[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Kinetics of 1,10-Phenanthroline Chelation. IV. Hydroxide, Cyanide, Azide and Ethylenediaminetetraacetate Ions with Tris-(1,10-phenanthroline)-nickel(II)

BY L. P. MORGENTHALER[1] AND D. W. MARGERUM[2]

RECEIVED MAY 20, 1961

Cyanide and azide ions were found to have no effect on the dissociation rate of the tris-(1,10-phenanthroline)-nickel(II) complex while hydroxide ion caused only a slight increase in the rate. The stability and dissociation kinetics of the complex $NiPh_2(OH)_2$ were studied. Both this complex and $NiPh_2(CN)_2 \cdot 2H_2O$ dissociate more rapidly than $NiPh_2(H_2O)_2$. Mixed complexes of Ni(II), Ph and EDTA were found and characterized in solution.

Introduction

It has been shown that hydroxide, cyanide and azide ions accelerate the dissociation rate of $FePh_3^{+2}$.[3,4] Previous workers have found that the rate of racemization of $NiPh_3^{+2}$ is slightly accelerated in basic solution[5,6] and that the racemization rate of $NiPh_3^{+2}$ is equal to its dissociation rate.[6] The present work has examined the dissociation rate of $NiPh_3^{+2}$ in the presence of hydroxide, cyanide, azide and ethylenediaminetetraacetate ions to see if the nickel complexes exhibit an enhancement in rate as do the iron(II) complexes. No enhancement was found. Several important mixed ligand complexes found during the kinetic investigations are reported.

Experimental

The apparatus used has been described.[4] Optical measurements were made on a Schmidt and Haensch polarimeter to ±0.01° with a 2 decimeter polarimeter tube. Racemic $NiPh_3Cl_2$ was prepared by the method of Pfeiffer and Tappermann.[7] The optical isomers were resolved as the iodide and perchlorate salts.[8] Racemization experiments were performed by adding the solid isomer to the solution containing the other components and dissolving it by rapid shaking. The concentration of salt was 1 to 3 mg. per ml., which gave initial rotations from 3 to 8°. The α_D for $NiPh_3I_2$ is about 1420°.

Diaquobis-(1,10-phenanthroline)-nickel(II) chloride was prepared by a modified procedure of Pfeiffer and Tappermann using 1:1 ethanol–water and concentrating under reduced pressure. The product was a light blue solid which became light green when dried over $Mg(ClO_4)_2$. When $NiPh_2(H_2O)_2Cl_2$ is dissolved in water the solution becomes violet.

Anal. Calcd. for $[NiPh_2(H_2O)_2]Cl_2$: C, 54.79; H, 3.83; N, 10.65. Found: C, 54.80; H, 4.00; N, 10.69.

Preparation of $[NiPh_2(CN)_2] \cdot 2H_2O$: A 1.0 *M* NaCN solution was added dropwise to 30 ml. of 0.053 *M* $NiCl_2$ until all of the precipitate had dissolved. Then 0.3 g. of 1,10-phenanthroline monohydrate dissolved in 170 ml. of water was added to the nickel solution. After standing 48 hr. the pink crystals were filtered and thoroughly washed with water. The solid was dried over $Mg(ClO_4)_2$. The compound is insoluble in water and only slightly soluble in methanol and ethanol. It is soluble in aqueous NaCN solutions, but the product is $Ni(CN)_4^{-2}$.

Anal. Calcd. for $[NiPh_2(CN)_2] \cdot 2H_2O$: C, 61.57; H, 3.98; N, 16.57. Found: C, 61.58; H, 4.03; N, 16.04.

Disodium dihydrogen ethylenediaminetetraacetate $[Na_2H_2Y]$ solutions were standardized potentiometrically with NaOH and with standard Mg^{+2} or Zn^{+2} solutions at *p*H 10 to a visual Eriochrome black-T end-point.[9] Analysis of Y^{-4} in the presence of Ni^{+2} and 1,10-phenanthroline was checked by an alternate titration with standard Zn^{+2} or Mg^{+2} at *p*H 10 to the potentiometric end-point as detected by a Sargent–Malmstadt titrator, using an amalgamated gold ring as indicator electrode and a carbon rod as reference electrode. HgY^{-2} was added to supply an indicator reaction.[10,11] Analysis for Y^{-4} also was performed in 0.4 *M* NaOH by measurement of the potential assumed by an amalgamated gold wire in the presence of HgY^{-2}. This potential was then compared to the potentials obtained from a series of standards.

Solutions were analyzed for 1,10-phenanthroline by extraction into dichloromethane from which it then was removed with 1 *M* sulfuric acid. The acid solution was neutralized and the 1,10-phenanthroline reacted with iron(II) at *p*H 5 to form the bright red complex $FePh_3^{+2}$, which was determined spectrophotometrically.[12,13] The dichloromethane extraction was carried out for 45 sec. followed by a five second rinse. The total extraction time was never over 2 min.

The quantity of 1,10-phenanthroline in solution also was measured spectrophotometrically at 343 and 335 mμ where the molar absorptivities of the 1,10-phenanthroline bonded to Ni^{+2} are 401 and 413, respectively, and for unbonded 1,10-phenanthroline the molar absorptivities are 47.8 and 145, respectively.

It was not possible to control ionic strength for many of the reactions as in 1 *M* salt solutions concentrations of $NiPh_3^{+2}$ greater than 1×10^{-4} *M* cause precipitation of the salt of the complex. The ionic strength could not be controlled in any of the procedures involving extraction as $NiPh_3^{+2}$ readily forms extractable ion-pairs which, in turn, introduce very large errors in the 1,10-phenanthroline analysis. Although NaOH was found to suppress the solubility of $NiPh_3I_2$ and $NiPh_3(ClO_4)_2$, it did not cause precipitation of $NiPh_3^{+2}$ or give an extractable ion-pair.

Results and Conclusions

Racemization of $NiPh_3^{+2}$.—The racemization rates of tris-(1,10-phenanthroline)-nickel(II) ion in the presence of sodium hydroxide showed a slight increase with increasing hydroxide ion concentration as shown in Table I. This increase, however, is quite small compared to the behavior of $FePh_3^{+2}$ and may be due to changes of the electrolyte concentration. Table I also indicates that the racemization rate is not affected by EDTA.

Dissociation of $NiPh_3^{+2}$ with Hydroxide.—Spectrophotometric observation of $NiPh_3^{+2}$ in

---

[1] Abstracted from a thesis submitted by L. P. Morgenthaler to the Graduate School of Purdue University, June 1961, in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] Address correspondence to this author.

[3] D. W. Margerum, *J. Am. Chem. Soc.*, **79**, 2728 (1957).

[4] D. W. Margerum and L. P. Morgenthaler, *ibid.*, **84**, 706 (1962).

[5] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **48**, 244 (1952).

[6] R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 1763 (1957).

[7] P. Pfeiffer and F. Tappermann, *Z. anorg. u. allgem. Chem.*, **215**, 273 (1933).

[8] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1949).

[9] W. Biedermann and G. Schwarzenbach, *Chimia (Switz.)*, **2**, 56 (1948).

[10] C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **30**, 947 (1958).

[11] C. N. Reilley, R. W. Schmid and D. W. Lambson, *ibid.*, **30**, 953 (1958).

[12] I. M. Kolthoff, D. L. Leussing and T. S. Lee, *J. Am. Chem. Soc.*, **72**, 2173 (1950).

[13] I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **73**, 390 (1951).

TABLE I

RACEMIZATION RATE CONSTANTS OF $NiPh_3^{+2}$ IN THE PRESENCE OF HYDROXIDE ION AT 25.00 ± 0.05°

$[OH^-]$, M	$k_{rac} \times 10^4$, min.$^{-1}$
1.0	9.8[a]
1.0	8.7[a]
2.0	11[a]
3.0	12[a]
pH 5.8	6.62
0.40	7.00
.60	7.20
.60	7.99
.70	8.01
.80	8.10
1.00	8.38
1.20	8.68
1.50	8.66
1.00	8.30
1.00	8.36[b]
1.00	7.21[c]

[a] $NiPh_3(ClO_4)_2$ was used for these rates. $NiPh_3I_2$ was used for all others. [b] 5.0×10^{-3} M Y^{-4} present. [c] 0.10 M Y^{-4} present.

TABLE II

EQUILIBRIUM CONSTANT FOR THE HYDROXIDE ION DISSOCIATION OF $NiPh_3^{+2}$

$[NiPh_3^{+2}]_0 = 1.00 \times 1.0^{-3}$, 25.0°

$[OH^-]$	$K \times 10^6$
5.00	3.2
4.00	2.3
3.00	2.9
2.00	2.5
1.00	3.1
1.00	2.1
0.50	2.0

$$\text{Av.}\quad K = 2.6 \times 10^{-6} = \frac{[NiPh_2(OH)_2][Ph]}{[NiPh_3^{+2}][OH^-]^2}$$

sodium hydroxide showed a slight decrease in the absorbance of the solution at 343 mμ which is characteristic of 1,10-phenanthroline bonded to nickel(II) ion, indicating that the complex was partially dissociating. To measure the extent of this dissociation solutions were prepared containing 1.00×10^{-3} M $NiPh_3Cl_2$ in 0.5 to 5.0 M NaOH. After several days at 25.0° each solution was analyzed for free 1,10-phenanthroline by the extraction procedure. From these data the equilibrium constants in Table II were calculated assuming the reaction in equation 1.

$$NiPh_3^{+2} + 2OH^- \rightleftarrows NiPh_2(OH)_2 + Ph \qquad (1)$$

The dissociation rate of $NiPh_3^{+2}$ in NaOH was measured in the same manner at 25.0°.

In general the rate curves were not very good because the back reaction became appreciable before much dissociation occurred. However, the values of the rate constants obtained were in agreement with the values of the racemization rate constants.

Dissociation of $NiPh_3^{+2}$ with EDTA and OH^-. The dissociation rate of solutions 5×10^{-4} M in $NiPh_3^{+2}$, containing a 10 to 40-fold excess of Y^{-4} as well as sodium hydroxide, were measured by the extraction procedure. The reaction observed is given by equation 2, which is discussed later.

$$NiPh_3^{+2} + Y^{-4} \longrightarrow NiPhY^{-2} + 2Ph \qquad (2)$$

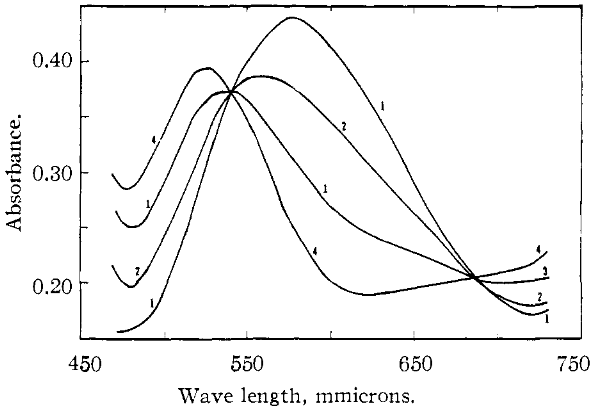

Fig. 1.—Disproportionation of dihydroxobis-(1,10-phenanthroline)-nickel (II): $[NiPh_2(OH)_2]_0 = 4.3 \times 10^{-3}$, $[NiPh_3^{+2}]_0 = 8.7 \times 10^{-4}$, $[NaOH] = 1.43 \times 10^{-2}$, 10 cm. cell, spectra scanning at 300 mμ/min. from right. Curves 1, 2, 3 and 4 are started 0.5, 5.0, 13.0 and 25.0 min. after mixing, respectively.

Excellent first order rate plots were obtained and the values of the dissociation rate constants in Table III are in good agreement with the racemization rate constants. The dissociation rate showed no dependence on the concentration of Y^{-4}.

Disproportionation of $NiPh_2(OH)_2$.—A freshly prepared solution of the diaquobis-(1,10-phenanthroline)-nickel(II) chloride is violet in color but immediately becomes green upon the addition of dilute NaOH. The accompanying pH changes indicate the rapid uptake of 2.0 hydroxide ions per nickel ion corresponding to the formation of the dihydroxo complex, $NiPh_2(OH)_2$. This complex disproportionates, eventually converting all the Ph to the tris complex.

$$3NiPh_2(OH)_2 \longrightarrow 2NiPh_3^{+2} + 4OH^- + Ni(OH)_2 \quad (3)$$

The disproportionation reaction proceeds before the precipitation of $Ni(OH)_2$ can be observed, which is consistent with the disproportionation of $NiPh_2(H_2O)_2^{+2}$ and with the favored stability of the tris complex compared to the bis in equation 1. Figure 1 is a repetitive spectral scan of the reaction at 25°. The isosbestic point at 543 mμ holds until a precipitate forms but the initial isosbestic point at 685 mμ begins to shift a little sooner. The disproportionation rate of the dihydroxo complex is much faster than that observed for the diaquo complex. The stepwise mechanism for equation 3 would be

$$NiPh_2(OH)_2 \xrightarrow{k_{2d}} NiPh(OH)_x + Ph$$

$$NiPh(OH)_x \xrightarrow{k_{1d}} Ni(OH)_2 + Ph$$

$$NiPh_2(OH)_2 + Ph \xrightarrow{\text{rapid}} NiPh_3^{+2} + 2OH^-$$

If the main absorbing species in Fig. 1 are only $NiPh_2(OH)_2$ and $NiPh_3^{+2}$, then k_{2d} is at least equal to 0.03 min.$^{-1}$ which is 30 times greater than the dissociation rate constant for $NiPh_2(H_2O)_2$.[14] If $NiPh(OH)_x$ forms and has an appreciable absorbance, then k_{2d} is even larger. The rate of the initial

[14] R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 4514 (1957).

TABLE III

FIRST-ORDER DISSOCIATION RATE CONSTANT OF $NiPh_3^{+2}$ IN THE PRESENCE OF Y^{-4} AND OH^-

$[Y^{-4}]_0/[NiPh_3^{+2}]_0$[a]	$[OH^-]$, M	$k \times 10^4$, min.$^{-1}$
40	1.0	11
40	1.2	11
20	1.2	9.5
20	1.0	10
10	1.0	11
10	0.1	8

[a] $[Y^{-4}]_0$ and $[NiPh_3^{+2}]_0$ refer to initial concentrations. $[NiPh_3^{+2}]_0 = 5.00 \times 10^{-4}$.

disproportionation reaction as observed spectrophotometrically did not change with 0.014, 0.025 and 0.8 M NaOH.

$NiPh_3^{+2}$ and Cyanide.—Dissociation of $NiPh_3^{+2}$ in the presence of CN^- gave $Ni(CN)_4^{-2}$ and 3 Ph as products. This was confirmed by the fact that $NiPh_2(CN)_2$ reacted rapidly with CN^- to form $Ni(CN)_4^{-2}$. The dissociation rate was followed spectrophotometrically by determining the bonded and unbonded 1,10-phenanthroline concentrations. The results in Table IV show that the dissociation rate is unchanged in the presence of NaCN. The dissociation rates of $NiPh_2(CN)_2$ and whatever $NiPh(CN)_x$ complex forms are much faster in NaCN than are the dissociation rates of $NiPh_2(H_2O)_2^{+2}$ and $NiPh(H_2O)_4^{+2}$. This is similar to the effect observed for $NiPh_2(OH)_2$.

TABLE IV

DISSOCIATION RATE CONSTANT OF $NiPh_3^{+2}$ IN THE PRESENCE OF CYANIDE AND AZIDE IONS AT 25°

M	$k \times 10^4$, min.$^{-1}$
0.6 CN^-	7.0[a]
0.8 CN^-	6.3[a]
1.0 CN^-	6.6[a]
1.2 CN^-	6.9[a]
1.4 CN^-	6.8[a]
0.8 N_3^-	7.0[b]
1.0 N_3^-	6.8[b]
1.2 N_3^-	7.1[b]

[a] $[NiPh_3^{+2}]_0 = 1.02 \times 10^{-4}$. [b] $[NiPh_3^{+2}] = 2.00 \times 10^{-4}$, $[EDTA] = 4 \times 10^{-3}$.

$NiPh_3^{+2}$ and Azide.—Solutions of $NiPh_3^{+2}$ in the presence of 1.2 M NaN_3 showed no release of 1,10-phenanthroline from the complex. In order to displace the reaction a 20-fold excess of Y^{-4} was added to an initial complex concentration of 2.00×10^{-4} M. The reaction observed was the displacement of two 1,10-phenanthrolines to give $NiPhY^{-2}$ in agreement with the OH^- and Y^{-4} system. Values for the rate constants are given in Table IV. The dissociation rate was not affected by the presence of azide ion.

Complexes of Ni^{+2} with Ph and Y^{-4}.—As indicated earlier the rate of dissociation of $NiPh_3^{+2}$ in the presence of EDTA agrees with the racemization and hydroxide dissociation rates only if the reaction in (2) occurs where instead of Y^{-4} releasing all three Ph from nickel it forms a stable complex retaining one Ph. Furthermore, the visible spectrum of a mixture of $NiPh_3^{+2}$ and Y^{-4} does not correspond to the possible summations of the spectra of $NiPh_3^{+2}$ and NiY^{-4}. A series of solutions of various Ph, Ni and Y^{-4} composition were prepared as given in Table V. In solutions 1 through 5 Y^{-4} was added to $NiPh_3^{+2}$ and after 21 days at 25.0° aliquots of the solutions were analyzed for Y^{-4} with the titrator.

Solutions 6 through 10 were prepared by adding 1,10-phenanthroline to NiY^{-2} and after 13 days at 25.0° they were analyzed for Y^{-4} titrimetrically using a visual indicator and also by the absolute potentiometric method. Aliquots of the solutions were analyzed for free 1,10-phenanthroline by both extraction and spectrophotometry. Although there was good agreement between methods for each analysis, the 1,10-phenanthroline analyses were considered the more accurate of the group. All of the solutions contained 0.4 M NaOH to maintain constant ionic strength and also to simulate the basic conditions under which the kinetics had been measured. All constants calculated from these data are apparent and not thermodynamic constants.

Solutions 1–5 in Table V indicate that for each Ph released one Y^{-4} is taken up by the nickel. It is not possible to account for this with only the complexes $NiPh_3^{+2}$, $NiPhY^{-2}$ and NiY^{-2}, but another mixed complex $NiPh_2Y^{-2}$ must be proposed. On the other hand, the data for solution 10 are consistent with the formation of $NiPhY^{-2}$ Three equilibria are postulated

$$NiPh_3^{+2} + Y^{-4} \xrightleftharpoons{K_1} NiPh_2Y^{-2} + Ph$$

$$NiPh_2Y^{-2} \xrightleftharpoons{K_2} NiPhY^{-2} + Ph$$

$$NiPhY^{-2} \xrightleftharpoons{K_3} NiY^{-2} + Ph$$

The extraction data for solutions 1–9 give as a best fit for the constants $K_1 = 0.12$ and $K_2 \cong 4 \times 10^{-4}$. K_3 was calculated directly from the solution 10 data assuming from the nearly quantitative disappearance of free Y^{-4} and free Ph that $NiPhY^{-2}$ was the primary species present. The value for K_3 is 4×10^{-6}. These constants are in agreement with the kinetic data where at lower $NiPh_3^{+2}$ concentrations the predominant product was $NiPhY^{-2}$. However, the product of the equilibrium constants $K_1 \cdot K_2 \cdot K_3 = K'$ is 1.9×10^{-10} in 0.4 M NaOH. On the basis of the stability constants for $NiPh_3^{+2}$ ($K = 10^{-24.3}$ over a range of 0.7 to 10^{-3} M ionic strength)[15] and NiY^{-2} ($K = 10^{18.6}$ at 0.1 M KCl),[16,17] the value of K' is calculated to be 2×10^{-6} at 0.1 M ionic strength. This discrepancy in K' values can be partially accounted for by a decrease in the stability of the NiY^{-2} complex due to the high ionic strength. Carini and Martell[18] have shown a factor of 10 decrease in the stability of CaY^{-2} in going from 0.1 to 0.4 M ionic strength. The formation of NaY^{-3} could account for another factor of 20. The effect of ionic strength and Na^+ complexing has not been reported for the 1,10-phenanthroline complexes. The discrepancy that

[15] D. W. Margerum, R. I. Bystroff and C. V. Banks, *J. Am. Chem. Soc.*, **78**, 4211 (1956).

[16] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[17] G. Schwarzenbach and E. Freitag, *ibid.*, **34**, 1503 (1951).

[18] F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5745 (1952).

TABLE V

COMPOSITION OF Ni^{+2}–Ph–Y^{-4} SOLUTIONS, ANALYSES FOR FREE [Ph] AND [Y^{-4}] AND VALUES FOR K_2 WHEN $K_1 = 0.12$

Soln. no.	$[Ni^{+2}]_{total}$ × 10^3	$[Y^{-4}]_{total}$ × 10^3	$[Ph]_{total}$ × 10^3	Free $[Y^{-4}]$ × 10^3	Free [Ph] × 10^3	$[Y^{-4}]_{bonded}$ × 10^3	$[Ph]_{bonded}$ × 10^3	K_2 × 10^4
1	7.14	2.86	21.42	1.53	1.19	1.33	20	..
2	5.56	4.44	16.68	3.01	1.65	1.43	15.03	6
3	5.00	5.00	15.00	3.31	1.62	1.69	13.38	5
4	4.54	5.46	13.62	3.84	1.61	1.62	12.01	4
5	4.16	5.84	12.48	4.17	1.59	1.67	10.89	..
6	1.12	4.51	3.09	3.6	0.69	0.9	2.40	6
7	1.12	2.25	3.09	1.4	.46	.9	2.63	4
8	1.12	1.13	3.09	0.4	.28	.7	2.81	2
9	1.12	1.13	2.06	.02	.10	1.11	1.96	3
10	1.12	1.13	1.03	.02	.03	1.11	1.00	..

still exists in our value of K' and the calculated value may be due to the 0.4 M NaOH. The proposed intermediates in every other way account for these data which were obtained from four different methods of analysis in solution. Attempts to crystallize the mixed complexes were unsuccessful.

Discussion

No effect on the dissociation rate of $NiPh_3^{+2}$ was observed with cyanide and azide ions. The effect from hydroxide ion is several orders of magnitude less than the effect with the $FePh_3^{+2}$ complex. Thus, the behavior of these three ions with the nickel(II) complex is in great contrast to their behavior with the iron(II) complex. A substitution mechanism based on the difference in the electronic configuration of nickel(II) and iron(II) is proposed to account for their behavior.[4,19]

The large increase in the rate of dissociation of $NiPh_2(OH)_2$ compared to $NiPh_2(H_2O)_2^{+2}$ is of interest and may be due to the effect of reduced charge on the ease of breaking the nickel(II)–1,10-phenanthroline bonds. The $NiPh_2(CN)_2$ system also is converted more rapidly to $Ni(CN)_4^{-2}$ than the dissociation rates of $NiPh_2(H_2O)_2^{+2}$ and $NiPh(H_2O)_4^{+2}$ would predict. Similarly, the $NiPh_2Y^{-2}$ complex must be more labile than $NiPh_2(H_2O)_2^{+2}$ because it is not observed as a reaction product in either the hydroxide ion or azide ion reactions with EDTA.

The mixed ligand complexes of Ni^{+2}–Ph–Y^{-4} are surprisingly stable considering the multidentate nature of both the chelate groups. There is no reason why this type of mixed complex would only occur for this system. The formation of mixed complexes of Y^{-4} and other mono or bidentate ligands may be a source of error in chelatometric analysis involving the use of masking agents or metallochromic indicators.

Acknowledgments.—The authors wish to express their thanks to the Research Corporation and to Purdue Research Foundation for their support of this work.

(19) J. W. Richardson, D. W. Margerum and L. P. Morgenthaler, to be published.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZ., AND UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

Selenium Dioxide Oxidations. I. Studies on the Mechanism of Oxidation of 1,2-Dibenzoylethane[1]

BY JOHN P. SCHAEFER[2]

RECEIVED MAY 22, 1961

The oxidation of 1,2-dibenzoylethane in 80% acetic acid by selenious acid to *trans*-1,2-dibenzoylethylene follows the rate law $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3]^{1/2}$. The reaction is both acid and base catalyzed and the rate expression in the presence of an excess of strong acid is $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3][HA]$ and in the presence of an excess of base $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3][OAc^-]$. The large kinetic isotope effect observed when the α-methylene hydrogens are replaced with deuterium is consistent with a rate-determining attack of an oxidizing selenium species on the diketone to form an enol-selenite ester which decomposes to give the unsaturated 1,4-diketone. Alternate mechanisms are discussed and criticized.

Since Riley's[3] initial investigation, numerous examples describing selenium dioxide as an oxidant for organic molecules have been reported[4]; however, little detailed mechanistic information is available. To clarify the mechanism of oxidation of 1,4-diketones to 1,4-enediones, we have carried out a study of the oxidation of 1,2-dibenzoylethane (I) to *trans*-1,2-dibenzoylethylene (II).

$$2C_6H_5COCH_2CH_2COC_6H_5 + SeO_2 \longrightarrow 2C_6H_5COCH{=}CHCOC_6H_5 + Se + 2H_2O \quad (1)$$

In 80% acetic acid–20% water solvent, yields of 80–85% of II were obtained; no 1,4-diphenyl-1,2,4-butanetrione (III) could be detected. A kinetic study of the reaction is complicated slightly

---

(1) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) Present address: Department of Chemistry, The University of Arizona, Tucson, Ariz.

(3) H. L. Riley, J. F. Morley and N. A. Friend, *J. Chem. Soc.*, 1875 (1932).

(4) N. Rabjohn, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Chap. 8.