γ then changes slowly into the stable β form. This fact conclusively shows that the calcium-stabilized γ-$Zn_3(PO_4)_2$ solid solutions are metastable.

The extent of the γ-solid solutions as a function of the radius of the stabilizing ion is given in Table V. As the radius of the stabilizing cation increases, the composition range of the solid solutions rapidly decreases. The calcium ion represents the limiting case for the existence of γ-solid solutions. Larger ions such as Sr^{2+} do not yield γ-solid solutions, whereas ions smaller than Ca^{2+} yield thermodynamically stable solid solutions.

TABLE V

COMPOSITION RANGE OF "γ-$Zn_3(PO_4)_2$" SOLID SOLUTIONS AS A FUNCTION OF THE RADIUS OF THE STABILIZING CATION

Compn range, mole % $Zn_3(PO_4)_2$	Stabilizing cation	Radius of ion, A	Ref
0–97	Mg^{2+}	0.67	7
4–27	Mn^{2+}	0.80	8
2–7	Cd^{2+}	0.97	9
Metastable	Ca^{2+}	0.99	This paper
Not observed	Sr^{2+}	1.12	2

Conclusions

β-$Ca_3(PO_4)_2$ takes a maximum of 10 mole % $Zn_3(PO_4)_2$ into solid solution. The $\beta \rightleftarrows \alpha$ inversion temperature increases rapidly as the concentration of $Zn_3(PO_4)_2$ increases. This behavior is the same as that observed in the $Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$[3] and $Ca_3(PO_4)_2$–$Sr_3(PO_4)_2$[2] systems.

One compound, $CaZn_2(PO_4)_2$, was found in the system. The compound melts congruently at 1048 ± 5° and has three stable polymorphs with the transition temperatures

$$\alpha \overset{870 \pm 25^\circ}{\rightleftarrows} \beta \overset{1013 \pm 7^\circ}{\rightleftarrows} \delta$$

A metastable phase, labeled γ-$CaZn_2(PO_4)_2$, was found to exist above 997 ± 22° by high-temperature X-ray diffraction. Only the α and δ forms were observed in quenched samples. δ-$CaZn_2(PO_4)_2$ forms solid solutions with $Zn_3(PO_4)_2$ extending from 66.7 to 74 mole % $Zn_3(PO_4)_2$. These solid solutions have a eutectoid at 894° and 70 mole % $Zn_3(PO_4)_2$. Slight amounts of $Ca_3(PO_4)_2$ go into solid solution in β- and δ-$CaZn_2(PO_4)_2$.

Approximately 1.5 mole % of $Ca_3(PO_4)_2$ goes into solid solution in β-$Zn_3(PO_4)_2$. The $\alpha \rightleftarrows \beta$ inversion temperature decreases as the Ca^{2+} concentration increases. Similar behavior was observed in other systems.[7–9]

γ-$Zn_3(PO_4)_2$ solid solutions were observed in the system, but these are metastable. The composition range of the γ-solid solutions is inversely related to the size of the stabilizing cation. The Ca^{2+} ion represents the limiting size for the existence of such solid solutions, and with calcium these are metastable. Ions smaller than Ca^{2+} produce stable γ-solid solutions whereas ions larger than Ca^{2+} do not even produce metastable γ-solid solutions.

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The Rate and Mechanism of the Iodine–Formate Reaction in Dimethyl Sulfoxide–Water Solvents

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The kinetics of the reaction $I_3^- + HCOO^- \rightarrow 3I^- + CO_2 + H^+$ have been studied spectrophotometrically in water, in pure dimethyl sulfoxide, and in several dimethyl sulfoxide–water mixtures. The reaction was found to be first order in triiodide ion, first order in formate ion, and inverse first order in iodide ion in the various solvents. Metal ion–formate ion-pair dissociation constants and values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from the kinetic data. The deuterium isotope effect using deuterioformate was examined and values of k_H/k_D were found to change from 2.2 in dimethyl sulfoxide to 3.8 in water. Values of the triiodide ion dissociation constants were measured and found to decrease as the mole fraction of dimethyl sulfoxide in the solvent increased. The mechanism proposed involves a rate-determining attack of iodine on the formate anion. Because water molecules strongly solvate the formate anion *via* hydrogen bonding, the rate of reaction decreases as the water content of the solvent increases.

Introduction

In this paper we report the results of a kinetic study of the iodine–formate reaction

$$I_3^- + HCOO^- \longrightarrow 3I^- + CO_2 + H^+ \qquad (1)$$

This work represents a continuation of our evaluation of solvent effects on inorganic reactions in water–dimethyl sulfoxide (DMSO) solvents.[2] In particular, our objective has been to examine changes in rate and

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[1] To whom inquiries should be addressed.

[2] J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

mechanism brought about by gradually replacing the polar, hydrogen-bonding solvent water with polar but aprotic DMSO. The iodine–formate system has been described by others in the literature,[3] but kinetic measurements have not been extended to nonaqueous solvents. Although the deuterium isotope effect using deuterioformate has been reported for the permanganate–formate reaction,[4,5] a comparable study apparently has not been made for the iodine–formate reaction. The results of deuterium substitution are of special interest because this system allows an evaluation of k_H/k_D as a function of solvent composition.

Experimental Section

Solvent.—Crown-Zellerbach commercial grade DMSO was purified by slowly heating a mixture containing 1.5 g of potassium hydroxide/l. of DMSO up to 125° over a period of 1 hr. The resulting yellow solution was then distilled at 72° (10 mm) through a 16-in. column packed with glass helices. The center 70% was redistilled and the resulting center fraction was retained for use. This treatment removed small amounts of reducing impurities and lowered the water content to approximately 0.03%. Solvent mixtures were prepared on a weight basis by slow addition of water, redistilled from basic permanganate, to a partially frozen sample of DMSO.

Reagents.—J. T. Baker reagent grade iodine was used as obtained. Reagent grade sodium formate, potassium perchlorate, and tetraethylammonium perchlorate (Eastman) were vacuum dried over phosphorus pentoxide. Potassium, sodium, and tetraethylammonium iodides and sodium perchlorate were recrystallized from water and vacuum dried over phosphorus pentoxide. Lithium and barium perchlorates were prepared by neutralizing the reagent grade hydroxides with 60% perchloric acid, recrystallizing from water, and vacuum drying at 100° over phosphorus pentoxide. Neutralization of 88.5% reagent grade formic acid with potassium hydroxide yielded potassium formate which was recrystallized from water and vacuum dried at 100° over phosphorus pentoxide. We were unable to prepare solid samples of tetraethylammonium formate with satisfactory purity. Solutions of this salt for the kinetic runs were prepared by mixing equivalent amounts of formic acid and 10% aqueous tetraethylammonium hydroxide and then adding enough DMSO to give the correct solvent composition.

Sodium deuterioformate of 98% minimum isotopic purity was obtained from Merck Sharp and Dohme of Canada Ltd. *Anal.* Calcd for NaDCOO: C, 17.4; D, 2.9. Found: C, 17.5; D, 2.8.

Kinetic Measurements.—The reaction was followed by measuring the absorbance at 380 mμ using a Beckman Model DU spectrophotometer. Except when low iodide concentrations were employed in the aqueous runs, iodine is essentially completely converted to triiodide ion, the only species which absorbs appreciably at 380 mμ. Independent experiments showed that Beer's law was obeyed in DMSO–H_2O solvents.

Separate solutions of formate and of triiodide, containing the required concentrations of iodide and perchlorate salts, were thermostated at the reaction temperature. After the solutions were rapidly combined and thoroughly mixed, a 4-ml sample was transferred to a 1-cm glass-stoppered silica cell. The cell was mounted in the cell holder and thermostated to within 0.1° of the desired temperature.

Although the reaction rate was not very sensitive to ionic strength, the ionic strength was maintained at 0.300 *M* in most of the runs by addition of potassium, sodium, or tetraethylammonium perchlorates. No attempt was made to exclude oxygen from the solutions because independent checks showed that the presence of excess oxygen did not affect the reaction rate. Since the analogous iodine–oxalate reaction is known to proceed in part *via* a photoinitiated radical process,[6,7] the effect of 365-mμ radiation was examined in several of the kinetic runs. One of two identical solutions was exposed continuously at 365 mμ using maximum slit width, while the second solution was exposed only long enough to obtain several absorbance values. The absorbance decreased at the same rate in both solutions.

The stoichiometry was checked in 75.0 and 94.5% DMSO (0.409 and 0.800 mole fraction DMSO, respectively) by allowing a known amount of iodine to react completely with an excess of formate. The final solution was diluted with water, boiled gently to expel CO_2, and titrated with sodium hydroxide. The ratio of moles of hydrogen ion produced per mole of iodine consumed was found to be 0.97 ± 0.03. Loss of formic acid during boiling may have led to the slightly low value observed.

Emf Measurements.—Values of the triiodide dissociation constant were determined from emf measurements on an iodine–iodide concentration cell with pure DMSO and three DMSO–H_2O solvents

$$\mathrm{Pt}|\mathrm{I_2}(a),\ \mathrm{I^-}(b)||\mathrm{I^-}(b'),\ \mathrm{I_2}(a')|\mathrm{Pt}$$

In most of these experiments, the cell consisted of platinum wires in the appropriate electrolyte solutions which were separated by a 0.1 *M* tetraethylammonium perchlorate salt bridge and two sintered-glass junctions. Several of the cells were constructed with only a sintered-glass junction separating the electrolytes. A Heath Model EUW-301 pH recording electrometer was used as a millivoltmeter for the emf measurements. Some of the cells showed an initial drift in voltage, which usually became constant after approximately 2 min.

Results

Rate Law.—The rate was found to be dependent on the concentrations of iodine, iodide, and formate anion. In most of the kinetic runs, the initial concentrations of iodide and of formate were chosen to be much greater than the initial total iodine concentration. Under these conditions, linear plots of ln $(A - A_\infty)$ *vs.* time were obtained, indicating a first-order dependence on triiodide ion. By varying the initial, excess concentrations of both formate and iodide, the slopes of the above plots were found to be proportional to $[\mathrm{HCOO^-}]/[\mathrm{I^-}]$. In the DMSO–$H_2O$ mixtures, these slopes were unaffected by addition of formic acid; thus, formate anion is the reactive species. The following rate law describes the kinetics in six DMSO–H_2O solvents and in 100% DMSO.

$$\text{rate} = \frac{k[\mathrm{I_3^-}][\mathrm{HCOO^-}]}{[\mathrm{I^-}]} \tag{2}$$

The rate constant was evaluated from the expression $k = S[\mathrm{I^-}]/[\mathrm{HCOO^-}]$, where $S = -\mathrm{d}\ln(A - A_\infty)/\mathrm{d}t$. In solvent water, reasonably large rates could be obtained only at rather low iodide concentrations. Under these conditions the rate was no longer strictly inversely proportional to the iodide concentration. However, the data were accommodated by the slightly modified rate law

$$\text{rate} = \frac{k(\Sigma\mathrm{I_2})[\mathrm{HCOO^-}]}{K_D + [\mathrm{I^-}]} \tag{3}$$

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[3] (a) B. F. Chow, *J. Am. Chem. Soc.*, **57**, 1437 (1935); (b) N. Dhar, *J. Chem. Soc.*, 707 (1917); (c) S. S. Doósay and W. V. Bhagwat, *Z. Anorg. Allgem. Chem.*, **216**, 241 (1934); (d) D. L. Hammick and M. Zvegintzov, *J. Chem. Soc.*, 1105 (1926); (e) A. v. Kiss and A. Urmánczy, *Z. Anorg. Allgem. Chem.*, **213**, 353 (1933); (f) M. Kunaszewska and E. Jozefowicz, *Zeszyty Nauk. Politech. Lodz., Chem.*, **14**, 11 (1964); *Chem. Abstr.*, **64**, 558e (1966).

[4] S. M. Taylor and J. Halpern, *J. Am. Chem. Soc.*, **81**, 2933 (1959).

[5] K. B. Wiberg and R. Stewart, *ibid.*, **78**, 1214 (1956).

[6] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **28**, 752 (1932).

[7] R. O. Griffith, A. McKeown, and A. G. Winn, *ibid.*, **29**, 369 (1933).

where K_D is the dissociation constant for triiodide ion. In these aqueous runs, the rate constant was evaluated from the expression $k = (1 + K_D/[I^-])S[I^-]/[HCOO^-]$, where $S = -d \ln (A - A_\infty)/dt$. Compared with runs in aqueous solution, all runs in 0.200–1.000 mole fraction of DMSO involved $[I^-] >> K_D$ and $\Sigma I_2 \cong [I_3^-]$. Thus, in solvents containing DMSO, rate law 3 becomes equivalent to rate law 2.

Runs in 100% DMSO and some of the runs in 0.800 and 0.900 mole fraction of DMSO involved $[HCOO^-]/[I_3^-]$ ratios in the range of only 17–30. Rate constants calculated for these runs were corrected for the error introduced by small decreases in formate ion concentration during the run.

Values of the first-order rate constant were determined in several solvent mixtures and found to be somewhat dependent upon the nature of the cation present and highly dependent on the fraction of DMSO in the solvent. The results[8] are given in Table I where the indicated cation was the only one present in the series of runs used to obtain the corresponding rate constant. A plot of the data in Table I shows that log k is nearly linearly dependent on the mole fraction of DMSO in the solvent.

Table I

Kinetic Data at 20.7° and 0.300 M Ionic Strength for Runs with a Single Cation Present

Mole fraction DMSO	M^+	Range of $[HCOO^-]$, M	Range of $[I^-]$, M	10^5k,[a] sec^{-1}
0	Na^+	$(7–20) \times 10^{-2}$	$(4–40) \times 10^{-3}$	2.43
0.200	Na^+	$(1–15) \times 10^{-2}$	$(3–50) \times 10^{-3}$	18.7
0.409	Na^+	$(4–6) \times 10^{-2}$	$(8–20) \times 10^{-2}$	206
0.409	K^+	$(1–15) \times 10^{-2}$	$(3–20) \times 10^{-2}$	248
0.409	$(C_2H_5)_4N^+$	$(1–4) \times 10^{-2}$	$(5–15) \times 10^{-2}$	373
0.600	K^+	$(5–27) \times 10^{-3}$	$(6–30) \times 10^{-2}$	1,600
0.700	K^+	$(4–11) \times 10^{-3}$	$(1–3) \times 10^{-1}$	3,800
0.800	K^+	$(1–9) \times 10^{-3}$	$(0.5–3) \times 10^{-1}$	8,120
0.800	$(C_2H_5)_4N^+$	$(3–10) \times 10^{-4}$	$(1–1.5) \times 10^{-1}$	21,100
0.900	K^+	$(1–2) \times 10^{-3}$	$(1–3) \times 10^{-1}$	18,500
1.000	K^+	$(5–12) \times 10^{-4}$	$(1.5–3) \times 10^{-1}$	49,800

[a] These values represent averages for 10–20 runs and have standard deviations in the range 2–5%. Initial total iodine concentrations were typically in the range $(2–5) \times 10^{-5}$ M. For complete data see ref 8.

Rate constants were also measured at several temperatures for potassium ion or tetraethylammonium ion solutions in both 0.409 and 0.800 mole fraction of DMSO. Average values are summarized in Table II and the corresponding activation parameters are reported in Table III.

Ion-Pair Constants.—As seen in Table I, the rate constant for sodium ion solutions is less than that for potassium ion solutions in 0.409 mole fraction of DMSO. This behavior is assumed to be due to ion pairing of the formate, since the ionic strength was 0.300 M in both solutions. In an attempt to distinguish between a specific ion-pair effect and the more general ionic strength effect, we carried out several experiments with tetraethylammonium ion, assuming it to have little or no tendency to ion pair with formate. Runs which were identical, except for variation in the concentration of tetraethylammonium perchlorate from 0 to 0.240 M, showed no change or trend in the rate constant within an experimental error of 3%. Although possible, it seems unlikely that an ion-pair effect cancels the ionic strength effect. Therefore, we assumed that the reaction rate is independent of ionic strength and that tetraethylammonium ion undergoes no appreciable ion pairing with formate.

Table II

Temperature Dependence of the First-Order Rate Constant

M^+	Temp, °C	Range of $[HCOO^-]$, M	Range of $[I^-]$, M	10^3k,[a] sec^{-1}
0.409 Mole Fraction of DMSO				
$(C_2H_5)_4N^+$	29.7	$(1–2) \times 10^{-2}$	2.01×10^{-1}	12.0
K^+	13.3	$(1.6–3) \times 10^{-2}$	3.66×10^{-1}	0.89
K^+	14.1	$(5–10) \times 10^{-2}$	$(5–10) \times 10^{-2}$	1.02
K^+	25.4	$(2–4) \times 10^{-3}$	1.61×10^{-2}	4.0
K^+	30.5	$(6–19) \times 10^{-3}$	$(1–2) \times 10^{-2}$	7.2
0.800 Mole Fraction of DMSO				
$(C_2H_5)_4N^+$	14.8	$(1–2) \times 10^{-3}$	1.50×10^{-1}	119
$(C_2H_5)_4N^+$	30.1	$(5–10) \times 10^{-3}$	2.21×10^{-1}	567
K^+	13.4	$(1–3) \times 10^{-3}$	1.00×10^{-1}	37.6
K^+	13.7	$(1.99) \times 10^{-3}$	$(1–2) \times 10^{-1}$	40
K^+	14.0	$(1–2) \times 10^{-3}$	1.00×10^{-1}	41
K^+	25.3	$(1–2) \times 10^{-3}$	2.98×10^{-1}	130
K^+	30.5	$(5–30) \times 10^{-4}$	$(1.6–3) \times 10^{-1}$	190

[a] Average values for several runs taken from data in ref 8.

Table III

Enthalpy and Entropy of Activation in DMSO–H_2O

Mole fraction of DMSO	K^+		$(C_2H_5)_4N^+$	
	$\Delta H^\ddagger$, kcal/mole	$\Delta S^\ddagger$, cal/mole deg	$\Delta H^\ddagger$, kcal/mole	$\Delta S^\ddagger$, cal/mole deg
0[a]	25.6			
0.409	19.6	−3	22.3	6
0.800	15.7	−10	17.3	−3

[a] Estimated from $\Delta H^\ddagger = 20.8$ kcal/mole for the bimolecular step in aqueous solution[3f] and ΔH° (K_D, I_3^-) = 4.8 kcal/mole: R. W. Ramette and R. W. Sanford, Jr., *J. Am. Chem. Soc.*, **87**, 5001 (1965).

The question next arises as to whether formate is partially or completely deactivated by ion pairing. Complete ion pairing with hydrogen ion, *i.e.*, formation of formic acid, was shown previously to deactivate formate entirely. Accordingly, it was assumed that metal ion pairs were unreactive, allowing us to determine ion-pair dissociation constants from the kinetic data. The assumptions above appear to be reasonable ones, since consistent dissociation constants were obtained over a range of concentrations.

Kinetic studies were carried out in three types of solutions. In type A, all solutions initially contained the same concentrations of tetraethylammonium formate and tetraethylammonium iodide, but varying concentrations of the metal perchlorate. Type-B solutions initially contained the same concentrations of potassium formate and potassium iodide, but varying concentrations of potassium perchlorate. In type C, all solutions initially contained the same concentrations of potassium formate and potassium iodide, but varying concentrations of the metal perchlorate. Dissociation constants were derived from data in type-A and -B solutions using

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[8] F. W. Hiller, Ph.D. Thesis, Oregon State University, Corvallis, Ore., 1967.

$$K_M = \frac{k}{k_0}(\Sigma HCOO^-) - \frac{k}{k_0 - k}(\Sigma M) \qquad (4)$$

where K_M is the ion-pair dissociation constant for cation M, ($\Sigma HCOO^-$) and (ΣM) are total initial formate and metal ion concentrations, respectively, k is the observed rate constant in the presence of metal ion, and k_0 is the rate constant observed when tetraethylammonium ion is the only cation present.[9] Similarly, for type-C solutions, eq 5 and 6 were employed

$$K_M = \frac{\Sigma M}{a} - \frac{k}{k_0}(\Sigma HCOO^-) \qquad (5)$$

$$a = \frac{k_0}{k} - 1 - \frac{\Sigma K^+}{\frac{k}{k_0}(\Sigma HCOO^-) + K_{K^+}} \qquad (6)$$

which make use of K_{K^+}, the dissociation constant for the potassium formate ion pair, obtained from the type-A and -B solutions.[9]

The results of these calculations are summarized in Table IV. In a given solvent, K_M decreases in the order $K^+ > Na^+ > Li^+ > Ba^{2+}$, consistent with the increasing charge/radius ratio of the cations. For a given cation, K_M is smaller in 0.800 mole fraction of DMSO than in 0.409 as expected from the correspondingly lower dielectric constant and anion-solvating capacity of DMSO.

TABLE IV

METAL–FORMATE ION-PAIR DISSOCIATION CONSTANTS AT 20.7° IN DMSO–H_2O[a]

K^+	Na^+	Li^+	Ba^{2+}
	0.409 Mole Fraction of DMSO		
0.46 (A)[b]	0.31 (C)	0.28 (A)	0.081 (A)
0.46 (B)		0.25 (C)	0.081 (C)
0.44 (C)			
	0.800 Mole Fraction of DMSO		
0.17 (A)	0.070 (C)	0.080 (A)	0.015 (A)
0.21 (B)		0.068 (C)	0.014 (C)
0.21 (C)			

[a] Average values of the dissociation constants, K_M, are based on five to ten kinetic runs with varying metal ion concentrations.[8] [b] Runs of types A, B, or C are described in the text.

Isotope Effect.—Kinetic runs using sodium formate-*d*, NaDCOO, were made in pure DMSO, water, and three DMSO–H_2O mixtures. Corresponding values of the first-order rate constants for deuterioformate, k_D, and values of k_H/k_D are given in Table V.

TABLE V

DEUTERIUM ISOTOPE EFFECT IN DMSO–H_2O AT 20.7°

	Mole fraction of DMSO				
	0	0.409	0.800	0.900	1.000
k_H, sec^{-1}	2.1×10^{-5}	2.3×10^{-3} [a]	0.081	0.187	0.46
k_D, sec^{-1}	5.6×10^{-6}	7.9×10^{-4}	0.032	0.078	0.21
k_H/k_D	3.8	2.9	2.5	2.4	2.2

[a] Solution contained both sodium and potassium ions; k_H was determined using dissociation constants from Table IV.

Triiodide Equilibrium.—Equilibrium constants, K_D, for the dissociation reaction

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (7)$$

were obtained in three DMSO–H_2O mixtures and in 100% DMSO, by emf measurements of iodine–iodide concentration cells, following the method of Parker.[10] Except in 0.200 mole fraction of DMSO where an iterative method was used, eq 8 was used to obtain K_D values from the data.

$$E \text{ (volts)} = 0.02925 \log \frac{(1/K_D)^3(a - b)^3(b' - a')^3}{a'b^2} \qquad (8)$$

Here, a and b represent initial molar concentrations of iodine and iodide, respectively, in one half-cell and a' and b', those in the second half-cell, such that $a > b$ and $b' > a'$.[11] The results are summarized in Table VI, which contains, for each solvent, a description of a typical cell and an average K_D value for several cells. The K_D values were not very dependent on the liquid junction, as results with or without a 0.1 *M* tetraethylammonium perchlorate salt bridge agreed, within experimental error. It is known that iodine and DMSO form a 1:1 complex,[12-14] and, at least in carbon tetrachloride as the solvent, this complex undergoes dissociation into $(CH_3)_2SOI^+$ and I^-.[13,15] This dissociation should be repressed in solutions containing excess iodide, but may have an influence on the K_D values, especially in 100% DMSO.

The triiodide dissociation constant decreases rapidly as the solvent changes from 0 to 0.409 mole fraction of DMSO, but is relatively insensitive to solvent com-

TABLE VI

EMF AND TRIIODIDE DISSOCIATION CONSTANTS OF REPRESENTATIVE IODINE–IODIDE CELLS IN DMSO–H_2O

Mole fraction of DMSO	$[I_2]$[a]	$[I^-]$	$[I_2]'$	$[I^-]'$	E, mv	$10^6 K_D$
0[e] (21°)						1230
0.200 (23°)	0.0727	0.0687	0.00723	0.1643	193[c]	200 (180)[b]
0.409 (22°)	0.1070	0.01580	0.02541	0.0921	407[d]	7 (10)[b]
0.409 (22°)	0.0598	0.0168	0.01193	0.1045	388[c]	10 (10)[b]
0.800 (22°)	0.1214	0.00990	0.01038	0.1053	476[d]	4 (4)[b]
1.000 (22°)	0.1079	0.00972	0.01137	0.1012	466[c]	4 (5)[b]

[a] Formal concentration in moles/l. [b] Average value of $K_D \cdot (I_3^-)$ for the several cells set up in this solvent. [c] With a 0.1 *M* $(C_2H_5)_4NClO_4$ salt bridge. [d] Without a salt bridge. [e] Value of $K_D(I_3^-)$ in aqueous solution taken from: R. W. Ramette and R. W. Sanford, Jr., *J. Am. Chem. Soc.*, **87**, 5001 (1965).

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(9) Equations 4–6 were derived from the expressions: $K_M = [M^{n+}] \cdot [HCOO^-]/[M^{n+}HCOO^-]$, for the ion-pair equilibrium, $M^{n+}HCOO^- \rightleftharpoons M^{n+} + HCOO^-$, $(\Sigma HCOO^-) = [HCOO^-] + \Sigma[M^{n+}HCOO^-]$, and, from the assumption that only ion pairs react, $[HCOO^-]/(\Sigma HCOO^-) = k/k_0$.

(10) A. J. Parker, *J. Chem. Soc., Ser. A*, 220 (1966).

(11) Neglecting activity coefficients, the concentration cell is described by $\Delta E = 0.02925 \log [(a - x)(b' - x')^2/(a' - x')(b - x)^2]$ and the triiodide equilibrium by $K_D = (a - x)(b - x)/x$ or $K_D = (a' + x')(b' - x')/x'$, where x and x' represent triiodide concentration. Equation 8 results from the assumption that $x \cong b$ when $a > b$ and $x' \cong a'$ when $b' > a'$, which is valid when $K_D \sim 10^{-5}$. In 0.200 mole fraction of DMSO, where $K_D \sim 10^{-4}$, the expressions above were solved, without approximation, for a consistent value of K_D.

(12) R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963).

(13) M. C. Giordano, J. C. Bazán, and A. J. Arvia, *J. Inorg. Nucl. Chem.*, **28**, 1209 (1966).

(14) P. Klaeboe, *Acta Chem. Scand.*, **18**, 27 (1964).

(15) M. A. Slifkin, *Spectrochim. Acta*, **21**, 1391 (1965).

position in the range 0.409 to 1.000 mole fraction of DMSO. The small value of $K_D = 5 \times 10^{-6}$ in 100% DMSO is consistent with the expected stability of highly polarizable species such as the triiodide ion in polar aprotic DMSO. The corresponding value of K_D in dimethylformamide is 0.15×10^{-6}.[10]

Discussion

Solvent Effect.—The rate law and presumably the mechanism as well are independent of solvent composition over the entire solvent range from pure water to 100% DMSO. The corresponding activated complex has the composition and charge, $I_2 \cdot HCOO^-$. The mechanism proposed for the reaction in aqueous solution[3] is consistent with all of our experimental results.

$$I_3^- \rightleftharpoons I_2 + I^- \qquad K_D \tag{9}$$

$$I_2 + HCOO^- \longrightarrow I_2 \cdot HCOO^- \qquad k_r \tag{10}$$

The slow step involves iodine attack on the formate anion, although one can only speculate about the nature of the following intermediates. This latter point will be discussed below in connection with the isotope rate effect.

In the mechanism above, the observed first-order rate constant is $k = K_D k_r$. Since the solvent effect on the rate-determining step is of interest, values of K_D as a function of solvent, obtained in this study, were used to determine values of the bimolecular rate constant, k_r. The required constants were taken from data in Tables I and VI and k_r correlated with solvent composition as shown in Figure 1. The attack of formate on iodine is greatly accelerated by replacing water with DMSO in the solvent, especially in the region below 0.409 mole fraction of DMSO. In an evaluation of halide ion nucleophilicities, we have observed a similar increase in reactivity of chloride and bromide ions in solvents of increasing DMSO content.[2] Parker, in his review of solvation in dipolar aprotic solvents, has observed that basic anions are greatly destabilized by replacing hydrogen-bonding water molecules with aprotic species, such as DMSO.[16] Consistent with this proposal, the reactivity of formate is high in DMSO-rich mixtures but decreases as the water content increases. Although changes in the solvent will also affect iodine and the activated complex, it is likely that interactions between DMSO and the large, polarizable iodine and activated complex species will largely tend to cancel.

Consistent with the arguments in favor of desolvation of formate ion in DMSO, the reaction rate increases in DMSO-rich solvents through a decrease in activation enthalpy (Table III). The decrease in activation entropy opposes but does not cancel the effect of the enthalpy term. The more positive values of $\Delta S^{\ddagger}$ in the water-rich solvents presumably correspond to a considerable decrease in order as water molecules bound to formate are partially released in attaining the transition state.

Isotope Effect.—The k_H/k_D values in Table V make it

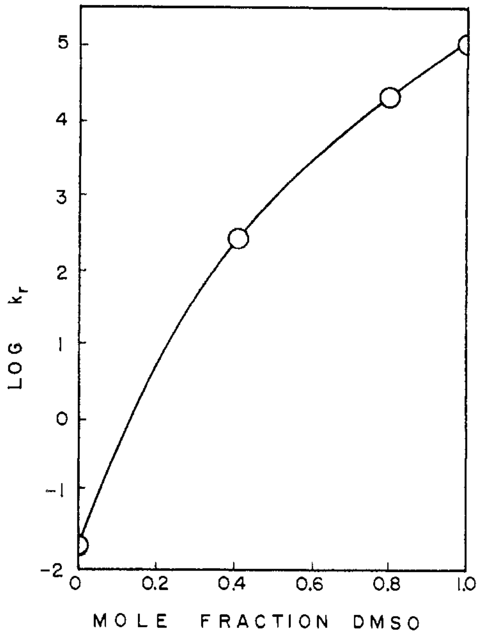

Figure 1.—Log of the bimolecular rate constant, k_r, *vs.* mole fraction of dimethyl sulfoxide in the solvent.

clear that the transition state involves cleavage of the carbon–hydrogen bond. However, the activated complex is asymmetrical with respect to hydrogen transfer, since the isotope effect observed is below the maximum possible for carbon–hydrogen bonds. The mechanism proposed must be consistent with this isotope rate effect and with the unusually large solvent variation of k_H/k_D. One plausible mechanism involves the reaction of formate with iodine, leading to the formation of formyl hypoiodite which could lose CO_2 in a final step.

$$I_2 + HCOO^- \rightleftharpoons HCOOI + I^- \tag{11}$$

$$HCOOI \longrightarrow CO_2 + H^+ + I^- \tag{12}$$

This sequence will be consistent with the inverse first-order iodide dependence only if one assumes that reaction 12 is much more rapid than the reverse step in reaction 11. However, the appreciable isotope effect observed rules out reaction 11 as a rate-determining step, since it involves no appreciable change in the carbon–hydrogen bond.

A rate-determining step involving proton transfer is also possible.

$$\begin{array}{l} B + HCOO^- + I_2 \longrightarrow BH^+ + CO_2I^- + I^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad CO_2 + I^- \end{array} \tag{13}$$

In reaction 13, a solvent molecule is presumed to function as the base in removing the proton developing in the transition state. (No second-order dependence on formate was observed, even though formate ion is the strongest base present in the DMSO–H_2O solvent.) However, proton transfer to a molecule of DMSO or of water seems inconsistent with the variation of k_H/k_D from 3.8 to 2.2, since this variation implies a remarkable sensitivity to the strength of the base, when, in fact, DMSO and water are of comparable basicity.[17]

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The kinetic isotope data, which thus eliminate hypoiodite formation and proton transfer as possible pathways, are consistent with transfer of a hydride ion from carbon to iodine

$$\begin{tikzcd} I_2 + HCOO^- \arrow[r] & I_2H^- + CO_2 \arrow[d] \\ & 2I^- + H^+ \end{tikzcd} \qquad (14)$$

Such a process involves carbon-hydrogen bond cleavage, the importance of which would depend on the water content of the solvent because of hydrogen bonding to the oxygen atoms of formate. Simultaneous interaction of iodine with one of the oxygen atoms may also be involved. This is suggested by the fact that $k_H/k_D = 3.4$ for the thallium(III) oxidation of formate,[18] a process which undoubtedly occurs *via* interaction of Tl^{3+} on the oxygen of formate. Our values of k_H/k_D in the range of 2.2 to 3.8 agree fairly closely with the thallium(III) value, but are considerably lower than $k_H/k_D = 7$, observed in the permanganate-formate reaction which is assumed to proceed *via* simple hydride transfer.[4,5]

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CONTRIBUTION FROM THE WESTERN RESEARCH CENTER,
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Complex Fluoro Cations. III.[1] Tetrafluoronitrogen(V) Cation, NF_4^+. Vibrational and Fluorine-19 Nuclear Magnetic Resonance Spectra of $NF_4^+AsF_6^-$

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Fluorine-19 nuclear magnetic resonance and infrared and Raman spectroscopy confirm the postulated ionic structure, NF_4^+-AsF_6^-, for the NF_3–F_2–AsF_5 adduct in the solid state and in HF solution. The NF_4^+ cation, with four equivalent fluorine atoms, has a tetrahedral configuration (point group T_d). The force constants of NF_4^+ are calculated and compared with those of NF_3 and isoelectronic species, BF_4^- and CF_4.

Introduction

The existence of an NF_3–F_2–AsF_5 adduct has recently been reported.[3,4] In a subsequent paper[1] we have described the synthesis and properties of this complex. On the basis of X-ray data, the high thermal stability, and theoretical considerations, the ionic structure, $NF_4^+AsF_6^-$, was proposed.[1] The object of this paper is to support further the proposed ionic nature and structure of this compound (in the solid state and in HF solution) by spectroscopic data. In addition, it is interesting to compare the bond strength (based on valence force constants) in NF_4^+ with that in NF_3 and isoelectronic BF_4^- and CF_4.

Experimental Section

The preparation of $NF_4^+AsF_6^-$ by the glow discharge of a 1:1 mole mixture of NF_3 and AsF_5 in the presence of excess fluorine has been described earlier.[1] In the sample used for the spectroscopic investigations, except for small amounts of CuF_2, none of the possible impurities, such as $NO^+AsF_6^-$ or complex copper salts, could be detected. The combined results of X-ray, infrared, mass spectral, and elemental analyses indicated that the sample contained at least 95% $NF_4^+AsF_6^-$ [1] (the remainder was CuF_2). Manipulations outside the vacuum line were done in the dry nitrogen atmosphere of a glove box.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1}. Samples of NF_4^+-containing salts, as dry powders, were placed between AgCl windows held in place by a screw-cap metal cell equipped with neoprene O rings.

Raman Spectra.—The Raman spectra were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 A) as the exciting line and saturated KNO_2 solution as the filter. For the solid complex, a Pyrex tube (7-mm o.d.) having an inner hollow glass cone for variable sample thickness or a glass-plunger type of reflection cell was used. Owing to the very fine particle size of the sample, the better spectra were obtained using the latter technique. The Raman spectrum of the complex in HF solution was taken using a technique described in the literature.[5]

^{19}F Nuclear Magnetic Resonance Spectra.—A Varian Associates Model HA-100 spectrometer operating at 94.6 Mcps was used to record the ^{19}F nuclear magnetic resonance spectra. Solid $NF_4^+AsF_6^-$ (0.15 g) was placed into a Teflon FEP tube equipped with a Monel bellows-seal valve (Hoke, M482M). The tube was connected to a vacuum line having only Monel and Teflon FEP construction. Purified liquid HF (~0.5 ml) was condensed into the tube. After allowing 1 hr for complete mixing at 25°, the clear solution above some undissolved material was transferred mechanically (decanted) into a Teflon FEP nmr tube (~4-mm o.d.). The nmr tube was "heat sealed" under vacuum

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