

Physical Properties of Some Halo-Nitrophenols

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IN THE course of a screening program in the search for chemicals selectively toxic to sea lamprey larvae (1), it was discovered that certain mononitrophenols containing halogens were effective. The toxic properties of six of these larvicides have been reported (2).

The use of these chemicals as larvicides in natural waters requires precise control of concentration. The concentration must be high enough to be effective against the lamprey larvae, yet not so high as to affect other aquatic species adversely. The concentration of the larvicide can be determined readily by colorimetric analysis.

This article reports certain properties of eight selective larvicides which were measured in connection with the development of colorimetric procedures. Details of the analysis for one of these, 3-trifluoromethyl-4-nitrophenol, have been reported (4).

EXPERIMENTAL

Compounds Studied. The sources and physical properties of the substituted phenols used are given in Table I.

Ultraviolet and Visible Spectra. The spectrum of each compound was determined with a Beckman DU Spectrophotometer (1-cm. cells) in three solvents: acid, 1% NaOH, and 95% ethanol. Stock solutions of the phenols (usually 500 p.p.m.) were prepared in 1% NaOH and in 95% ethanol.

Table I. Experimental Purification Conditions for Substituted Nitrophenols

Compound	Condition	Recrystallization Solvent	M.P., ° C.
Halo-4-Nitrophenol			
2-Bromo-	Commercial	Benzene-Petroleum ether	110-12
3-Bromo-	Synthesized by authors ^a	^b	134-35
2-Chloro-	Commercial	Benzene	112-12.5
2,5-Dichloro-	Commercial	Benzene	114.5-16
3-Trifluoromethyl-	Commercial	Benzene-Petroleum ether	75-6
Halo-2-Nitrophenol			
5-Chloro-	Commercial	Petroleum ether, low b.p. ^c	39.0
3,4,6-Trichloro-3-Trifluoromethyl-	Commercial	Petroleum ether	91-2 71-3

^a Nitration of *m*-bromophenol in acetic acid (3). ^b Crude product m.p. 112°-15° C. was dissolved in acetone and chromatographed over Al₂O₃. Elution with benzene gave a solution from which the pure compound separated upon addition of petroleum ether. ^c Sample steam distilled before recrystallization.

Portions of these were then diluted to suitable concentrations. To prepare the acidic solutions, the 1% NaOH stock solution was used. The pH of the solution was decreased below 3 by the cautious addition of dilute HCl. In all determinations, the instrument was balanced against the appropriate solvent. The maxima and molar absorptivities obtained are reported in Table II.

Each of the phenols shows an absorption maximum in the neighborhood of 400 m μ in 1% NaOH solution. At this value of λ_{max} , Beer's law is followed up to a concentration of 30 p.p.m. (Figure 1).

Potentiometric Titrations. The phenol (2 mmoles) was dissolved in water (usually 900 ml.) and titrated with 0.1000*N* NaOH. The pH was measured at intervals with a Beckman Zeromatic pH meter. The p*K* was calculated at three different points on the titration curve (approximately 40, 50, and 60% neutralization). The average of these three values and the average deviation from the mean are reported in Table III for each phenol.

As the solution became more alkaline, the absorbance in

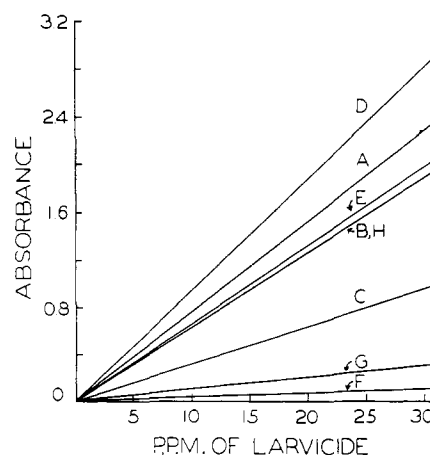


Figure 1. Variation of absorbance with concentration of compounds in 1% NaOH as determined with a Beckman DU Spectrophotometer (1-cm. cell)

- A. 2-Bromo-4-nitrophenol (402 m μ)
- B. 3-Bromo-4-nitrophenol (397 m μ , indistinguishable from H)
- C. 5-Chloro-2-nitrophenol (408 m μ)
- D. 2-Chloro-4-nitrophenol (402 m μ)
- E. 2,5-Dichloro-4-nitrophenol (393 m μ)
- F. 3,4,6-Trichloro-2-nitrophenol (410 m μ)
- G. 3-Trifluoromethyl-2-nitrophenol (405 m μ)
- H. 3-Trifluoromethyl-4-nitrophenol (395 m μ , indistinguishable from B)

Table II. Absorption Maxima and Molar Absorptivities of Larvicides

Compound	Acid		1% NaOH		95% Ethanol	
	λ_{max} , M μ	$\epsilon \times 10^{-4}$	λ_{max} , M μ	$\epsilon \times 10^{-4}$	λ_{max} , M μ	$\epsilon \times 10^{-4}$
2-Bromo-4-nitrophenol	318	0.78	402	1.69	235	0.81
					317	0.84
					405	0.14
3-Bromo-4-nitrophenol	246	0.484	397	1.37	242	0.74
	312	0.521			305	0.56
5-Chloro-2-nitrophenol	287	0.520	408	0.522	279	0.685
	340	0.311			339	0.390
2-Chloro-4-nitrophenol	316	0.833	402	1.71	315	0.826
2,5-Dichloro-4-nitrophenol	248	0.551	393	1.33	280	0.819
					340	0.480
3,4,6-Trichloro-2-nitrophenol	293	0.209	243	1.05	292	0.461
			310	0.336		
			410	0.0913		
3-Trifluoromethyl-2-nitrophenol	281	0.358	295	0.518	286	0.489
			405	0.234		
3-Trifluoromethyl-4-nitrophenol	280	0.193	300	0.465	290	1.47
			395	1.313		

Table III. Acidity Characteristics of Larvicides

Compound	pK, Average	Minimum pH for Maximum Absorbance
2-Bromo-4-nitrophenol	5.29 \pm 0.01	6.5
3-Bromo-4-nitrophenol	6.31 \pm 0.01	8.0
5-Chloro-2-nitrophenol	6.43 \pm 0.01 ^a	8.5
2-Chloro-4-nitrophenol	5.30 \pm 0.02	6.0
2,5-Dichloro-4-nitrophenol	4.64 \pm 0.01	5.5
3,4,6-Trichloro-2-nitrophenol	3.63 \pm 0.04	5.0
3-Trifluoromethyl-2-nitrophenol	5.60 \pm 0.00	7.5
3-Trifluoromethyl-4-nitrophenol	6.07 \pm 0.03	8.0

^a Value obtained from titration in 30:70 ethanol:water (v./v.).

determinations, the instrument was calibrated by recording the 6.24-micron line of polyethylene film on the paper immediately before the spectrum was run. The principal bands for each of the phenols are given in Table IV.

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Table IV. Principal Infrared Bands of Larvicides

Halo-Nitrophenol							
2-Bromo-4-	3-Bromo-4-	5-Chloro-2-	2-Chloro-4-	2,5-Dichloro-4-	3,4,6-Trichloro-2-	3-Trifluoro-methyl-2-	3-Trifluoro-methyl-4-
Microns							
2.95	2.95	3.20	2.90	3.10	3.00	2.90	3.00
6.30	6.20	6.20	6.30	6.40	6.50	6.25	6.00
6.60	6.30	6.35	6.70	6.60	7.20	6.50	6.20
7.60	6.60	6.60	7.50	7.20	7.90	6.75	6.50
8.00	7.55	7.65	8.00	7.40	8.40	7.60	6.70
8.55	7.70	7.90	8.50	7.60	8.60	7.95	6.90
9.00	8.40	8.10	9.00	8.00	8.80	8.50	7.55
9.70	8.95	8.50	9.60	8.25	10.45	8.75	7.85
11.10	9.70	9.15	11.10	8.80	11.10	9.05	8.00
11.25	11.05	9.30	11.20	9.20	11.40	9.40	8.50
12.05	11.50	9.40	12.00	10.35	12.40	10.75	8.75
13.40	12.15	10.90	13.40	11.10	13.45	11.65	9.10
14.50	13.40	11.35	14.00	11.65	14.30	12.45	10.90
	14.70	11.50		11.75		13.20	11.20
		11.85		13.25		13.85	11.35
		12.10		13.60		14.60	11.80
		13.30					11.90
		14.50					13.25
		14.90					13.35
							14.15

the neighborhood of 400 m μ increased because of increasing concentration of phenolate ion. Eventually, a pH was reached above which further increases produced little or no change in absorbance. The absorbance of each phenol was examined as a function of pH using a Bausch and Lomb Spectronic 20 Spectrophotometer. The minimum pH for maximum color development is also reported in Table III. If analysis is to be carried out at these wave lengths, this pH value represents the minimum degree of alkalinity that must be developed in the analytical solution if reliable results are to be obtained.

Infrared Spectra. Infrared spectra were determined on a Perkin Elmer Infracord (NaCl prism) as Nujol mulls. In all

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