On the Mechanism of the Extraction of Uranyl Nitrate by Tributyl Phosphate II. Infrared Study

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The uranium extraction by TBP (tri-*n*-butyl phosphate) has been studied by many workers especially from the standpoint of distribution equilibrium. For the extraction of uranyl nitrate by TBP, the following mechanism was presented by Moore[1].

$$UO_2^{2+}(aq.)+2NO_3^-(aq.)+2TBP(org.)\rightleftharpoons [UO_2(NO_3)_2](TBP)_2(org.) \quad (1)$$

Naito, one of the present authors, has given an analytical method for studying the extraction mechanism and applied it to a uranyl nitrate extraction system[2]. As a result of this analysis, it was shown that the extraction of nitric acid (Eq. 2) competes with that of uranyl nitrate (Eq. 1), when uranyl nitrate is extracted by TBP from a nitric acid solution,

$$H^+(aq.)+NO_3^-(aq.)+TBP(org.)\rightleftharpoons HNO_3\cdot TBP(org.) \quad (2)$$

However, the results obtained by the partition study were not enough to demonstrate how the TBP complex was formed from the species involved in the extracted system. In this paper the authors present the results of the infrared study concerning the mechanism of extraction. At first, discussions for the systems TBP-water, TBP-nitric acid and TBP-uranyl nitrate are given individually, and secondly the extraction mechanism of the system TBP-uranyl nitrate-nitric acid is presented.

Experimental

Perkin-Elmer Model 12C and 321 Spectrometers equipped with rock salt prisms were used in the infrared measurement. The liquid cell was constructed from spacers and frames made by polyethylene with silver chloride windows, since the usual cell made from metal spacers and frame with alkaline halide windows is attacked by nitric acid and a considerable loss of nitric acid takes place. The above-mentioned non-metallic cell, designed and constructed by the present authors, was quite useful for this experiment and the detail of the design will be reported elsewhere.

The concentration of nitric acid was determined by titration against standard alkali, and the water content in the TBP phase was determined by the Karl-Fisher titration method. The uranium concentration was determined by the alkaline peroxide method. TBP was purified by refluxing with 0.5% aqueous sodium hydroxide according to the method shown by Alcock et al.[3] In some cases, the purified TBP was further distilled in vacuo in order to remove a trace of water. Analytical-grade uranyl nitrate (after recrystallization), nitric acid and carbon tetrachloride were used.

Results and Discussion

Spectra of Pure TBP.—First of all, tentative assignment of TBP itself will be explained in order to analyze the spectra of the systems described below. The spectrum of pure TBP is shown in Fig. 1. Two bands at 2911 and 2840 cm^{-1} are assigned to CH stretching frequencies of *n*-butyl group. Two bands at 1459 and 1382 cm^{-1} are assingned to CH_3 and CH_2 deformation frequencies of *n*-butyl group, respectively. A strong band at 1270 cm^{-1} is assigned to P=O stretching frequency according to Bellamy[4]. A triplet band at 1059, 1027 and 991 cm^{-1} is assigned to the P–O–C group. The assignment of the weak bands at 1237, 1168, 1149, 1119, 959 and 910 cm^{-1} is not clear at present.

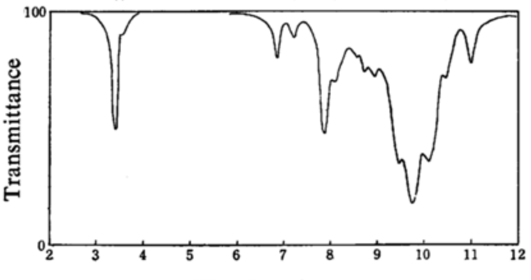

Fig. 1. Infrared spectra of pure TBP capillary.

TBP-Water System.—The infrared spectra of the system TBP-water, obtained by Cobb, have

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[1] R. L. Moore, *AECD-3196* (1951).
[2] K. Naito, This Bulletin, 33, 363 (1960).
[3] K. Alcock et al., *Trans. Faraday Soc.*, 52, 39 (1956).
[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., John Wiley and Sons, Inc., New York (1958), p. 258.

been mentioned in the paper by Alcock et al.[3] He has shown that as water is added to pure TBP the band due to the P=O group at 1283 cm^{-1} is shifted to 1267 cm^{-1} and a shift of 16 cm^{-1} suggests the formation of weak hydrogen bonding (with water) at P=O oxygen.

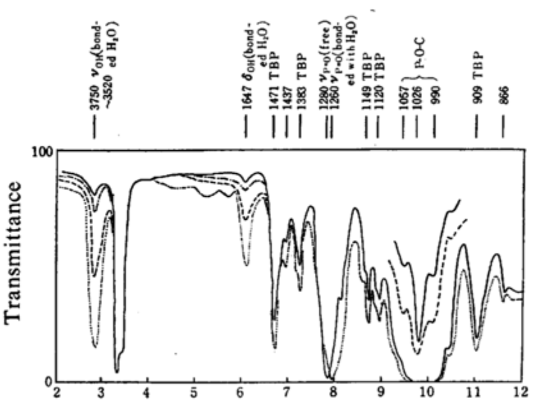

Fig. 2. Infrared spectra of TBP-H_2O system. Thickness : 0.015 mm.

—— No. 1, (0.968 mg. water per ml. of solution)

-·-·- No. 2, (5.98 mg. water per ml. of solution)

---- No. 3, (31.9 mg. water per ml. of solution)

······ No. 4, (64.0 mg. water per ml. of solution)

The spectra for this system obtained by the authors are shown in Fig. 2. Samples No. 1, 2, 3 and 4 contain 0.968, 5.93, 31.9 and 64.0 mg. water per ml. of solution, respectively. It is observed from Fig. 2 that as water is added to pure TBP the band due to P=O at 1280 cm^{-1} is shifted to 1260 cm^{-1} in agreement with Cobb's result. At the same time an increase in intensities of bands at 3750~3550 and 1647 cm^{-1}, is observed which are assigned to the stretching and deformation vibrations of the OH group respectively. The positions of these two bands are near to those of stretching and deformation vibrations of free water and this fact also suggests the formation of weak hydrogen bonding between P=O oxygen and water molecules.

Since the positions of the absorption bands due to P–O–C at 1057, 1026 and 990 cm^{-1} have no appreciable change by the addition of water, it is concluded that in this system water does not bond with the P–O–C group.

TBP-Nitric Acid System.—The samples for TBP-nitric acid system were prepared as follows: 5% carbon tetrachloride solution of TBP was shaken with aqueous solution of nitric acid having various concentrations (where the volume ratio of the organic phase to the aqueous is equal to unity). After separating the organic phase from the aqueous phase, the former was used as a sample. A 5% TBP solution was used for the reason that the adequate intensities of bands can be obtained with 0.1 mm. spacer. The results of analysis for nitric acid and water contents in these samples are summarized in Table I.

TABLE 1. RESULT OF ANALYSIS FOR THE SAMPLES OF TBP-NITRIC ACID SYSTEM

Sample No.	Initial conc. (aqueous phase) of HNO_3, M	Equilibrium conc. HNO_3, M	(TBP phase) of H_2O, M
1	0	0	0.0250
2	0.995	0.0095	0.0328
3	3.41	0.099	0.0368
4	5.14	0.151	0.0267
5	7.10	0.173	0.0211
6	9.23	0.188	0.0239
7	10.83	0.192	0.0250

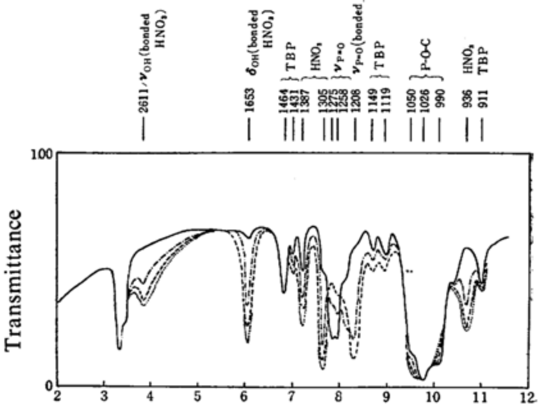

Fig. 3. Infrared spectra of TBP-HNO_3 system. Thickness 0.1 mm.

—— No. 2, (0.995 N HNO_3)

-·-·- No. 3, (3.41 N HNO_3)

---- No. 4, (5.14 N HNO_3)

······ No. 5, (7.10 N HNO_3), No. 6, (9.23 N HNO_3) and No. 7, (10.83 N HNO_3)

The infrared spectra obtained for these samples are shown in Fig. 3. As the concentration of nitric acid in the TBP phase increases, the intensities of bands due to P=O at 1275 cm^{-1} and 1258 cm^{-1} decrease and one at 1208 cm^{-1} rises in its place. It is not clear at present whether the branches of the doublet due to P=O are assigned to the free and bonded (with water) P=O respectively or are to be considered as a solvent effect caused by dilution with carbon tetrachloride. A new band at 1208 cm^{-1} is assigned to bonded P=O with nitric acid. The shift amounts to 50～66 cm^{-1} and this fact suggests a strong bonding between P=O and nitric acid. In the case of samples No. 5—7. the bands at 1275 and 1258 cm^{-1} almost disappear and the same spectra are obtained for all of these samples. Accordingly in the case of samples No. 5—7 all molecules of the TBP are entirety bonded with nitric acid at their P=O bonds. This is in agreement with the analytical data shown in Table I.

The triplet band assigned to the P–O–C group (1050, 1026 and 990 cm^{-1}) shows a change to some extent in samples No. 2—5 in which the increase in nitric acid content brings the increase in the intensity of the band at 1050 cm^{-1} together with the decrease in that at 990 cm^{-1}, whereas the intensity of the band at 1026 cm^{-1} remained unchanged. However, in the case of samples No. 5—7, little change is observed at the P–O–C band. Though it is not easy to interpret the above-mentioned change of spectra due to the P–O–C group, it may be attributed directly to the complex formation at P=O in view of the parallel nature between the spectra of the P–O–C group and that of the P=O group.

The bands at 2611 and 1653 cm^{-1}, the intensities of which are roughly proportional to the content of nitric acid in the TBP phase, are assigned to the stretching and deformation vibrations of the OH group, respectively. The band at 2611 cm^{-1} is shifted obviously from the band due to free OH stretching vibration, so that the formation of strong hydrogen bonding is also confirmed.

The intensities of bands at 1387 and 1305 cm^{-1} are also roughly proportional to the nitric acid content although the former band is overlapped with the band due to the deformation vibration of CH_3 groups of TBP at 1381 cm^{-1}. These two bands are then assigned to the bonds of the bonded nitric acid. It was found by Kamiyama[5] that when an alkaline halide window is used instead of a silver chloride window, a *single band* at 1387 cm^{-1}, which is assigned to the absorption due to the nitrate ion, appeared instead of these two bands*. It was interpreted as the result of the exchange reaction between alkaline halide and nitric acid in the TBP phase, which in turn formed nitrate ion at the surface of the window, so that the use of an alkaline halide window in this case should be strictly avoided. Tuck[6] described briefly the infrared spectra of the TBP-nitric acid system and found bands at 1400 and 810 cm^{-1}, which are assigned to the ionic organic nitrate. The discrepancy between his result and the authors' may have originated from the fact that he used an alkaline halide window.

The intensity of the band at 936 cm^{-1} is also roughly proportional to the content of nitric acid in the TBP phase. Thus the bands at 2611, 1653, 1387, 1305 and 936 cm^{-1} have the same tendency with respect to the content of nitric acid in the TBP phase, and therefore these bands are useful as the indication for bonded nitric acid in TBP phase.

TBP-Uranyl Nitrate System. — The samples used here consist of the following three samples: No. 1; 5% TBP solution (carbon tetrachloride is used as a diluent) saturated with uranyl nitrate monohydrate, No. 2; sample No. 1 was diluted with 5% TBP solution (the volume ratio equals 1 : 1), No. 3; sample No. 1 was diluted with 5% TBP solution (the volume ratio equals 5 : 1).

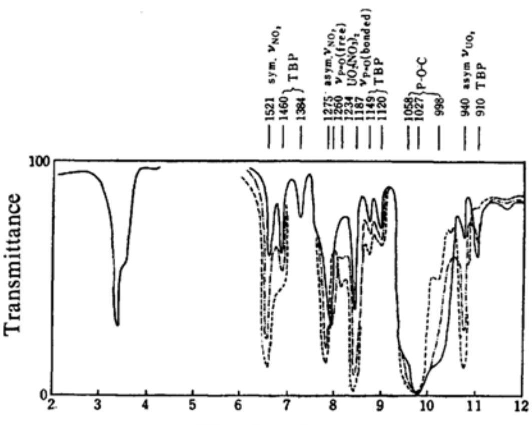

Fig. 4. Infrared spectra of TBP-$UO_2(NO_3)_2$ system. Thickness: 0.1 mm.
---- No. 1 (TBP saturated with $UO_2(NO_3)_2$)
-·-·- No. 2 (1/2 diluted solution of No. 1)
—— No. 3 (1/6 diluted solution of No. 1)

The infrared spectra obtained for these samples are shown in Fig. 4. As the solution is diluted, the intensity of the band at 1187 cm^{-1}, which the authors assign to P=O bonded with uranyl nitrate, decreases and that at 1260 cm^{-1}, due to free or bonded (with water) P=O rises in its place. The shift of frequency between the two bands amounts to 70 cm^{-1} and this fact suggests the strong complex formation between P=O and uranyl nitrate.

The triplet band assigned to P–O–C group at 1058, 1027 and 998 cm^{-1} also shows a similar appreciable change with dilution. As uranyl nitrate content in the TBP phase increases, the intensity of the band at 1058 cm^{-1} increases

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[5] H. Kamiyama, unpublished.

[6] D. G. Tuck, *J. Chem. Soc.*, **1958**, 2783.

* Miller et al. mentioned that the ionic nitrates of alkali metals illustrates the point group D_{3h}, where the strong nitrate asymmetrical stretching frequency is centered in the region of 1380 cm^{-1} and no splitting occurs. F. A. Miller and C. H. Wilkins, *Analyt. Chem.*, **24**, 1253 (1952).

and one at 998 cm^{-1} decreases, whereas one at 1027 cm^{-1} shows little change. As in the case of TBP-nitric acid system, the change of P-O-C band may be directly related to the complex formation at P=O.

The intensities of bands at 1521, 1275, 1234 and 940 cm^{-1} are roughly proportional to the uranyl nitrate content. The band at 940 cm^{-1} is assigned to the uranyl group[7]. According to Ferraro, the former two bands are assigned to NO_2 asymmetric and symmetric stretching of covalent nitrate, respectively[8]. The assignment of the band at 1234 cm^{-1} is not clear at present.

TBP-Uranyl Nitrate-Nitric Acid System.—It is known that when uranyl nitrate is extracted from an aqueous solution of nitric acid by TBP, the extraction peak of uranyl nitrate appears at nitric acid concentration of 5~6 mol./l. in the aqueous phase. As an illustration, the result obtained by McKay is shown in Fig. 5[9]. The existence of such a peak was concluded by Naito as the result of competition to form TBP complex between uranyl nitrate and nitric acid[2]. The mechanism of extraction was described as follows; in low nitric acid concentration the extraction of uranyl nitrate predominates over the extraction of nitric acid which serves merely as a salting-out agent, whereas the increase in nitric acid concentration promotes the extraction of nitric acid into the TBP phase with the progressive replacement of uranyl nitrate by nitric acid. This illustrates the existence of the peak in the extraction curve.

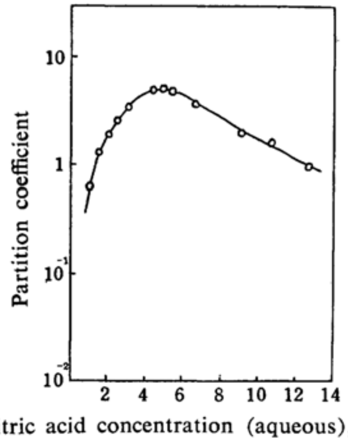

Fig. 5. Extraction of $UO_2(NO_3)_2$ by TBP. Kerosine is used as a diluent. (The original curve by H. A. C. McKay)

The mechanism obtained by the partition study was checked by the infrared spectroscopy as follows:

Replacement of Nitric Acid by Uranyl Nitrate.—Fig. 6 shows the infrared spectra in which the replacement of nitric acid by urany nitrate in TBP phase is demonstrated. The samples were prepared as follows: 5% carbon tetrachloride solution of TBP was shaken with aqueous solution of 5 N nitric acid containing uranyl nitrate of various concentrations (where the volume ratio of organic phase to the aqueous equals unity). After separating the organic phase from the aqueous phase, the former was used as a sample. The initial concentrations of uranyl nitrate in aqueous phase for samples No, 1, 2, 3 and 4 were 0.05, 0.1, 0.3 and 0.5 M, respectively.

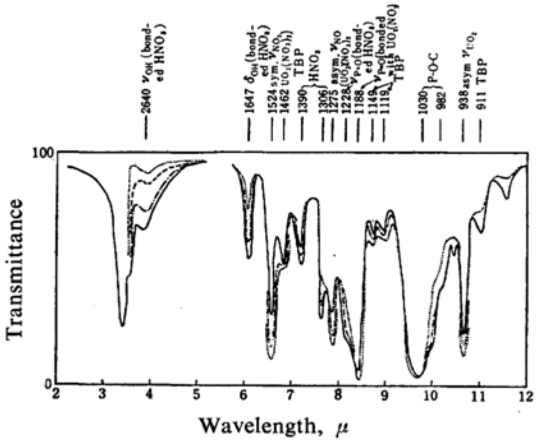

Fig. 6. Infrared spectra of TBP-$UO_2(NO_3)_2$-HNO_3 system. (a) Replacement of nitric acid by uranyl nitrate. Thickness: 0.1 mm.

—— No. 1 (Initial concentration of $UO_2(NO_3)_2$: 0.05 mol./l.)
-·-·- No. 2 (Initial concentration of $UO_2(NO_3)_2$: 0.1 mol./l.)
---- No. 3 (Initial concentration of $UO_2(NO_3)_2$: 0.3 mol./l.)
······ No. 4 (Initial concentration of $UO_2(NO_3)_2$: 0.5 mol./l.)

In the spectra of Fig. 6, the bands at 1228 and 1188 cm^{-1} are assigned to the P=O bonded with nitric acid and uranyl nitrate respectively as mentioned above. As going from sample No. 1 to No. 4, the intensity of the band at 1228 cm^{-1} decreases and the one at 1188 cm^{-1} rises in its place. At the same, the intensities of the bands at 1524, 1275 and 940 cm^{-1}, which are assigned to the vibrations of uranyl nitrate, increase and those of the bands at 2640, 1647, 1390 and 1306 cm^{-1}, which are assigned to the vibrations of nitric acid, decrease.

One can obviously observe from these facts that when going from sample No. 1 to No. 4, the concentration of uranyl nitrate in the TBP phase increases, while that of nitric acid decreases, and that all sites at the P=O group initially occupied by nitric acid are progressively replaced by uranyl nitrate.

Replacement of Uranyl Nitrate by Nitric Acid.—Fig. 7 shows the infrared spectra of samples in which nitric acid expels uranyl nitrate. The samples were prepared as follows: 5% carbon tetrachloride solution of TBP was shaken with an aqueous solution of uranyl nitrate (0.05 M) containing nitric acid of various concentrations (where the volume ratio of the organic phase to the aqueous one equals unity). The initial concentrations of nitric acid in aqueous phase of sample No. 1, 2 and 3 are 2, 6 and 12 mol./l., respectively.

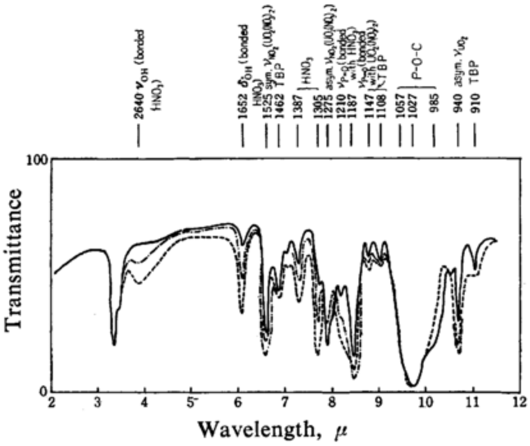

Fig. 7. Infrared spectra of TBP-UO$_2$(NO$_3$)$_2$-HNO$_3$ system. (b) Replacement of uranyl nitrate by nitric acid. Thickness: 0.1 mm.

—— No. 1 (Initial concentration of HNO$_3$: 2 mol./l.)

-·-·- No. 2 (Initial concentration of HNO$_3$: 6 mol./l.)

---- No. 3 (Initial concentration of HNO$_3$: 12 mol./l.)

When going from sample No. 1 to No. 3, the intensity of the band at 1210 cm^{-1} due to P=O bonded with nitric acid increases, on the other hand that at 1187 cm^{-1} due to P=O bonded with uranyl nitrate shows a maximum in sample No. 2. At the same time, the intensities of the bands at 2640, 1652, 1387 and 1305 cm^{-1}, which are assigned to the vibrations of nitric acid, increase and those at 1525, 1275 and 940 cm^{-1}, which are assigned to the vibrations of uranyl nitrate, show a maximum at sample No. 2, except for one at 1275 cm^{-1}. The band at 1275 cm^{-1} of sample No. 1 is overlapped with the band due to free or bonded (with water) P=O at 1275~1258 cm^{-1}, therefore this band only looks to be irregular.

Thus it is evidently seen from these facts that when going from sample No. 1 to No. 3 the concentration of nitric acid in the TBP phase increases monotonously, while that of uranyl nitrate shows a maximum in sample No. 2. Therefore the peak of extraction of uranyl nitrate from nitric acid solution appears at 5~6 M of nitric acid concentration in aqueous phase beyond which the sites of P=O occupied by uranyl nitrate are progressively replaced by nitric acid.

In conclusion, the above-mentioned infrared study confirms the competition between uranyl nitrate and nitric acid in TBP phase and is in good agreement with the result obtained by the partition study.

Summary

The complex formation of TBP in the systems TBP-water, TBP-nitric acid, and TBP-uranyl nitrate was confirmed by means of infrared spectroscopy. The infrared spectra of uranyl nitrate in the system TBP-nitric acid-uranyl nitrate lead to the conclusion that the competition extraction of both uranyl nitrate and nitric acid takes place during the extraction process.

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[7] e. g. see B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, **1958**, 3965.

[8] J. R. Ferraro, *J. Inorg. Nucl. Chem.* **10**, 319 (1959).

[9] H. A. C. Mckay, Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1955, vol. 7, p. 314.