[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

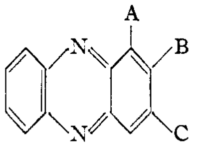
Oxidation–Reduction. II. Catalysis of the Titanous Chloride–Iodine Reaction by Quinones and Phenazines

BY CARL E. JOHNSON, JR.,[1] AND S. WINSTEIN

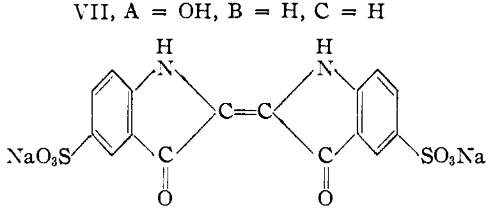
A series of compounds, including quinones, phenazines and quinoxalines, has been surveyed for catalytic effects on the titanous chloride–iodine reaction. A few of these have proven to be effective catalysts at concentrations as low as 10^{-7} *M*. Equations 1, 2 and 5 summarize the three types of rate law required to describe the kinetics of catalysis by different compounds in the series, k_b, k_c and κ_c being constants at any particular acid, iodide ion and catalyst concentration. Even closely related substances may catalyze the reaction with different rate laws.

P. A. Shaffer has reported[2] the catalysis of the titanous chloride–iodine reaction by phenazines, pyocyanine, indigosulfonates, rosindulin, flavins, indophenols and anthraquinone and naphthoquinone sulfonates, but quantitative and kinetic data have not been available. However, the report by B. Gaspar[3] that as little as one part in 100,000 of 2,3-diaminophenazine in a photographic developing solution has a distinct accelerating effect on the destruction of certain azo dyes by colloidal silver deposits, suggests that some of the catalysts enumerated by Shaffer may be effective in very small concentrations. Gaspar[3] lists also 2-hydroxy-3-aminophenazine, quinoxaline and 2,3-diphenylquinoxaline among the most efficient catalysts for the reductive cleavage of azo dyes by silver.

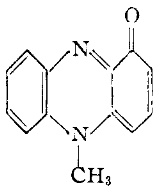
In this paper we present the results of an initial kinetic survey of the catalytic properties of a number of compounds toward the titanous chloride–iodine reaction, discussed in the previous paper.[4] The compounds tested were: 2-hydroxy-3-aminophenazine (I); indigo carmine (II); β-hydroxyphenazine (III); sodium anthraquinone-1,5-disulfonate (IV); pyocyanine (V); sodium anthraquinone-β-sulfonate (VI); α-hydroxyphenazine (VII); 2,3-dimethylquinoxaline (VIII); 2,3-diphenylquinoxaline (IX); *p*-toluenesulfonic acid; *p*-benzoquinone; and hydroquinone.



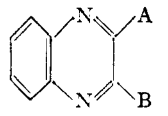
I, A = H, B = OH, C = NH_2
III, A = H, B = OH, C = H
VII, A = OH, B = H, C = H



II



V



VIII, A = B = CH_3
IX, A = B = C_6H_5

Experimental

Materials.—Eastman Kodak Co. white label sodium anthraquinone β-sulfonate (VI) was recrystalllized twice from hot redistilled water and dried in a vacuum over calcium chloride.

Anal. Calcd. for $C_{14}H_7O_5SNa$: C, 54.20; H, 2.26. Found: C, 53.95; H, 2.29.

Stock solutions, 10^{-3} *M*, were prepared by dissolving weighed amounts of the dry salt in redistilled water.

Sodium anthraquinone 1,5-disulfonate (IV) in crude form was obtained through the courtesy of the Organic Chemicals Division of E. I. du Pont de Nemours and Co. It was separated from insoluble impurities by continuous extraction with water, the soluble portion recrystallized twice from hot water, and the crystals dried in vacuum.

Anal. Calcd. for $C_{14}H_6O_8S_2Na$: C, 40.80; H, 1.46. Found: C, 40.84; H, 1.69.

β-Hydroxyphenazine (III), pyocyanine (V) hydrochloride and α-hydroxyphenazine (VII) were obtained through the courtesy of Dr. P. W. Preisler of the Washington University Medical School in the same degree of purity as the samples used in his measurements of oxidation–reduction potentials.[5] Stock solutions were made up by dissolving weighed amounts of the compounds in 0.1 *M* hydrochloric acid.

2-Hydroxy-3-aminophenazine (I) was prepared by the method of Ullmann and Mauthner[6] and recrystallized once from alcohol.

Eastman Kodak Co. white label 2,3-dimethylquinoxaline (VIII) was recrystallized twice from redistilled water; m.p. 105.5–106.3° (reported[7] 106°). Stock solutions, 10^{-3} *M*, were made up by dissolving weighed amounts of the compound in redistilled water.

The 2,3-diphenylquinoxaline IX, prepared by condensation of benzil with *o*-phenylenediamine, was recrystallized twice from alcohol; m.p. 125.5° (reported[8] 126°).

Commercial samples of hydroquinone and benzoquinone were recrystallized twice from redistilled water. Available samples of indigo carmine (II) and *p*-toluenesulfonic acid were used without further purification.

The water, hydrochloric acid, potassium iodide, potassium chloride, titanous chloride and iodine employed were the same as those used in the study of the uncatalyzed reaction between titanous chloride and iodine.[4]

Apparatus and Procedure.—The reaction vessel and all other apparatus used in these experiments were described previously,[4] as was the procedure for carrying out the rate measurements at 25°, with the exception that the catalyst was always placed in the compartment of the reaction flask containing the titanous chloride when the constituents were measured out. The method for analyzing the reacting mixture for triiodide was also the same as that used in the case of the uncatalyzed reaction.

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[2] P. A. Shaffer, *Cold Springs Harbor Symposium Quant. Biol.*, **VII**, 50 (1939).

[3] B. Gaspar, U. S. Patent 2,270,118 (1942).

[4] C. E. Johnson, Jr., and S. Winstein, THIS JOURNAL, **73**, 2601 (1951).

[5] P. W. Preisler and L. H. Hempelmann, *ibid.*, **58**, 2305 (1936); *ibid.*, **59**, 141 (1937).

[6] F. Ullmann and F. Mauthner, *Ber.*, **35**, 4303 (1902).

[7] S. Gabriel and A. Sonn, *ibid.*, **40**, 4850 (1907).

[8] O. Fischer, *ibid.*, **24**, 720 (1891).

TABLE I

COMPARISON OF HALF-TIMES FOR THE REDUCTION OF IODINE

Run no.	(Ti^{III}) 10^5 M	(I_3^-) 10^5 M	Average (H^+) M	Average (I^-) M	Catalyst	(catalyst) M	$t_{1/2}$, min.	$t_{1/2}$, uncat., min.
1[a]	1000	251.5	0.347	0.180	p-HOC_6H_4OH	5.45×10^{-5}	50	50–51
2[a]	1000	251.5	.347	.180	p-HOC_6H_4OH	1.91×10^{-4}	49	50–51
3[b]	1000	251.5	.347	.180	p-HOC_6H_4OH	1.09×10^{-4}	17	50–51
4[c]	1000	251.5	.347	.180	p-OC_6H_4O	1.02×10^{-4}	26	50–51
5	1000	251.5	.347	.180	VI	5.00×10^{-5}	6	50–51
6	1000	251.5	.347	.180	VI	2.50×10^{-5}	11	50–51
7[c]	1007	258.0	.306	.072	p-OC_6H_4O	4.30×10^{-5}	19	28–30
8[d]	1007	258.0	.306	.072	p-OC_6H_4O	8.60×10^{-5}	3	28–30
9	1007	258.0	.306	.072	I	2.50×10^{-6}	0.5	28–30
10	1007	258.0	.306	.072	I	1.00×10^{-7}	9	28–30
11	1007	258.0	.306	.072	VIII	2.34×10^{-6}	24	28–30
12[e]	2130	250.0	.344	.179	p-$CH_3C_6H_4SO_3H$	5.00×10^{-4}	25	28
13	2130	250.0	.344	.179	p-$CH_3C_6H_4SO_3H$	1.00×10^{-1}	27	28
14	1094	244.0	.177	.179	VIII	1.00×10^{-4}	24	29–31
15	1112	244.0	.177	.179	IX	1.00×10^{-5}	27	29–31
16	967	237.0	.325	.098	II	5.00×10^{-7}	4	35
17	1039	245.0	.101	.098	IV	5.00×10^{-6}	4.5	11
18	1031	245.0	.101	.098	III	8.30×10^{-7}	4	11
19	938	246.0	.104	.098	VII	1.44×10^{-5}	5.5	12
20	1035	246.0	.101	.098	V	2.71×10^{-6}	8	11
21	1063	251.5	.101	.098	VI	1.00×10^{-5}	3.5	11

[a] Catalyst solution one day old. [b] Catalyst solution nine weeks old. [c] Catalyst solution freshly prepared. [d] Catalyst solution four days old. [e] In Runs 12 to 21, KCl added to give an ionic strength of 1.025 ± 0.007 M.

Results and Discussion

By plotting the triiodide concentration against time, drawing a smooth curve through the 6 or 7 available points and noting the time coördinate at which the smooth curve crosses the ordinate representing 50% triiodide consumption, the half-times for the reduction of iodine could be determined. In this way the catalytic efficiency of the various substances could be judged. The results are summarized in Table I. The next to the last column in Table I gives the half-times which may be compared with the half-times for the corresponding uncatalyzed reactions shown in the last column.

Half-times.—It may be seen from lines 9 and 10 of Table I that 2-hydroxy-3-aminophenazine (I) was the most efficient catalytic compound tested. It reduces the half-time for reduction of iodine by titanous chloride from 28–30 minutes in the absence of catalyst to 0.5 minute when (I) was present in a concentration of 2.50×10^{-6} M and to 9 minutes when (I) was present in a concentration of 1.00×10^{-7} M.

Line 16 shows that indigo carmine (II) was next in order of decreasing catalytic activity, a 5.00×10^{-7} M concentration of this compound lowering the half-time for reaction by a factor of nine. The third most active catalyst proved to be β-hydroxyphenazine (III), this material cutting the half-time by a factor of approximately three at a concentration of only 8.30×10^{-7} M (line 18).

Sodium anthraquinone 1,5-disulfonate (IV) at a concentration of 5.00×10^{-6} M (line 17) reduces the half-time for reduction to about half the uncatalyzed value. In line 20 it is seen that pyocyanine (V) lowers the half-time by about one-third at a concentration of 2.71×10^{-6} M. The half-time has been reduced by more than two-thirds by sodium anthraquinone β-sulfonate (VI) at a concentration of 1.00×10^{-5} M (line 21), and finally, at a concentration of 1.44×10^{-5} M α-hydroxyphenazine (VII) (line 19) cuts the half-time by a factor of 2. Although the catalytic activities of the last four compounds are nearly equal, it appears that they may be rated in order of decreasing efficiency as they are listed above.

The compounds 2,3-dimethylquinoxaline (VIII) and 2,3-diphenylquinoxaline (IX), 1.00×10^{-4} M and 1.00×10^{-5} M, respectively, (lines 14 and 15) give little or no reduction of half-times. At concentrations of 5.00×10^{-4} M and 1.00×10^{-1} M, p-toluenesulfonic acid (lines 12 and 13), which was tested to rule out any effect of the sulfonic acid or sulfonate ion group, did not reduce half-times appreciably.

With hydroquinone and benzoquinone aging of the catalyst stock solutions was a problem. Stock solutions of hydroquinone not more than one day old showed no appreciable tendency to catalyze the reaction as may be seen in lines 1 and 2 of Table I where no important change in half-times is noted for concentrations of 5.45×10^{-5} M and 1.91×10^{-4} M. Line 3, on the other hand, shows that when hydroquinone from a nine week old 10^{-3} M stock solution was added at a concentration of 1.09×10^{-4} M the half-time for the reduction of iodine was reduced to less than one-half its former value. Aging of the 10^{-3} M stock solution of p-benzoquinone also results in increased catalytic ability. This may be seen by comparing experiments in lines 4 and 7, in which freshly prepared catalyst solution was used, with that shown in line 8, in which the catalyst solution had stood in the laboratory for four days. Line 8 shows a much greater reduction of half-time per concentration unit than does either line 4 or 7. Contrary to our experience with hydroquinone, however, we were not able to prepare a *p*-benzoquinone solution without catalytic activity, even when used soon after preparation. No mechanistic significance should be attached to this fact since the experimental procedure of placing the benzoquinone in the titanous chloride compartment of the reaction flask in the thermostat 15–30 minutes before starting the reaction should automatically give the same results whether one starts with quinone or hydroquinone. One plausible explanation for the phenomenon is that the quinone reacts in aqueous solution to give catalytic products faster than does the hydroquinone and that we did not succeed in using a solution in which this reaction had not already set in.

Summarizing, it may be observed that those substances which show catalytic action, compounds I through VII, may be rated roughly in decreasing order of efficiency on a molar basis by means of their Roman numerical designations, compound I being effective at concentrations of the order of 10^{-7} *M* and compound VII at concentrations of the order of 10^{-5} *M*. It is interesting to contrast the inactivity of diphenylquinoxaline (IX) with the strong catalytic activity of, in some ways, similar compounds such as β-hydroxyphenazine (III), but any discussion of this must await the demonstration of the mechanism or mechanisms of the catalyzed reactions.

Rate Laws.—For some of the catalyzed reactions the rate law was scrutinized starting with values of the slope, $-d(I_3^-)/dt$, of the plots of (I_3^-) *vs.* time, determined at a number of points with the aid of a tangent meter. The same assumptions were made, as in the study of the uncatalyzed reaction,[4] concerning the constancy of (H^+) and (I^-), the approximation that (I_3^-) is equal to total iodine, and the predominance of Ti^{III} and Ti^{IV} as Ti^{+++} and TiO^{++}, respectively.

Considering the possible rate laws for the catalyzed reactions, the quinone type of catalysis could be due, as pointed out previously,[4] simply to the incursion of reaction steps faster than the uncatalyzed one, each one involving one of the catalyst species and the reducing or oxidizing agent. Even on this basis the rate law could be complex. The simplest cases which may be visualized are those which have as the rate-determining step of the alternate oxidation and reduction of the catalyst, either reduction of the totally oxidized form of the catalyst or oxidation of the totally reduced form.

In case the reduction is the slower, and thus rate-determining, the rate law in equation 1 would apply, κ_c being proportional to the first power

$$-d(I_3^-)/dt = \kappa_c(Ti^{III}) \qquad (1)$$

of the catalyst concentration. If the oxidation is rate-determining the rate law takes the form of equation 2, k_b being proportional to the first power

$$-d(I_3^-)/dt = k_b(I_3^-) \qquad (2)$$

of the catalyst concentration. These rate-laws were obeyed by the catalyzed reactions in the case of some of the catalysts.

One kind of kinetic behavior was observed with pyocyanine (V) and α-hydroxyphenazine (VII) as catalysts. Plots of $[-d(I_3^-)/dt]/(Ti^{III})$ *vs.* triiodide gave straight lines with positive slope and intercept. The slope and intercept may be corrected to represent only the catalysis by subtracting from them slope and intercept values due to the corresponding uncatalyzed reaction, calculated from equations 3 and 4 where k is the uncatalyzed slope and κ the uncatalyzed intercept.[4] These corrections disclose that the catalyzed reaction contributes a large increase

$$k = 0.0545/(H^+)(I^-) + 0.0640/(H^+) \qquad (3)$$

$$\kappa = 8.95 \times 10^{-5}/(H^+) \qquad (4)$$

in intercept but no increase in slope. Thus the rate of the catalyzed reactions with pyocyanine and α-hydroxyphenazine is independent of iodine concentration and obeys the rate law of equation 1, the corrected intercept being equal to κ_c. One κ_c value for catalysis by V and several for catalysis by VII at different values of (H^+) are listed in Table II. In the case of α-hydroxyphenazine (VII) the approximate proportionality of κ_c to the first power of the catalyst concentration may be seen by comparing Run 21 with 22 and 23 with 24 in Table II.

TABLE II

SUMMARY OF RATE CONSTANTS FOR SEVERAL CATALYSTS

(I^-) 0.098 *M* for all runs except 0.342 *M* in Run 6 and 0.505 *M* in Run 20. (I_3^-) 0.0025 *M* for all runs. Equivalent or 100% excess (Ti^{III}). Rate constants listed for runs marked with an asterisk represent the average of two or more determinations.

Run no.	Catalyst	10^6 (catalyst)	Average (H^+)	k_c, mole^{-1} liter min.$^{-1}$	$10^3\ \kappa_c$, min.$^{-1}$
1*	VI	10.00	0.101	7.66	12.57
2*	VI	10.00	.177	7.77	5.21
3	VI	25.00	.177	17.81	12.79
4*	VI	10.00	.329	3.10	1.69
5*	VI	25.00	.329	7.95	4.31
6	VI	50.00	.319	6.81	8.82
7*	VI	25.00	.633	2.65	2.61
8*	IV	5.00	.101	8.08	2.55
9*	IV	5.00	.117	4.60	2.75
10	IV	5.00	.177	2.50	2.00
11	IV	10.00	.329	2.68	2.00
12	IV	25.00	.481	3.50	4.80
13	IV	25.00	.633	3.40	2.90
14	III	0.83	.101	6.30	8.9
15	III	0.83	.177	6.30	7.3
16	III	1.66	.329	8.50	8.3
17	III	3.32	.329	17.60	13.0
18	III	1.66	.633	4.70	6.5
19	VII	14.37	.104	...	17.3
20	VII	14.37	.104	...	18.0
21	VII	6.83	.155	...	7.1
22	VII	14.37	.155	...	14.8
23	VII	17.10	.641	...	7.4
24	VII	34.20	.641	...	15.1
25	V	2.71	.101	...	4.0

Another type of kinetic behavior was observed in catalysis by indigo carmine II. When $-d(I_3^-)/dt$, from which had been subtracted a small correction for uncatalyzed reaction rate under the same conditions, was plotted as ordinate *vs.* (I_3^-) a line through the origin resulted. The dependence of the rate of the catalyzed reaction on the first power of the triiodide concentration indicates that catalysis here obeys the rate law of equation 2, the slope of the line through the origin, equal to k_b of equation 2, being 0.137 min.$^{-1}$.

In addition to the two simple rate laws of equations 1 and 2 which were found to apply in the cases just discussed, still a third type was found necessary to describe catalysis of the reaction by β-hydroxyphenazine (III), sodium anthraquinone 1,5-disulfonate (IV) and sodium anthraquinone β-sulfonate (VI). For these substances as catalysts plots of $[-d(I_3^-)/dt]/(Ti^{III})$ *vs.* triiodide concentration gave straight lines having both larger slopes and larger intercepts than those corresponding to the uncatalyzed reactions. After correction for concurrent uncatalyzed reaction, the rate law in this case can be expressed by equation 5

$$-d(I_3^-)/dt = k_c(Ti^{III})(I_3^-) + \kappa_c(Ti^{III}) \qquad (5)$$

k_c being the corrected slope and κ_c the corrected intercept of the lines. Values of k_c and κ_c (equation 5) from the data for the three compounds III, IV and VI, are given in Table II. While the data are fragmentary, they do give some indication of the dependence of the constants on catalyst concentration. Thus for β-hydroxyphenazine (III), k_c is proportional to catalyst concentration while κ_c which is less reliable is roughly so. This is true also in the case of sodium anthraquinone β-sulfonate. With sodium anthraquinone 1,5-disulfonate IV, no runs at the same (H^+) with different concentrations of catalyst are available, so the dependence of rate constants on catalyst concentration is not clearly visible without a more adequate treatment of the dependence of rate on (H^+). However, it is clear that both k_c and κ_c rise with catalyst concentration.

Even the short survey here reported shows how differently may various catalysts of the quinone–phenazine class behave in the titanous chloride–iodine reaction. Thus we have the rate law 2 for indigo carmine II. For pyocyanine V and α-hydroxyphenazine VII, we have the rate law 1, as though reduction of the catalyst is rate-determining. Making the structural change from α-hydroxyphenazine (VII) to β-hydroxyphenazine (III) gives the rate law 5 which is also followed by the anthraquinone derivatives IV and VI. The rate law 5 corresponds to two terms in the rate, one the same as for rate law 1, the other an additional term proportional to both titanous ion and iodine. The latter third order term is especially interesting since it corresponds to a rate-determining transaction involving the reducing agent, titanous ion, the catalyst and the oxidizing agent, iodine.

The dependence of rate on hydrogen ion concentration can be involved, as is illustrated by the data in Table II. For example, while k_c for VI does not increase when (H^+) is decreased from 0.177 to 0.101 *M*, for IV it increases rapidly.

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LOS ANGELES, CALIF. RECEIVED JULY 13, 1951

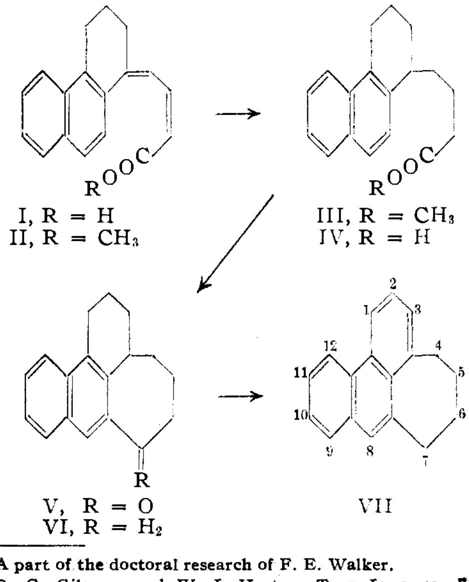
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Seven-membered Ring Compounds. III. 4,5,6,7-Tetrahydrocyclohepta[jk]phenanthrene

BY W. J. HORTON AND F. E. WALKER[1]

The structure of 4,5,6,7-tetrahydrocyclohepta[jk]phenanthrene has been established by two independent syntheses. The synthesis of 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VIII) from benzosuberone has been improved and it has been shown that VIII is attacked in position 2 or 3 by succinic anhydride.

In a previous investigation[2] the peri-cyclization of γ-tetrylbutyric acid was brought about in excellent yield by the use of phosphorus pentoxide in orthophosphoric acid. In a similar manner, from 1-keto-1,2,3,4-tetrahydrophenanthrene and methyl γ-bromocrotonate, γ-1-(1,2,3,4-tetrahydrophenanthryl)-butyric acid (IV) has been prepared in four steps and submitted to cyclization. This acid (IV) has been made previously[3a,b] as an intermediate in the synthesis of chrysenes and the process used here is that of Cook.[4] There appear to be no attempts to cyclize this acid using the conventional methods.



I, R = H
II, R = CH_3

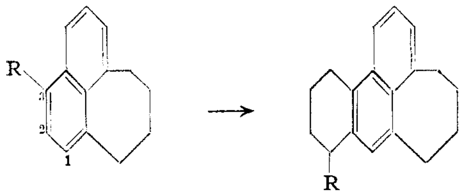
III, R = CH_3
IV, R = H

V, R = O
VI, R = H_2

VII

The phosphorus pentoxide–phosphoric acid procedure converted the acid IV to a viscous oil V which could not be crystallized. The oil, however, formed a crystalline semicarbazone in excellent yield. Decomposition of the semicarbazone (Wolff–Kishner) gave the hydrocarbon VI and dehydrogenation of VI over palladium–charcoal produced VII which crystallized with ease and formed a picrate.

By analogy with acenaphthene and α-methylnaphthalene, it might be predicted that 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VIII) would be attacked at position 3 by electrophilic reagents. The following series of reactions conclusively demonstrate that the point of attack is position 3 or 2 and position 3 is thought to be the more likely. The hydrocarbon VIII gave an aroylpropionic acid (IX) when treated with succinic anhydride and aluminum chloride in nitrobenzene. The keto acid IX was reduced to the arylbutyric acid X. Cyclization of the acid chloride of X by means of stannic chloride gave a ketone XI. The non-cyclization of X to the alternate position 4 is of interest since the difficulties of such a second peri-cyclization have been noted[5] in the case of the formation of a second five-membered ring. The ketone XI was reduced to the carbinol XII by



VIII, R = H
IX, R = $CO(CH_2)_2COOH$
X, R = $(CH_2)_3COOH$

XI, R = O
XII, R = OH

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[1] A part of the doctoral research of F. E. Walker.

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