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Equilibrium and Rate Data on Some Arsenite Transesterification Reactions

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The arsenite transesterification reaction $As(OCH_3)_3 + HOR \rightleftharpoons As(OCH_3)_2OR + HOCH_3$ (with R equaling benzyl and *t*-butyl) has been studied in acetonitrile solvent. With benzyl alcohol, K, $\Delta H°$, and $\Delta S°$ are 3.6 (25 °C), 5.0 kJ mol^{-1} and 27 J mol^{-1} K^{-1} respectively; with *t*-butyl alcohol, the values are 0.36 (25 °C), 4.0 kJ mol^{-1}, and 5 J mol^{-1} K^{-1} respectively. The rate law for the approach to equilibrium in the case of benzyl alcohol is:

$$\frac{-\mathrm{d}[As(OCH_3)_3]}{\mathrm{d}t} = k'_f[As(OCH_3)_3][HOCH_2Ph]^2 - k'_r[As(OCH_3)_2(OCH_2Ph)][HOCH_3][HOCH_2Ph].$$

A mechanism which explains the unusual law has been postulated. The slower *t*-butyl alcohol reaction proceeds by a different mechanism which apparently involves catalysis by small amounts of water in the solvent. The steric effects are very significant.

Arsenious acid $As(OH)_3$ and related arsenic(III) compounds are potent inhibitors of enzymes which have a mercaptan function near the active site. Thus, understanding the rates and equilibria of these arsenic compounds is important.

A few studies of replacement rates in arsenic(III) compounds have been carried out. These include an ^{17}O NMR line-broadening investigation of the exchange between arsenite ions and water1) and a quantitative study of the hydrolysis of arsenite triesters.2) In both instances, the rates were too fast for classical rate techniques. Some less definitive studies of the glycol complexing of arsenite ions,3) of the arsenite catalysis of arsenate-oxygen exchange with water,4) and 2-mercaptoethanol complexing of arsenite ions5) gave results also indicating rapid replacement in the arsenic coordination sphere.

In the present work, data on the arsenite transesterification reaction:

$$As(OCH_3)_3 + HOR \rightleftharpoons As(OCH_3)_2(OR) + HOCH_3, \quad (1)$$

with R equaling benzyl and *t*-butyl, have been obtained. With benzyl alcohol, the rates have been found to be rapid; on the other hand, with *t*-butyl alcohol, the reactions are much slower. The mechanisms are strikingly different.

Experimental

Chemicals. Trimethyl arsenite, also known as trimethoxyarsine, $As(OCH_3)_3$, was prepared by two methods,6,7) both of which were found satisfactory. $AsCl_3$ (Aldrich, ultrapure) was used as obtained. All the other materials for the preparations (ether, hexane, triethylamine, and methanol) were dried according to standard procedures.8) The product was characterized by NMR and chloride-ion analysis to see if any side products such as $As(OCH_3)_2Cl$ were present. The $As(OCH_3)_3$ was found to be at least 99.993% pure.

Benzyl alcohol and *t*-butyl alcohol were dried by the usual methods.8) Acetonitrile, which was employed as the reaction solvent, was normally distilled twice from P_2O_5; drying is important because any significant amount of water in acetonitrile will cause cloudiness or turbidity when the arsenite ester is dissolved. In some experiments, we used acetonitrile vigorously dried by the following procedure: 1) The acetonitrile was distilled. 2) It was then stirred with P_2O_5 (about 0.04 g per 10 g of CH_3CN). 3) It was redistilled, collected over 4 Å Molecular Sieves (which had been previously dried by heating in a vacuum oven), and shaken occasionally for 2 h. 4) It was again distilled, and then stored over Molecular Sieves. The dried solvent was taken up just before use by means of a Pasteur pipet with a glass-wool filter.

Equipment. For the benzyl alcohol kinetic runs, a Bruker WP60 FT NMR apparatus was coupled to a specially constructed stopped-flow apparatus based on the design of Couch *et al.*9) The glass tips of the syringes were constructed so that the two solutions were fed directly into the NMR tube. The equilibrium data and kinetic results for the slower *t*-butyl alcohol runs were obtained with the Bruker instrument or with a Varian EM-360 NMR apparatus.

Reaction Analyses. The concentration of the reactant and product species were determined by measuring their NMR peak heights and by comparing them with the known initial concentration of trimethyl arsenite. These peak heights correlated well with the integrated areas, and mass balance was also tested.

Results

Proton NMR. For both equilibrium and rate experiments, the analysis were based on the proton-NMR-line intensities. The chemical-shift assignments in acetonitrile are as follows: $C\underline{H}_3OH$, 3.31 ppm; $(C\underline{H}_3O)_3As$ and $(C\underline{H}_3O)_2AsOCH_2Ph$, both 3.53±0.03 as one line; $PhC\underline{H}_2OH$, 4.59 ppm; $PhC\underline{H}_2OAs(OCH_3)_2$, 4.87 ppm; $C_6\underline{H}_5CH_2OH$, 7.35 ppm; $(C\underline{H}_3)_3COH$, 1.19 ppm; and $(C\underline{H}_3)_3COAs(OCH_3)_2$, 1.37 ppm.

Table 1. Equilibrium constants with benzyl alcohol

t/°C	$[As(OCH_3)_3]_0$/M	$[HOCH_2Ph]_0$/M	K
25	2.75	0.93	3.66
	2.71	1.21	3.58
	2.21	1.70	3.69
	2.06	1.87	3.51
	2.02	1.87	3.51
−25	2.06	1.87	2.34
−20	2.06	1.87	2.38
−15	2.06	1.87	2.65
−11	2.06	1.87	2.93
20	2.06	1.87	3.43
28	2.06	1.87	3.51

Equilibria. The transesterification reaction, Eq. 1, proceeds rapidly to a convenient degree when trimethyl arsenite and the alcohol are in the concentration range from 1 to 3 M.[†]

Some results for the benzyl-alcohol reaction are given in Table 1. At 25 °C, the average value or K from these data is 3.59±0.08 (standard deviation), while from the results in Table 3 it is 3.49±0.04. The temperature dependence of K gives $\Delta H^\circ=5.0\pm0.3$ kJ mol^{-1} and $\Delta S^\circ=27\pm1$ J mol^{-1} K^{-1}. It is important to mention that the evidence for the formation of some $(PhCH_2O)_2As(OCH_3)$ was indicated by a significant increase in the apparent binding constant when there was an excess of benzyl alcohol, therefore, all of the present results are given for the condition, $[PhCH_2OH]_0<[As(OCH_3)_3]_0$ so as to minimize this complication.

Some results with *t*-butyl alcohol are presented in Table 2. The average of the first three values of K therein is 0.364±0.010. Under the kinetics conditions (see below), the observed value was 0.29±0.03. The thermodynamic quantities based on the Table 2 data are $\Delta H^\circ=4.0\pm0.4$ kJ mol^{-1} and $\Delta S^\circ=5.2\pm1.1$ J mol^{-1} K^{-1}. From the equilibrium constant based on the kinetic data in Table 5, the values of ΔH° and ΔS° were found to be 4.2±0.5 kJ mol^{-1} and 6±2 J mol^{-1} K^{-1} respectively; these values are considered somewhat less accurate than those based on the Table 2 data.

Kinetics with Benzyl Alcohol. The stoichiometry of the reaction may be represented as:

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2C \tag{2}$$

with C standing for each product (since they are present in equal concentrations). For purposes of calculation and plotting, it is initially assumed that the orders match the stoichiometry; this assumption can be checked in order to obtain the correct rate law. Thus, the tentative law;

$$\frac{-d[A]}{dt} = k_f[A][B] - k_r[C]^2 \tag{3}$$

is employed. This is converted to the integrated form:

$$\frac{1}{Q}\ln\left\{\frac{([A]_0-[A]_e)([A]-[A]_e+Q)}{([A]-[A]_e)([A]_0-[A]_e+Q)}\right\} = (k_f-k_r)t, \tag{4}$$

where $Q=[1/(K-1)]\{K^2([B]_0-[A]_0)^2+4[A]_0[B]_0K\}^{1/2}$, where the subscripts 0 and e designate the initial and equilibrium states, and where K is obtained for each run separately. If the left-hand side is plotted *versus* the time t, (k_f-k_r) is obtained from the slope; with $K=k_f/k_r$ on the basis of microscopic reversibility, k_f and k_r can be evaluated.

Table 2. Equilibrium constants with *t*-butyl alcohol

t/°C	$[As(OCH_3)_3]_0$/M	$[HOC(CH_3)_3]_0$/M	K
25	3.10	1.65	0.362
	2.82	2.74	0.374
	2.43	3.01	0.355
28	2.82	2.74	0.374
36	2.82	2.74	0.382
45	2.82	2.74	0.404
56	2.82	2.74	0.419
66	2.82	2.74	0.448

As may be seen in Fig. 1a, the plots are linear, with the results from experiments at variable concentrations given in Table 3. The values of k_f and k_r at variable $[As(OCH_3)_3]$ and constant $[PhCH_2OH]$ are essentially constant. On the other hand, when the benzyl alcohol concentration is varied, k_f and k_r both increase in proportion to the concentration; this indicates that the true order is larger by one than the assumed order. Furthermore, the fact the rate plots shown in Fig. 1a are linear over the measured course of reaction suggests that both forward and reverse reactions involve the initial concentration of benzyl alcohol, $[PhCH_2OH]_0$, which may be equated the total alcohol concentration at any time t, $\{[PhCH_2OH]_t+[CH_3OH]_t\}$.

Employing the corrected rate law consistent with the observed results:

$$\frac{-d[As(OCH_3)_3]}{dt} = k_1[As(OCH_3)_3][HOCH_2Ph][HOCH_2Ph]_0 - k_2[As(OCH_3)_2(OCH_2Ph)][HOCH_3][HOCH_2Ph]_0, \tag{5}$$

and the preliminary data in Table 3, the average values of k_1 and k_2 obtained are 0.349±0.008 M^{-2} s^{-1} and 0.100±0.002 M^{-2} s^{-1}. The values of k_1 and k_2 are calculated by using the relations, $k_1=k_f/[HOCH_2Ph]_0$

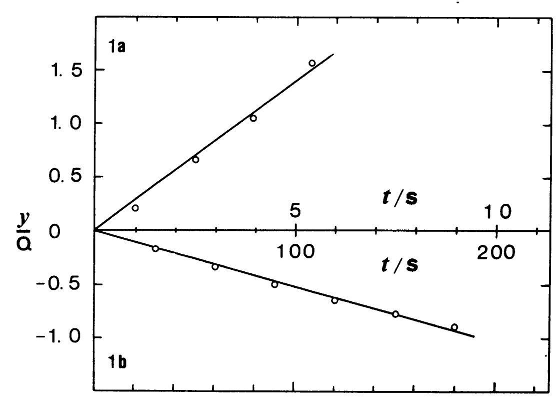


Fig. 1. Rate plots for arsenite transesterification reactions with (a) $[As(OCH_3)_3]=2.02$ M, $[HOCH_2Ph]=1.16$ M, and (b) $[As(OCH_3)_3]=1.69$ M, $[HOC(CH_3)_3]=1.07$ M. The ordinate is the left side of Eq. 4.

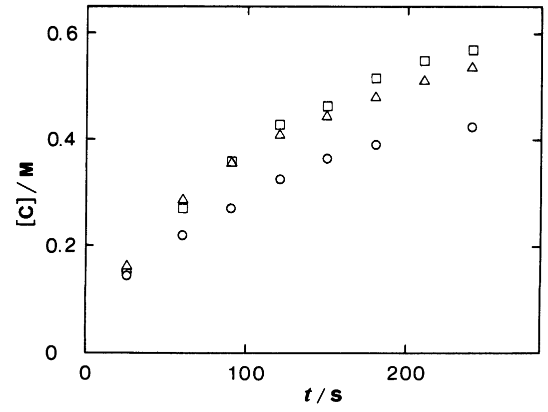


Fig. 2. Plot of $[As(OCH_3)_2OC(OCH_3)_3]$ as a function of time for $[As(OCH_3)_3]_0=2.02$ M, and ○: $[HOC(CH_3)_3]=1.07$, △: 1.67, and □; 2.07 M.

[†] 1 M=1 mol dm^{-3}.

TABLE 3. RATE RESULTS FOR BENZYL ALCOHOL[a)]

$[As(OCH_3)_3]_0$/M	$[PhCH_2OH]_0$/M	$k_f/M^{-1}\ s^{-1}$	$k_r/M^{-1}\ s^{-1}$	$K^{b)}$	$k_1/M^{-2}\ s^{-1}$ [c)]	$k_2/M^{-2}\ s^{-1}$ [d)]
2.02	1.16	0.397	0.115	3.45	0.342	0.099
2.02	1.40	0.497	0.145	3.48	0.355	0.102
2.02	1.87	0.651	0.186	3.50	0.348	0.099
1.17	1.16	0.394	0.113	3.49	0.340	0.097
1.51	1.16	0.415	0.117	3.55	0.358	0.101

a) At 25 °C in the acetonitrile solvent. b) $K=k_f/k_r$. c) $k_1=k_f/[HOCH_2Ph]_0$. d) $k_2=k_r/[HOCH_2Ph]_0$.

TABLE 4. RATE RESULTS FOR *t*-BUTYL ALCOHOL[a)]

$[As(OCH_3)_3]_0$/M	$[HOC(CH_3)_3]_0$/M	$10^3k_f/M^{-1}\ s^{-1}$	$10^3k_f/M^{-1}\ s^{-1}$	$K^{b)}$	$10^3k_3/s^{-1}$ [c)]	$10^3k_4/s^{-1}$ [d)]
2.03	2.07	1.12	3.60	0.31	2.32	7.45
2.03	1.67	1.51	4.63	0.33	2.52	7.73
2.03	1.07	1.87	7.11	0.26	2.00	7.61
1.69	1.07	1.92	7.04	0.27	2.05	7.53
1.25	1.07	1.95	7.11	0.28	2.09	7.61

a) At 25 °C in acetonitrile. b) $K=k_f/k_r$. c) $k_3=k_f[HOC(CH_3)_3]_0$. d) $k_4=k_r[HOC(CH_3)_3]_0$.

and $k_2=k_r/[HOCH_2Ph]_0$ respectively.

It was not possible to obtain the activation parameters because the stopped-flow injector did not have a temperature-control attachment.

The catalysis of the transesterification reaction is important. 1-Pentanethiol, *p*-toluenesulfonic acid, and 2,4-dimethylpyridine, all at concentrations near 10^{-2} M, accelerated the reaction to such an extent that equilibrium was reached in times comparable to or less than the time necessary for getting the first data point.

Kinetics with t-Butyl Alcohol. It is possible to treat the initial rate data for this alcohol in a manner (*i.e.*, Eq. 4) identical with that used for benzyl alcohol. However, the slope is now negative (as would be expected for $K<1$), and the alcohol concentration effect on the slope was in the opposite direction.

A typical plot is shown in Fig. 1b, and the data are presented in Table 4. As the *t*-butyl alcohol concentration increased, the preliminary rate constants decreased. This change in the rate constant indicates that the order assumed in the derivation is too large; these constants vary in such a manner as to indicate that the correct order in *t*-butyl alcohol is zero. This surprising conclusion can be visualized in the plots of the concentration of the product against the time shown in Fig. 2. The initial slopes must be essentially identical because the 30-second points for all three alcohol concentrations are the same, within the limits of experimental error.

The recalculation of the k_f and k_r data in Table 4 on the basis of the corrected rate law:

$$\frac{-d[As(OCH_3)_3]}{dt} = k_3\frac{[As(OCH_3)_3][HOC(CH_3)_3]}{[HOC(CH_3)_3]_0} - k_4\frac{[As(OCH_3)_2(OC(CH_3)_3)][HOCH_3]}{[HOC(CH_3)_3]_0} \qquad (6)$$

was then carried out. The two constants, k_3 and k_4, from Table 4 have values of $(2.20\pm0.22)\times10^{-3}$ s^{-1} and $(7.59\pm0.10)\times10^{-3}$ s^{-1} respectively.

The rates for the *t*-butyl alcohol reaction were measured at five temperatures from 30 to 60 °C; these are given in Table 5. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for k_3 are 15 ± 1 kJ mol^{-1} and -253 ± 4 J mol^{-1} K^{-1}; for k_4, the corresponding numbers are 10 ± 1 kJ mol^{-1} and -258 ± 5 J mol^{-1} K^{-1} respectively.

TABLE 5. DEPENDENCE OF *t*-BUTYL ALCOHOL RATE CONSTANT ON TEMPERATURE[a)]

t/°C	$10^3k_3/s^{-1}$	$10^3k_4/s^{-1}$	$K^{b)}$
30.0	1.20	3.24	0.369
36.5	1.41	3.59	0.392
45.0	1.77	4.45	0.397
53.0	1.98	4.78	0.414
61.0	2.25	5.15	0.438

a) In acetonitrile, $[As(OCH_3)_3]=2.025$ M, and $[HOC(CH_3)_3]=1.073$ M. b) $K=k_3/k_4$.

The *t*-butyl alcohol reaction with $As(OCH_3)_3$ was found not to be catalyzed by 2,4-dimethylpyridine, *p*-toluenesulfonic acid, or 1-pentanethiol.

The rate law (Eq. 6) in the forward direction shows a dependence on only a single species: this might suggest a unimolecular reaction. However, the activation parameters give evidence that such a suggestion can not be correct. A low $\Delta H^{\neq}$ value and a very negative $\Delta S^{\neq}$ value can only be explained if considerable bond formation between several species is taking place in the transition state and in equilibria prior to the transition state. A further piece of evidence that other species are present in the transition state is the slight difference in rate constants in Tables 4 and 5, the data for which were obtained using different batches of a solvent. It seems possible that the rate-limiting step in the transesterification reaction was the reaction of $As(OCH_3)_3$ with a trace amount of water in the acetonitrile. This hypothesis was tested by treating the solvent so as to dry it beyond the normal purification procedure. The rate decreased greatly, by about three powers of ten; the resulting halftime was about one week at room temperature. Because of other complications, however, the further study of this very slow transesterification was not possible.

Discussion

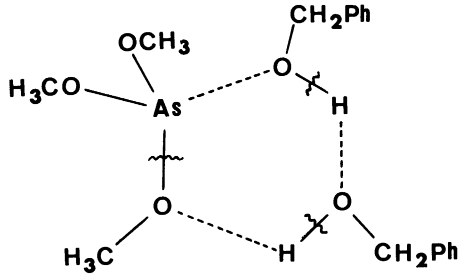
General. From prior arsenite-rate studies,[1-5] it was expected that the transesterification reaction would be rapid, with a cleavage of the arsenic-oxygen bond. The observed rates with benzyl alcohol are indeed rapid, although slightly slower than the oxygen-exchange process[1] and the ester hydrolysis.[2] Low values of $\Delta H^{\neq}$ and negative values of $\Delta S^{\neq}$ are found for all three reactions; presumably this is a characteristic of replacements in the arsenite-coordination sphere.

Equilibria. The K value found for benzyl alcohol is 3.6. This can be converted (using the appropriate statistical factor of 3) to the corrected value of 1.2. The reaction is slightly endothermic (5.0 kJ $\mathrm{mol^{-1}}$). The entropy is (after correction for the statistical factor) +18 J $\mathrm{mol^{-1}\ K^{-1}}$.

For *t*-butyl alcohol, the value of K is near 0.3; after statistical correction, it is 0.1. An enthalpy (4.0 kJ $\mathrm{mol^{-1}}$) comparable to the case of benzyl alcohol was found. The decrease of a power of ten in the equilibrium constant shows up as a lower entropy ($\Delta S^\circ = +5$ J $\mathrm{mol^{-1}\ K^{-1}}$; after correction, −4).

The difference in the equilibrium constants can be traced completely to the entropy contribution. It seems probable that As–O free rotations, which are probably active in $As(OCH_3)_3$, may be shut down in $As(OCH_3)_2OC(CH_3)_3$ because of the large *t*-butyl group. For one carbon-carbon free rotation, the entropy contribution is about 16 J $\mathrm{mol^{-1}\ K^{-1}}$;[10] even if the rotation about the arsenic-oxygen bond is less important, three such rotations could easily be sufficiently active to explain a loss of 22 J $\mathrm{mol^{-1}\ K^{-1}}$.

Kinetics with Benzyl Alcohol. The rate of this transesterification was rapid as expected; on the other hand, the rate law was somewhat of a surprise. Nevertheless, it is readily explicable in terms of a mechanism. The second benzyl alcohol molecule is presumably present in order to accomplish the necessary proton transfer (without an energy-costly charge-separation process) in a transition state of this type:



The dashed lines indicate bonds being formed; bonds being cleaved are denoted by a bond line crossed by a wavy line. A recent study of the arsenate ester/alcohol transesterification reaction indicated hydrogen-bonding, and a transition state similar to the above had to be considered.[11]

The energetic basis for additional (over stoichiometry) molecules has been discussed in some detail in relation to the peroxide oxidation of neutral nucleophiles.[12] Two examples of reactions which are catalyzed by extra protic molecules and involve proton transfer in the transition state are the oxidation of dialkyl sulfides by hydrogen peroxide[13] and the hydration of carbonyl compounds in mixed solvents.[14]

In the present case, at least two proton transfers are involved; these could take place synchronously or in a stepwise fashion. One arsenic-oxygen bond is being broken, while another is being formed, at essentially the same time. Since the rate plots as shown in Fig. 1a are linear over the measured course of the reaction, it appears that benzyl alcohol and methanol have similar proton-transrer capabilities.

Kinetics with t*-Butyl Alcohol.* For this alcohol, the half-time for the reaction is about one power of ten longer (in a normally purified solvent) than for benzyl alcohol; this slower rate makes it possible to follow the process using normal NMR line-intensity techniques. Now, however, the initial rate is independent of the entering alcohol concentration, and the experimental rate law given in Eq. 6 which was found to give a quantitative fit of the data most certainly cannot be complete. The activation parameters show that other particles must be present in the transition state, and evidence has been presented that the trace of water in the acetonitrile solvent acts as a catalyst. This leads to the following mechanism:

$$\begin{aligned} &As(OCH_3)_3 + H_2O \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} As(OCH_3)_2OH + HOCH_3, \\ &As(OCH_3)_2OH + HOC(CH_3)_3 \\ &\quad \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} As(OCH_3)_2OC(CH_3)_3 + H_2O. \end{aligned} \tag{7}$$

The steady-state rate law derived from Eq. 7 is:

$$\begin{aligned} -\frac{d[As(OCH_3)_3]}{dt} &= k_1'[H_2O][As(OCH_3)_3]R/(1+R) \\ &\quad - k_4'[H_2O][As(OCH_3)_2OC(CH_3)_3]/(1+R), \end{aligned} \tag{8}$$

where $R = k_3'[HOC(CH_3)_3]/k_2'[HOCH_3]$. Equation 8 reduces to Eq. 6 if $R \gg 1$ to give $k_3 = k_1'[H_2O]$ and $k_4 = k_2'k_4'[H_2O]/k_3'$.

The fit to Eq. 6 was, in fact, not perfect (notice the slight curvature of the points in Fig. 1b). A three-parameter fit to Eq. 8 is considerably better. The results of a nonlinear least-squares fit are:[15] $k_1'[H_2O] = 3.5 \times 10^{-3}\ \mathrm{s^{-1}}$, $k_4'[H_2O] = 1.5 \times 10^{-3}\ \mathrm{s^{-1}}$ and $k_3'/k_2' = 0.15$. Since k_1' is just the rate constant for hydrolysis, we can use the known value, 4.4 $\mathrm{M^{-1}\ s^{-1}}$,[2] to obtain an estimate of the water concentration in the acetonitrile solvent, 8×10^{-4} M, which is not an unreasonable value.

For this transesterification study, *t*-butyl alcohol was chosen because the bulk of the large alkyl group was expected to bring about interesting effects; such turned out to be the case. Compared to the benzyl-alcohol results, the K value is very low and this is reflected in the fact that k_4 is larger than k_3. The binding difference of a factor of ten is due wholly to the lower value of ΔS, and this may be related to the loss of internal rotations in the product, the mixed ester.

The direct reaction of *t*-butyl alcohol with trimethyl arsenite is exceedingly slow, if it occurs at all, and this allows the entry of a mechanism which seems to be based on catalysis by very small concentrations of water in the solvent. Finally, the discrimination constant, k_3'/k_2', reflects the fact that *t*-butyl alcohol (in spite of its probably larger nucleophilicity) is larger than the competing methanol.

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References

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

2) C. D. Baer, J. O. Edwards, P. H. Rieger, and C. M. Silva, *Inorg. Chem.*, accepted for publication.

3) G. L. Roy, A. L. Laferriere, and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **4**, 106 (1957).

4) A. Okumura, N. Yamamoto, and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 3633 (1973).

5) J. O. Edwards, T. Mallouk, and P. H. Rieger, unpublished results.

6) M. Moedritzer, *Inorg. Syn.*, **14**, 181 (1968).

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

8) J. A. Riddick and W. S. Bunger, "Organic Solvents," in "Techniques of Chemistry, " 3rd ed, ed by A. Weissberger, Wiley, New York (1971), Vol. 2, Chap. V, pp. 572—877.

9) D. A. Couch, O. W. Howarth, and P. Moore, *J. Phys. E. Sci. Inst.*, **8**, 831 (1975).

10) J. O. Edwards, unpublished calculations.

11) a) C. D. Baer, J. O. Edwards, M. J. Kaus, T. G. Richmond, and P. H. Rieger, *J. Am. Chem. Soc.*, **102**, 5793 (1980); b) C. D. Baer, Ph. D. Thesis, Brown university, 1980.

12) R. Curci, R. DiPrete, J. O. Edwards, and G. Modena, "Hydrogen-Bonded Solvent Systems," ed by A. K. Covington and P. Jones, Taylor and Francis, London (1968), pp. 303—321.

13) M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *J. Am. Chem. Soc.*, **90**, 3209 (1968).

14) R. P. Bell, J. P. Millington, and J. M. Pink, *Proc. R. Soc. London, Ser. A*, **303**, 1 (1968).

15) Although the overall fit of Eq. 8 to the experimental data is good, the parameters are strongly correlated; the values given are, therefore, rough estimates at best.