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.*, $AgCl_2^- > ReO_4^- > Cl^-$.

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

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The empirical form of the rate law for the reaction 2NP(VII) + HCOOH = 2Np(VI) + $2H^+$ + CO_2 at constant hydrogen ion concentration is $-d[\mathrm{Np(VII)}]/dt = k'[\mathrm{Np(VII)}][\mathrm{HCOOH}]$. 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 2.64×10^{-2} M^{-1} sec^{-1} and 5.10×10^{-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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(2) Member, Argonne National Laboratory Faculty Research Participation Program, 1971.

(3) For a resumé, see K. B. Wiberg, Ed., "Oxidations in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(4) J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, **5** (1969).

(5) R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **92**, 3028 (1970).

(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.

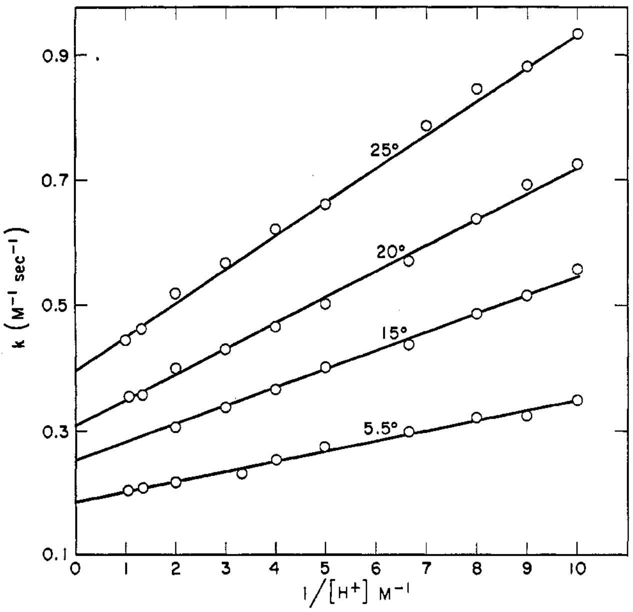

Figure 1.—[H^+] and temperature dependencies of k'. $I = 1.0$ with $LiClO_4$. Listed for each temperature are $10^4[Np(VII)]_0$ (M), $10^2[HCOOH]_0$ (M), number of independent determinations: 5.5°, 3.03, 3.62, 18; 15.0°, 3.78–3.99, 1.83–3.63, 16; 20.0°, 3.69, 1.83, 20; 25.0°, 3.84–19.9, 0.458–3.83, 42.

by a least-squares computation in terms of (1). The absorptivity data for a given experiment were reproduced by this expression to within 0.002–0.003 OD unit. The magnitude of the precision indices estimated for the rate parameters (based on external consistency) and the spread in the reproducibility of such a parameter are illustrated by the following data. At 25.0°, $I = 1.0$, $[H^+] = 0.101$, $[Np(VII)]_0 = (4.04\text{–}4.13) \times 10^{-4}$ M, and $[HCOOH]_0 = 1.83 \times 10^{-2}$ M, the values computed for $10^2 \cdot k'$ (sec^{-1}) were 1.732 ± 0.003, 1.770 ± 0.003, 1.699 ± 0.004, 1.753 ± 0.005, 1.783 ± 0.002, and 1.778 ± 0.003.

Results and Discussion

The formal stoichiometry for the reaction under consideration is

$$2Np(VII) + HCOOH = 2Np(VI) + CO_2 + 2H^+ \qquad (2)$$

The following observations provide evidence that is consistent with eq 2. (a) The sole metal ion reduction product that could be determined spectrophotometrically was Np(VI). (b) There was no detectable reaction between Np(VI) (10^{-3} M) and formic acid (to concentrations of 2 M) at 25°. (c) The gas produced when Np(VII) was reduced in solutions containing excess formic acid was determined by mass spectrometric scan to be CO_2.[9]

Kinetics of the Reaction.—The variation of the apparent first-order rate parameter, k', is linear as a function of the initial formic acid concentration. At 25°, $I = 1.0$, $[Np(VII)]_0 = 4.04 \times 10^{-4}$ M, $[H^+] = 0.101$ M, and 4.0×10^{-3} M < $[HCOOH]_0$ < 38.0×10^{-3} M, the values computed for the slope and intercept of the line (based on 21 independent determinations) are 0.933 ± 0.008 M^{-1} sec^{-1} and (1.7 ± 11.9) × 10^{-5} sec^{-1}. The empirical form of the rate law at constant hydrogen ion concentration based on these data is

$$-d[Np(VII)]/dt = k[Np(VII)][HCOOH] \qquad (3)$$

The variation of the second-order rate parameter as a function of hydrogen ion concentration and temperature is presented in Figure 1. At each temperature the data were adequately correlated by the relation

$$k'' = a + b/[H^+] \qquad (4)$$

At 5.5, 15.0, 20.0, and 25.0° respectively values computed for a (M^{-1} sec^{-1}), 10^2b (sec^{-1}) were 0.1887 ± 0.0028, 1.588 ± 0.045; 0.2561 ± 0.0097, 2.93 ± 0.16; 0.3102 ± 0.0043, 4.103 ± 0.085; and 0.4015 ± 0.0067, 5.38 ± 0.10.

These parameters are assumed to be a measure of parallel reaction paths. Based upon this interpretation apparent energies of activation calculated for the paths independent of and inverse in hydrogen ion respectively are 6.44 ± 0.29 and 10.5 ± 0.2 kcal/mol.

Table I summarizes the results obtained for the effect on the rate parameter of varying the concentration of the supporting electrolytes, lithium perchlorate or sodium perchlorate, at a constant initial acidity.

TABLE I[a]

$LiClO_4$				$NaClO_4$	
I	k	I	k	I	k
0.25	1.05	1.45	0.865	0.55	0.978
0.50	1.02	1.70	0.810	1.05	0.910
0.75	1.00	1.95	0.788	1.75	0.772
1.20	0.936	3.55	0.583	3.55	0.576

[a] At 25°, $[H^+] = 0.101$ M, $[Np(VII)]_0 = 4.04 \times 10^{-4}$ M, and $[HCOOH]_0 = 1.84 \times 10^{-2}$ M. Units of k are M^{-1} sec^{-1}. Values are the average of two to four independent determinations.

Deuterium Isotope Effects.—Figure 2 summarizes the variation of the second-order rate parameter with change in the mole fraction of D_2O.

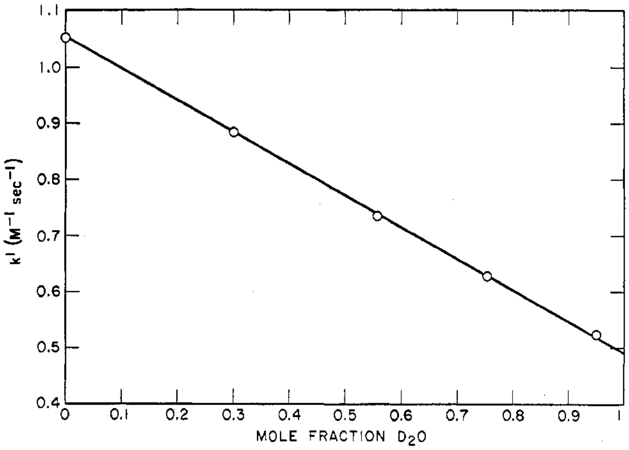

Figure 2.—Variation of k' as a function of the mole fraction of D_2O. $[D^+] = 0.100$ M; $I = 0.167$; temperature 25°; $[HCOOD]_0 = 0.0181$ M; $[Np(VII)]_0 = 3.68 \times 10^{-4}$ M. There were 10 determinations.

The rate parameter varies linearly with the reciprocal of the hydrogen ion concentration even when the ionic strength varies; *i.e.*, it is determined by the concentration of the acid. In Figure 3, the results obtained for such experiments with $HClO_4$–H_2O and $DClO_4$–D_2O are summarized. Values computed for the intercept (M^{-1} sec^{-1}), slope (sec^{-1}) in the H and D systems respectively are 0.3828 ± 0.0092, (7.17 ± 0.31) × 10^{-2}; and 0.377 ± 0.014, (1.70 ± 0.17) × 10^{-2}.

The change in the rate parameter for the oxidation of DCOOH with variation of the hydrogen ion con-

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[9] The amount of gas produced was of the order of magnitude calculated on the basis of eq 2.

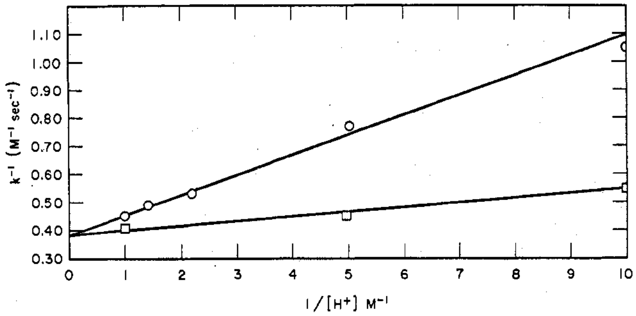

Figure 3.—[H^+] and [D^+] dependence of k' at 25°: ○, $HClO_4$, $[HCOOH]_0 = 1.79 \times 10^{-2}\ M$, $[Np(VII)]_0 = 4.0 \times 10^{-4}\ M$, 10 determinations; □, $DClO_4$, mole fraction of D_2O = 0.951, $[HCOOD]_0 = 1.81 \times 10^{-2}\ M$, $[Np(VII)]_0 = 4.0 \times 10^{-4}\ M$, 8 determinations.

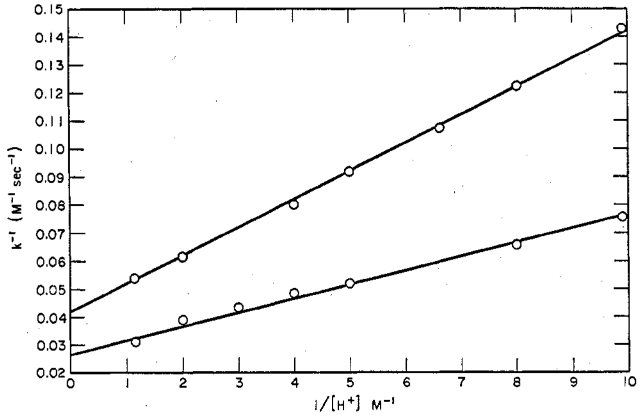

Figure 4.—k' as a function of [H^+] at I = 0.933: lower line, 24.8°, $[DCOOH]_0$ = 1.135 M, 14 determinations; upper line, 34.4°, $[DCOOH]_0$ = 0.0659 M, 17 determinations.

centration is presented in Figure 4. The data were adequately correlated by eq 4 with respective values for 10^2a (M^{-1} sec^{-1}), 10^3b (sec^{-1}) of 2.64 ± 0.12, 5.10 ± 0.20; and 4.206 ± 0.013, 10.00 ± 0.26 at 24.8 and 34.4°. Within the context of the assumptions previously noted, apparent energies of activation for the paths independent of and inverse in hydrogen ion respectively are 8.92 and 12.8 kcal/mol.[10]

Discussion

The available data are not sufficient to distinguish between a reaction scheme of successive 1-equiv steps or a sequence such as

$$Np(VII) + HCOOH \longrightarrow Np(V) + CO_2 + 2H^+ \qquad (5)$$

$$Np(VII) + Np(V) \longrightarrow 2Np(VI) \quad \text{(rapid)} \qquad (6)$$

The term in the rate law inverse in hydrogen ion concentration may reflect a preequilibrium of the formic acid

$$HCOOH = H^+ + HCOO^- \qquad (7)$$

While such an interpretation is not unique, it is consistent with the following observations. (1) The solvent isotope effect data summarized in Figure 4 yield b_H/b_D = 4.2 ± 0.5, a value comparable in magnitude to the ratio of the respective ionization constants of 2.9.[11,12] (2) In the kinetic studies on the oxidation of formic acid by reagents as diverse as permanganate[13] and hexaaquocobalt(III)[14] such an inverse hydrogen ion term has been reported. (3) This type of kinetic path has not been observed for the reduction of Np(VII) by H_2O,[4] Tl(I),[5] or Hg(I).[15]

A comparison of the rate constants for the two paths is of interest and is feasible based on the assumption that the equilibrium (eq 7) provides the mechanism for the occurrence of the inverse hydrogen ion dependence of the empirical rate law. When the rate constants $k_1 = a$ and $k_2 = b/K$,[16] the value calculated for k_2/k_1 is 300. This result is qualitatively in accord with the concept that a reaction between the formate ion and a cation would be favored on electrostatic considerations over a reaction between Np(VII) and the neutral formic acid molecule.

The values calculated for the primary kinetic deuterium isotope effect are 15.2 for k_1 and 9.95 for k_2. Values of this magnitude are generally considered to indicate a significant amount of H–C bond rupture in the dissociation of the activated complex. It should be noted that b_H/b_D = 10.5 and therefore the interpretation that the mechanisms for the two paths are similar (*i.e.*, significant C–H bond rupture) is not dependent upon the validity of the assumption concerning the ionization of formic acid prior to the rate-determining step.

The differences in the energies of activation are of primary importance in describing the change of rate parameters when deuterium is substituted for hydrogen. The small differences in values computed for the entropies of activation act to increase rather than decrease the values of the rate parameters.

The most important aspect of the present investigation is the large deuterium primary kinetic isotope effect. The oxidation of formic acid by Np(VII) proceeds at a rate more rapid than for any system previously studied which is consistent with the ideas previously advanced correlating such an increase with an increase in the redox potential of the metal ion couple. The concomitant increase in the magnitude of the deuterium kinetic isotope effect may well be a reflection of the specific character of the oxidant.

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[10] It was not experimentally expedient to vary the temperature over a wider range. At temperatures significantly greater than 35° the volatility of the deuterioformic acid was significant. At temperatures below 25° the concentrations of DCOOH necessary to prevent competition from the oxidation of water were far greater than those under which eq 3 was demonstrated to be valid.

[11] W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937).

[12] The data summarized in Figure 3 demonstrate that the difference between a mole fraction of 0.95 and 0.97 for D_2O (conditions under which the rate parameters and ionization constants, respectively, were determined) does not markedly influence the comparison. The differences between the ratios may well reflect differences in the pertinent activity coefficient ratios.

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

[14] T. J. Kemp and W. A. Waters, *Proc. Roy. Soc., Ser. A*, **274**, 480 (1963).

[15] M. A. Thompson, J. C. Sullivan, and E. Deutsch, *J. Amer. Chem. Soc.*, **93**, 5667 (1971).

[16] Ionization constant of formic acid of 1.77×10^{-4} is from R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955, p 496; G. A. Ropp, *J. Amer. Chem. Soc.*, **82**, 4252 (1960), determined a value of 1.06 for K_H/K_D.