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An Infrared Spectroscopic Investigation of the Hydrogenation of Cinnamate Ions Catalyzed by $Co(CN)_5H^{3-}$ in Aqueous Solution

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The hydrogenation of cinnamate ions in aqueous solution catalyzed by $Co(CN)_5H^{3-}$ has been studied by measuring the decrease of cinnamate concentration. This was done by measuring the ir intensity of a band characteristic of the C=C stretching of the cinnamate ion. The rate constants thus obtained could be transformed into the bimolecular rate constant as the concentration of the catalytically active species $Co(CN)_5H^{3-}$ was also determined by ir intensity measurements.

The activation energy was estimated to be $E_a = 13 \pm 1$ kcal/mole.

INTRODUCTION

The ability of the cobalt(II)–cyanide system to catalyze the hydrogenation of olefinic bonds is now well documented (*1*). Especially the selectivity claimed (*2*) for the homogeneous hydrogenation of polyunsaturated acids has created a great interest in this and similar systems.

In order to increase the understanding of the mechanism of such homogeneous hydrogenations we have performed a series of investigations on the action of $Co(CN)_5H^{3-}$ and its analogues on a model system. As such a model system we chose the cinnamate ion as it is one of the simplest unsaturated compounds easily soluble in water.

Furthermore, we set out to use an infrared spectroscopic technique for the analysis of the reaction. The progress of the hydrogenation reaction is related to a decrease of the concentration of molecules containing a carbon–carbon double bond. As the $\nu_{C=C}$ vibration of the cinnamate ion gives a rather well-defined absorption band in the infrared spectrum, ir intensity measurements constitute an easy way of following the reaction. Using this approach the hydrogenation experiments simplified merely to bubbling purified hydrogen at atmospheric pressure through the reaction solution. Taking samples directly from the reaction mixture one can also determine by ir techniques the *actual* amount of catalyst present, i.e., $[Co(CN)_5H^{3-}]$. This has been done by measuring the ν_{CN} absorption intensity of the complex.

This approach made it easy to perform the kinetic measurements for a series of temperatures, thereby making it possible to calculate the activation energy of the rate determining step.

EXPERIMENTAL METHODS

Technique of Analysis

As the frequency of the $\nu_{C=C}$ vibration of the cinnamate ion is about 1640 cm^{-1} it is not possible to make observations directly on the aqueous solutions, water absorbing heavily in this region. Therefore, an extraction technique was chosen, viz, to extract an ion pair of tetrabutylammonium cinnamate into chloroform. In this way it was easy to measure the 1640 cm^{-1} absorption intensity and obtain a calibration curve of A_{1640} versus cinnamate concentration. Then, by withdrawing a sample from the reaction mixture it was possible to determine the concentration of free cinnamate at any time.

Method

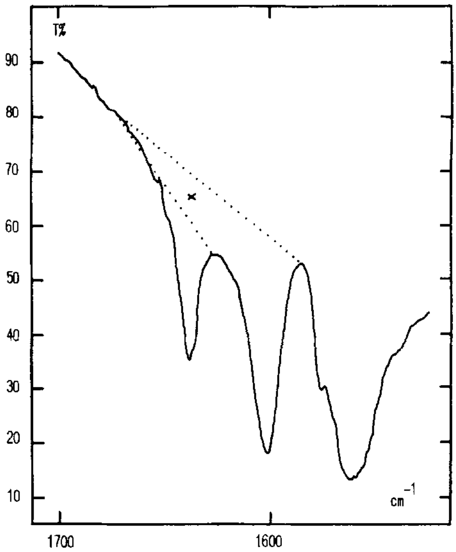

FIG. 1. Example of ir analysis of cinnamate concentration. Spectrum of the chloroform phase. The estimation of the proper background value of the cinnamate C═C band (×) (45°C, t = 1 hr).

The reaction vessel was a round bottom vessel, volume 250 ml. In one neck a funnel was adapted. A solution of $CoCl_2$ was introduced into the funnel and a mixture of sodium cinnamate and sodium cyanide was introduced into the vessel. The solution in the vessel was stirred by means of a motor of the pneumatic type giving a rapid, but nonvibrating, rotation to the stirrer. The temperature was controlled by a thermometer, a relay and a heating mantle. Both solutions were flushed with hydrogen for 10 min before mixing. The hydrogen was purified from traces of oxygen by passing it through alkaline hydroquinone. After mixing, a sample was withdrawn for analysis. Thereafter samples were withdrawn at regular intervals (cf. Table 1). A typical mixture had the following composition: in the reaction vessel 100 ml (0.175 M Na cinnamate + 0.325 M NaCl) + 60 ml 1 M NaCN and in the funnel 30 ml 0.334 M $CoCl_2$. For every analysis 5 ml of the reaction mixture were withdrawn (siphon) and mixed with 1 ml 0.2 M Bu_4NBr and 6 ml chloroform. The mixture was shaken, thermostated, shaken and finally separated with an ordinary separation funnel. A typical ir spectrum of the resulting extract is shown in Fig. 1 illustrating the absorbance measurement. The method of Kimmer (*3*) was used to obtain a proper background and thus to estimate the absorbance.

TABLE 1
EXPERIMENTAL RESULTS[a]

	[S](mM)						
Temp (°C) Time (hr):	0	1	2	3	4	5	6
30	95	93	84	75	67	66	
45	80	78		57	45		
50	88	87	65		42		26
60	93	70	50		27		12

[a] The cinnamate concentration [S], as a function of time. C_{Co} = 52.8 mM; C_{CN} = 316 mM; [S_0] = 92 mM.

At various times during the hydrogenation a sample was withdrawn under a protective atmosphere and immediately transferred to an infrared cell (CaF_2, 0.05 mm). The spectrum was run against a sodium cinnamate solution as reference.

The chemicals were of analytical grade and were used without further purification. A Perkin-Elmer PE 521 infrared spectrophotometer was used.

RESULTS

The measured kinetic series for the different temperatures are given in Table 1. The rate constants (k_2) were obtained from a least square computation using the original cinnamate concentration (0.092 M) and the measured value at time zero with equal weight. The rate constants thus obtained

TABLE 2
RATE CONSTANTS

Temp (°C)	$k_2 \times 10^3$ (min^{-1})	[Co(CN)$_5$H^{3-}] (mean value) M	$k_1 \times 10^2$ (min^{-1} M^{-1})
30	1.3 ± 0.1	0.045	2.9
45	2.6 ± 0.3	0.038	6.9
50	3.5 ± 0.3	0.036	9.7
60	5.6 ± 0.2	0.025	22.3

are given in Table 2. The rate law is written as

$$\frac{d[S]}{dt} = -k_1[\mathrm{Co(CN)_5H}][S], \qquad (1)$$

in accordance with previous studies by Basters *et al.* (4).

Assuming a constant value of the cobalt pentacyanohydride during a kinetic run (Table 3) we can write

$$\frac{d[\mathrm{S}]}{dt} = -k_2[\mathrm{S}]. \qquad (2)$$

This relation was supported by the experimental data. k_2 is transformed into the bimolecular constant k_1 by dividing with the actual concentration of the catalytically active $Co(CN)_5H^{3-}$. This concentration was calculated from the above-mentioned spectra of the aqueous solutions. In such a spectrum four bands can be observed, ν_{CN} of $Co(CN)_5^{3-}$ (2083 cm^{-1}, s), ν_{CN} of $Co(CN)_5H^{3-}$ (2096 cm^{-1}, sh), ν_{CoH} of $Co(CN)_5H^{3-}$ (1888 cm^{-1}, w) and a medium strong band at 2124 cm^{-1} which probably corresponds to ν_{CN} of the oxidation and/or decomposition products of $Co(CN)_5^{3-}$. These bands have been studied in detail by one of us (*5*) and the results will be published soon. There is also the possibility that ν_{CN} of $Co(CN)_5H^{3-}$ of the cyanide ion *trans* to the hydride ion will appear in the same region as the absorption due to the "oxidation products." This matter will be discussed later (*5*), but is of no importance in this merely analytical context.

Notice (Table 3) that the concentration of $Co(CN)_5H^{3-}$ is rather constant while the oxidation products increase in most cases at the cost of the concentration of $Co(CN)_5^{3-}$. Also the sum of the concentration of the components is somewhat larger than the total cobalt concentration. This may be partly due to the difficulty in drawing proper base lines but probably also to the fact that we have used the extinction coefficient (*5*) of $Co(CN)_6^{3-}$ for the "oxidation-product" band. As there might very well be other oxidation or decomposition products this choice may not be the best one.

In principle, there is also the possibility to obtain the concentration of $Co(CH)_5H^{3-}$ from the ν_{Co-H} band. This band, however, is weaker and determinations made in this way would tend to be uncertain.

After the constants k_1 had been calcu-

TABLE 3
EXPERIMENTAL VALUES OF THE CONCENTRATIONS OF $Co(CN)_5H^{3-}$ (2096 cm^{-1}), $Co(CN)_5^{3-}$ (2083 cm^{-1}) AND "OXIDATION PRODUCTS" (2124 cm^{-1})[a]

	Time (hr)					
	2			4		
Temp (°C)	[Co(CN)$_5$H^{3-}]	[Co(CN)$_5$$^{3-}$]	[ox prod]	[Co(CN)$_5$H^{3-}]	[Co(CN)$_5$$^{3-}$]	[ox prod]
30	45	5	8	45		
45	37	19	7	40	16	8
50	36	13	11	35	8	14
60	24	11	12	26	19	8

[a] All concentrations in mM. Total concentration C_{Co} = 53 mM.

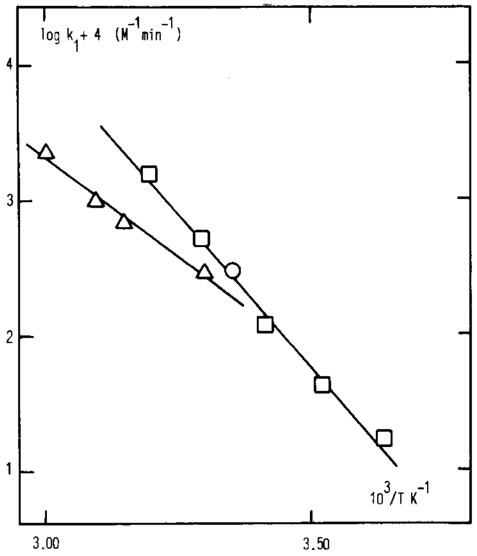

FIG. 2. Arrhenius plots of the present data (△) and those given by Simandi and Nagy (*6*) (□). The k_1 value obtained by Basters *et al.* (*4*) is also included (○).

lated in this way, they were used for an Arrhenius plot (Fig. 2). From the slope a value of the activation energy (E_a) of 13 ± 1 kcal/mole, is derived.

DISCUSSION

This investigation has been performed mainly to test a certain experimental technique, i.e., infrared absorption measurements, for studying hydrogenation reactions. It is therefore of great interest to compare earlier results reached for the same system. The work of Simandi and Nagy (*6*) merits special attention. By a detailed kinetic analysis they could determine the rate constant of the rate determining step

$$\mathrm{Co(CN)_5H^{3-}} + \mathrm{S^-} \xrightarrow{k_1} \mathrm{SH\cdot^-} + \mathrm{Co(CN)_5^{3-}}. \quad (3)$$

This constant has the same meaning as the one we have used in Eq. (1) and we can therefore directly compare the results of Simandi and Nagy (*6*) with ours. This is done in Fig. 2. One notices a fair agreement of the two sets and also between these and the point originating from the work of Basters *et al.* (*4*). It must be remembered when making this comparison that the ionic strengths at which the three investigations were performed are different: $I = 0.75$ *M* (present work), $I = 1.0$ *M* [Simandi and Nagy (*6*)] and $I \approx 1.4$ *M* [Basters *et al.* (*4*)]. As both schools seem to agree (*4,6*) that the rate determining step is described by the relation (*3*), i.e., a reaction involving ions of similar charges, one should expect a salt effect on the rate constant. Within the accuracy of the determinations one cannot detect such an effect. This most probably is caused by the rather small variation of activity coefficients at this range of ionic strength. Most definitely one is outside the range where the Debye–Hückel limiting law is valid.

Although we cannot contribute to the elucidation of the mechanism of the reaction with this investigation—we merely rely on the results of other workers—we can perhaps add some new data for the determination of the energy of activation.

In a recent paper Simandi and Bundo (*7*) have compared activation energies for the reaction of $\mathrm{Co(CN)_5H^{3-}}$ with cinnamate, muconate and sorbate ions. Because of the similar electronic structure of these ions the authors were led to suggest the activation energies to be rather similar. They found (*6*), however, that the value for cinnamate was unexpectedly (*7*) high. Inspection of Fig. 2 now tells us that even if our suggested value of $E_a = 13$ kcal/mole is perhaps somewhat low, the one used by Simandi and Budo (*7*) is probably too high. However, a compromise using all the experimental points, thus covering a wider temperature range, will give a value of the activation energy close to that of the muconate system, i.e., 15 kcal/mole.

Other studies have been performed on this system. Thus Takahashi *et al.* (*8*) report the rate law $R = k[\mathrm{A}]^{1.2}[\mathrm{B}]^{0.6}$, [A] meaning the concentration of the "complex" and [B] that of the organic ion. Incidentally, they report an apparent total activation energy of 16 kcal/mole, i.e., rather close to our value.

A similar investigation by Strohmeier and Iglauer (*9*) on the two-phase hydrogenation of styrene gave an activation energy (estimated by us) that is even less than that found here ($E_a \approx 7 \pm 2$ kcal/mole).

The approach made by Simandi and Budo in discussing the relation between energy of activation and electronic structure of the organic ion seems most fruitful. It appears to the authors, though, that the relation between the energy of activation and the vibrational energies of the Co–H bond will be of complementary value.

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