many possibilities that velocity measurements alone are of little assistance in establishing the complete mechanisms. It is not improbable that each of the following reactions contributes in some instances to the instability of the systems: self-condensation and self-oxidation of the oxidant, the addition of the elements of water, reaction with the reductant.

Summary

By means of a "discontinuous titration" method it has been possible to determine the oxidation–reduction potentials of systems which are so unstable that the half-life period for the decomposition of the oxidant is of the order of one-tenth to one-half minute. With the systems formed by *p*-aminophenol and two of its N-alkyl derivatives the variation of the potential with the hydrogen-ion concentration has been studied in the *P*H range 1–8, and the basic dissociation constants have been determined from the results. Seven systems have been studied and the more important constants found are summarized in Tables XV and XVI.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA]

PRELIMINARY STUDY ON THE ANTIRACHITIC PROPERTIES OF SHRIMP OIL

BY F. P. BROOKS,[1] ROY F. ABERNETHY AND F. C. VILBRANDT[2]

RECEIVED AUGUST 4, 1930 PUBLISHED DECEMBER 18, 1930

Shrimp oil is the ether-soluble oil obtained when the waste of the shrimp industry is extracted. It has been obtained by the authors[3] in their study on the utilization of shrimp waste. A later chemical study of this oil showed the presence of 19% of cholesterol, the presence of which led to the study of the oil for its antirachitic properties.

This investigation consisted in the feeding study of the oil on white rats, which had become rachitic by special feeding. Standard cod liver oil and shrimp oil were fed at the same time to get a relation of the antirachitic properties of the oil. After three generations of breeding, the selected young rats were fed on Sherman's growth diet B consisting of 66.7 g. of whole wheat, 33.3 g. of whole milk and 1.3 g. of sodium chloride, until they were twenty-eight days old. Part of the series was continued on this diet to serve as normal controls, another part was fed Steenbock's diet 2965[4] for the production of rickets. When they had developed the rickets,

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[3] F. C. Vilbrandt and R. F. Abernethy, "Utilization of Shrimp Waste," Fisheries Document 1078 (1930).

[4] H. Steenbock and A. Black, *J. Biol. Chem.*, **64**, 263 (1924).

which condition was shown by x-ray pictures and outward appearances, the rachitic rats were divided into three divisions. The first division was fed cod liver oil, the second division was fed shrimp oil and the third division was continued on the rachitic diet. The oils were added to the rachitic diet and the feeding test was continued for a period of five days. There were four groups of rats, (1) the rachitic and (2) the normal rats to serve as extreme controls and the two classes of rats one of which was fed cod liver oil and the other shrimp oil.

In this investigation three methods of measuring the amount of cure in the rats were used: (a) McCollum's[5] line test; (b) percentage of ash in the bone[6] and (c) the amount of calcium and phosphorus in the blood. The line test and the determination of the calcium and phosphorus in the blood were made by Dr. F. P. Brooks. (These data are not available and are material for a separate and more extensive paper by Dr. Brooks.) The ash determinations on the bone and the calcium and phosphorus determinations on the ash were made according to the Standard Methods.[7] The data in Table I and II will show there was some cure by the shrimp oil, but also that there was less cure in the second series than there was in the first.

In the first series of determinations 16 rats were used. At the age of twenty-eight days twelve rats were fed the Steenbock diet 2965 for four weeks. At the end of this time x-ray pictures and the outward appearance showed the animals to be rachitic. After the animals were found to be sufficiently rachitic, four of the twelve were fed shrimp oil with the rachitic diet, four were fed the rachitic diet with cod liver oil added and the other four were fed the rachitic diet. They were fed this oil diet for five days and then the sixteen rats were killed, the blood was taken for analysis and the bones from the rear legs were removed for the line test and the ash determination. The blood from the four rats of one group was combined to get a sufficient quantity for analysis. The bones were preserved in acetone until analyzed.

The Effect of Treated Feeds on Ash in Bones.—The results for the rat noted K are abnormal; the amount of food consumed by this rat was small, hence the results on this rat are not taken into consideration in determining the average. Examination of the data will disclose that the rachitic rat had the smallest percentage of ash and the control the highest. The rachitic rats that were fed the oils show some cure by being between the two extremes.

[5] E. V. McCollum, *J. Biol. Chem.*, **51**, 41 (1922).

[6] F. S. Hammett, *ibid.*, **64**, 415 (1925).

[7] Bethke, Steenbock and Nelson, *ibid.*, **58**, 76 (1923); J. O. Halverson and Olaf Bergeim, "The Preparation of *N*/100 Permanganate Solutions," *J. Ind. Eng. Chem.*, **10**, 119 (1918); R. E. G. Mahin, "Quantitative Analysis," **1922**, p. 453.

TABLE I

AMOUNT OF ASH IN BONES

Condition of rats	Notation	% Ash	Condition of rats	Notation	% Ash
Rachitic	A	43.55	Cod liver oil fed	I	44.71
Rachitic	B	41.54	Cod liver oil fed	J	44.71
Rachitic	C	45.62	Cod liver oil fed	K	40.00
Rachitic	D	43.61	Cod liver oil fed	L	47.37
Average		43.58	Average		45.59
Shrimp oil fed	E	46.77	Normal controls	M	53.93
Shrimp oil fed	F	45.33	Normal controls	N	54.30
Shrimp oil fed	G	47.65	Normal controls	O	52.47
Shrimp oil fed	H	44.54	Normal controls	P	54.77
Average		46.07	Average		53.82

Effect of Treated Feeds on Calcium and Phosphorus in Bones.—As in the determination of the percentage of the ash, the percentage of the calcium and of the phosphorus shows that the shrimp oil has some curative properties on rachitic rats.

TABLE II

CALCIUM AND PHOSPHORUS CONTENT OF ASH

Condition of rats	Notation	Calcium, % Bone	Calcium, % Ash	Phosphorus, % Bone	Phosphorus, % Ash
Rachitic	A	16.78	38.54	7.81	17.94
Rachitic	B	15.65	37.26	6.64	16.13
Rachitic	C	16.22	37.70	8.43	18.60
Rachitic	D	16.95	38.90	...	...
Average		16.40	38.10	7.63	17.56
Shrimp oil	E	18.05	38.59	8.59	18.34
Shrimp oil	F	17.55	38.61	8.30	18.30
Shrimp oil	G	18.14	38.07	9.09	19.08
Shrimp oil	H	16.81	37.80	8.12	18.24
Average		17.64	38.27	8.52	18.49
Cod liver oil	I	17.49	38.83	8.07	18.10
Cod liver oil	J	16.23	38.26	...	...
Cod liver oil	K	15.60	38.90	...	...
Cod liver oil	L	17.45	39.20	...	...
Average		16.69	38.79	8.07	18.10
Controls	M	20.32	37.64	10.05	18.64
Controls	N	20.11	36.91	9.45	17.23
Controls	O	19.55	37.00	8.65	16.30
Controls	P	20.63	37.85	...	...
Average		20.15	37.35	9.54	17.39

Summary

In the investigation of the antirachitic properties of shrimp oil it was found from the analysis of the blood and the bones that the oil had proper-

ties akin to cod liver oil that tended to cure the rachitic rats. From an examination of the data it is found in the first series that the shrimp oil was as potent as the cod liver oil. The second series showed some cure but less than the cod liver oil, probably due to the increasing rancidity of the shrimp oil.

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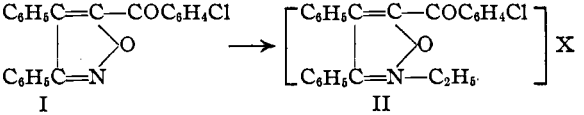
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PSEUDO BASES IN THE ISOXAZOLE SERIES. THIRD PAPER

BY E. P. KOHLER AND C. L. BICKEL

RECEIVED AUGUST 12, 1930 PUBLISHED DECEMBER 18, 1930

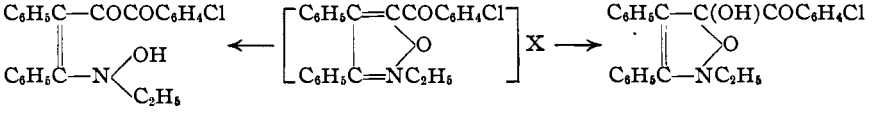
The pseudo bases that have been described in earlier papers of this series are derived from isoxazoles in which all available positions are filled with hydrocarbon residues. In all these cases the rearrangement of the true base results in a pseudo base in which the hydroxyl group occupies the 5-position. In order to determine whether this mode of rearrangement is altered by an acidic group in this position, we have alkylated a ketonic isoxazole and studied the behavior of the resulting salts toward bases



I II

The ethylation presented no difficulties and the salts could be manipulated in the same manner as those described heretofore. When they were shaken at a low temperature with aqueous sodium bicarbonate or sodium hydroxide and ether, the organic material immediately passed from the aqueous to the ethereal layer and when the ethereal solution was acidified the salts were regenerated. The alkylated ketonic isoxazole, therefore, forms a pseudo base in the usual manner.

By cautious manipulation of its ethereal solution it was possible to isolate the pseudo base as a colorless crystalline compound. Ozonization of this compound yielded equivalent quantities of benzoic and *p*-chlorobenzoic acids, and a halogen-free substance which has not been identified. This result shows that the rearrangement, as usual in this series, leads to a 5-hydroxy compound, and it leaves but two possible formulas for the pseudo base



III IV

The lack of color in our pseudo base definitely excludes formula III which represents an α-diketone that would be intensely yellow. The