Reduction of α-Keto Acids by Low-Valent Metal Ions. 1. Reaction of Aqueous Chromous Ion with Pyruvic Acid

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Abstract: Chromous ion reacts in acidic aqueous solutions only with the carbonyl form of pyruvic acid. In fact, the first stage in the reaction is essentially a kinetic titration of this form. Hydrated pyruvic acid reacts only after being transformed into the carbonyl form by an acid catalyzed reaction. The product is a binuclear, partly bidentate complex of chromium(III) with lactic acid, which eventually undergoes hydrolysis. The overall stoichiometry of the reaction is 2:1. The kinetics were studied in detail by the stop-flow technique. The redox steps in the reaction were found to be very fast; they are completed within the time of mixing. This observation provides the basis for a correlation of the two-electron transfer from Cr^{2+} (aqueous) to "free" pyruvic acid with one-electron-transfer reactions in which pyruvic acid plays the role of the mediating ligand.

Introduction

The aspects of the interaction between low-valent metal ions and various organic compounds that have been studied so far in our laboratories[2] can be classified into the following categories: complex formation, hydrogenation of carbon–carbon double bonds, isomerization of olefins, activation and exchange of olefinic hydrogens with hydrogens from the solvent, selective reduction of the carboxyl group in the pyridine carboxylic acids, and report (this paper) on the selective reduction of the ketonic carbonyl in the reaction of chromous ion with pyruvic acid in acid aqueous solutions.

In 1926 Conant and Cutter[3] observed that chromous and vanadous salts reduce a variety of compounds including α-keto acids. So far as we know, no other study on this reaction has been reported since then. Yet a more systematic study of the reactions of pyruvic acid (**1, 2**) with Cr^{2+} (aqueous) seemed to us interesting for the following reasons. Firstly, further investigation of the selective patterns in the interaction between strongly reducing metal ions and organic compounds seems warranted. Secondly, the reduction by Cr^{2+} (aqueous) and other low-valent metal ions of pyruvatopentamminecobalt(III) and of other complexes with related ligands has been extensively investigated.[4] In this case the electron is, of course, transferred from the reducing metal ion to Co^{III}, whereas in our case two electrons end up on the "free" [5] α-carbonylcarboxylic ligand. Nevertheless, comparison of the two systems can be expected to enhance the understanding of both. Finally, in the enzymatic reduction of pyruvate by reduced diphosphoropyridine nucleotide it has been postulated[6] that the mechanism involves hydride transfer to the carbonyl group. Our system then could, in some respects, serve as a model of this more complicated biological system.

Experimental Section

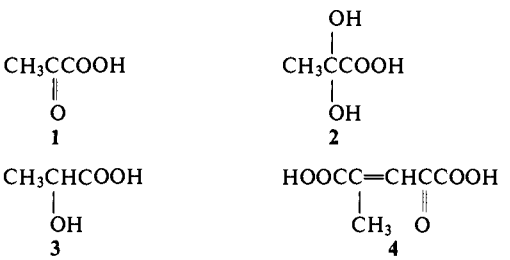
Materials. Triply distilled water was used in all experiments. Solutions of chromium(II) perchlorate were prepared from the corresponding Cr^{III} solutions electrolytically, under an atmosphere of deoxygenated argon. Unreacted chromous ion was determined by adding an aliquot of a deaerated Fe^{III} solution in aqueous H_2SO_4 and titrating the resulting Fe^{II} with standard Ce^{IV} amperometrically on a Metrohm A. G. Herisau potentiograph, Mo 436. Dimer-free pyruvate was supplied by Fluka and stored at ~0 °C. Stock solutions were prepared immediately before use, because sodium pyruvate slowly dimerizes upon prolonged standing.

Stoichiometry. The stoichiometry of the overall reaction was determined by adding an excess of Cr^{II} solution to a solution of pyruvic acid and titrating the excess of Cr^{II} after the reaction was completed. The stoichiometry was also determined with excess pyruvic acid. In this case analysis of the remaining pyruvic acid was done polarographically, using a Metrohm AG Herisau rapid polarograph.

Chromatographic Separations. The chromatographic separations were done on a Dowex-50W×2 cation-exchange resin in the atmosphere of dry argon. The chromium species were eluted with perchloric acid of various concentrations following the procedure described by King and Dismukes.[7] The charge of the complex species was determined by titrating the hydrogen ions released upon absorption on a sample of resin.

Reaction Products. The organic product of the reaction, which is obtained after hydrolysis of the Cr^{III} complexes, was isolated from the reaction mixture by extraction with ether. Its identification was done by elemental analysis and NMR spectrum. The only product in the reaction is lactic acid (**3**).

Kinetic Measurements. The kinetics were followed spectrophotometrically by observing the change in absorbance due to the formation of the Cr^{III} complexes. The hydrolysis stage of the reaction was followed on a Cary 14 spectrophotometer, all other stages using an Applied Photophysics Ltd. stop-flow apparatus.



Abbreviations: For the keto (carbonyl) form of pyruvic (**1**) we use the abbreviation k-pyr, for the hydrated form (**2**), h-pyr, for pyruvic without specifying the form, pyr, and for lactic, lc.

Results

Reaction Stages, Products, and Stoichiometry. The first two stages in the reaction between Cr^{2+} (aqueous) and pyruvic acid are clearly shown in the typical stop-flow trace reproduced in Figure 1. The first stage is too fast to be followed under any of the experimental conditions that we have tried and it is manifested by an increase of the absorbance within a time scale shorter than the dead time of the stop-flow instrument. The second stage, corresponding to a further increase in absorbance, takes place within the time range of the instrument. The product of the second stage eventually hydrolyzes (third stage), but, since this hydrolysis takes several days, it can easily be chromatographically separated and characterized. Thus, it was found to contain two Cr^{III} ions bound to each reduced organic ligand and to have a charge of +4. This complex is the only product at the end of the second stage of the reaction between Cr^{2+} and pyruvic acid. The final organic product (after hydrolysis) is lactic acid and the overall stoichiometry 2:1. NMR spectra show that, after prolonged standing, reaction mixtures containing excess pyruvic acid contain also the dehydrated

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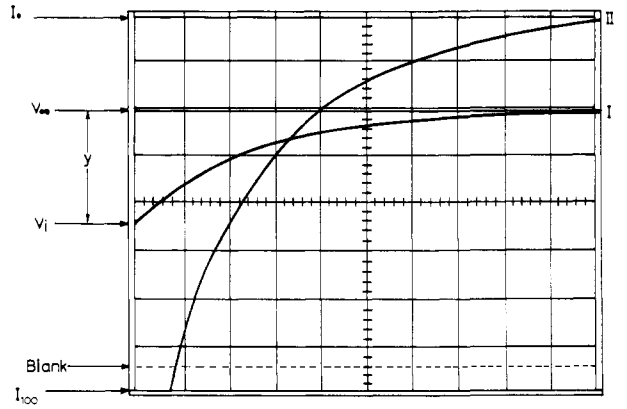

Figure 1. Stop-flow traces for the reaction of Cr^{II} with pyruvic acid: $[Cr^{II}]$ = 0.04 M, [pyr] = 0.005 M, $[HClO_4]$ = 0.65 M, and temperature of 31 °C. Ordinate gives voltage values which are proportional to transmittance. For trace I transmittance limits 0 and 100% are shown in the diagram. Trace II was taken under the same conditions as trace I but at four times higher sensitivity. Abscissa shows the time (100 ms/div).

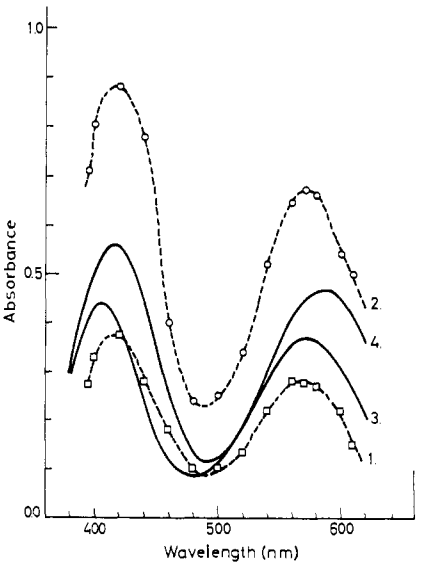

Figure 2. Variation of A_i and A_f with wavelength is shown by curves 1 and 2 correspondingly: [pyr] = 0.0075 M, $[Cr^{II}]$ = 0.0165 M, $[HClO_4]$ = 0.50 M, and stop-flow cell length of 2.0 cm. Curves 3 and 4 give the variation of absorbance vs. wavelength for Cr^{III} aqueous and Cr^{III}–O–Cr^{III} aqueous correspondingly: $[Cr^{III}]$ = 0.0150 M, $[Cr^{III}$–O–$Cr^{III}]$ = 0.010 M, and 2.0-cm cell.

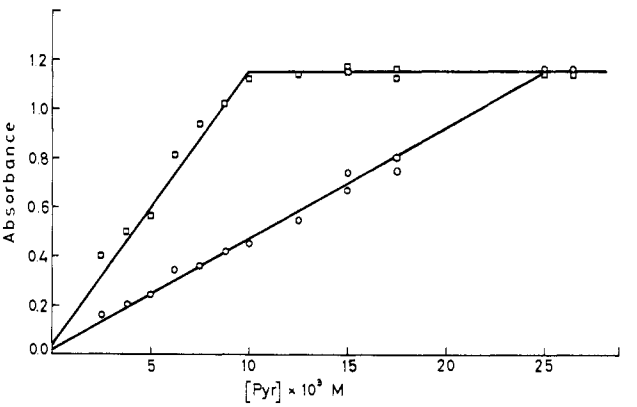

Figure 3. Variation of A_i (○) and A_f (□) with the total ligand concentration at constant total metal ion concentration $[Cr^{II}]_0 = 2 \times 10^{-2}$ M and $[HClO_4]$ = 0.33 M.

form of the dimeric pyruvic acid (**4**). The time scale for the formation of this product, however, is generally long compared with the time scale of the reactions investigated. Blank experiments showed that the formation of this compound is due to the catalytic action of Cr^{III} on pyruvic acid in acidic aqueous media, similar to that of Ni^{II} and Zn^{II}.[8]

Spectrophotometric Investigation. The absorbance at "zero time", A_i, and "infinite time", A_f, was monitored in the stop-flow apparatus as a function of wavelength from ~390–600 nm. The results for $[Cr^{II}]_0 = 1.6 \times 10^{-2}$ M, $[pyr]_0 = 7.5 \times 10^{-3}$ M, and $[HClO_4]$ = 0.5 M are given in Figure 2. The two curves, for A_i and A_f, differ only by a constant multiplication factor. They can be made to coincide if the values for A_i are multiplied by 2.4. It is also noted that both A_i and A_f are essentially independent of hydrogen ion concentration and temperature (10–37 °C).

Included in Figure 2 for comparison are the spectra of the monomeric and dimeric Cr^{III}.

Figure 3 is a typical plot of A_i and A_f as a function of the total ligand concentration, for constant total metal ion concentration. The sharp intercept of the two linear parts for A_f shows that only one complex of high stability is present in the solution. The total ligand concentration at the intercept is half the total metal ion concentration, corresponding to a 2:1 metal to ligand ratio,[9] the same as that found after the chromatographic separation. Thus, the product obtained at the end of the second stage is obviously the binuclear complex of Cr^{III} with lactic acid, abbreviated Cr_2lc^{4+}.

"Zero time" absorbance vs. total ligand concentration also shows a sharp intercept, indicative of a single complex species of high stability, but at a metal to ligand ratio 1:1.25. This rather peculiar ratio, together with the fact that the spectra corresponding to A_i and A_f (Figure 2) differ only by a constant multiplication factor, provides the key for the interpretation of the results (vide infra).

Kinetics. The second stage of the reaction was followed under pseudo-first-order conditions, keeping the concentrations of Cr^{II} and hydrogen ion in excess. The results are given in Table I. It is significant to note that the values of the observed first-order rate constant, k^1_{obsd}, given in this table were calculated from the oscilloscope traces (e.g., Figure 1) using the formula

$$\log \frac{A_f - A_t}{A_f - A_0} = \frac{k^1_{obsd}}{2.303} t \qquad (1)$$

which is based on the assumption that the concentration of the precursor of Cr_2lc^{4+} is proportional to $A_f - A_t$.

It is seen from the data in Table I that k^1_{obsd} is independent of the initial chromous ion and pyruvic acid concentration, but varies linearly with hydrogen ion concentration. Figure 4 is a plot of k^1_{obsd} vs. $[H^+]$. From the slope of the line we obtain the second-order rate constant $k^2_{obsd} = 2.9 \pm 0.1$ M^{-1} s^{-1}. Also, from the data in Table I the activation parameters were calculated on the basis of k^2_{obsd} as follows: activation enthalpy $\Delta H^{\ddagger} = 16.1 \pm 0.4$ kcal mol^{-1}; activation entropy $\Delta S^{\ddagger} = 4.5 \pm 0.4$ cal mol^{-1} deg^{-1}.

The data in Table I also show that k^1_{obsd} does not depend on the excess concentration of Cr^{II}. This means that there is no Cr^{II} concentration term in the rate law. Moreover it should be noticed that Table I includes entries in which the excess of chromous ion over pyruvic acid is only twofold. This is because even in this small excess the data fit perfectly first-order kinetics (Figure 5). Yet, when the ratio of the initial chromous ion over pyruvic acid becomes <2, the situation changes abruptly: the data no longer fit eq 1 (Figure 5), or for that matter any analogous equation derived on the assumption of an order other than first. Further decrease of the ratio of $[Cr^{2+}]_0$ over $[pyr]_0$ results in a decrease of $(A_f - A_i)$ and, when initial concentrations of pyruvic acid exceed those of chromous

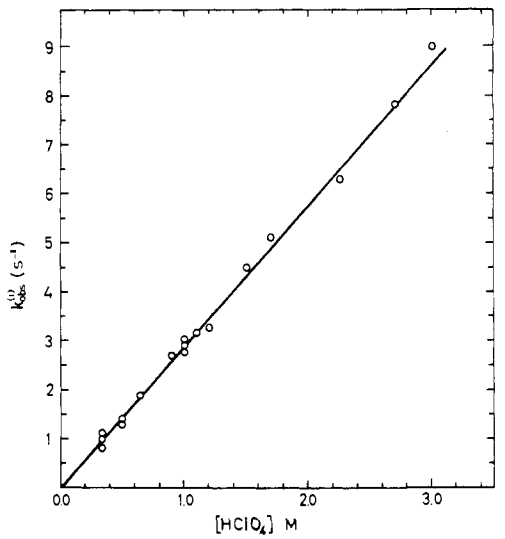

Figure 4. Plot of k^1_{obsd} vs. acid concentration using data from Table I. Second-order rate constant, k^2_{obsd} 2.9 ± 0.1 M^{-1} s^{-1}.

Table I. Kinetic Data for the Reduction of Pyruvic Acid by Cr^{II}

Temp, °C	[Cr^{II}] × 10^2 M	[pyr] × 10^2 M	[$HClO_4$], M	A_i	A_f	k^1_{obsd}, s^{-1}
10.0	4.00	0.50	0.65	0.240	0.600	0.49
15.0	4.00	0.50	0.65	0.250	0.610	0.72
24.0	3.20	0.50	0.65	0.280	0.600	1.95
24.0	3.47	0.25	1.00			3.00
31.0	4.00	0.50	0.65	0.270	0.580	3.65
38.0	4.00	0.50	0.65	0.300	0.600	6.67
47.0	4.00	0.50	0.65	0.350	0.590	9.60
22.0	2.00	0.50	0.33	0.210	0.580	0.65
24.0	1.10	0.50	0.90			2.70
27.0	3.50	0.50	2.70	0.270	0.600	10.30
24.0	2.25	0.50	0.50	0.220	0.580	1.30
24.0	2.25	0.50	0.50	0.280	0.580	1.40[a]
24.0	3.20	0.80	1.00	0.360	0.860	2.90
23.0	3.20	0.25	1.00	0.140	0.320	2.50
26.0	3.25	0.50	1.20	0.250	0.600	3.90
25.5	4.25	0.50	1.10			3.70
28.0	6.75	0.50	3.00	0.270	0.580	13.00
24.0	3.55	0.50	2.25	0.350	0.620	6.30
24.0	3.40	0.50	1.70	0.280	0.580	5.17
24.0	9.05	0.50	1.50	0.300	0.600	4.50
24.0	9.50	0.50	0.35	0.220	0.580	0.97
24.0	9.50	0.25	0.35	0.110	0.280	1.10
24.0	2.00	0.25	0.33	0.160	0.400	0.89
24.0	2.00	0.38	0.33	0.200	0.500	1.00
24.0	2.00	0.50	0.33	0.240	0.560	1.05
24.0	2.00	0.62	0.33	0.340	0.810	0.97
24.0	2.00	0.75	0.33	0.360	0.940	0.88
24.0	2.00	0.88	0.33	0.420	1.020	0.97
24.0	2.00	1.00	0.33	0.450	1.090	1.05
24.0	2.00	1.25	0.33	0.550	1.140	0.92[b]
24.0	2.00	1.50	0.33	0.740	1.150	0.90[b]
14.0	2.00	1.75	0.33	0.790	1.160	0.96[b]

[a] Concentration of ClO_4^- of 2 M was achieved by adding $NaClO_4$. [b] Values of k^1_{obsd} were computed by using eq 9.

ion the difference ($A_f - A_i$) becomes zero; in excess pyruvic the second stage of the reaction is missing.

The kinetics of the hydrolysis of Cr_2Ic^{4+} were not investigated in detail, but it seems that the reaction takes place in two successive first-order acid-independent stages as expected for an octahedral Cr^{III} complex.

Discussion

It has been stated (vide supra) that both A_i and A_f correspond to stable complexes. In fact, these complexes are identical, in spite of the apparent difference in metal to ligand ratios and of the fact that one seems to be transformed into the other.

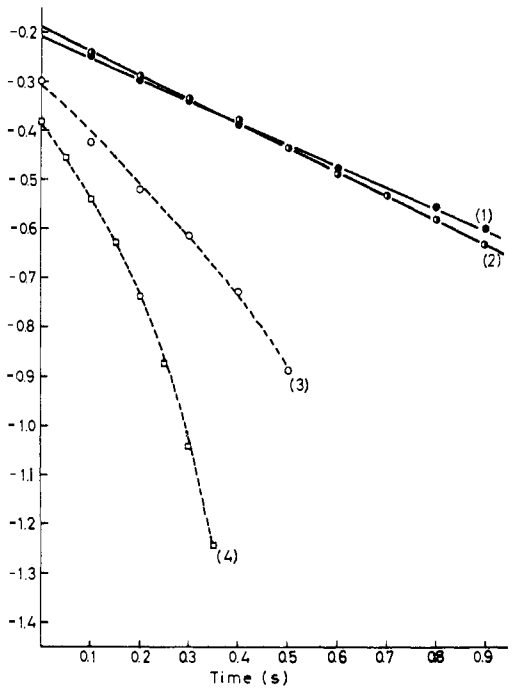

Figure 5. Plot of kinetic data using eq 1 ordinate corresponds to log log ($V_\infty + y)/V_\infty$ (see Figure 1). For all four cases shown, total Cr^{II} and $HClO_4$ concentrations are constant (0.020 and 0.33 M, respectively). Ligand, Pyr, concentrations are different. Successive values of $[pyr]_0$ for curves 1–4 are 0.0088, 0.0100, 0.0125, and 0.0175 M.

The arguments supporting this claim can be summarized as follows. Firstly, the spectra (Figure 2) differ only by a constant multiplication factor. Secondly, if the complex corresponding to A_i were simply the precursor of Cr_2Ic^{4+}, the plot of A_i vs. $[pyr]_0$ at constant $[Cr^{2+}]_0$ should have shown a break at a "reasonable" value of the metal to ligand ratio, such as 2:1 or 1:1. The break is instead observed at a ratio of 1:1.25. Finally, kinetics fit first-order plots only for values of $[Cr^{2+}]_0/[pyr]_0$ larger than value of ~2:1. The discontinuity observed at this value (Figure 5), from good to bad fit, is reminiscent of a titration curve and is, indeed, a kind of kinetic titration.

Thus, the conclusion is inescapably reached that a fraction of Cr_2Ic^{4+} is formed at "zero time" (<10 ms) and the rest is formed at the second stage of the reaction, with kinetics first order in pyruvic acid and hydrogen ion, but zero order in chromous ion. In other words, part of pyruvic acid reacts immediately upon mixing and the remainder reacts only after transformation into the more reactive form. The rate-determining step in the second stage of the Cr^{2+}–pyruvic acid reaction is this transformation rather than any redox or complex formation step. All complexation and reductive steps of the reactive form of pyruvic acid are completed within 10 ms.

On the basis of this conclusion all pieces of evidence given in the results now fall nicely into place. Thus, the multiplication factor in the spectra (Figure 2) indicates that 41.5% of total pyruvic acid in solution exists in a form which reacts with chromous ion upon mixing. An independent estimate of 40% for this content is also obtained from the break in the plot of A_i vs. $[pyr]_0$.

On the basis of NMR studies, Becker[10] concluded that in dilute aqueous solutions 65% of undissociated pyruvic acid exists in the hydrated form (**2**) and the rest (35%) in the keto form (**1**). Becker's experiments were performed with concentrated solutions (2.0 M in pyruvic acid) and the value for dilute

solutions was approximately estimated using Ostwald's law of dilution. Our reactive form (~40%) can, therefore, be safely identified as the keto form and the slow step in the second stage of the reaction as the hydrogen ion catalyzed transformation of the hydrated into the carbonyl form:

$$CH_3C(OH)_2COOH \xrightarrow{k_1} CH_3COCOOH + H_2O \quad (I)$$

The values 8.6×10^{-3} and 2.5×10^{-4} mol L^{-1} were reported[10] for the dissociation constants of the keto and hydrated forms, respectively. Under the conditions of our experiments ($[H^+] > 0.33$ M), the dissociated forms can, therefore, be neglected.

In view of these findings, in the first-order relation

$$\log \frac{C}{C_0} = \frac{k_1}{2.303} t \quad (2)$$

k_1 must be identified with k^1_{obsd}, and

$$C_0 = [\text{h-pyr}]_0 \quad (3)$$

$$C = [\text{h-pyr}]_0 - [\text{h-pyr}]_t \quad (4)$$

where $[\text{h-pyr}]_0$ is the initial concentration of the hydrated form of pyruvic acid and $[\text{h-pyr}]_t$ the concentration reacted at time t, given by

$$[\text{h-pyr}]_t = \frac{(A_t - A_i)}{\epsilon \ell} \quad (5)$$

Therefore

$$\log \frac{(A_t - A_i)}{\epsilon \ell [\text{h-pyr}]_0} = -\frac{k_1}{2.303} t \quad (6)$$

In applying eq 6 three cases should be distinguished.

If $[\text{pyr}]_0 \leq 0.5[Cr^{2+}]_0$ the initial absorbance corresponds to $0.4[\text{pyr}]_0$ and after the second stage all pyruvic acid added has reacted. Therefore

$$[\text{pyr}]_0 = A_f/\epsilon \ell \quad (7)$$

and

$$[\text{h-pyr}]_0 = \frac{(A_f - A_i)}{\epsilon \ell} \quad (8)$$

Substituting eq 8 into eq 6 we obtain eq 1 (with k^1_{obsd} replaced by k_1). Under these conditions this equation is therefore valid, but it does not represent transformation of a precursor complex to Cr_2Ic^{4+}. If $0.4[\text{pyr}]_0 > 0.5[Cr^{2+}]_0$ or $[\text{pyr}]_0 > 1.25[Cr^{2+}]_0$, all chromous ion has been consumed upon mixing, there is no second stage anymore, $A_f = A_i = A_t$, and eq 6 has no meaning.

In the intermediate case, i.e., for $1.25[Cr^{2+}]_0 > [\text{pyr}]_0 > 0.5[Cr^{2+}]_0$, eq 7 and 8 and therefore 1 are not valid and this is why in this region the corresponding plots are not linear. Equation 6, however, can still be used in the form

$$\log \frac{0.6[\text{pyr}]_0 - \frac{1}{\epsilon \ell}(A_t - A_i)}{0.6[\text{pyr}]_0} = -\frac{k_1}{2.303} t \quad (9)$$

Applying eq 9 on the data for initial pyruvic acid concentrations in the range between $1.25[Cr^{2+}]_0$ and $0.5[Cr^{2+}]_0$, using absorptivities from Figure 2, we obtain good straight lines (Figure 6). This fit provides an excellent cross check of the data and of the interpretation.

Our values for the activation parameters and the rate constant at 25 °C of reaction I are also in very good agreement with the activation energy (14.5 ± 1.2 kcal mol^{-1}) and the rate constant ($k^2_{obsd} = 2.8 \pm 0.5$ M^{-1} s^{-1}) obtained by another method[11] (pressure jump). In the light of this agreement and the absence of a Cr^{II} term in the rate law, we suggest that,

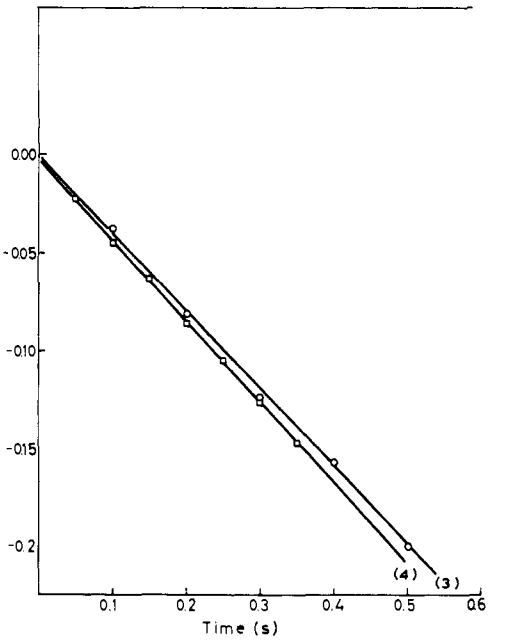

Figure 6. Data from curves 3 and 4 of Figure 5 are replotted here using eq 9. Ordinate in this plot corresponds to

$$\log \frac{0.6[\text{pyr}]_0 - (1/\epsilon \ell) \log V_i/(V_\infty + y)}{0.6[\text{pyr}]_0}$$

V_i, V_∞ and y are explained in Figure 1. Curves 3 and 4 of Figure 5 become straight lines in this plot giving values for k^1_{obsd} of 0.92 and 0.95 s^{-1}, correspondingly.

under the conditions of our experiments, catalysis of reaction I by Cr^{II} is insignificant compared with the catalysis by hydrogen ions. Although catalysis of the pyruvic acid dimerization reaction by metals has been reported,[8] no similar effect for reaction such as I has ever been studied.

A comparison with the reaction of Cr^{2+} (aqueous) with pyruvatopentamminecobalt(III)[4] is also instructive. Thus, it should first be recalled that in our case electron transfer *to* the ligand is over within the time of mixing (<10 ms). In the case of the pyruvato complex electron transfer *through* the ligand is considerably slower ($k = 10^4$ M^{-1} s^{-1}). Yet, in the case of the cobalt complex, there is definitely no reduction of the ligand, even with excess chromous ion. If the "free" ligand is readily reduced so, why is the ligand bound to Co^{III} or to Cr^{III} in the product so inert? And why is the reaction of the free ligand so much faster? Reduction of the "free" ligand *after* it is liberated from the Co^{II} coordination sphere does not have to be considered, since within the time scale of the redox reaction the ligand is not really liberated but it is simply transferred to the Cr^{II} coordination sphere.

A tentative answer to these questions is simply that the transient $CH_3C^-(=OCr^{III})COOCo^{III}$ has no site for simultaneous facite attack by another Cr^{2+}. In fact, we are tempted to suggest that many of the reducible organic ligand mediating in electron transfer between metal ions do not undergo two-electron reduction themselves, simply because they do not have a third (polar) site for attack by another low-valent metal ion. Electrostatic repulsions resulting from the accumulation in a small space of too many positive charges will certainly play an important role in this case, but they can perhaps be minimized by a selection of ligands having polar groups remote from each other.

In the reduction of "free" pyruvic acid, the two electrons go directly into the low-lying empty orbital of the ligand. In view of the high rates, involvement of higher lying orbitals can safely be excluded.[12] In the case of the pyruvato complex, the electron ends up at the Co^{III} "hole", but through the same low-lying

acceptor orbital, as perturbed by the central ion, etc. This is true whether electron transfer takes place by a conjugatively stabilized radical-cation transition state as suggested by Gould[4c] or by a resonance mechanism following preparation of the acceptor and donor sites as suggested by Price and Taube.[4b] If, then, for a given reducing agent, this orbital were the main factor in determining the energy barrier, it would have been reasonable to expect the transfer of one electron to Co^{III} to be at least as fast as the transfer of the two electrons to the "free" ligand. The fact then that this is not the case indicates that the rate is determined by other factors, e.g., preparation of the acceptor and donor sites as suggested by Price and Taube.

In continuing the comparison it is also interesting to note that the product Cr_2lc^{4+} obtained in the reaction of Cr^{2+} (aqueous) with "free" pyruvic acid has ϵ_{max} 59 at λ_{max} 420 nm and ϵ_{max} 45 at λ_{max} 570 nm. These absorptivity values indicate that one of the two Cr^{III} ions forms with the ligand a chelated ring. In contrast, the product, and presumably the activated complex as well, in the reduction of the pyruvato complex of Co^{III} is monodentate. In fact it has been suggested[4b,c] in this case that chelation in the activated complex is not an important factor in determining the relative rates. Extension of this conclusion to include the reduction of the "free" ligand as well cannot be made offhand. The differences in rates between the bound and the unbound ligand are clearly associated with structural differences.

Acknowledgments. The authors thank Mrs. K. Kaplany-Aravany for secretarial assistance and Mrs. E. Kissa-Meidany for laboratory assistance. We also thank the Analytical Laboratory of N.R.C. "Demokritos" for analytical work.

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Electron Spin Resonance Line-Width Alternation and Na^+ Transfer in the Ion Pairs of 3,5-Dinitropyridine

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Received August 17, 1977

Abstract: An ESR study of the ion pairs of 3,5-dinitropyridine with alkali metals in tetrahydrofuran and 1,2-dimethoxyethane is reported. The analysis of the ESR spectra of the ion pair with Na^+ after the addition of sodium tetraphenylborate shows an intermolecular cation transfer between $DNP^-{\cdot}Na^+$ and $Na^+BPh_4^-$. Kinetic parameters are compared with those of the corresponding reaction of *m*-dinitrobenzene. The interpretation of the ion pairs structure is supported with ab initio calculations of the electrostatic potential generated by the 3,5-dinitropyridine radical anion. The spin distribution in the ion pair is computed by the McLachlan method modified according to McClelland. The same method is adopted to study the exchange mechanism by evaluating the association energy for the triple ions.

Introduction

Line-width alternation effects in the ESR spectra of a number of ion pairs obtained by alkali metal reduction of aromatic substrates have been widely investigated.[2] These effects are generated by the relative motions of the counterions causing various magnetic field modulations; thus the line width is essentially a kinetic parameter, and allows a description of the ion pair dynamics.

Following a research on radical ions of nitropyridine derivatives,[3-5] we have previously determined the hfs constants of the free radical anion of 3,5-dinitropyridine (DNP) obtained by electrolytic reduction in different solvents.[6,7]

In this paper we report an ESR study of ion pair association of DNP with alkali metals in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). Information on the structure of the ion pairs is also obtained by the electrostatic potential method based on an ab inito wave function.[8-10]

In particular we investigate the rate and the mechanism of sodium exchange reaction in the $DNP^-{\cdot}Na^+$ system when another source of metal ions, such as sodium tetraphenylborate ($NaBPh_4$), is added to the solution.

A comparative analysis of the ESR spectra of *m*-dinitrobenzene (MDNB)–sodium after the addition of $NaBPh_4$[11] is presented.

Experimental Section

DNP was obtained following the method suggested by Plazek,[12] mp 106 °C. $NaBPh_4$ (Fluka) was used without additional purification.

0002-7863/78/1500-3132$01.00/0