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High-Conductivity Solid Electrolytes. Tropyllium Iodide–Silver Iodide System

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Since the discovery[1-3] of the family of high-conductivity solid electrolytes MAg_4I_5 (M = K, Rb, NH_4), we have carried out an extensive search for high ionic conductivity in other AgI double-salt systems. We have previously reported the discovery of many compounds of high ionic conductivity in the systems QI–AgI, where Q^+ is an ammonium ion[4-6] or a sulfonium ion.[7] The high Ag^+ mobility in these compounds has been attributed to the unique crystal structures characterized by face-sharing iodide polyhedra, forming channels of Ag^+ sites through the structure, and by a large excess of vacant Ag^+ sites in the unit cell.[8-11]

In this paper we report our investigation of the tropyllium iodide (C_7H_7I)–silver iodide system, the first examination of a stable carbonium ion system.

Experimental Section

Using the method of Kursanov and Vol'pin[12] for the preparation of tropyllium chloride, a stirred mixture of 41 g of PCl_5 in 500 ml of CCl_4 was treated dropwise with 9 g of cycloheptatriene in 50 ml of CCl_4. The system was protected by a $CaCl_2$ tube. After addition of the triene was complete, the heavy slurry was stirred for 2 hr at room temperature and was then filtered through a coarse frit. The collected filtrate was cooled in Dry Ice and 20 ml of H_2O was added dropwise with stirring. Much heat and HCl were evolved. After warming to 25°, 50 ml of 55% HI was added to the solution of C_7H_7Cl, followed by 200 ml of acetone. Bright red crystals of C_7H_7I separated, were collected, washed with acetone, and stored in vacuo.

Mallinckrodt reagent grade AgI was used without further purification. The AgI–C_7H_7I compositions were prepared by the paste preparation procedure previously described.[4] The measurement of the density of the electrolytes has also been described.[4] The conductivities were measured using the cell Ag, $RbAg_4I_5$–sample–Ag, $RbAg_4I_5$ as previously reported.[4,13] All measurements were made at 22°.

Results

The experimentally determined densities and specific conductivities are shown in Table I. Contact resistances[13] were not determined; the reported values for the specific conductivities therefore represent a lower limit. Our experience[4] indicates that the corrected values would be 5–8% higher.

Discussion

The observed maximum in specific conductivity around 80–85 mol % of AgI, while not as sharp as that observed in other systems,[4,6-8] indicates that at least one compound with specific conductivity greater than that of AgI is formed in this system. More work would be necessary to establish the exact stoichiometry of the conductive compound (or compounds). The fact that the electrochemical cell Ag–$C_7H_7I{\cdot}4AgI$–C, $(CH_3)_4NI_9$ has the correct potential of 0.63 V indicates that the conduction is primarily ionic, rather than electronic.[14]

Table I. Density and Specific Conductivity in the Tropyllium Iodide–Silver Iodide System

Mol % of AgI	Density, g/cm^3	Specific conductivity, (ohm cm)$^{-1}$
75	4.16	5.04×10^{-3}
80	4.42	5.84×10^{-3}
85	4.69	5.78×10^{-3}
90	4.97	5.30×10^{-3}
95	5.33	1.94×10^{-3}
100	5.75	4.00×10^{-4}

The highest conductivity we have observed for onium iodide–silver iodide compounds is 0.06 (ohm cm)$^{-1}$ (e.g., for diethyldimethylammonium[4] and quinuclidinium[6]); the maximum conductivity shown in Table I is an order of magnitude less, but still an order of magnitude greater than the conductivity of pure AgI. The inorganic compound $RbAg_4I_5$ has a specific conductivity of 0.26 (ohm cm)$^{-1}$.

The work presented here supports our previous conclusions[4,6,7] that there are a multitude of QI–AgI solid electrolytes exhibiting high ionic conductivity and that the Q^+ ion, whether ammonium, sulfonium, or, as in this case, carbonium, serves merely to stabilize a structure through which the Ag^+ ion can move freely.[15] The most important characteristic of the Q^+ ion seems to be its size, rather than its composition and structure.[4,6]

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Registry No. AgI, 7783-96-2; C_7H_7I, 1316-80-9.

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Interaction of Cobalt(II)–Glycylglycine Chelates with Molecular Oxygen. Species in Solution[1a]

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The nature of the factors governing the properties of cobalt oxygen complexes has recently elicited considerable interest.[2-4]

Cobalt complexes of amino acids and dipeptides which interact with dioxygen have received particular attention as models for biological metal–dioxygen interaction.

The cobalt(II)–glycylglycine system has been studied in some detail[5-9] but is still poorly understood, as such studies have failed to concentrate on all the molecular species in solution. In particular, it has previously been generally assumed[6-8] that only the bis-glycylglycine chelate interacted with molecular oxygen, such assumption being based primarily on Fallab's widely accepted contention[7,10] that only complexes which contain three nitrogens in the coordination sphere could interact with oxygen. This "3 N" rule, however, has recently been disproved by studies of the cobalt complexes of the isomeric ethylenediaminediacetic acids.[2a,4]

Nakon and Martell[9] have proposed the existence of a mono(glycylglycine)cobalt–oxygen complex as a catalytic intermediate, yet the question of whether such an assignment is correct is complicated by the fact that the low equilibrium constant for metal–glycylglycine complex formation prohibits the study of an isolated 1:1 system, as a large excess of ligand is required to inhibit precipitation of the metal.

We have undertaken kinetic studies in an attempt to resolve this question, by combining kinetic and equilibrium data to elucidate which molecular species do in fact react with dioxygen.

Experimental Section

Materials. Glycylglycine hydrochloride was obtained from Sigma Chemical Co. and was used without further purification. Cobalt(II) solutions were standardized by EDTA titration using murexide as an indicator.

Kinetic Experiments. Kinetics of the interaction of oxygen with cobalt(II)–glycylglycine species were followed spectrally on a Durrum Jasco D150 stopped-flow spectrophotometer by monitoring the increase in absorbance of a characteristic metal–ligand charge-transfer band at ~352 nm. Large excess quantities of ligand (Co:GG < 1:8) were required to maintain homogeneity. In a typical experiment, equilibrated solutions of cobalt and glycylglycine at a high pH were prepared under nitrogen with rigorous exclusion of air and were allowed to react with oxygenated strong base (1.0 *M* KOH or NaOH). A minimum tenfold excess of complex over oxygen was maintained, and good pseudo-first-order kinetics were obtained.

Results and Discussion

Concentration distributions for the species of interest were calculated by a Newton Raphson iterative method, utilizing the critical stability constants reported by Smith and Martell.[11] The results of these calculations are given in Table I.

Having resolved the raw data into the important molecular species, the refined data were subjected to the following treatments. First, it was assumed that only the bis(glycylglycine)cobalt chelate reacts with molecular oxygen, and on this basis a rate constant (k_1) giving the best fit for all data was calculated by a standard least-squares procedure. In a second treatment it was assumed that both the bis-glycylglycine chelate and the mono-glycylglycine chelate promote the combination of cobalt with dioxygen, to form two oxygen complexes which would absorb at or around 352 nm. Thus the observed absorbance change and value of k_{obsd} would be due to a sum of the contributions of the $Co_2(GG)_4O_2$ and $Co_2(GG)_2O_2$ complexes, and $k_{\text{obsd}} = k_1'[\text{CoGG}] + k_1''[\text{Co(GG)}_2]$. Here the constants k_1' and k_1'' include not only the rate constant but a constant of the form ϵ'/ϵ'' which accounts for the differences (if any) in the molar extinction coefficients of the different complexes at the wavelength observed. Best values for k_1' and k_1'' were calculated by a linear least-squares procedure.

Both our own data and raw data reported by Watters and Wilkins, which we have resolved with respect to molecular species, were considered. We have repeated some of their measurements and found them to be in excellent agreement with our own results. These results are presented in Table II.

Table I. Equilibrium Concentrations of 1:1 and 2:1 Glycylglycine–Cobalt(II) Complexes at pH 11

Total ligand, mmol	Metal total, mmol	[ML], *M*	$[ML_2]$, *M*
20.06[a]	0.28	5.91×10^{-5}	2.18×10^{-4}
10.06[a]	0.28	9.59×10^{-5}	1.74×10^{-4}
20.20[a,b]	1.10	2.44×10^{-4}	8.42×10^{-4}
10.10[a,b]	0.55	1.86×10^{-4}	3.24×10^{-4}
10.00[b]	1.00	3.68×10^{-4}	5.88×10^{-4}
10.00[b]	0.50	1.76×10^{-4}	3.05×10^{-4}

[a] Reference 5. [b] This study.

Table II. Calculated and Observed First-Order Rate Constants (sec^{-1})

k_{obsd}	$k_1[ML_2]^c$	Diff	$k_1'[ML]^c + k_1''[ML_2]^c$	Diff
2.6[a]	2.8	0.2	2.6	0
2.3[a]	2.26	0	2.24	0.1
10.5[a]	10.9	0.4	10.6	0.1
4.4[b]	4.2	0.2	4.6	0.2
8.4[b]	7.6	0.8	8.6	0.2
4.2[b]	3.9	0.3	4.3	0.1

[a] Reference 5. [b] This study. [c] Best values; $k_1 = 1.3 \times 10^4$ M^{-1} sec^{-1}; $k_1' = 0.75 \times 10^4$ M^{-1} sec^{-1}; $k_1'' = 1.0 \times 10^4$ M^{-1} sec^{-1}.

Although the fit obtained by considering only the bis-glycylglycine species is reasonably good, it seems apparent that the consideration of an active mono-glycylglycine chelate results in an improved description of the kinetics of the system.

Since such an improvement might, in fact, be due merely to the introduction of any second parameter, the results were subjected to a multiple-regression analysis to determine the statistical significance of the description obtained relative to the description utilizing only the bis chelate. For the data in Table I, the correlation coefficient obtained considering only $Co(GG)_2$ is $r_{12}^2 = 0.95$. The correlation coefficient $R_{1.23}^2 = 0.99$. The coefficient of partial correlation is $r_{13.2}^2 = (R_{1.23}^2 - r_{12}^2)/(1 - r_{12}) = 0.8$. Subjecting these results to a *t* test $[t = (r_{13.2}^2(n))/(1 - r_{13.2}^2)^{1/2}]$ shows significance at the 2% level; i.e., the chance of the observed improvement occurring by the introduction of a nonsignificant variable is less than 2%.

Thus we can state with some assurance that the consideration of oxygen complexation by the CoGG species results in a statistically and, by inference, physically meaningful description of the system. This result lends support to the earlier catalytic studies of Nakon and Martell and points out the importance of obtaining and applying equilibrium data in interpreting kinetic studies of such complexes.

The probable oxygen binding of the CoGG complex is further supported by the interaction of the cobalt(II)–glycylglycinemonoacetic acid (GGMA)[13] complex at high pH. Earlier studies had shown complexes of glycylglycinediacetic acid (GGDA) to be inactive in promoting the combination of cobalt with molecular oxygen. The complex $[\text{CoGGDA}]^{2-}$, however, has an overall negative charge of 2, which might inhibit the formation of the formally negative peroxide bridge required in oxygen complex formation. Thus the difference in oxygen affinity of the various peptide derivatives may be a matter of simple electrostatics.

We are pursuing further studies of these complexes.

Registry No. Cobalt, 7440-48-4; glycylglycine, 556-50-3; oxygen, 7782-44-7.

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Mechanism of Formation of Bis(pyridine)oxoosmium(VI) Esters. Effect of Pyridine Activity on the Apparent Rate Law

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In previous work from this laboratory,[1] we suggested that the kinetics of formation of the title compounds could be explained by a three-term rate law

$$v = k_0[\mathrm{OsO_4}][\mathrm{S}] + k_1\beta_1[\mathrm{OsO_4}][\mathrm{S}][\mathrm{py}] + k_2\beta_2[\mathrm{OsO_4}][\mathrm{S}][\mathrm{py}]^2$$

where py = pyridine and S = substrate.

In accordance with this proposal, linear plots of $(k_\psi - k_0[\mathrm{S}])/[\mathrm{S}][\mathrm{py}]$ vs. [py] were observed under pseudo-first-order conditions (OsO_4 concentration limiting) from which values of $k_1\beta_1$ and $k_2\beta_2$ were evaluated. Estimates of β_1 and β_2 were obtained from absorbance changes of OsO_4–pyridine mixtures as a function of pyridine concentration.

However, discrepancies appeared on closer analysis of our data: (1) plots of the absorbance changes of OsO_4–pyridine mixtures which assumed the existence of both $OsO_4 \cdot py$ and $OsO_4 \cdot 2py$ were not linear over the entire concentration range;[1] (2) the square term in pyridine concentration assumed importance in the kinetic analysis at lower concentrations than required by the data on complex formation; (3) examination of the ir and Raman spectra of concentrated solutions of OsO_4 and pyridine showed no bands other than those attributable to OsO_4, $OsO_4 \cdot py$, and pyridine.[2]

This situation is resolved by our observation that plots of the square of pyridine activity[3] vs. k_ψ are linear over the entire pyridine concentration range investigated (Figure 1). We conclude that there is no significant term which is first order in pyridine and that the fit of the data to the three-term rate law is an algebraic consequence of the fact that as the quantity of pyridine increases, the $(k_\psi - k_0[\mathrm{S}])/[\mathrm{S}]a_{\mathrm{py}}$ term becomes increasingly larger than the corresponding term in [py], while the a_{py} term itself becomes increasingly smaller than the [py] term (Figure 2). Kirby and Jencks[4] have previously observed apparent self-association of pyridine with consequent kinetic deviations. The rate law is thus

$$v = k_0[\mathrm{OsO_4}][\mathrm{S}] + k_2'[\mathrm{OsO_4}][\mathrm{S}]a_{\mathrm{py}}^2$$

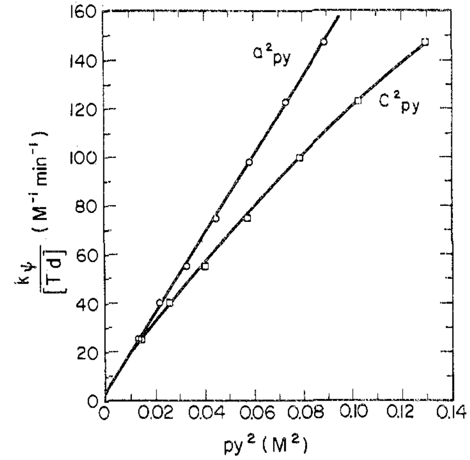


Figure 1. Kinetics of the reaction of osmium tetroxide with thymidine (Td) as a function of the quantity of pyridine present. The data are taken from ref 1a, Figures 3 and 4. C^2_{py} is the square of pyridine concentration; a^2_{py} is the square of pyridine activity.

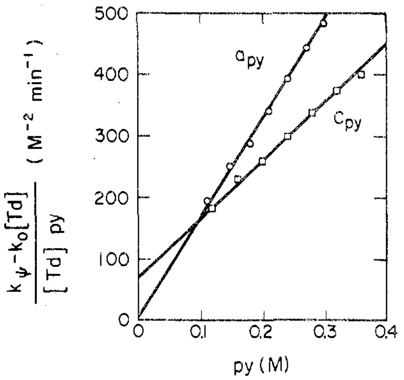
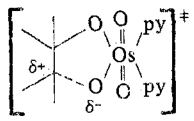
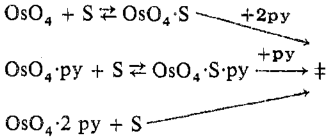


Figure 2. Linear plots of $k_\psi/[\mathrm{py}]$ vs. [py] using either pyridine concentration or activity. Note the y intercept for the concentration plot which gave rise to the spurious k_1 term. The data are taken from ref 1a, Figures 3 and 4.

This rate law is in accordance with an activated complex which contains two pyridine ligands



We write this species with partial bond formation to account for the high stereospecificity of the reaction.[5] We cannot, however, with the data at hand, adequately distinguish among the possible pathways which might lead to this activated complex



Our preference is for the second pathway which also fits Burton's data[6] on the ammonia–OsO_4 reaction and our observations on the α,α′-dipyridyl–OsO_4 system. Burton[6] observed only 1:1 complex formation between OsO_4 and ammonia but second-order kinetic dependence on ammonia concentration over the same range. The activity coefficient of ammonia, in contrast to that of pyridine, is essentially constant and equal to 1 under Burton's conditions.[7] We find that although the α,α′-dipyridyl–OsO_4 stability constant is very small, the rate