

stated⁷ to require a tyrosine side-chain for activity. We are at present engaged in studying the action on tyrosine of other choline-esterase inhibitors and in attempts to isolate O-phosphorylated tyrosine from the reaction products of suitable choline-esterase inhibitors with chymotrypsin and other sensitive enzymes. Full details of our work will be published elsewhere in due course.

(7) I. W. Sizer, *J. Biol. Chem.*, **160**, 547 (1945).

IMPERIAL COLLEGE OF
SCIENCE AND TECHNOLOGY,
LONDON S. W. 7, ENGLAND

R. F. ASHBOLT
H. N. RYDON

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THE EXCHANGE REACTION BETWEEN COBALTOUS AND COBALDIC IONS IN PERCHLORIC ACID SOLUTION

Sir:

Previous investigators¹ found that under their conditions the rate of electron transfer between cobaltous and cobaltic ions was complete within the time of separation. Since the possibility existed that their results were due to exchange induced by the separation method, we have reinvestigated the exchange using a non-precipitation method.

We find that, at low cobalt concentrations, the rate is measurable. In our experiments, separation of the cobaltous and cobaltic species was effected by adding the exchange mixture to an ammoniacal solution of sodium Versenate,² acidifying the resulting solution with HNO₃, adding NH₄CNS and extracting the cobalt (II) with methylisobutyl ketone. Each fraction was then converted to a cobalt (III) "Versenate" complex for gamma counting and spectrophotometric analysis. Early experiments established that the separation method gave satisfactory activity and material balances (100 ± 5%) when both fractions were examined. In later work, only the specific activity of the Co (III) fraction was measured since this, together with the infinite time specific activity is sufficient to determine the fraction exchange. About 30 or 40% of the Co(III) was reduced to Co(II) during the separation, but a negligible amount of reduction occurred in the exchange mixture before separation. The amount of induced exchange was large (ca. 20%) but fairly reproducible.

Co⁺³ was prepared by electrolysis of a perchloric acid solution of cobaltous perchlorate.

The tracer was Co⁶⁰ obtained from Oak Ridge. Experiments were usually done with cobaltous tracer, but one experiment using cobaltic tracer gave results which were consistent with the other data.

The exchanges reported in Table I were carried out in the dark, although experiments showed that no appreciable effects were caused by light of ordinary laboratory intensity.

An experiment done in a vessel packed with glass beads indicated that catalysis by glass surfaces is negligible.

(1) S. A. Hoshowsky, O. G. Holmes and K. J. McCallum, *Can. J. Research*, **27B**, No. 4, 258 (1949).

(2) The sodium salt of ethylenediaminetetracetic acid, manufactured by Bersworth Chemical Co.

The data for several of our experiments are given in Table I. All runs were made at 0° and in 1 M HClO₄. The reaction obeyed the usual exponential rate law with four or five points on each curve. The constancy of the product of half-time and total cobalt concentration shows the reaction to be second order, presumably first order in each of the two cobalt ions. The average bimolecular rate constant is calculated to be 46 liter-mole⁻¹ min.⁻².

TABLE I
ELECTRON TRANSFER BETWEEN COBALTOUS AND COBALDIC IONS AT 0° AND 1 M HClO₄

Total	Co(molarity × 10 ³) Co ⁺²	Co ⁺³	T _{1/2} (min.) (±0.5 min.)	T _{1/2} × total Co(× 10 ³)
0.717	.124	.593	22.0	1.58
1.33	.14	1.19	11.5	1.53
1.47	10.8	1.59 ^a
2.93	.27	2.66	4.8	1.41
3.03	~1.5	~1.5	4.8	1.45 ^b
				Av. 1.51

^a Glass beads added. ^b Tracer added as Co⁺³.

Experiments are under way to investigate the induced exchange and to study the kinetics of the reaction in detail.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

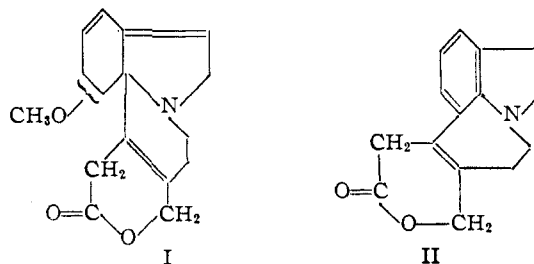
NORMAN A. BONNER
JOHN P. HUNT

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THE STRUCTURES OF β-ERYTHROIDINE AND APO-β-ERYTHROIDINE¹

Sir:

Previously we have suggested partial structures for apo-β-erythroidine and certain other derivatives.^{2,3} Additional evidence, which we are now presenting, makes it possible to assign structures I and II to β-erythroidine and apo-β-erythroidine, respectively.



Apo-β-erythroidine, a dihydroindole derivative, contains a δ-lactone ring, has no terminal methyl group and yields 7-carboxyisatin on oxidation.² These results indicate a tricyclic nucleus having fused five-, six- and seven-membered rings. Hofmann degradation studies have now demonstrated the presence of two —CH₂—CH₂— groups attached to the nitrogen atom, making it necessary to place the lactone ring as shown. The evidence for this is the appearance in the Hofmann degradation products of the characteristic absorption peaks in the infrared associated with the —CH=CH₂

(1) Aided by a grant from the United Cerebral Palsy Association.

(2) M. F. Grundon and V. Boekelheide, *THIS JOURNAL*, in press.

(3) V. Boekelheide and E. Agnello, *ibid.*, **73**, 2286 (1951).