was unsuccessful. Based on present estimates, the reaction should be exothermic by about 20 kcal/mol. A further attempt to observe this reaction seems warranted.

From our previous estimate[6] of the lattice energy of $NF_4^+F^-$ as 147 kcal/mol and accessory data cited therewith and above, we estimate the enthalpy of formation of that substance to be -4 ± 10 kcal/mol. Decomposition to NF_3 and F_2 at 25° is therefore exothermic by 26 ± 10 kcal/mol. Nevertheless, the formation of $NF_4^+F^-$ at low temperatures is thermodynamically reasonable since NF_4^+ is stable with respect to its likely decomposition products, F^- is stable, and their union to form $NF_4^+F^-$ is favored by the lattice energy. The crystal is probably only kinetically stable, even at low temperatures, with respect to decomposition to nitrogen trifluoride and fluorine.

The formation of $NF_4^+F^-$ in the irradiation of mixtures of nitrogen trifluoride and fluorine at low temperatures therefore appears to be a reasonable possibility. The dependence of the yield on the mole ratio of fluorine to nitrogen trifluoride suggests that the rate of the reaction depends on the limited solubility of the latter substance in the former. The yield should be capable of enhancement by use of a stirred reactor. The alternative possibility for the product of this reaction,[34] $NF_4^+HF_2^-$ *via* a possible hydrogen fluoride impurity, seems unlikely for several reasons. (1) Precautions were taken to remove hydrogen fluoride and water from the reagents. (2) If the product had been $NF_4^+HF_2^-$, we are confident that we would have observed HF^+ in the mass spectrum of the decomposition products; we saw no trace of it. (3) The decomposition temperature of $NF_4^+HF_2^-$ is given by Tolberg, *et al.*,[35] as about 230°K, whereas our product decomposed below 143°K.

Further investigation of the radiation-induced reaction between nitrogen trifluoride and fluorine at low temperatures appears to be merited. Additional confirmation of NF_5 as a product could be obtained by improved mass spectrometry designed to detect fluorine in the decomposition products and by laser-Raman spectroscopy, which was not available to us when the experiments described herein were done.

Acknowledgments.—The work reported here was supported in large part by the Advanced Research Projects Agency under Contract No. DA-31-124-ARO (D)-54, monitored by the U. S. Army Research Office, Durham, N. C. The preparation of significant quantities of NF_4BF_4 was supported in part by a subcontract from the Dow Chemical Company, under Contract No. FO4611-67-C-0025 supported by the U. S. Air Force. We are grateful to Dr. G. C. Sinke and the Thermochemical Laboratory of Dow Chemical Company for permission to quote from their thermochemical results prior to publication. We are grateful also to Dr. W. E. Tolberg of Stanford Research Institute for useful discussions and to Dr. K. O. Christe of the Rocketdyne Division, North American Rockwell, Inc., for discussions and for assistance with the spectroscopic characterization of NF_4BF_4.

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[34] We are grateful to a referee for pointing out to us this possibility.

[35] W. E. Tolberg, R. T. Rewick, G. R. Zeilenga, M. P. Dolder, and M. E. Hill, submitted for publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Extraction of Some Anions from Molten Lithium Nitrate–Potassium Nitrate by Tetraoctylphosphonium Nitrate in Polyphenyl or 1-Nitronaphthalene Solvent

BY ZOILO C. H. TAN*[1] AND J. W. IRVINE, JR.

Received October 29, 1971

Tetraoctylphosphonium nitrate (TOPN) in a polyphenyl or 1-nitronaphthalene solvent has been used to extract perrhenate, chloride, and $AgCl_2^-$ ions from a eutectic molten salt mixture of $LiNO_3$–KNO_3 at 150°. The distribution coefficients of perrhenate and of chloride with TOPN in polyphenyl are comparable to those obtained previously with tetraheptylammonium nitrate (THAN), while the distribution coefficient of $AgCl_2^-$ in TOPN is greater. Distribution coefficients using 1-nitronaphthalene as the organic solvent are somewhat higher for ReO_4^- both with the phosphonium salt and with the ammonium salt. The dependence of the perrhenate distribution on the temperature and solute concentration was also studied with both polyphenyl and 1-nitronaphthalene. As in the case with THAN, the distribution of the anions is interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. The equilibrium constants for the anion-exchange and the dimerization constants were derived from the distribution data. Both quaternary salts polymerized strongly even at low solute concentrations although polymerization in 1-nitronaphthalene is less than that in polyphenyl. Also, the polymerization of the ammonium salt is stronger than that of the phosphonium salt in either solvent.

Introduction

Tetraheptylammonium nitrate (THAN) has been used to extract simple and complex anions from a $LiNO_3$–KNO_3 eutectic melt.[2] The distribution of the anions between the melt and the extractant has been interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. It was of interest to extend these studies to other organic extractants having ion-exchange characteristics.

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[1] Research Laboratories, Eastman Kodak Co., Rochester, N. Y. 14650.

[2] I. J. Gal, J. Mendez, and J. W. Irvine, Jr., *Inorg. Chem.* **7**, 985 (1968).

For an extension of this work, a new extractant, tetra-*n*-octylphosphonium nitrate (TOPN), was synthesized. A eutectic mixture of *o*-terphenyl, *m*-terphenyl, and biphenyl (designated as "polyphenyl") or 1-nitronaphthalene was used as the organic solvent. The eutectic mixture of $LiNO_3$–KNO_3 was the molten salt phase in all studies. The distribution of the anionic species ReO_4^-, Cl^-, and $AgCl_2^-$ between the nitrate melt and TOPN in polyphenyl solvent was studied. The distribution of ReO_4^- was also studied with 1-nitronaphthalene as the organic solvent in an effort to study the effect of variation in the dielectric constant of the solvent on extraction. The extraction of ReO_4^- with 1-nitronaphthalene as solvent was also determined with THAN as the extractant.

Experimental Section

The preparation of THAN, polyphenyl solvent, and eutectic nitrate melt and the procurement of the radioactive tracers ^{186}Re, ^{38}Cl, and ^{110m}Ag are described elsewhere.[2]

Preparation of Tetra-*n*-octylphosphonium Nitrate.—The method followed for the intermediate iodide is based on that suggested by Jerchel[3] and refined by Elhanan.[4] Tri-*n*-octylphosphine (M and T Chemicals Inc.) and 1-iodooctane (Eastman White Label) were mixed in the molar ratio of 1.1:1. Absolute ethyl alcohol was added to the mixture at the ratio of 1.5 ml of alcohol to 0.1 mol of tri-*n*-octylphosphine used. The mixture was stirred and refluxed for 5 hr at ~110°. Subsequent cooling at room temperature yielded a white crystalline mass. The tetra-*n*-octylphosphonium iodide was recrystallized several times from analytical grade ethyl acetate until it was pure white; after being dried under vacuum for 48 hr, it had a measured melting point of 88–89.5°.

Seventy-three grams of the iodide salt was dissolved in 180 ml of reagent grade toluene. The solution was shaken with 150 ml of 4 *N* $NaNO_3$ solution for about 30 min with an automatic shaker. After discarding the aqueous phase, the organic solution was shaken again with freshly prepared 4 *N* $NaNO_3$ solution. The shaking process was repeated at least 20 times or until the content of iodide in the washed solution was negligible. The final traces of iodide in the organic solution were removed by adding 25 ml of 0.1 *N* $AgNO_3$ solution. After separating the aqueous phase and precipitate, the organic phase was filtered and washed with water until tests showed that Ag^+ and I^- were absent. The solution was evaporated to dryness and then dried under vacuum for 48 hr. The solid product, recrystallized twice from a mixture of ethyl acetate and petroleum ether (bp 30–60°) and dried under vacuum for 48 hr, had a measured melting point of 65–66.5°. The yield was 80%. *Anal.* Calcd for $C_{32}H_{68}NO_3P$: C, 70.4; H, 12.55; N, 2.56; P, 5.67. Found: C, 69.65; H, 12.75; N, 2.52; P, 5.77.

1-Nitronaphthalene.—This compound was Eastman White Label grade with a melting point of 56.5–58.5°. Prior to use, it was melted and passed through a heated column of activated alumina (Alcoa, Grade F-1, 14–28 mesh).

Procedure for Determining Distribution Coefficients.—The experimental technique, using radioactive isotopes, was described previously.[2] In all extraction processes, an equilibration time of 60 min, sufficient to obtain equilibrium, was chosen. The molal distribution coefficient, *D*, of an anionic species was calculated as

$$D = \frac{\text{counts/(min)(g of organic solvent phase)}}{\text{counts/(min)(g of salt phase)}}$$

Each distribution coefficient is the average of at least two independent measurements. The standard deviation of the distribution coefficient is 1–4%, except in the range of *D* of 10^{-3} or lower (or *D* of 10^2 or higher), where it is up to 10%. Concentrations are expressed in molality, unless otherwise specified.

Results and Discussion

TABLE I

DISTRIBUTION COEFFICIENT, *D*, OF ReO_4^- AND Cl^- BETWEEN MOLTEN $LiNO_3$–KNO_3 AND TOPN IN POLYPHENYL AS A FUNCTION OF INITIAL TOPN CONCENTRATION C^i_{TOPN}[a]

C^i_{TOPN}, *m*	$D_{ReO_4^-}$	D_{Cl^-}
0	$\sim 10^{-5}$	$< 10^{-5}$
4.89×10^{-4}	1.73×10^{-2}	
1.00×10^{-3}	3.36×10^{-2}	1.04×10^{-4}
2.02×10^{-3}	6.42×10^{-2}	2.36×10^{-4}
3.00×10^{-3}	9.14×10^{-2}	
5.00×10^{-3}	1.45×10^{-1}	4.90×10^{-4}
8.00×10^{-3}	2.15×10^{-1}	
1.00×10^{-2}	2.67×10^{-1}	1.05×10^{-3}
2.00×10^{-2}	5.04×10^{-1}	2.01×10^{-3}
3.00×10^{-2}	7.60×10^{-1}	3.19×10^{-3}
5.00×10^{-2}	1.27	4.01×10^{-3}
8.00×10^{-2}	2.12	
1.00×10^{-1}	2.57	9.07×10^{-3}

[a] $C^i_{ReO_4^-} \approx 1.6 \times 10^5$ *m*; $C^i_{Cl^-} = 7.97 \times 10^{-2}$ *m*; temperature 150 ± 1°.

The Distribution of ReO_4^- and Cl^- with TOPN in Polyphenyl.—Representative extraction data for ReO_4^- and Cl^- at 150 ± 1° are given in Table I, as the distribution coefficient, *D*, *vs.* initial TOPN concentration C^i_{TOPN} at constant initial anion (X^-) concentration C^i_X in the melt. The distribution coefficients of both ReO_4^- and Cl^- increase with increasing TOPN concentration. An analysis of the data indicates that below a TOPN concentration of about 5×10^{-3} *m*, the distribution of X^- follows the simple anion exchange represented by

$$M^+X^- + \overline{TNO_3} \rightleftharpoons \overline{TX} + M^+NO_3^-$$

$$K_d = \frac{[\overline{TX}][M^+NO_3^-]\gamma_{MNO_3}}{[\overline{TNO_3}][M^+X^-]\gamma^*_{MX}} \qquad (1)$$

where $\overline{TNO_3}$ represents the tetraoctylphosphonium nitrate ion pair, $\overline{TX}$ is a similar ion pair with anion X^- instead of NO_3^-, $M^+ = 0.42Li^+ + 0.58K^+$, γ and γ^* are the activity coefficients with respect to the standard state (defined as $\gamma_{MNO_3} = 1$ when its mole fraction $X_{MNO_3} = 1$) and reference state (defined as $\gamma^*_{MX} = 1$ when $X_{MX} \rightarrow 0$), K_d is the equilibrium constant for the ion-exchange reaction, and the bar refers to the species in the organic phase. Figure 1 shows the dependence of the experimental values of *D* from Table I on the equilibrium concentration of TOPN monomer calculated by the method described previously.[2] The slope of the lower portion of each curve approaches unity, which confirms the reaction represented by eq 1.

At low initial concentration of ReO_4^- in the melt and TNO_3 concentration over a range of 5×10^{-4} to 3×10^{-2} *m*, it was possible to explain the ReO_4^- extraction by assuming four species in the organic phase, $\overline{TReO_4}$, $\overline{TReO_4 \cdot TNO_3}$, $\overline{TNO_3}$, and $\overline{(TNO_3)_2}$. The equilibrium constant (K_d) for the extraction of ReO_4^- and the two dimerization constants defined as

$$K_{20} = \frac{[\overline{(TNO_3)_2}]}{[\overline{TNO_3}]^2} \qquad (2)$$

and

$$K_{11} = \frac{[\overline{TNO_3 \cdot TX}]}{[\overline{TNO_3}][\overline{TX}]} \qquad (3)$$

were determined by the methods described previously.[2] These constants are given in Table II. The upper curve of Figure 1 shows that the equation

$$D = \frac{[\overline{TX}] + [\overline{TNO_3 \cdot TX}]}{[M^+X^-]} \qquad (4)$$

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(3) D. Jerchel, *Ber.*, **76**, 601 (1943).

(4) J. Elhanan, personal communication, 1967.

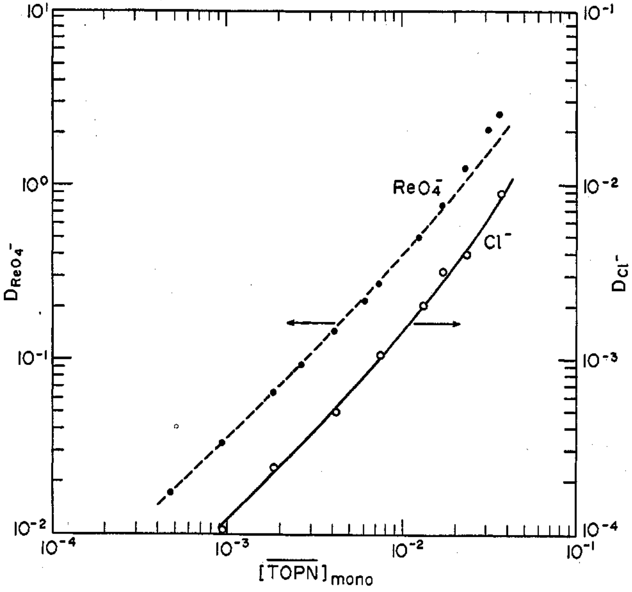

Figure 1.—Plot of the distribution coefficient, D, of ReO_4^- and Cl^-, against the equilibrium molality of $\overline{TOPN}$ monomer in polyphenyl, $\overline{[TOPN]}_{mono}$; temperature 150 ± 1°: ●, ReO_4^-; ○, Cl^-. $[ReO_4^-] \approx 1.6 \times 10^{-5}$ *m* initially in the melt; $[Cl^-] \approx 7.97 \times 10^{-2}$ *m* initially in the melt. The broken curve is the theoretical curve for ReO_4^- calculated from eq 4.

TABLE II

EQUILIBRIUM CONSTANTS AT 150 ± 1° (MOLALITY SCALE)

Symbol	Eq	Equil	Organic sol	Equil const	Source
K_d	1	ReO_4^-–$\overline{TReO_4}$	TOPN in polyphenyl	410	This work
	1	ReO_4^-–$\overline{TReO_4}$	TOPN in 1-nitronaphthalene	912	This work
	1	ReO_4^-–$\overline{TReO_4}$	THAN in polyphenyl	420	Ref 2
	1	ReO_4^-–$\overline{TReO_4}$	THAN in 1-nitronaphthalene	920	This work
	1	Cl^-–$\overline{TCl}$	TOPN in polyphenyl	0.77	This work
	1	Cl^-–$\overline{TCl}$	THAN in polyphenyl	2.1	Ref 2
K_{20} (dimerizn)	2	$\overline{(TOPN)_2}$	TOPN in polyphenyl	25	This work
	2	$\overline{(TOPN)_2}$	TOPN in 1-nitronaphthalene	20	This work
	2	$\overline{(THAN)_2}$	THAN in polyphenyl	50	Ref 2
	2	$\overline{(THAN)_2}$	THAN in 1-nitronaphthalene	32	This work
K_{11} (assocn)	3	$\overline{TNO_3 \cdot TReO_4}$	TOPN in polyphenyl	10	This work
	3	$\overline{TNO_3 \cdot TReO_4}$	TOPN in 1-nitronaphthalene	10	This work
	3	$\overline{TNO_3 \cdot TReO_4}$	THAN in polyphenyl	59	Ref 2
	3	$\overline{TNO_3 \cdot TReO_4}$	THAN in 1-nitronaphthalene	24	This work
K_d	7	$AgCl_2^-$–$\overline{TAgCl_2}$	TOPN in polyphenyl	35,000	This work
	7	$AgCl_2^-$–$\overline{TAgCl_2}$	THAN in polyphenyl	2510	Ref 2

TABLE III

DISTRIBUTION COEFFICIENT, D, OF CHLORIDE BETWEEN MOLTEN $LiNO_3$–KNO_3 AND TOPN IN POLYPHENYL AS A FUNCTION OF INITIAL CHLORIDE CONCENTRATION $C^i_{Cl^-}$ IN THE MELT[a]

D_{Cl^-}	$C^i_{Cl^-}$, *m*	D_{Cl^-}	$C^i_{Cl^-}$, *m*
1.11×10^{-3}	6.00×10^{-2}	4.09×10^{-4}	5.00×10^{-1}
1.05×10^{-3}	7.97×10^{-2}	3.87×10^{-4}	7.00×10^{-1}
9.49×10^{-4}	1.00×10^{-1}	3.76×10^{-4}	8.00×10^{-1}
5.57×10^{-4}	1.97×10^{-1}	3.54×10^{-4}	1.00
4.41×10^{-4}	3.00×10^{-1}		

[a] $C^i_{TOPN} = 1.00 \times 10^{-2}$ *m*; temperature 150 ± 1°.

and the values of the equilibrium constants in Table II describe fairly well the distribution of tracer ReO_4^- over a range of TOPN concentration of three orders of magnitude. The points are the experimental values of D, while the curve is the theoretical curve from eq 4 which is set by the values found for K_d, K_{20}, and K_{11}. The increasing slope of the ReO_4^- curve at high TOPN concentration can be explained by the formation of higher polymeric species in the organic phase that are neglected in the present treatment.

At a given concentration of TOPN, increasing the ReO_4^- concentration from 1.6×10^{-5} *m* (Table I) to 1.00×10^{-3} *m* does not change the distribution coefficient of ReO_4^-. Further increase in ReO_4^- concentration, however, tends to decrease the distribution coefficient especially at low TOPN concentration. For example, at 1×10^{-2} *m* ReO_4^-, the decrease in average values of D range from about 18% at 1×10^{-3} *m* TOPN and 9% at 3×10^{-2} *m* TOPN to 0% at 1×10^{-1} *m* TOPN. This is explained as due to the saturation of TOPN with ReO_4^- as will be discussed in more detail later. The standard deviation of D at these concentrations of TOPN was mentioned previously to be 1–4%.

The lower curve of Figure 1 is a plot of the experimental values of chloride. By means of the dimerization constant, K_{20}, for TOPN, the extraction of chloride can be explained also by eq 4 assuming $\overline{TCl}$ as the principal chloride species in the organic solvent. The theoretical curve of the chloride distribution is not calculated since the distribution coefficients of chloride are 2–3 orders of magnitude lower than those of perrhenate; therefore, the error inherent with these low values of D is too large to demonstrate the presence of the polymeric species if their formation constants are small compared to K_{20}. Also, the addition of inactive (K,Li)Cl into the melt to constitute a concentration of about 5×10^{-2} *m* is necessary to obtain reproducible distribution data.

The dependence of D on the Cl^- concentration is summarized in Table III. At 1 *m* chloride concentration in the melt, only about 3.5% of TOPN is in the chloride form. It is, therefore, reasonable to assume that at up to 1 *m* chloride concentration in the melt, $\overline{TCl}$ is still the principal chloride species in the organic solvent. Thus, the decrease of D with increasing chloride concentration in the melt can be attributed to changes in the activity coefficients of the nitrate and chloride components of the melt. The dependence of D on the chloride concentration in the melt follows the simple relation[2]

$$\log \left(D \frac{[M^+NO_3^-]}{\overline{[TNO_3]}} \right) = \log K_d - 2b_{NO_3-Cl}X_{Cl} \qquad (5)$$

Here X_{Cl} is the mole fraction of chloride in the melt, and b_{NO_3-Cl} is a constant containing the difference between the interaction energy terms of anions NO_3^- and Cl^-. It was found that $b_{NO_3-Cl} = 0.85$. The equilibrium constant, $K_d = 0.77$, as given in Table II, is obtained from the intercept of a plot of eq 5. It

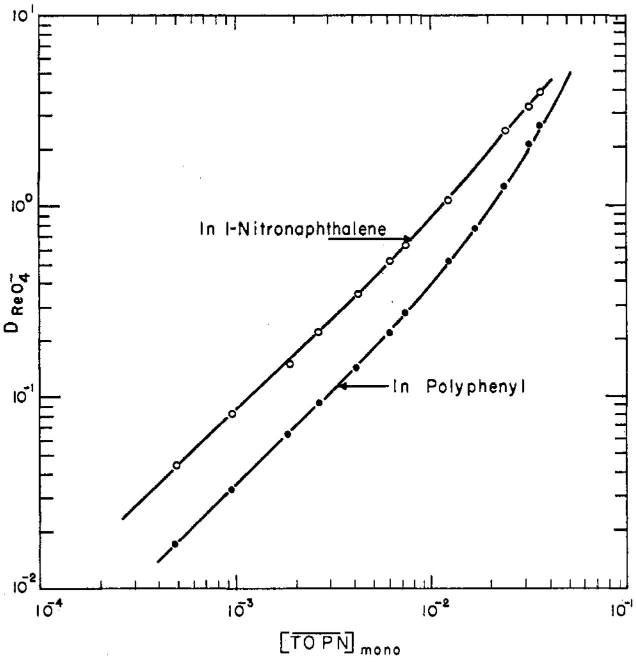

Figure 2.—The effect of dielectric constant of the solvent upon the extraction of ReO_4^-. Plot of log D against log $[\overline{TOPN}]_{mono}$. $[ReO_4^-]$ = 1.6 × 10^{-5} m initially in the melt; temperature 150 ± 1°: ●, in polyphenyl solvent; ○, in 1-nitronaphthalene solvent.

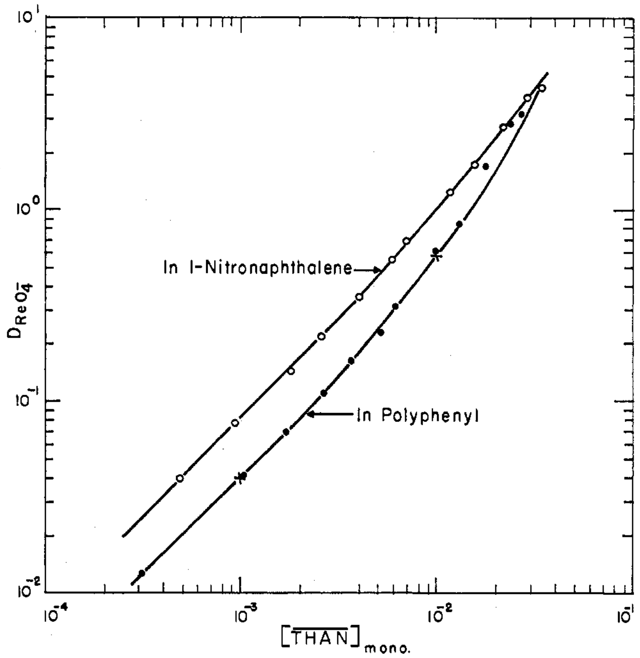

Figure 3.—The effect of dielectric constant of the solvent upon the extraction of ReO_4^-. Plot of log D against log $[\overline{THAN}]_{mono}$. $[ReO_4^-]$ = 1.6 × 10^{-5} m initially in the melt; temperature 150 ± 1°: ●, in polyphenyl solvent, data of Gal;[2] ×, this work; ○, in 1-nitronaphthalene solvent.

refers to the dilute solution as reference state, defined by $\gamma^*_{Cl} = 1$ for $X_{Cl} \rightarrow 0$.

Extraction of ReO_4^- with a Solvent of Higher Dielectric Constant.—In an attempt to study the effect of changing the dielectric constant of the solvent upon the extraction, 1-nitronapthalene was used instead of polyphenyl in the extraction of ReO_4^- by TOPN and THAN at 150 ± 1°. The results of the distribution of ReO_4^- with TOPN in 1-nitronaphthalene are compared with the distribution data obtained from polyphenyl in Figure 2. Although 1-nitronaphthalene has an extrapolated dielectric constant value of ϵ = 14.26 at 150°,[5] which is relatively large compared with the low-dielectric polyphenyl, where ϵ = 2.4 for biphenyl at 150°,[6] the observed effect on the extraction of ReO_4^- is not large. As shown in Figure 2, at lower TOPN concentration, the distributions of ReO_4^- in 1-nitronaphthalene as solvent are about 2–2.5 times that in polyphenyl as solvent, while at higher TOPN concentration, the difference in the distribution is very small. A similar observation (Figure 3) was obtained with THAN in 1-nitronaphthalene when compared with the results in polyphenyl.[2]

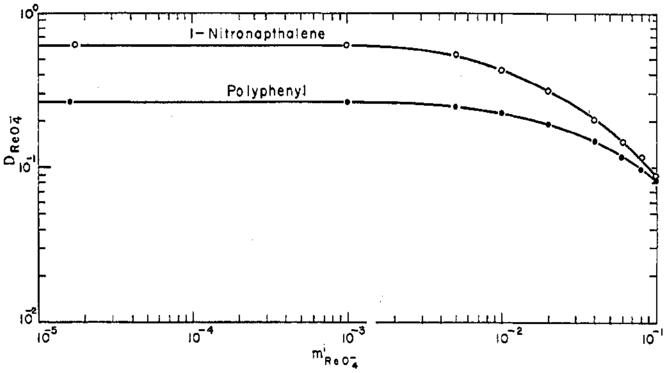

Figure 4.—Dependence of the distribution of ReO_4^- on ReO_4^- concentration at 150 ± 1° under constant TOPN concentration in organic solvent, $[\overline{TOPN}]$ = 1.00 × 10^{-2} m: ●, in polyphenyl solvent; ○, in 1-nitronaphthalene solvent.

The polymerization of both extractants in 1-nitronaphthalene is less than that in polyphenyl as evident from the lower values of the dimerization constant K_{20} in Table II and smaller increase of the slope of the distribution curves in 1-nitronaphthalene at high TOPN concentrations (Figures 2 and 3). In either solvent, TOPN is less associated than is THAN. This is evident from Table II, where the dimerization constants, K_{20}, of TOPN and THAN are 25 and 50, respectively, in polyphenyl and 20 and 30, respectively, in 1-nitronaphthalene. A similar trend in the self-association of these two salts has been observed by Gal[7] from osmometric measurements.

The Dependence of ReO_4^- Distribution on ReO_4^- Concentration.—The effect of ReO_4^- concentration on the distribution coefficient of ReO_4^- was studied with TOPN in both polyphenyl and 1-nitronaphthalene as solvents. The results at 1 × 10^{-2} m TOPN are summarized in Figure 4. In both cases, D is almost constant at low ReO_4^- concentration up to 1 × 10^{-3} m ReO_4^- and begins to drop at about 5 × 10^{-3} m ReO_4^-. This is due mainly to the saturation of TOPN with ReO_4^- in the organic phase. As the ReO_4^- concentration in the melt is increased, it can be calculated that the equilibrium concentration of ReO_4^- in the or-

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(5) S. K. K. Jatkar and V. K. Phansalkar, *J. Univ. Poona, Sci. Technol.*, **No. 22**, 65 (1962).

(6) "Handbook of Chemistry and Physics," C. D. Hodgman, Ed., 42nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 2521.

(7) I. J. Gal, I. Paligoric, and V. G. Antonijević, *J. Inorg. Nucl. Chem.*, **32**, 1645 (1970).

TABLE IV

DISTRIBUTION COEFFICIENT, D, OF ReO_4^- BETWEEN MOLTEN $LiNO_3$–KNO_3 AND TOPN IN POLYPHENYL (OR 1-NITRONAPHTHALENE) AS A FUNCTION OF INITIAL TOPN CONCENTRATION IN THE ORGANIC SOLVENT, C^i_{TOPN}, AND VARYING TEMPERATURE[a]

Polyphenyl		1-Nitronaphthalene	
C^i_{TOPN}, m	D	C^i_{TOPN}, m	D
150 ± 1°			
0	1×10^{-5}	0	2.25×10^{-3}
9.94×10^{-4}	3.36×10^{-2}	1.00×10^{-3}	8.08×10^{-2}
3.00×10^{-3}	9.14×10^{-2}	3.03×10^{-3}	2.19×10^{-1}
1.00×10^{-2}	2.67×10^{-1}	1.00×10^{-2}	6.17×10^{-1}
3.00×10^{-2}	7.60×10^{-1}	3.00×10^{-2}	1.57
1.00×10^{-1}	2.57	1.00×10^{-1}	3.88
160 ± 1°			
0	1×10^{-5}	0	2.07×10^{-3}
9.99×10^{-4}	3.00×10^{-2}	1.03×10^{-3}	6.31×10^{-2}
3.00×10^{-3}	8.18×10^{-2}	3.00×10^{-3}	1.78×10^{-2}
9.98×10^{-3}	2.41×10^{-1}	1.00×10^{-2}	5.44×10^{-1}
3.00×10^{-2}	7.17×10^{-1}	3.00×10^{-2}	1.40
1.00×10^{-1}	2.52	1.00×10^{-1}	3.64
170 ± 1°			
0	1×10^{-5}	0	1.74×10^{-3}
1.00×10^{-3}	2.82×10^{-2}	1.00×10^{-3}	5.45×10^{-2}
3.00×10^{-3}	7.67×10^{-2}	3.00×10^{-3}	1.53×10^{-1}
9.97×10^{-3}	2.19×10^{-1}	9.98×10^{-3}	4.74×10^{-1}
3.00×10^{-2}	6.48×10^{-1}	3.00×10^{-2}	1.25
1.00×10^{-1}	2.26	1.00×10^{-1}	3.23

[a] $[ReO_4^-] \approx 1.6 \times 10^{-5}$ m initially in the melt.

ganic solution approaches the initial concentration of TOPN as a limit.

The foregoing shows that in contrast to the behavior found in the extraction of trivalent metal halides in acidic aqueous system,[8,9] the distribution of ReO_4^- as a function of ReO_4^- concentration in molten salt shows a similar trend both in the low-dielectric solvent (polyphenyl) and in the high-dielectric solvent (1-nitronaphthalene). That is, the distribution coefficient, D, increases with decreasing ReO_4^- concentration C^i_X and becomes independent of C^i_X below 1×10^{-3} m.

The Effect of Temperature upon the TOPN Extraction of ReO_4^-.—The dependence of ReO_4^- distribution upon temperature was studied in both polyphenyl and 1-nitronaphthalene solvent at 150 ± 1, 160 ± 1, and 170 ± 1°. A distinct temperature dependence of D was found in both solvents as shown in Table IV. The K_d values in Table V were obtained by extrapolating to $C^i_{TOPN} = 0$ the plots of log $[D[MNO_3]/C^i_{TOPN}]$ *vs.* C^i_{TOPN} assuming that at low TOPN concentration, the equilibrium monomer concentration of TOPN is equal to C^i_{TOPN}. The values of D used in the plot were corrected for D_0, the distribution coefficient of ReO_4^- due to the extraction of pure solvent.

A plot of the logarithm of K_d *vs.* the reciprocal of the absolute temperature yields a straight line. The enthalpy changes, entropy changes obtained from the slope of this curve, and the standard free energy calculated from the relation $\Delta G° = -RT \ln K_d$ are given in Table V. These values are the thermodynamic quantities that pertain to the reaction represented by eq 1.

TABLE V

EQUILIBRIUM CONSTANTS, K_d, AT VARYING TEMPERATURE AND THERMODYNAMIC QUANTITIES OF THE REACTION BETWEEN ReO_4^- AND TOPN REPRESENTED BY EQ 1[a]

	Polyphenyl			1-Nitronaphthalene		
	150°	160°	170°	150°	160°	170°
K_d	410	351	308	912	695	592
$\Delta G°$, kcal mol^{-1}		−5.06			−5.72	
$\Delta H°$, kcal mol^{-1}		−5.80			−8.14	
$\Delta S°$, eu		−1.75			−5.72	

[a] $[ReO_4^-] \approx 1.6 \times 10^{-5}$ m in the melt.

The Distribution of $AgCl_2^-$ with TOPN in Polyphenyl.—In the presence of chloride in the molten salt phase, it is assumed that silver is present as the species Ag^+, AgCl, and $AgCl_2^-$. At low chloride concentration, silver is extracted into the organic phase as $\overline{TAg^I\text{–}NO_3}$ complexes and $\overline{TAgCl_2}$. The distribution coefficient of silver between the melt and the organic phase is, therefore, a sum of the distribution of Ag^+ and $AgCl_2^-$ species in the melt. However, at the higher chloride concentration, at which the silver in the melt is principally in the form of $AgCl_2^-$, the silver species extracted into the organic phase will be, mostly, $\overline{TAgCl_2}$ so that

$$D = \frac{[\overline{TAgCl_2}]}{C_{Ag}} = \frac{[\overline{TAgCl_2}]}{[Ag^+] + [AgCl] + [AgCl_2^-]} \qquad (6)$$

Here C_{Ag} is the total concentration of silver in the melt.

The distribution ratio of silver to chloride between a melt approximately 0.3 and 0.5 m in MCl and 8×10^{-4} m in $AgNO_3$ and an organic phase 1×10^{-2} m TOPN in polyphenyl was determined using 260-day ^{110m}Ag and 37-min ^{38}Cl as tracers in two samples of this melt. The results are shown in Table VI. These data, subject to experimental error of 5–10%, showed that at these chloride concentrations in the melt, the ratio of Cl to Ag in the extracted species is 2:1 indicative of $\overline{TAgCl_2}$ as the extracted species.

On the basis of this result, the distribution of silver can be described by the ion-exchange equilibrium

$$M^+AgCl_2^- + \overline{TNO_3} = \overline{TAgCl_2} + M^+NO_3^-$$

$$K_d = \frac{[\overline{TAgCl_2}][M^+NO_3^-]\gamma_{MNO_3}}{[\overline{TNO_3}][M^+AgCl_2^-]\gamma^*_{MAgCl_2}} \qquad (7)$$

Defining the "degree of formation" of $AgCl_2^-$ as[10]

$$\alpha_2 = \frac{[AgCl_2^-]}{C_{Ag}} \qquad (8)$$

and introducing (6) and (8) into (7)

$$\log D = \log K_d + \log [\overline{TNO_3}] + \log \left(\frac{\alpha_2 \gamma^*_{MAgCl_2}}{[M^+NO_3^-]\gamma_{NO_3}}\right) \qquad (9)$$

At constant concentration of MCl and tracer amounts of silver, the last term of eq 9 is constant. A plot of log D *vs.* log $[\overline{TNO_3}]$, the equilibrium concentration of TOPN monomer, should give a straight line with slope of +1. This is the case of the upper curve in each set of curves in Figure 5 (open circles) for a melt 0.2 and 0.3 m in MCl. The lower curves are plots of D as a function of initial total concentration of TOPN (filled circles). As shown, at lower concentration of TOPN, the curves are linear with both slopes approaching +1. The increasing slope of the curves at higher TOPN

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TABLE VI

THE Cl:Ag RATIO IN THE ORGANIC PHASE[a]

Initial molality in melt		Distribution coeff		Equil molality in organic phase		Molality of Cl bound to Ag in organic phase,	Mole ratio
m^i_{Cl}	m^i_{Ag}	D_{Cl}	D_{Ag}	$\overline{m_{Cl}}$	$\overline{m_{Ag}}$	$\bar{m}'_{Cl}$	$\bar{m}'_{Cl}/\overline{m_{Ag}}$
0.300	8.60×10^{-4}	3.84×10^{-3}	1.24	1.15×10^{-3}	5.18×10^{-4}	1.02×10^{-3}	1.97
0.300	...	4.30×10^{-4}	...	1.29×10^{-4}	...	...	
0.500	8.10×10^{-4}	2.10×10^{-3}	1.08	1.05×10^{-3}	4.42×10^{-4}	8.65×10^{-4}	1.95
0.500	...	3.81×10^{-4}	...	1.90×10^{-4}	...	...	

[a] [TOPN] = 1.00×10^{-2} *m* in polyphenyl; temperature 150 ± 1°.

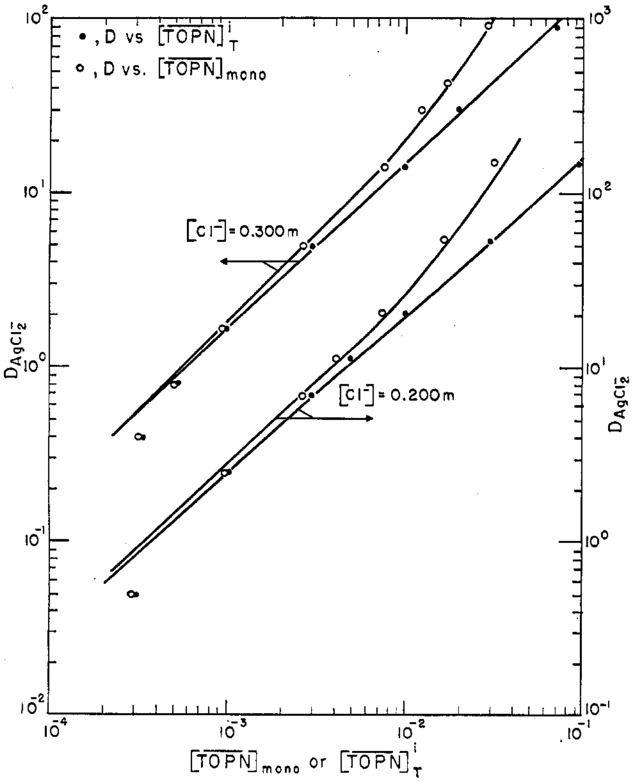

Figure 5.—Dependence of the distribution coefficient of $AgCl_2^-$ on TOPN concentration in polyphenyl at 150 ± 1°C. $[Ag^+] \approx 1.5 \times 10^{-6}$ *m* initially in the melt; $[Cl^-] = 0.300$ *m*, 0.200 *m* initially in the melt: ○, *D vs.* $\overline{[TOPN]}_{mono}$, the equilibrium monomer concentration of TOPN; ●, *D vs.* $\overline{[TOPN]}^i_T$, the initial total concentration of TOPN in polyphenyl.

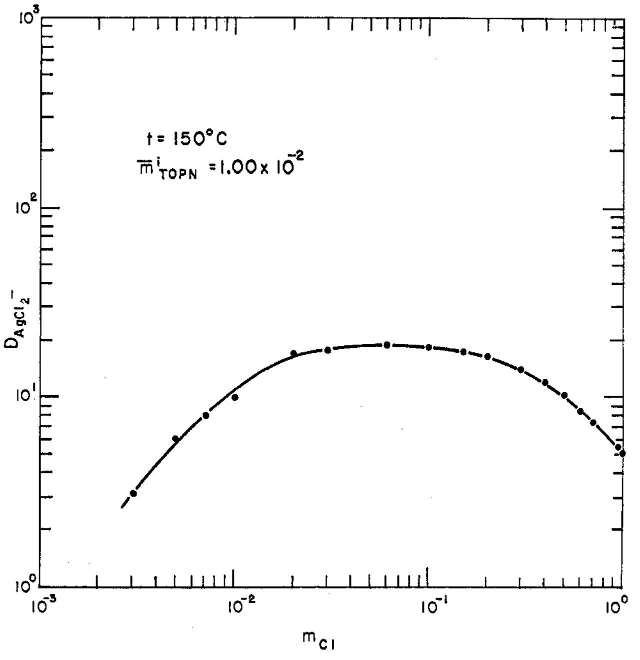

Figure 6.—Dependence of the distribution coefficient *D* of $AgCl_2^-$ on chloride concentration. $m^i_{TOPN} = 1.00 \times 10^{-2}$ in polyphenyl; temperature 150 ± 1°.

concentration is probably due to the formation of $[\overline{TAgCl_2}]_2$ homopolymer.

Equation 9 can be rewritten as[2]

$$\log \left(D \frac{[M^+NO_3^-]}{\overline{[TNO_3]}}\right) = \log K_d + \log \alpha_2 + \Lambda X_{Cl} \qquad (10)$$

where $\Lambda = b_{MCl-MAgCl_2} - b_{MNO_3-MAgCl_2} - b_{MNO_3-MCl}$. b_{A-B} is the interaction energy between A and B defined earlier. The dependence of *D* on the concentration of MCl is shown in Figure 6. A plot of log $(D[M^+NO_3^-]/\overline{[TNO_3]})$ *vs.* X_{Cl}, the mole fraction of chloride in the melt, yields a straight line with an intercept value of K_d = 35,000. The slope of the line is Λ, with a value of −8.01. This value of Λ and the value of b_{NO_3-Cl} obtained from the chloride extraction were used to calculate the activity coefficients of the anionic species present in the melt. At low concentration of MCl ($\leq 2 \times 10^{-2}$ *m* in the melt), the activity coefficients of all species were calculated to be close to unity and the solution can be assumed to behave ideally. As more MCl is added, more $AgCl_2^-$ is formed in the melt and the value of *D* increases. If MCl is added when $AgCl_2^-$ is the principal silver species in the melt and $\overline{TAgCl_2}$ is the principal silver species in the organic phase, then *D* reaches a maximum. Further addition of MCl causes the activity coefficients of the species in the melt to decrease; probably higher chloride complexes of silver form, causing *D* values of $AgCl_2^-$ to decrease.

The stability constants K_1 and K_2 for the species AgCl and $AgCl_2^-$, respectively, were recalculated on the molality scale from α_2 values obtained from eq 10 using the curve-fitting methods described by Rossotti and Rossotti.[2,11] The values obtained are $K_1 = 300 \pm 20$, $K_2 = 117 \pm 10$. These values are in good agreement with those obtained from solvent extraction measurement,[2] solubility measurement,[12] and electromotive force measurement.[13,14]

Comparison of the Extraction Power of THAN and TOPN on the Anionic Species ReO_4^-, Cl^-, and $AgCl_2^-$

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from Molten Salts.—A comparison of the results obtained in this work with those obtained by Gal[2] shows that THAN and TOPN are comparable in extraction power for ReO_4^- and Cl^-. Within experimental error, the distribution coefficients of ReO_4^- and Cl^- with TOPN as the extractant are essentially the same as those obtained with THAN in the same solvent. The distribution coefficient of Cl^- with TOPN, however, decreases faster with increasing chloride concentration, especially for $[Cl^-] > 1 \times 10^{-1}\ m$.

For $AgCl_2^-$, however, TOPN is a much better extractant. The distribution coefficient of $AgCl_2^-$ at 150° in the presence of 0.2 *m* Cl^-, for example, is $D = 2.37$ at $3.00 \times 10^{-2}\ m$ THAN in polyphenyl,[2] while $D = 52.6$ using the same concentration of TOPN under similar conditions (*cf.* Figure 5).

TOPN is found to be thermally more stable than THAN. A 1.5-g sample of TOPN heated in air for 1 hr at 150° decreased only 0.07% in weight, while similar treatment of THAN caused a weight loss of 0.6%.[2] Furthermore, it was observed that upon heating, THAN changes to a yellowish color at a faster rate than TOPN.

The high distribution coefficient of $AgCl_2^-$ suggests that TOPN might be a desirable extractant for other metal halide and metal nitrate complexes from molten eutectic salt mixtures. The order of extractability of the various ions studied is the same with both extractants, *i.e.*, $AgCl_2^- > ReO_4^- > Cl^-$.

Acknowledgment.—The authors are grateful to the late Professor C. D. Coryell for much helpful discussion and criticism. The partial financial supports made available by the U. S. Atomic Energy Commission under Contract No. AT-(30-1)-305 and the Massachusetts Institute of Technology Chemistry Department for awarding Z. C. H. T. a Forris Jewett Moore Memorial Fellowship are appreciated.

CONTRIBUTION FROM THE COLLEGE OF ST. CATHERINE, ST. PAUL, MINNESOTA 55116,
AND ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439

A Kinetic Study of the Oxidation of Formic Acid by Neptunium(VII) in Aqueous Perchloric Acid Solution[1]

BY MARY THOMPSON[2] AND JAMES C. SULLIVAN*

Received December 15, 1971

The empirical form of the rate law for the reaction $2NP(VII) + HCOOH = 2Np(VI) + 2H^+ + CO_2$ at constant hydrogen ion concentration is $-d[Np(VII)]/dt = k'[Np(VII)][HCOOH]$. At 25° and $I = 1.0$, $k' = a + b/[H^+]$ where $a = 0.4015\ M^{-1}\ sec^{-1}$ and $b = 5.38 \times 10^{-2}\ sec^{-1}$. Apparent energies of activation for the respective parameters are 6.44 and 10.5 kcal/mol. There is no solvent deuterium effect on the *a* parameter but one of 4.2 for *b*. The respective values of *a* and *b* for the reaction with DCOOH (25°, $I = 1.0$) are $2.64 \times 10^{-2}\ M^{-1}\ sec^{-1}$ and $5.10 \times 10^{-3}\ sec^{-1}$ with apparent energies of activation 8.92 and 12.8 kcal/mol. The primary kinetic isotope effects form the basis for the suggestion that the mechanism is similar for the two reaction paths.

The results obtained in kinetic studies of the oxidation of formic acid by a number of different metal ions have been presented.[3] The salient features of such studies in perchlorate media appear to be as follows: (a) the empirical form of the rate law is first order in oxidant and reductant with terms independent and inverse in hydrogen ion concentration; (b) there is an apparent correlation between increasing values of the redox potentials of the metal ions and rate parameters and decreasing values of the primary isotopic kinetic effect. In this article we present the results obtained with Np(VII) as the oxidant. This reagent has a redox potential >-2.0 V,[4] which provides a greater thermodynamic driving force for the reaction than the oxidants utilized in previous studies. The results to be presented thus extend the range over which the oxidation of formic acid can be compared to thermodynamic properties of the oxidant. In addition the results provide further information on the chemical dynamic behavior of Np(VII) in acid media.

Experimental Section

Reagents.—The preparation and standardization of the Np(VII), $HClO_4$, $LiClO_4$, and $NaClO_4$ solutions have been previously described.[5] The D_2O was purified by distillation from alkaline permanganate and was 99.7% isotopically pure.[6] Deuterioperchloric acid and deuterioformic acid were obtained from commercial sources.[7] Baker reagent grade formic acid was twice recrystallized.

Procedures.—The spectrophotometric kinetic studies have been previously detailed.[5] A CEC mass spectrometer was used in the identification of the gaseous product.[8]

The reactions were carried out with a large excess of formic acid to minimize possible complications due to the oxidation of water by Np(VII). Under the experimental conditions utilized the kinetic data could be adequately described by the usual integrated form of the first-order rate law expressed as

$$A = A_\infty + (A_0 - A_\infty)e^{+kt} \qquad (1)$$

Each kinetic experiment was monitored for at least 3 half-lives. Between 20 and 30 absorbance–time data points were adjusted

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* Address correspondence to this author at Argonne National Laboratory.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Member, Argonne National Laboratory Faculty Research Participation Program, 1971.

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(6) We are indebted to Dr. H. L. Crespi of the Chemistry Division for providing the purified D_2O.

(7) $DClO_4$ was obtained from Diaprep, Inc., and DCOOH from Stohler Isotope Chemicals.

(8) We are indebted to A. Engelkemeir for these measurements.