1402 Inorg. Chem. 1983, 22, 1402-1404

Electronic. The electronic spectra of ~10^{-4} M solutions of the isolated products showed peaks that corresponded with the ruthenium(II) nitrile analogues of the starting oximes.[2b,5] These spectra were also in good agreement with the solution spectra of the reaction solution before product isolation. The infrared and electronic spectral data are summarized in Table I.

Discussion

The reaction between $(H_3N)_5RuH_2O^{2+}$ and aldoximes produces ruthenium(II) nitrile compounds, as indicated by their characteristic infrared and electronic spectral properties. These observations can be explained by a stepwise mechanism in which $(H_3N)_5RuOH_2^{2+}$ produced by reduction of $(H_3N)_5RuOH_2^{3+}$ undergoes substitution by the oxime ligand, followed by rapid dehydration to the nitrile product (eq 1–3).

$$(H_3N)_5RuOH_2^{3+} \xrightarrow[\text{slow}]{\text{Zn/Hg}} (H_3N)_5RuOH_2^{2+} \quad (1)$$

$$(H_3N)_5RuOH_2^{2+} + HON{=}CHR \xrightarrow[\text{fast}]{k_s} [(H_3N)_5RuN(OH){=}CHR^{2+}] + H_2O \quad (2)$$

$$[(H_3N)_5RuN(OH){=}CHR^{2+}] \xrightarrow[\text{very fast}]{k_d} (H_3N)_5RuN{\equiv}Cr^{2+} + H_2O \quad (3)$$

This facile conversion contrasts greatly with the much more strenuous conditions (e.g., prolonged refluxing in glacial acetic acid) normally required for the dehydration of aldoximes and thus provides an unequivocal demonstration of the driving force provided by the Ru(II) center, via back-bonding, in going from the sp^2 to sp hybridization on nitrogen. An estimate of the rate of reaction 2 for R = CH_3 was obtained from a competition reaction in which equimolar $HON{=}CHCH_3$ and pyridine were used. A product ratio of $(H_3N)_5RuN{\equiv}CCH_3^{2+}$ to $(H_3N)_5Ru(py)^{2+}$ of 2.3 to 1 was found. Using the published rate constant[6] for the pyridine reactions leads to $k_s \simeq 0.2$ M^{-1} s^{-1} in good agreement with that reported for imidazole,[6] which contains a chemically similar (nonaromatic, sp^2) nitrogen.

With 4-pyridinecarboxaldoxime at high concentration, the only product detectable is $(H_3N)_5RuN{\equiv}Cpy^{2+}$, establishing almost exclusive attack of $(H_3N)_5RuOH_2^{2+}$ at the oxime group. This enhanced preference for oxime compared to the competition reaction described above may be due in part to a deactivation of the pyridine site in this ambidentate ligand. The appearance of a second visible peak in product formed at lower oxime concentration cannot be due to the presence of linkage isomer (which should be concentration independent); we believe it represents the bridged dimer formed when $(H_3N)_5RuOH_2^{2+}$ is generated in the presence of $(H_3N)_5Ru{\equiv}Cpy^{2+}$ at depleted oxime levels. For 2-pyridinecarboxaldoxime steric as well as electronic effects are probably involved. In the case of the 2- and 3-pyridinecarboxaldoximes, the only product observed was the cyanopyridine complex. These results parallel those found for the corresponding cyanopyridine complexes where direct substitution produces only the cyano-bound isomers.[5,7]

Similar reactivity has been found for oximes containing α-carbonyl groups. These reactions produce a ruthenium(II) nitrile product and carboxylic acid via C–C bond scisson.[8]

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Registry No. $[(H_3N)_5RuN{\equiv}CCH_3](ClO_4)_2$, 41654-94-8; $[(H_3N)_5RuN{\equiv}CC_6H_5](ClO_4)_2$, 26259-25-6; $[(H_3N)_5RuN{\equiv}C\text{-}2\text{-}C_4H_4N](ClO_4)_2$, 28589-23-3; $[(H_3N)_5RuN{\equiv}C\text{-}3\text{-}C_4H_4N](ClO_4)_2$, 30897-96-2; $[(H_3N)_5RuN{\equiv}C\text{-}4\text{-}C_4H_4N](ClO_4)_2$, 85096-98-6; $[(H_3N)_5RuCl]Cl_2$, 18532-87-1; $(H_3N)_5RuOH_2^{2+}$, 21393-88-4; $HON{=}CHCH_3$, 107-29-9; $HON{=}CHC_6H_5$, 932-90-1; $HON{=}CH\text{-}2\text{-}C_4H_4N$, 873-69-8; $HON{=}CH\text{-}3\text{-}C_4H_4N$, 1193-92-6; $HON{=}CH\text{-}4\text{-}C_4H_4N$, 696-54-8.

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(6) Shepard, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.

(7) Allen, R. J.; Ford, P. C. *Inorg. Chem.* **1972**, *11*, 679.

(8) Guengerich, C. P.; Schug, K. R. *Inorg. Chem.* **1983**, *22*, 181.

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Reaction Kinetics of Several Alkyl Arsenite Hydrolyses

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Arsenic compounds are known for their toxicity and are pollutants from some industrial processes.[2,3] On the other hand, certain arsenic compounds enhance the growth of poultry and swine, and there is evidence to suggest that it is an essential element in rat physiology.[4] In order to more fully understand the role of arsenic compounds in physiological systems, we have been investigating the kinetic behavior of simple systems containing As–O bonds with the arsenic in the 5+[5–8] and 3+[9,10] states. The hydrolysis of trialkyl arsenites (reactions 1–3)

$$H_2O + As(OR)_3 \xrightarrow{k_1} HOAs(OR)_2 + ROH \quad (1)$$

$$H_2O + HOAs(OR)_2 \xrightarrow{k_2} (HO)_2AsOR + ROH \quad (2)$$

$$H_2O + (HO)_2AsOR \xrightarrow{k_3} H_3AsO_3 + ROH \quad (3)$$

has been shown to occur with exclusive As–O bond fission.[11] We report here the kinetics of the first step (reaction 1) for $As(OR)_3$ (R = Me, Et, *i*-Pr), as well as the cage arsenite (4-methyl-2,6,7-trioxa-1-arsabicyclo[2.2.2]octane), and for R = Et we report an indication of the rates of reaction 2 and/or 3.

Experimental Section

Materials. The trialkyl arsenites were prepared by a variety of methods[12,13] although the methods of Brill and Campbell[14] were found to be the most convenient. The compounds were characterized by NMR, IR, and boiling point data. The cage arsenite, previously prepared by Verkade and Reynolds,[15] was obtained by the transesterification reaction of trimethyl arsenite with 2-(hydroxymethyl)-2-methyl-1,3-propanediol. Stoichiometric amounts of the

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(1) (a) Providence College. (b) Brown University.

(2) Sarquis, M. *J. Chem. Educ.* **1979**, *56*, 815.

(3) Dagani, R. *Chem. Eng. News* **1981**, *59* (Sept 16), 29.

(4) Underwood, E. R. In "Trace Elements in Human and Animal Nutrition"; Academic Press: New York, 1977; pp 424–428.

(5) Baer, C. D.; Edwards, J. O.; Kaus, M. J.; Richmond, T. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1980**, *102*, 5793.

(6) Baer, C. D.; Edwards, J. O.; Rieger, P. H. *Inorg. Chem.* **1981**, *20*, 905.

(7) Richmond, T. J.; Johnson, J. R.; Edwards, J. O.; Rieger, P. H. *Aust. J. Chem.* **1977**, *30*, 1187.

(8) White, P. J.; Kaus, M. J.; Edwards, J. O.; Rieger, P. H. *J. Chem. Soc., Chem. Commun.* **1976**, 429.

(9) Edwards, J. O.; Okumura, A.; Rieger, P. H.; Toyomi, Y., unpublished data on transesterification reactions of $As(OCH_3)_3$.

(10) Copenhafer, W. C.; Rieger, P. H. *J. Am. Chem. Soc.* **1978**, *100*, 3776.

(11) Ford, G. C.; Edwards, I. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *2*, 95.

(12) Klement, R.; Rueber, R. *Ber. Dtsch. Chem. Ges. B* **1935**, *68*, 1761.

(13) Moedritzer, M. *Inorg. Synth.* **1968**, *14*, 181.

(14) Brill, T. B.; Campbell, N. C. *Inorg. Chem.* **1973**, *12*, 1884.

(15) Verkade, J. G.; Reynolds, L. T. *J. Org. Chem.* **1960**, *25*, 663.

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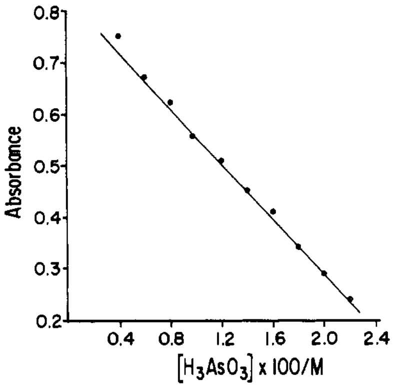

Figure 1. Absorbance of indicator solution, $[H_2In] = 1.5 \times 10^{-2}$ M and $[NaOH] = 2.8 \times 10^{-2}$ M, vs. arsenous acid in acetonitrile/30% H_2O.

reagents were stirred overnight in a stoppered flask with a small amount of acetonitrile. After removal of solvent and methanol, the crude $As(OCH_2)_3CCH_3$ was sublimed under vacuum at 57 °C. The product, clear rhombic crystals, was obtained in ~50% yield (no attempt was made to maximize yield); mp, 39–40 °C vs. lit. mp 41–42 °C. Phenol red indicator (Fisher Scientific) was used without further purification. Other reagents and solvents were prepared and purified as previously reported.[5,6]

Procedure. The hydrolysis reactions were followed on a Durrum-Gibson D110 stopped-flow spectrometer by utilizing an indicator method similar to that previously reported.[6] Since the pK_a's of the indicator, phenolphthalein, and the product, arsenous acid, are similar (9.2 and 9.29, respectively), there was concern that the observed absorbance might not be linear in product concentration. However, as shown in Figure 1, the indicator absorbance was in fact a satisfactory linear function of added arsenous acid. Also nothing in any of the rate runs suggested other than such a linear relationship. Thus, in a typical hydrolysis experiment, one drive syringe of the apparatus contained an acetonitrile/water stock solution of indicator (H_2In hereafter), tetraethylammonium bromide (to maintain constant ionic strength), and sodium hydroxide to give, after mixing $[H_2O] = 13.0$ M, $[H_2In] = 0.015$ M, $[NaOH] = 0.027$ M, and $[Et_4NBr] = 0.20$ M. The second syringe contained triethyl arsenite in CH_3CN to give after mixing $[As(OEt)_3] = 0.020$ M. The absorbance was monitored on an oscilloscope and the trace photographed for data analysis.

Rates were determined at four or more temperatures over a 30 °C range; about ten runs were done at each temperature to average out any temperature fluctuations during the experiment. Photographs were digitized by hand over the first half-life of the reaction, and pseudo-first-order constants were calculated by a linear least-squares fit of $-\ln (A_t - A_\infty)$ vs. time with a TRS-80 Model I microcomputer.

Results and Discussion

The hydrolysis intermediates, $(RO)_2AsOH$ and $ROAs(OH)_2$, are expected to be somewhat stronger acids than arsenous acid.[16] On the other hand, pK_2 for $ROAs(OH)_2$ and pK_2 and pK_3 for $As(OH)_3$ are large so that at most one proton can be transferred to the absorbing indicator species In^{2-}. Since the indicator absorbance responds to formation of the two intermediates as well as the ultimate product, a linear first-order plot is expected only if (a) the rates of reactions 2 and 3 are very rapid compared to that of reaction 1 or (b) the rate of one of the final two steps is much slower than that of the preceding step(s). Case b can be eliminated in that the total absorbance changes for the reactions studied always corresponded to values expected from Figure 1; much larger changes would have occurred if stoichiometric amounts of the mono- or dialkylated species were present. This was not surprising as previous work[6] had shown that the first step in the hydrolysis of trialkyl arsenates is rate determining. However, in this work it was found that under conditions where $[H_2O] >> [As(OR)_3]$ first-order plots were not entirely linear over several half-lives. Deviations from linearity were small in all cases but qualitatively similar in that the initial rates were somewhat more rapid and the final rates somewhat slower than expected for a first-order process. The most reasonable explanation would be that case a almost applies but with one or both of the final steps of the hydrolyses being approximately 5–10 times as rapid as the first step. Thus the observed deviations can be attributed to the presence of significant concentrations of the acidic intermediates. As a check on the order with respect to $As(OR)_3$ an initial rate study was performed for triethyl arsenite. The results are given in Figure 2 where $\Delta A/\Delta t$ is plotted as a function of initial $[As(OEt)_3]$. The linearity of Figure 2 confirms the order of 1. For the sake of internal consistency k_{obsd} values were determined from data taken over 1 half-life. We can, therefore, express the rate as

$$-d[As(OR)_3]/dt = k_{obsd}[As(OR)_3] \quad (4)$$

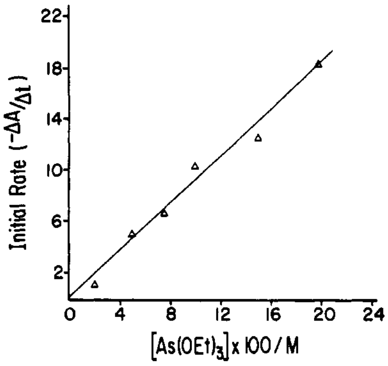

Figure 2. Plot of initial rate, (Δ absorbance)/(Δ time), vs. triethyl arsenite concentration in acetonitrile/30% H_2O.

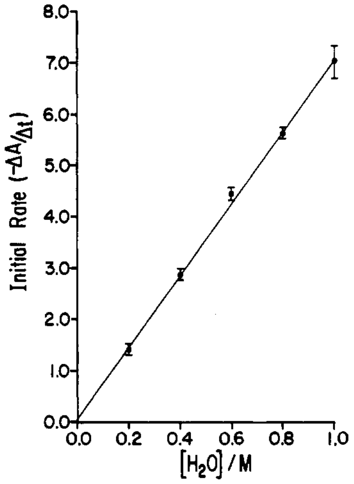

Figure 3. Initial rate, (Δ absorbance)/(Δ time), of trimethyl arsenite hydrolysis, $[As(OMe)_3] = 0.05$ M, vs. water concentration with methanol as solvent.

where k_{obsd} contains any dependence of the rate on water concentration. Conditions and resulting k_{obsd} values for the various arsenities are reported in Table I. The temperature dependence of the trimethyl arsenite hydrolysis was determined in methanol at relatively low water concentrations due to the rapid rate and to the low indicator solubility in acetonitrile.

An experiment was performed to obtain more direct evidence of the presence of the hydrolysis intermediates. Phenol red (pK_a = 7.9), a more acidic indicator, was employed. This indicator is more sensitive to the intermediates than to arsenous acid, due to the relative pK_a values. It was expected, therefore, that there would be an initial, rapid decrease in absorbance followed by an increase in absorbance as arsenous acid is

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[16] Guthrie, J. P. *Can. J. Chem.* **1978**, *56*, 2342.

Table I. Experimental Conditions and k_{obsd} Values[a]

ester	solvent	$[H_2O]$/M	temp/°C	k_{obsd}/s^{-1}
methyl	MeOH	0.092	20.3	0.57
			29.2	0.89
			39.3	1.35
			48.0	2.06
methyl	CH_3CN	17.3	25.0	76
ethyl	CH_3CN	13.0	15.3	2.58
			25.0	3.22
			35.0	6.75
			46.5	10.9
isopropyl	CH_3CN	13.0	9.8	0.053
			15.0	0.069
			26.0	0.123
			37.0	0.208
			44.0	0.284
cage	CH_3CN	13.0	15.0	49
			25.0	54
			36.0	69
			45.0	86

[a] The average standard deviation on k_{obsd} values was 7%.

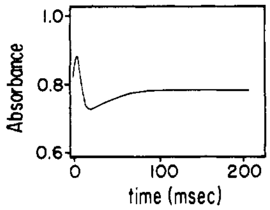

Figure 4. Stopped-flow oscilloscope trace of triethyl arsenite hydrolysis monitored with phenol red indicator at 598 nm. $[As(OEt)_3] = 2.62 \times 10^{-3}$ M; [phenol red] = 2.5×10^{-4} M.

formed. This is what was observed in the oscilloscope trace reproduced in Figure 4.

Experiments determining k_{obsd} at concentrations of water from 13 to 20 M were performed. In general, plots of k_{obsd} vs. $[H_2O]$ were linear in this range, although scatter was present. An initial rate study was done with triethyl arsenite to further clarify the order with respect to water. Methanol was employed as solvent to allow low water concentrations to be used, and a plot of $\Delta A/\Delta t$ vs. $[H_2O]$, Figure 3, was linear. We conclude, therefore, that the general rate law for the compounds studied has the following form at low water concentrations:

$$-d[As(OR)_3]/dt = k_1[As(OR)_3][H_2O] \qquad (5)$$

We approximate k_1 values where low water concentrations were not possible as $k_1 = k_{obsd}/[H_2O]$ and use the values so derived in the determination of activation parameters. Of course, no such approximation was necessary in the case of the trimethyl arsenite hydrolysis in methanol. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained and values of k_1 at 25 °C are reported in Table II. It should be noted that the values of $\Delta S^{\ddagger}$ are subject to systematic error of up to 20%; however, this error is not sufficient to alter the interpretation.

For the trialkyl arsenites the rate decreases by roughly an order of magnitude with each substitution of a carbon atom in the alkyl group, triisopropyl arsenite hydrolyzing some 300 times more slowly than trimethyl arsenite. The activation enthalpies are small for the trialkyl arsenites, and the activation entropies are large and negative. These results are in accord with previous work involving oxygen exchange between arsenite monoanion and water[9]: $k_{25} = 167$ s^{-1}, $\Delta H^{\ddagger} = 25$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -120$ J K^{-1} mol^{-1}. They are also remarkably similar to results on the rates of hydrolysis of arsenate triesters[6] and pyroarsenate ion[7] and the rates of alcohol exchange with arsenate triesters[5] where activation enthalpies ranged from 0 to 50 kJ mol^{-1} and activation entropies from −100 to −200 J K^{-1} mol^{-1}. As in these other cases, a highly associative mechanism is indicated with the probable formation, in this case, of a four-coordinate intermediate.

Table II. Rate Constants and Activation Parameters

ester	k_{25}/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
methyl[a]	8.3	33 ± 1	−116 ± 5
methyl[b]	4.4		
ethyl[b]	0.29	35 ± 5	−138 ± 17
isopropyl[b]	0.0086	34 ± 3	−170 ± 2
cage[b]	4.7	12 ± 2	−190 ± 7

[a] CH_3OH as solvent. [b] CH_3CN/30% H_2O as solvent.

The results obtained with the cage arsenite, on the asumption that the basic features of the mechanism are the same, would suggest that attack of the incoming nucleophile, H_2O, occurs on a face of the arsenite defined by two oxygen atoms and the lone pair of electrons. If attack were to take place on the unique face, defined by the three oxygen atoms, the formation of four-coordinate arsenic would be expected to be more energetically unfavorable than for the trialkyl arsenites. Approach to the arsenic atom from this direction would be sterically hindered by the cage structure, and coordination of the incoming nucleophile, H_2O would require considerable bond breaking in at least one of the rings of the cage. The observed rate constant, $k_1 = 4.7$ M^{-1} s^{-1}, and activation parameters, $\Delta H^{\ddagger} = 12$ kJ mol^{-1} and $\Delta S^{\ddagger} = -190$ J K^{-1} mol^{-1}, certainly do not support such a mechanism. We conclude, therefore, that nucleophilic attack occurs "back side" to the leaving alkoxy group. The considerably lower value of $\Delta H^{\ddagger}$, compared with those of the trialkyl arsenites, is interesting. Possible explanations are (1) the incoming nucleophile is less hindered sterically, allowing for a closer approach to the arsenic in the transition state compared to the case of the trialkyl esters, and thus more bond formation, (2) there is some alleviation of ring strain in the cage upon formation of the proposed four-coordinate intermediate, and (3) some combination of (1) and (2) occurs.

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Registry No. $As(OMe)_3$, 6596-95-8; $As(OEt)_3$, 3141-12-6; As-$(OPr\text{-}i)_3$, 39936-83-9; 4-methyl-2,6,7-trioxa-1-arsabicyclo[2.2.2]octane, 22223-55-8.

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Comparative Studies of the Kinetics of Macrocycle Dissociation from Nickel(II) in the Presence of Excess Copper Ion and 1,10-Phenanthroline

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Previously, the thermodynamics of complexation and the kinetics of formation[2] and dissociation (in the presence of

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