

ratio of the activity coefficients of all the species is constant. It follows that

$$(I^- \cdot A_n) = \frac{\Sigma(I^-)}{K \frac{(H)}{(A)} + 1} \quad (7)$$

where

$$\Sigma(I^-) = (I^- \cdot A_n) + (H \cdot I^- \cdot A_{n-1}) = (KI)$$

In line with the foregoing comments, the rate of exchange R for the benzyi iodide exchange reaction is now expressed as

$$R = k_1(I^- \cdot A_n)(BzI) \quad (8)$$

Substitution of equation 7 into equation 8 gives

$$R = \frac{k_1}{K \frac{(H)}{(A)} + 1} (KI)(BzI) \quad (9)$$

and comparison of equation 3 with equation 9 reveals that

$$\frac{k_1}{k} = \frac{K(H)}{(A)} + 1 \quad (10)$$

where k_1 is the specific reaction rate in pure acetone. Plots of k_1/k versus $(H)/(A)$ proved to be linear in accordance with equation 10 and the values of K obtained from the slopes are 80, 25 and 15 for phenol, ethanol and water, respectively. The value of K for the *p*-NO₂BzI exchange reaction in acetone-ethanol mixtures turned out to be the same as that for benzyl iodide, indicating that only solvation of the iodide ion is of primary importance as previously assumed in the derivation

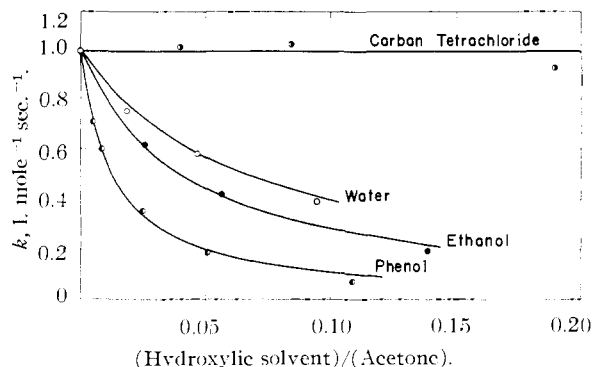


Fig. 1.—The variation of k for benzyl iodide with the ratio (hydroxylic solvent)/(acetone) as calculated from equation 10. The points are experimentally determined values for k .

of equation 10. The curves shown in Fig. 1 represent the variation of k with the ratio $(H)/(A)$ as calculated from equation 10 using the values of K mentioned above; the points represent the experimentally determined values for k .

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[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

Thermodynamics for the Extraction of Uranyl Nitrate and Nitric Acid by Esters of the Types $(RO)_3P=O$ and $(RO)_2RP=O$ ¹

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The thermodynamic quantities, ΔH , ΔF and ΔS , were obtained for the extraction of uranyl nitrate and of nitric acid by twenty-one compounds of the types $(RO)_3P=O$ and $(RO)_2RP=O$. The values of ΔS suggest that a very open structure is retained by the extractant molecules when they are bound to uranyl nitrate. The strength of the bonds formed with the uranyl ion is substantially altered as substituents on the phosphorus atom are replaced by various radicals. A partial correlation with Kharasch's² electronegativity scale was obtained for the substituents. When ΔF for the extraction of uranyl nitrate was plotted against ΔF for the extraction of nitric acid, a straight line was obtained. However, the fit of the data to the straight line is only approximate. Evidence was obtained that an extra order-disorder transition accompanies extraction of uranyl nitrate by certain extractants, but not with others.

Introduction

The utility of tri-*n*-butyl phosphate (TBP) suggests that other trialkyl phosphates and possibly dialkyl alkylphosphonates might be even more advantageous in processing irradiated uranium. Burger³ and the author⁴ of this paper have published data that indicate that there are such advantageous compounds. However, these earlier data were obtained at single temperatures, and, therefore, do not permit calculation of ΔH and

ΔS for the extraction reaction of uranium with the compounds that were tested.

It was felt that values for ΔH and ΔS might throw some light in a fundamental way on the effect of altering the substituents around the phosphorus atom.

Experimental

The thermodynamic quantities were calculated from the variation in the extraction coefficient for uranium over the temperature range, 0 to 50°. In two cases the range was extended to >80°.

The standard conditions chosen were 1.00 *M* nitric acid in the aqueous phase and 0.050 *M* extractant diluted with *n*-dodecane in the organic phase. These conditions gave extraction coefficients of conveniently measurable size. From the work of McKay and co-workers⁵ and from work in

(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 769 (1955).

(3) L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958).

(4) T. H. Siddall, *Ind. Eng. Chem.*, **51**, 41 (1959).

(5) H. A. C. McKay and T. V. Healy, *Rec. trav. chim.*, **75**, 730 (1956).

TABLE I
THERMODYNAMIC QUANTITIES FOR THE EXTRACTION OF URANYL NITRATE, 25°

Extractant	$-\Delta F \pm 1\%$	$\Delta H \pm 3\%$	$-\Delta S \pm 3\%$	Eq. for $-\Delta F$	ΔC_p
Tri- <i>n</i> -propyl phosphate	1740	5800	13.6	$= 16.89T - 1.239 \times 10^4 + \frac{2.713}{T} \times 10^6$..
Tri- <i>n</i> -butyl phosphate	1840	6300	15.0	$= 2.62T - 4.208 \times 10^3 + \frac{1.570}{T} \times 10^6$	35
Tri- <i>n</i> -amyl phosphate	1970	6300	14.4	$= 9.35T - 7.903 \times 10^3 + \frac{2.112}{T} \times 10^6$..
Tri- <i>n</i> -hexyl phosphate	2010	6500	15.1	$= 0.20T - 2.621 \times 10^3 + \frac{1.363}{T} \times 10^6$..
Triisobutyl phosphate	1740	6600	16.2	$= -16.24T + 6.579 \times 10^3$..
Tri- <i>sec</i> -butyl phosphate	2240	6900	15.6	$= -15.56T + 6879$..
Trimethyllyl phosphate	1450	3100	5.6	$= 21.81T - 1.323 \times 10^4 + \frac{2.437}{T} \times 10^6$..
Triisoamyl phosphate	2020	6200	14.1	$= 2.40T - 3.613 \times 10^3 + \frac{1.465}{T} \times 10^6$..
Tris-(3-methyl-2-butyl) phosphate	2120	6600	15.1	$= 9.91T - 8.301 \times 10^3 + \frac{2.228}{T} \times 10^6$..
Tri-3-amyl phosphate	2040	7100	16.9	$= 19.71T - 1.473 \times 10^4 + \frac{3.248}{T} \times 10^6$..
Trineopentyl phosphate	1620	5400	12.7	$= 20.59T - 1.446 \times 10^4 + \frac{2.963}{T} \times 10^6$	66
Tricyclopentyl phosphate	2500	7800	17.6	$= -17.62T + 7.753 \times 10^3$..
Tris-(4-methyl-2-amyl) phosphate	1910	6200	14.3	$= 8.66T - 7.547 \times 10^3 + \frac{2.049}{T} \times 10^6$..
Tricyclohexyl phosphate	2890	6900	13.6	$= -13.58T + 6.936 \times 10^3$..
Tribenzyl phosphate	$\sim 0^a$
Tris-(2-ethylhexyl) phosphate	2090	6200	13.8	$= 13.79T - 6.198 \times 10^3$..
Di- <i>n</i> -butyl <i>n</i> -butylphosphonate	4000	7600	12.2	$= -12.16T + 7.621 \times 10^3$	0
Di- <i>n</i> -amyl <i>n</i> -amylphosphonate	4010	7800	12.8	$= -12.77T + 7.821 \times 10^3$..
Di- <i>n</i> -butyl cyclohexylphosphonate	4090	8100	13.4	$= -13.35T + 8.069 \times 10^3$..
<i>n</i> -Butylphenyl <i>n</i> -butylphosphonate	1020	5700	15.8	$= 9.28T - 9.235 \times 10^3 + \frac{2.232}{T} \times 10^6$..
Bis-(2-ethylhexyl) chloromethylphosphonate	1480	5700	14.3	$= -14.32T + 5.660 \times 10^3$..

^a Extrapolated from higher temperatures.

this Laboratory, second-order effects due to extractant molecule interaction are essentially eliminated when the extractant is diluted to 0.05 *M*.

Nitric acid was determined by titration with Ba(OH)₂ in a nitrogen atmosphere to a phenolphthalein end-point. These determinations also permitted the calculation of the thermodynamic quantities for the extraction of nitric acid.

U²³³ was used without substantial isotopic dilution. The extraction coefficients were determined by counting aliquots of both phases for alpha activity. The concentration of uranium in the aqueous phase was kept in the range 10⁻⁵ to 10⁻⁴ *M*.

The U²³³ was repurified by extraction with diethyl ether every few days. This was done to eliminate the extraneous alpha activity which would be due to the growth of daughters of U²³². The U²³³ stock contained a small quantity of U²³².

The *n*-dodecane was obtained as the "olefin-free" grade from the Humphrey-Wilkinson Company and was further purified by passage through a column packed with Linde's 13X molecular sieve.

The extractants were obtained from several sources or were synthesized in this Laboratory. The source of each compound is indicated in Table II. The extractants were purified by one of several methods as indicated in Table II. Triple crystallization was the preferred technique of purification. In two instances, the extractants themselves were crystallized. In others the addition compound that was formed with uranyl nitrate was crystallized. No method of crystallization was found for some of the extractants, and those were purified by molecular distillation. As a matter of interest, solid addition compounds of tri-*n*-butyl phos-

phate also were formed with zirconium and lanthanum nitrates.

The experiments were performed by mixing phases in a container inside a stoppered Dewar flask. The extraction reaction of uranium is so rapid that one minute of thorough mixing was found to be sufficient to obtain equilibrium. In the case of tri-*n*-propyl phosphate, it was necessary to pre-equilibrate the aqueous phase with organic phase at each temperature. Tri-*n*-propyl phosphate is significantly soluble in 1.00 *M* nitric acid. Temperature was measured to 0.1° by means of an Ertco Precision Thermometer.

Results and Discussion

The results of the measurements of the thermodynamic quantities for the extraction of uranyl nitrate by twenty-one compounds are given in Table I and for nitric acid in Table II. Standard errors have been assigned to the various thermodynamic quantities except for ΔC_p ; there are large and undetermined uncertainties in ΔC_p . All the errors have been expressed in percentage except for ΔH for the extraction of nitric acid. Accurate determination of values of ΔH for the extraction of nitric acid was not feasible because of the smallness of the values. The thermodynamic quantities are given in calories or entropy units.

Nitric acid is extracted and the extractant bound to nitric acid must be subtracted from the total

TABLE II
THERMODYNAMIC QUANTITIES FOR THE EXTRACTION OF NITRIC ACID, 25°

Extractant	ΔH ± 100 , cal.	ΔF $\pm 2\%$	ΔS $\pm 10\%$	Source of extractant	Purification of extractant
Tri- <i>n</i> -propyl phosphate	0	1400	-4.7	Synthesis ROH + POCl ₃ + C ₃ NH ₅	Molecular distillation
Tri- <i>n</i> -butyl phosphate	-600	1410	-6.7	Commercial Solvents Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Tri- <i>n</i> -amyl phosphate	-300	1440	-5.8	Synthesis ROH + POCl ₃ + C ₅ NH ₅	Molecular distillation
Tri- <i>n</i> -hexyl phosphate	-400	1420	-6.1	Synthesis ROH + POCl ₃ + C ₆ NH ₅	Molecular distillation
Triisobutyl phosphate	-700	1440	-7.2	Shea Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Tri- <i>sec</i> -butyl phosphate	-400	1230	-5.5	Synthesis ROH + POCl ₃ + C ₅ NH ₅	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Trimethylalyl phosphate	-200	1830	-6.8	Shea Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Triisoamyl phosphate	-300	1380	-5.6	Monsanto Chemical Co. and Victor Chemical Works	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Tris-(3-methyl-2-butyl) phosphate	-500	1260	-5.9	Synthesis ROH + POCl ₃ + C ₅ NH ₅	Crystallized compd. with UO ₂ (NO ₃) ₂ from ethanol
Tri-3-amyl phosphate	-400	1300	-5.8	Synthesis ROH + POCl ₃ + C ₅ NH ₅	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Trineopentyl phosphate	-600	1360	-6.6	F. I. du Pont de Nemours, Inc.	Crystallized trineopentyl phosphate, itself, from hexane
Tricyclopentyl phosphate	-500	1130	-5.5	Synthesis RBr + Ag ₃ PO ₄	Ppt. UO ₂ (NO ₃) ₂ in hexane, dissolved in benzene, stripped UO ₂ (NO ₃) ₂ and recycled twice
Tris-(4-methyl-2-amyl) phosphate	-400	1410	-5.1	Synthesis ROH + POCl ₃ + C ₅ NH ₅	Molecular distillation
Tricyclohexyl phosphate	-600	1240	-6.2	Synthesis ROH + POCl ₃ + C ₆ NH ₅	Crystallized tricyclohexyl phosphate, itself, from aq. methanol
Tribenzyl phosphate	...	>2800 ^a	...	Synthesis RBr + Ag ₃ PO ₄	Same procedure as with tricyclopentyl phosphate
Tris-(2-ethylhexyl) phosphate	-100	1410	-5.1	Victor Chemical Works	Partial crystallization of compd. with UO ₂ (NO ₃) ₂
Di- <i>n</i> -butyl <i>n</i> -butylphosphonate	-600	850	-4.9	Virginia-Carolina Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Di- <i>n</i> -amyl <i>n</i> -amylphosphonate	-700	880	-5.3	Shea Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Di- <i>n</i> -butyl cyclohexylphosphonate	-600	780	-4.6	Shea Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
<i>n</i> -Butylphenyl <i>n</i> -butylphosphonate	-300	1740	-6.8	Shea Chemical Company	Crystallized compd. with UO ₂ (NO ₃) ₂ from hexane
Bis-(2-ethylhexyl) chloromethylphosphonate	0	1750	-5.9	Monsanto Chemical Company	Molecular distillation

^a Extrapolated from higher temperatures.

concentration of extractant in order to write the correct value for

$$K_u = \frac{U_o}{(U_a(P_f)^2(NO_3^-)^2)} = \frac{E^0/a}{(P_f^2)(NO_3^-)^2}$$

where K_u is the equilibrium constant for the extraction reaction of uranyl nitrate: $UO_2^{++} + 2NO_3^- + 2P_f \rightleftharpoons UO_2(NO_3)_2 \cdot 2P$ and $U_a = UO_2^{++}$ (in the aqueous phase); $U_o = UO_2(NO_3)_2 \cdot 2P$ (in the organic phase); P_f = the uncomplexed extractant (in the organic phase); $E^0/a = U_o/U_a$, or the extraction coefficient for uranium; NO_3^- = the nitrate concentration in the aqueous phase. The similar expression for nitric acid is

$$K_h = \frac{(HNO_3 \cdot P)}{(H^+)(NO_3^-)(P_f)}$$

Entropy Effects.—Significant negative contributions to ΔS for the extraction of uranyl nitrate do not arise from crowding of the alkyl groups away from the phosphoryl oxygen and subsequent inhibition of internal rotation. Hence, the possibility for rather open structures must exist in the bound extractant molecules. That crowding toward the extreme folded-away position is not the case is indicated by the rather constant values of ΔS for series; tri-*n*-butyl, tri-*n*-amyl and tri-*n*-hexyl phosphates. In fact, a very open structure must be maintained; otherwise such extremes as tris-(4-methyl-2-amyl) phosphate and tricyclohexyl phosphate would show quite different values of ΔS . Also, if crowding were a factor, increased restriction of the rotation of the alkyl group as a whole would be expected. Yet the phosphonates, with one alkyl group an atom nearer the center of the molecules, show *less* negative values for ΔS than do the trialkyl phosphates.

The value of ΔS for trimethylalyl phosphate is markedly smaller than for the other extractants. The value of $-\Delta H$ is also much smaller and indicates weaker bonds to the uranyl group. Possibly the weakening of these bonds permits a wider variety of vibrational states and more freedom in the uranium complex than would otherwise be the case.

Enthalpy Changes.—Substantial alterations in ΔH for the extraction of uranyl nitrate are obtained by changing substituents on the phosphorus atom. The effects of replacing an alkyl group by an alkoxy group and of introducing the chlorine atom or phenyl group already have been reported^{3,4} and are to be expected on the basis of a consideration of electroinductive effects.

It is perhaps surprising that differences in aliphatic radicals should have rather large effects on ΔH . It can be seen in Table I that the complete substitution of the cyclopentyl radical for butyl or other 1-alkyl radicals promotes trialkyl phosphates to the status of dialkyl alkylphosphonates as far as ΔH is concerned. Smaller but still significant gains are made with 3-amyl, cyclohexyl or 2-butyl radicals.

Rather fine details of structure must be responsible for the effects on ΔH . Although in the cases of the 4-methyl-2-amyl and 3-methyl-2-butyl radicals the alkoxy linkages are also through secondary carbon atoms, no or only barely sig-

nificant effect is observed. Apparently the secondary linkage is necessary, but not sufficient for a large effect. Perhaps the more general requirement is symmetry.

Even though it might not be possible to rationalize all of the detailed effects of introducing different hydrocarbon substituents on the phosphorus atom, it would seem possible to arrive at some order based on the electronegativity of the substituents. On this basis more electronegative radicals would decrease the electron density that the phosphoryl oxygen has available for bonding. It would be expected that the proper correlation would involve ΔH , rather than ΔF , since ΔH is a relative measure of bond strength.

The values of ΔH for the extraction of uranyl nitrate as a function of hydrocarbon substituent are in accord with Kharasch's² electronegativity scale—with three exceptions. The exceptions are tri-*n*-pentyl phosphate, tribenzyl phosphate and trimethylalyl phosphate. The tri-*n*-pentyl group may fail of proper placement because of steric effects, but the value of ΔS does not support the steric hypothesis. Five groups, cyclopentyl, isobutyl, 4-methyl-2-amyl, 3-amyl and 3-methyl-2-butyl, are lacking Kharasch's scale, and others are only represented by similar radicals.

Data from other sources show that the benzyl group does not always act as though it were relatively electropositive. It is true that benzylamine is an unusually strong base, but benzyl

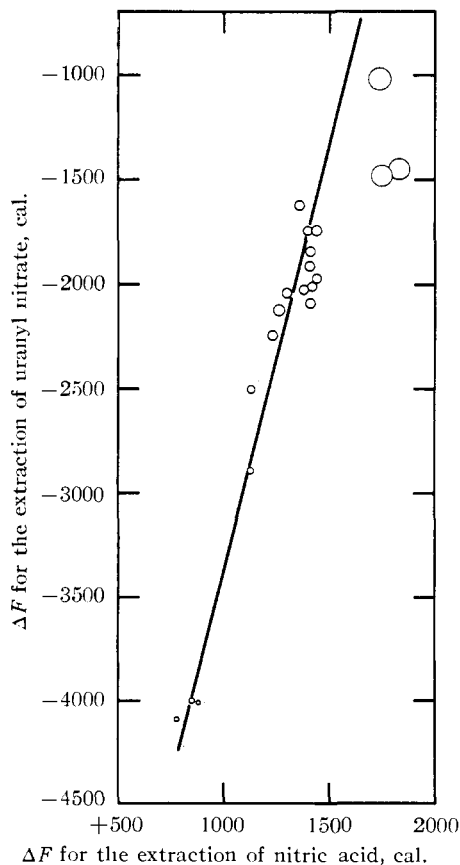


Fig. 1.—The affinity of extractants for uranyl nitrate versus the affinity for nitric acid.

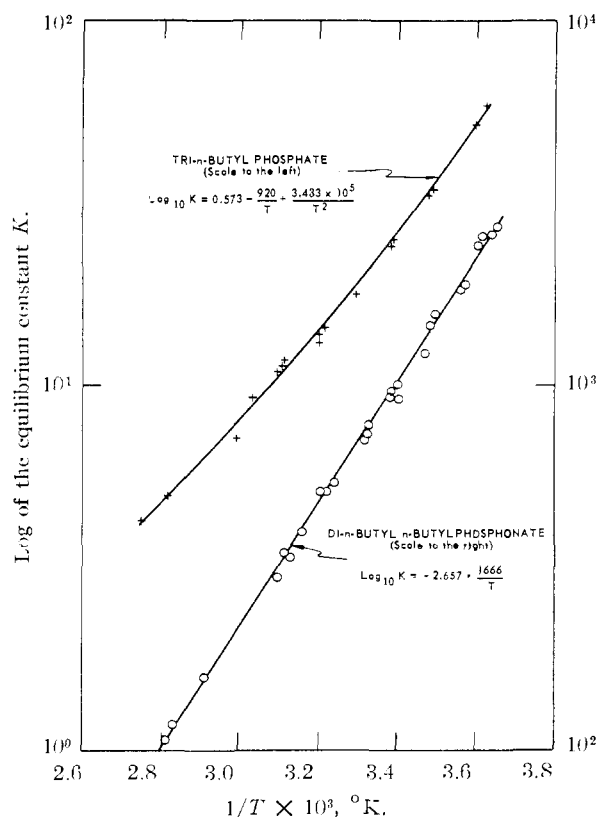


Fig. 2.—Extraction of $\text{UO}_2(\text{NO}_3)_2$ by tri-*n*-butyl phosphate and by di-*n*-butyl *n*-butylphosphonate.

ether is a very poor solvent for uranyl nitrate as compared to the alkyl ethers. Gordy and Stanford⁶ give spectroscopic evidence that benzylamine forms abnormally strong hydrogen bonds with methyl alcohol, but weak bonds are formed by benzyl esters and benzaldehyde with methyl alcohol. It is tempting to conclude that for some reason the benzyl radical has the expected effect when nitrogen is the electron donor, but not when oxygen is the donor. Because of common elements of structure, it would not be surprising if the allyl radical followed the same trend.

(6) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 179 (1940).

On the Connection between the Extractant Strength for Uranyl Nitrate and for Nitric Acid.—Figure 1 shows that any simple connection between bonding to the uranyl ion and bonding to nitric acid is no more than a rough approximation. The rough approximation may have a certain practical usefulness, but represents only a partial fundamental connection. In this figure ΔF at 25° for the extraction of uranyl nitrate is plotted against ΔF for the extraction of nitric acid. A straight line has been drawn through the data. The size of the circles indicates the approximate standard error in the data; several of the data depart drastically from a linear relationship.

It is evident from the data in Tables I and II that a similar plot of ΔH 's would fail. This is true even though a simple relation between ΔH 's is more to be expected than one between ΔF 's, since ΔH is directly connected with differences in bond strength and not ΔF .

Change in Heat Capacity.—For those compounds with a listed value for ΔC_p in Table I it is felt that the experimental data definitely establish that there is curvature in ΔF (or $\log K$) as a function of $1/T$. Plots of the experimental data for TBP and DBBP are given in Fig. 2. The temperature range of the experiments with these two extractants was extended to $>80^\circ$ in order to obtain a better statistical situation. In other cases the least squares equations for $\log K$ were carried out as $\log K = a + b/T + c/T^2$. This was done only because a slightly better fit was obtained for purposes of interpolation. In these other cases the reality of the curvature is not sufficient to assign a value to ΔC_p . Even in the cases of definite curvature the values given for ΔC_p are only approximations.

The linearity of $\log K$ as a function of $1/T$ in the case of DBBP and the definitely established curvature in the case of TBP and trineopentyl phosphate show that at least one order-disorder reaction, more or less, is more important for the extraction reaction in one case than in the other. There is a mechanism for either absorbing or generating heat that is important in one case and not in the other.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Activation Energy of the U(IV)-U(VI) Electron Exchange Reaction in the Water-Ethanol System

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The rate of the exchange reaction between U(IV) and U(VI) is measured at 25, 30, 35 and 40° in mixed ethanol-water solvents of composition 30, 60, 90 and 98 volume % in ethanol. The activation energy decreases when the alcohol concentration is increased, and this corresponds to the increase in rate already observed. Light and wall effects, which could account for some orders close to zero, are ruled out by appropriate runs.

In a previous paper¹ Mathews, Hefley and Amis have reported that the U(IV)-U(VI) exchange re-

(1) D. M. Mathews, J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, **63**, 236 (1959).

action has orders which vary with the solvent composition in the water-ethanol system. It is obviously impossible to compare rigorously the rate constants in different media, as a consequence of