CLEAVAGE BY HALOGENS OF CARBON—COBALT BONDS IN ORGANOMETALLIC COMPLEXES OF COBALT(III)

III *. KINETICS AND MECHANISM OF THE REACTIONS OF ORGANOBIS(DIMETHYLGLYOXIMATO)COBALT(III) COMPLEXES WITH IODINE IN CHLOROFORM

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Summary

The kinetics of the reaction between organocobaloximes, $RCo(DH)_2H_2O$, and iodine have been investigated. They reveal the participation of an $RCo(DH)_2H_2O \cdot I_2$ intermediate which undergoes intramolecular transalkylation and acts as an electrophile towards a second organocobaloxime molecule. The trend in reactivity as the R group is varied is discussed.

Introduction

The kinetics of carbon—cobalt bond cleavages [1—16] by electrophilic metal ions have been widely studied, but for the corresponding reactions with halogens only the stereochemistry and product analyses are reported [17—24]. We now describe the results of kinetic investigations of the reactions between organo-bis(dimethylglyoximato)Cobalt(III) complexes and iodine in chloroform. It has been previously shown that these complexes react with ICl by electrophilic cleavage, without participation of radicals [22]. We used iodine instead of ICl as the electrophile because of its greater stability in chloroform. We assume that the mechanism of the reaction does not change; an oxidative dealkylation can be excluded, in view of the weaker oxidizing powder of iodine [25], and no evidence for a radical process has been found.
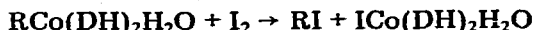
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* For Part II see ref. 22.

Results

Products identification and stoichiometry

The reactions examined, in chloroform at 25°C, were

$$RCo(DH)_2H_2O + I_2 \rightarrow RI + ICo(DH)_2H_2O$$

(R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, CH_2Cl, $C_6H_5CH_2$, C_6H_5)

The iodocobaloxime was isolated and identified by elemental analysis and the organic halides were identified by GLC and NMR spectra. The stoichiometry was confirmed for an excess of either organocobaloxime or iodine; the amount of organic halide was quantitatively determined by GLC; the excess of iodine tritated with $Na_2S_2O_3$ and, in both cases, the 1 : 1 consumption of reactants was confirmed for all complexes *.

Kinetic determinations

The reactions cannot be conveniently followed spectrophotometrically owing to the strong absorption of both reagents over the whole accessible UV-visible region. Therefore the reaction was followed by titration (with $Na_2S_2O_3$) of remaining iodine in solutions containing an excess of the complex. Obviously the kinetics in presence of excess of iodine cannot be studied in this manner.

The measurements were carried out in chloroform containing 0.5% ethanol at 25°C (at 40°C for the phenyl derivative). First order behavior was observed over a large extent of reaction for all the complexes, except for the methyl derivative, for which some acceleration occurs after one-half life. This could be attributed to a catalysis by reaction products; the addition of $ICo(DH)_2H_2O$ to the solution enhances this behavior and increases the overall reaction rate.

For CH_3- and $C_6H_5CH_2$-$Co(DH)_2H_2O$ the pseudo first-order constants, k_{obsd}, show a linear dependence on [RCo] (Fig. 1) and the data are in agreement with the rate expression:

$$-\frac{d[I_2]}{dt} = k_2[RCo][I_2]$$

The k_2 values are reported in Table 1. For C_2H_5-, n-C_3H_7-, i-C_3H_7-, C_6H_5-$Co(DH)_2$-H_2O, the plot of k_{obsd} vs. [RCo] is more complicated, as shown in Fig. 2 for R = C_2H_5. At low concentrations it is linear, but a positive deviation becomes evident as the concentration is increased. In this range a good fit is obtained by plotting k_{obsd} vs. $[RCo]^2$. The rate expression in the whole range of concentrations is:

$$-\frac{d[I_2]}{dt} = k_2[RCo][I_2] + k_3[RCo]^2[I_2]$$

The k_{obsd} expression is:

$$k_{obsd} = k_2[RCo] + k_3[RCo]^2$$

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* When R = CH_2Cl and the reaction is carried out in presence of excess iodine a second mole of halogen is consumed. It is probable that in this case the organic halide formed reacts with iodine: $CH_2ClI + I_2 \rightarrow CHClI_2 + HI$.
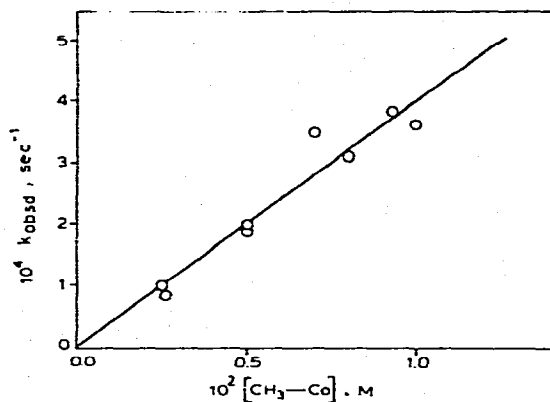
Fig. 1. Plot of the pseudo first-order rate constants vs. [CH₃Co] for the reaction of $CH_3Co(DH)_2H_2O$ with I_2.
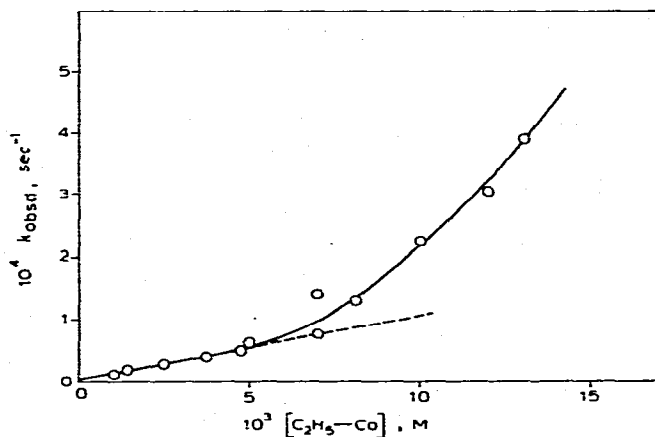
Fig. 2. Plot of the pseudo first-order rate constants vs. [C₂H₅Co] for the reaction of $C_2H_5Co(DH)_2H_2O$ with I_2.

TABLE 1

RATE CONSTANTS FOR THE REACTION BETWEEN $RCo(DH)_2H_2O$ AND I_2 [a]

R	$10^3 k_2$ (mol^{-1} s^{-1})	k_3 (mol^{-2} s^{-1})	n	10^4 [I₂] mol	10^3 [RCo] mol
C₇H₇	(86.58 ± 8.3)		10	2.5—5	1—8
CH₃	(19.93 ± 0.82)		8	5—10	2.5—10
i-C₃H₇	(11.2 ± 1.5)	2.44 ± 0.18	9	1.25—5	0.5—15
C₂H₅	(7.43 ± 1.88)	1.45 ± 0.26	12	1.25—5	1.0—13
CH₂Cl [b]	(5.65 ± 1.47)		8	2—5	1.2—9.3
n-C₃H₇	(0.69 ± 0.72)	2.17 ± 0.19	6	5	2.5—12
C₆H₅	(0.22 ± 1.07)	1.71 ± 0.17	7	5	2.7—9

[a] Temperature 25.0 ± 0.1°C, except for R = C₆H₅ (40 ± 0.1°C), solvent chloroform; data obtained by least squares regressions, errors are standard deviations, n is number of sets of observations. [b] The pre-equilibrium constant K for R = CH₂Cl is 122 ± 50 mol^{-1}.
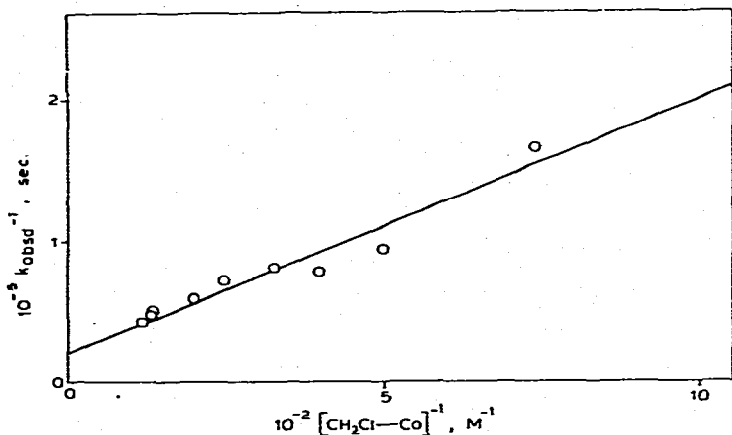
Fig. 3. Plot 6f the reciprocal of the pseudo first-order k_{obsd} vs. $[CH_2ClCo]^{-1}$ for the reaction of CH_2ClCo-$(DH)_2H_2O$.

The k_2 and k_3 values are obtained as intercept and slope of the plot of $k_{obsd}/[RCo]$ vs. $[RCo]$ (Table 1). For $CH_2ClCo(DH)_2H_2O$, the graph of k_{obsd} against $[RCo]$ curves from linearity at high concentrations of the latter, while a strictly linear relationship is obtained between the reciprocals of these quantities (Fig. 3). Thus:

$$k_{obsd} = \frac{k_2[RCo]}{1 + K[RCo]}$$

where K is the pre-equilibrium constant of a reaction leading to the formation of a 1 : 1 complex between $CH_2ClCo(DH)_2H_2O$ and iodine:

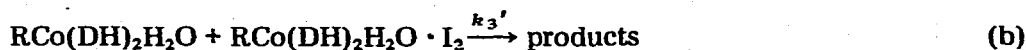$$CH_2ClCo(DH)_2H_2O + I_2 \overset{K}{\rightleftharpoons} CH_2ClCo(DH)_2H_2O \cdot I_2$$
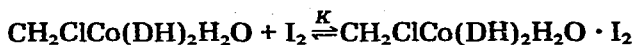
and k_2 is the usual second-order rate constant (Table 1).

Discussion

For R = C_2H_5-, i-C_3H_7-, n-C_3H_7- and C_6H_5-$Co(DH)_2H_2O$ the rate dependence on $[RCo]^2$ at high $[RCo]$ suggests a two stages mechanism, involving the pre-equilibrium:

$$RCo(DH)_2H_2O + I_2 \overset{K}{\rightleftharpoons} RCo(DH)_2H_2O \cdot I_2 \qquad\qquad (a)$$
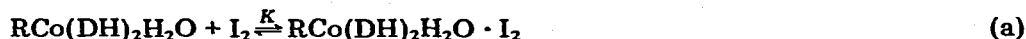
preceding a bimolecular rate determining step:

$$RCo(DH)_2H_2O + RCo(DH)_2H_2O \cdot I_2 \overset{k_3'}{\longrightarrow} products \qquad\qquad (b)$$

where the complex $RCo(DH)_2H_2O \cdot I_2$ (I) acts as an electrophile. On this assumption, k_{obsd} is:

$$k_{obsd} = \frac{k_3' K[RCo]^2}{1 + K[RCo]} \quad \text{(with } k_3 = k_3' K\text{).}$$

As at high concentrations k_{obsd} is linear in $[RCo]^2$, i.e. $k_{obsd} = k_3[RCo]^2$, it must follow $K[RCo] < 1$.

Another mechanism is also consistent with a 1 : 1 stoichiometry and a linear dependence of k_{obsd} on $[RCo]^2$, viz.:

$$2\ RCo(DH)_2H_2O \rightleftharpoons [RCo(DH)_2H_2O]_2$$

$$[RCo(DH)_2H_2O]_2 + I_2 \rightarrow products$$
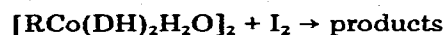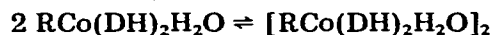
in which the formation of a dimeric compound is involved. This alternative seems less probable because no evidence has been found for the existence of such a compound in chloroform in the range of the concentrations examined. Infact no deviation from the Lambert—Beer law was observed, at least for $[RCo] \leqslant 5 \times 10^{-3}$ mol and a determination of molecular weight indicates that n-$C_3H_7Co(DH)_2H_2O$ is monomeric in solution at $[RCo] = 1.35 \times 10^{-2}$ mol. On the contrary, complexes of the type $RCo(chel) \cdot I_2$ have been isolated in chloroform and toluene for chel = salen, acacen (see experimental) *. Thus, the presence of the third-order term in the rate expression for R = C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_5, can probably be ascribed to formation of complex I.

For R = CH_2Cl, the presence of an analogous complex accounts for the form of the k_{obsd} expression of the second-order term. For R = CH_3 the existence of the complex I cannot be deduced from plots of k_{obsd} vs. $[RCo]$ or $[RCo]^2$, but the formation of a 1 : 1 adduct between substrate and halogen was proved by a series of experiments performed with comparable concentrations of the reagents.

The second-order constants, $k_{1:1}$, were obtained from the slope of the plot of $1/[I_2]_{total}$ vs. t [26], where $[I_2]_{total} = [I_2]_{free} + [RCo(DH)_2H_2O \cdot I_2]$. For all complexes, except for the methyl derivative, the constants do not vary when the initial concentrations are varied, and are equal to the k_2 values obtained under pseudofirst-order conditions.

For $CH_3Co(DH)_2H_2O$ the $k_{1:1}$ values are always smaller than the k_2 values, but increase as the initial concentrations are lowered (Fig. 4). This behaviour can be explained if the complex I is formed in solution, so that:

$$k_{1:1} = \frac{k_2}{(1 + K[I_2]_{free})^2}$$

As the initial concentrations of reactants are raised, $[I_2]_{free}$ also increases and $K[I_2]_{free}$ is not negligible compared with unity **. In the same range of concentrations, $k_{1:1}$ for the ethyl derivative is always equal to k_2, so that for this compound the product $K[I_2]_{free}$ must be <1.

From the above results it can be concluded that $K_{Me} > K_{Et}$. Since K for $CH_2ClCo(DH)_2H_2O$ is greater than for those of all the other complexes, the full sequence is $K_{CH_2Cl} > K_{Me} > K_{Et}$.

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* Salen = N,N'-ethylenebis(salicylideneiminato); acacen = N,N'-ethylenebis(acetylacetoneiminato).

** It should be noted that since in every run $[I_2]_{free}$ decreases with time, the plot of $1/[I_2]_{total}$ vs. t, should show a poisitive deviation when the product $K[I_2]_{free}$ in the denominator of $k_{1:1}$ decreases. In our experiments the deviation was not evident, because the very slow reaction was followed over only a small extent.
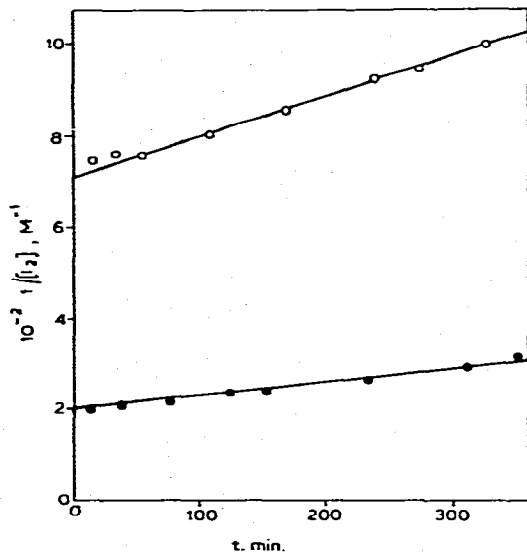
Fig. 4. Second-order plot for the reaction of $CH_3Co(DH)_2H_2O$ and I_2 with equal initial concentrations. ○ 1.2×10^{-3}, ○ 5.0×10^{-3} mol.

Since CH_3 and Cl have almost identical bulk [27] but opposite electronic effects, the decrease of K from R = CH_2Cl to R = C_2H_5 must be attributed to the greater $+I$ effect of the R group rather than to steric effects.
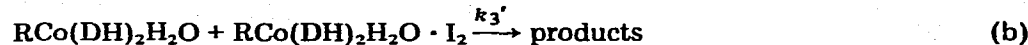
The existence of a pre-equilibrium having been demonstrated for all the complexes, the second-order term can be ascribed to intramolecular transalkylation of the intermediate:

$$RCo(DH)_2H_2O \cdot I_2 \xrightarrow{k_2'} \text{products} \tag{c}$$

or to direct reaction between substrate and iodine:

$$RCo(DH)_2H_2O + I_2 \xrightarrow{k_2''} \text{products} \tag{d}$$

Both hypotheses lead to a formally analogous expression for the second-order term. Consequently, at least two mechanisms are consistent with the kinetic data for all the complexes over the whole range of concentrations. The first mechanism is the sum of the steps a, b and c:

$$RCo(DH)_2H_2O + I_2 \underset{}{\overset{K}{\rightleftharpoons}} RCo(DH)_2H_2O \cdot I_2 \tag{a}$$

$$RCo(DH)_2H_2O + RCo(DH)_2H_2O \cdot I_2 \xrightarrow{k_3'} \text{products} \tag{b}$$

$$RCo(DH)_2H_2O \cdot I_2 \xrightarrow{k_2'} \text{products} \tag{c}$$
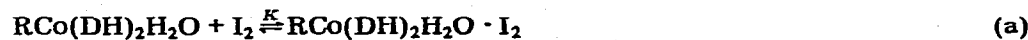
the other is the sum of the steps a, b and d:

$$RCo(DH)_2H_2O + I_2 \underset{}{\overset{K}{\rightleftharpoons}} RCo(DH)_2H_2O \cdot I_2 \tag{a}$$

$$RCo(DH)_2H_2O + RCo(DH)_2H_2O \cdot I_2 \xrightarrow{k_3'} \text{products} \qquad \text{(b)}$$

$$RCo(DH)_2H_2O + I_2 \xrightarrow{k_2''} \text{products} \qquad \text{(d)}$$
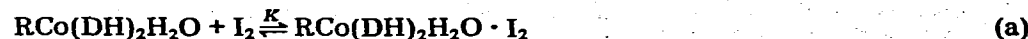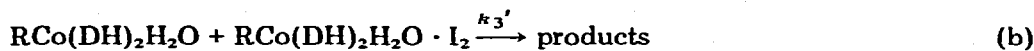
The expressions of k_{obsd} are respectively:

$$k_{obsd} = \frac{k'_2 K[RCo]}{1 + K[RCo]} + \frac{k'_3 K[RCo]^2}{1 + K[RCo]} \ (k_2 = k'_2 K)$$

and

$$k_{obsd} = \frac{k''_2 [RCo]}{1 + K[RCo]} + \frac{k'_3 K[RCo]^2}{1 + K[RCo]} \ (k_2 = k''_2).$$

The second-order term predominates for R = CH$_3$, CH$_2$Cl, C$_6$H$_5$CH$_2$ at all concentrations, and for R = C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, C$_6$H$_5$ at lower concentrations; the third-order term predominates only for the latter group of complexes at higher concentrations. Except for the chloromethyl derivative the product $K[RCo]$ is always <1.

Two considerations lead us to favour the first scheme.
1) In scheme a b c, the ratio $v_2/v_3 = k'_2/k'_3[RCo]$ is independent of the value of the pre-equilibrium constant K; in scheme a b d, the ratio $v_2/v_3 = k''_2/k''_3 K[RCo]$ depends on K and the third-order term becomes more important compared with the second order term as K become greater. Since the complexes giving the largest K values, viz. CH$_2$Cl and CH$_3$-Co(DH)$_2$H$_2$O, do not exhibit the third-order term in the range of concentrations used, the ratio v_2/v_3 appears to be independent of K, in accord with scheme (a) (b) (c).
2) The k_2 values are about equal for C$_2$H$_5$- and CH$_2$Cl-Co(DH)$_2$H$_2$O. At first sight this seems anomalous, because the bulk of the two R groups is very similar, but the charge density on the α carbon, and therefore its susceptibility to electrophilic attack, is much greater for the ethyl derivative than for the chloromethyl derivative, in which an electro-donating CH$_3$ is replaced by an electron-withdrawing Cl. This behaviour can be explained by assuming that k_2 consists of the products $k'_2 K$, in accord with the scheme (a) (b) (c). The relatively large value of k_2 for R = CH$_2$Cl is then due to the contribution of K, which is unusually high for this complex.

A common feature of these electrophilic substitutions appears to be the intermediate formation of a 1 : 1 adduct between the organocobaloxime and iodine. This is not surprising since 1 : 1 adducts of the type CH$_3$Co(chel) $\cdot$ I$_2$ (Chel = salen, acacen) have been isolated, and intermediates of the type RCo-(Chel)H$_2$O $\cdot$ Hg^{2+} (Chel = salen, (DO)(DOH)pn * have been detected from the kinetics of the transalkylation reactions [3].

As far as the second-order rate constants is concerned the sequence:

$$C_6H_5CH_2 > CH_3 > i\text{-}C_3H_7 > C_2H_5 > CH_2Cl > n\text{-}C_3H_7 \qquad (1)$$
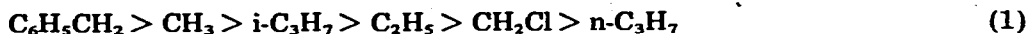
differs from that obtained for the reactions of electrophilic substitutions with

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* (DO)(DOH)pn = 1-diacetylmonoximeimino-3-diacetylmonoximatoiminopropane.

Hg^{2+} e Tl^{3+} [5,9]:

$$CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_3H_7 > CH_2Cl \qquad (2)$$

Actually the rate sequence for the n-alkyl derivatives is the same if one excludes the chloromethyl derivative, for which the large value of k_2 has been attributed to the contribution of K (see above). It is commonly accepted that sequence 2 is determined by steric effects and the inertness of the i-propyl derivative is due to its steric hindrance. On the other hand, in our case the k_2 constants only slightly vary with the bulk of group R, and the reaction of $i\text{-}C_3H_7Co(DH)_2H_2O$ is relatively fast. Therefore the electrophilic substitution reactions with halogens seem less sterically dependent than the corresponding reactions with metal ions. It is possible that the steric and electronic effects are counterbalanced.

In reactions of Br_2 with organochromium complexes a similarly weaker effect of the R group on the rate, compared to those with Hg^{2+}, was noted by Espenson [28], and was attributed to the different extent of solvation of the electrophiles. In our case such an argument cannot easily be used because the reactions with Hg^{2+} were performed in water [5] and those with halogens in chloroform. In order to determine the solvent effect in the reactions with iodine, further studies in oxygenated polar solvents are in progress.

An analogous analysis could be made for the third-order rate constants, k_3. However the data are now more difficult to interpret because the substrate and the electrophile i.e. complex I, vary simultaneously.

Experimental

Materials

The organocobaloximes were prepared as previously reported [22]. The reagent used as iodine bisublimate (C. Erba) and the solvent chloroform (C. Erba reagent grade), containing 0.5% of C_2H_5OH (content checked by GLC).

Products

The iodocobaloximes were isolated and identified by elemental analysis. We report, was an example, the analysis of the product from $CH_3Co(DH)_2H_2O$ and I_2. (Found: C, 22.7; H, 3.76; N, 12.7. $C_8H_{16}N_4O_5CoI$ calcd.: C, 22.13; H, 3.71; N, 12.9%.)

The organic halides were identified by GLC and NMR spectra. Chromatographic analyses were carried out with 2 m column of carbowax with a C. Erba Model G.T. Gaschromatograph. NMR spectra were recorded on a JEOL C60 HL spectrometer. The UV-visible spectra were recorded by a Perkin–Elmer 356 spectrophotometer.

Preparation of $CH_3Co(chel)I_2$ (chel = salen, acacen)

To 1 mmol of $CH_3Co(Chel)$ suspended in chloroform or toluene, about 5 ml of a solution 0.2 M of iodine in the some solvent were added. After few minutes the precipitate was filtered off, washed with the same solvent, and dried. (Found: C, 34.3; H, 2.4; N, 4.51. $C_{17}H_{18}O_2N_2CoI_2$ calcd.: C, 34.3; H, 2.94; N, 4.71%.) (Found: C, 27.1; H, 3.6; N, 5.01. $C_{13}H_{21}O_2N_2CoI_2$ calcd.: C, 28.3; H, 3.8; N, 5.11%.)

Kinetic determinations

The iodine concentrations was determined by titration with a potentiograph Metrohm E 336 equipped with a combined electrode Pt, Ag/AgCl. Samples of 10 ml of the solution were removed periodically and transferred to a titration cell, cooled in ice and flushed with nitrogen. About 10 ml of an aqueous solution of 10% NaI and 1 ml of concentrated CH_3COOH were added and the solution diluted to 60 ml with C_2H_5OH and titrated against 5×10^{-1} N $Na_2S_2O_3$.

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