
Department of Agricultural Chemistry and
Environmental Health Sciences Center, Oregon State University
Corvallis, Ore. 97331

Carbaryl (N-methyl-1-naphthylcarbamate) has been shown by STEWART, et al. (1967) and LAMBERTON and CLAEYS (1970) to degrade after estuarine application to products which are toxic to some marine species, and solution pH, light and temperature have been shown by LAMBERTON and CLAEYS (1970) and KARINEN, et al. (1967) to be significant factors in determining the rate and pathway of degradation. We have studied the kinetics of the hydrolysis of carbaryl in simple NaOH solutions and have found that the mechanism given by DITTERT and HIGUCHI (1963) and BENDER and HOMER (1965) for methylcarbamates appears to apply and adequately describes observed hydrolysis rates in sea water as well. Light irradiation of carbaryl solutions of various pH has shown that it is the naphthoxide ion produced by carbaryl hydrolysis in basic solution which is particularly sensitive to photooxidation. One photooxidation product has been identified.

During this investigation a paper by ALY and EL-DIB (1971) appeared in which the hydrolysis of carbaryl and three other carbamate insecticides was studied in NaOH solution and in phosphate buffers. Our kinetic results in general confirm their findings for NaOH media and are presented only in summary form. However, their results on buffered media, which were taken to indicate a difference in hydrolysis rate constants between sea and distilled water, appear to be in error.

Materials and Methods

Because the products of carbaryl are weakly acidic, base is consumed by the reaction above pH 8.5. A Radiometer syringe titrator was used in the pH-stat mode to monitor OH^- consumption.

---

[1] Research supported by N.I.E.H. Grant No. ES-00210 from the U.S. Public Health Service, and the manuscript issued as Technical Paper No. 3350 from Oregon Agricultural Experiment Station. Presented at the 163rd National ACS Meeting, Boston, 1972.

[2] N.I.E.H. Postdoctoral Trainee, to whom correspondence should be addressed. Current address: U.S.D.A./A.R.S., Southern Weed Science Laboratory, Stoneville, MS 38776.

Bulletin of Environmental Contamination & Toxicology,
Vol. 9, No. 5 © 1973 by Springer-Verlag New York Inc.

Using the titrator, 99 ml of distilled deionized water was brought to the required pH and 1 ml of a 95% ethanol solution of recrystallized carbaryl was then added. 0.1 N NaOH was used for titrant, and pseudo-first-order titration curves were obtained in all cases. Convenient reaction times were obtained in the pH range 9.0-10.0 and calculated second-order rate constants were independent of the pH.

Hydrolyses were run in a dark-amber glass bottle which was immersed in a water bath, and the solution was kept under a nitrogen atmosphere. Temperature control was to within 0.01°C; pH control and reproducibility was within 0.03 unit. Initial carbaryl concentrations were 3 x 10^{-4}M.

A 100W Hanovia high-pressure xenon-arc lamp, which closely simulates solar radiation, was used for irradiation of basic solutions of carbaryl in the cavity of a Varian E-4 EPR spectrometer. A mass spectrum of the products was obtained by acidification of the extract onto the direct inlet probe of a Varian Mat Gmbh CH-7 spectrometer. Silica gel G TLC plates of the extract were also developed using 9:1 benzene-acetone.

Results and Discussion

Observed pseudo-first-order half-lives and calculated second-order hydrolysis rate constants are given in Table 1 along with some previously reported values for comparison.

An Arrhenious plot (ln k_2 vs. 1/T °K) shows good agreement of the data, considering the wide range of experimental conditions, except for the higher temperatures and the uncertain point for 3.5°C of KARINEN, et al. (1967). Thus, there appears to be little difference in carbaryl hydrolysis rate constants in NaOH solution vs. sea water, and ALY and EL-DIB's (1971) reported much larger hydrolysis rate constant in pH 7, 8, 9, and 10 phosphate buffers, at 20°C, appears to be in error. Since their difference is a constant one for the 4 pH's, the disparity cannot be ascribed to the slight phosphate catalysis observed by BENDER and HOMER (1965).

We note in passing that the measurement of the (constant) titration rate of a saturated carbaryl solution, with excess carbaryl present, allows, with certain assumptions given by OHNISHI and TANABE (1971), the calculation of solubility. We obtained solubilities using this method of 114 ppm and 67 ppm at 24 and 12°C, respectively, which are considerably higher than previous estimates, e.g., 40 ppm at 30°C as reported by DAVID, et al. (1960). The value at 12°C also agrees well with that obtained from a Beers-law calculation on the UV spectrum of a saturated solution, but further investigation is needed.

TABLE 1

Reference	pH or [OH^-]	Temp. °C	$t_{\frac{1}{2}}^{obs}$	10^2 x k_2
ALY and EL-DIB (1971)	9 x 10^{-5}M	3	32 min.	0.242
"	"	13	11	0.691
"	"	23	3.8	2.04
"	"	33	1.4	5.37
this work	10.0 pH	12	99	0.7
"	"	25	20	3.4
"	"	35	8	9.0
"	9.8	25	27	4.3
"	9.5	25	58	3.8
"	9.2	25	116	3.8
"	9.0	25	173	4.0
KARINEN, et al. (1967)	8.0 (sea water)	3.5	1 mo.	0.08
"	"	17	4.8 d.	1.0
"	"	20	3.5	1.4
"	"	28	1.0	4.6

The data from ALY and ED-DIB (1971) are in simple NaOH solutions; the data from KARINEN, et al. (1967) are calculated from their reported extents of hydrolysis in sea water aquaria after a single time period.

In weakly acidic solutions carbaryl and 1-naphthol are stable for weeks in either the dark or under laboratory light. Furthermore, base-hydrolysis of carbaryl in the dark leads to formation of 1-naphthol as the only naphthyl product, as determined by UV spectra. In ordinary room light, however, basic 1-naphthol, or hydrolysed-carbaryl solutions, turn yellow, then amber within 24 hours. Thus, it is the basic form of 1-naphthol, 1-naphthoxide ion, which appears to be especially light-sensitive. BRYSON and MATTHEWS (1963) report the pK_a of 1-naphthol to be 9.40 and thus an appreciable amount of 1-naphthoxide (6% at pH 8.2) will be present in marine environments, and the photodegradation of this species appears to be the most important nonbiological route for further changes, after hydrolysis, in the naphthyl moiety of carbaryl.

In a recent report, TOMKIEWICZ et al. (1971) reported the observation of phenoxide ion photooxidation in aqueous NaOH. Using a flow system and Hg-Xe arc irradiation in the microwave cavity of an EPR spectrometer, the EPR signal of *p*-benzosemiquinone and two oxybenzosemiquionones were identified. Using their technique with 1-naphthol we obtained a weak EPR signal using Xe radiation but were unable to resolve the complex signal which the naphthyl species no doubt exhibit. However, acidification of the resulting amber solution immediately removed the color, and extraction with ether removed all UV-absorbing species. The resulting extract gave a 1-naphthol spot plus a broad orange smear on TLC plates, and the mass-spectrum of the extract was almost totally attributable to 1-naphthol and 2-hydroxy-1,4-naphthoquinone (lawsone). The latter has a quite characteristic fragmentation pattern, and identification was confirmed by the mass spectrum of the 2-methoxy analogue, obtained on treatment of the extract with diazomethane. Both materials gave mass spectra in agreement with those reported by BOWIE, et al. (1965).

Thus, it might be worthwhile to look for lawsone residues in the environment where carbaryl has been extensively used. However, lawsone is itself no doubt light sensitive, and 1-naphthol may form other photooxidation products under different conditions: weeks-old basic carbaryl solutions gave 5-7 colored TLC spots besides 1-naphthol, when exposed for that time to room (fluorescent) illumination. None of these products have been identified.

References

ALY, O. M., and M. A. EL-DIB: Water Research 5, 1191 (1971).

BENDER, M. L., and R. L. HOMER: J. Org. Chem. 30, 3976 (1965).

BOWIE, J. H., D. W. CAMERON, and D. H. WILLIAMS: J. Amer. Chem. Soc. 87, 5094 (1965).

BRYSON, A., and R. W. MATTHEWS: Aus. J. Chem. 16, 401 (1963).

DAVID, W. A., R. L. METCALF, and M. WINTON: J. Econ. Entomol. 53, 1021 (1960).

DITTERT, L. W., and T. HIGUCHI: J. Pharm. Sci. 52, 852 (1963).

KARINEN, J. F., J. G. LAMBERTON, N. E. STEWART, and L. C. TERRIERE: J. Ag. Food Chem. 15, 148 (1967).

LAMBERTON, J. G., and R. R. CLAEYS: J. Ag. Food Chem. 18, 92 (1970).

OHNISHI, R., and K. TANABE: Bull. Chem. Soc. Japan 41, 2647 (1971).

STEWART, N. E., R. E. MILLEMAN, and W. P. BREESE: Trans. Am. Fisheries Soc. 96, 25 (1967).

TOMKIEWICZ, M., A. GROEN, and M. COCIVERA: J. Amer. Chem. Soc. 93, 7102 (1971).