338. *Extraction of Ceric Nitrate by Solvents.*

By A. W. Wylie.

It is shown that ceric nitrate can readily be extracted into ethyl ether if the solution is made 5—6N. in nitric acid and if peroxide-free solvent is employed. The method is convenient for separation of small quantities of pure cerium from mixtures of lanthanon nitrates. These nitrates, which are inappreciably extracted under the conditions used, act as mild " salting out " agents for ceric cerium. The complex is shown to consist of $H_2[Ce(NO_3)_6]$ or a mixture of this substance and $H[Ce(NO_3)_5(H_2O)]$. Extraction of nitric acid in various solvents has been investigated, and the results have been interpreted in terms of the structure of the solvents and the formation of oxonium nitrates. Notable extraction of cerium is found only in solvents which readily extract nitric acid from aqueous solutions. It is considered that the complex, though largely un-ionised, may be held in the solvent phase by van der Waals and oxonium-type forces.

EXTRACTION of ceric nitrate from aqueous solutions with ethyl ether was reported by Imre (*Z. anorg. Chem.*, 1927, **164**, 214) who suggested the method as suitable for purification of cerium. The extraction has been reinvestigated with mixed lanthanon nitrates, and has been found quite as convenient as classical methods for preparation of small quantities of pure cerium. Considerably greater extraction was obtained than reported by Imre, whose results were probably vitiated by reduction of cerium before analysis.

The nitric acid concentration was found to be critical for the extraction, an acidity not less than 5N. being desirable. The cerium concentration was relatively unimportant. Mixed neodymium–praseodymium nitrates in the aqueous phase have a beneficial effect on the extraction of cerium, acting as a useful salting out agent in 5N-acid at sufficiently high salt concentrations.

Both ceric nitrate and nitric acid may be rapidly and quantitatively recovered from ether by back-extraction into water. A disadvantage of the extraction procedure is the partial reduction of ceric to cerous cerium occurring when the aqueous phase is kept for a long time in bright daylight or warmed to expel ether. Ether peroxides also cause rapid reduction of ceric cerium. The usual end product of the extraction is therefore an acid solution of ceric nitrate containing a variable proportion of cerous nitrate. Reduction of cerium in the ether phase is very slow with pure solvent, but ultimately causes separation into a cerium-free. ether–nitric acid layer, and an ether-saturated, cerous nitrate–nitric acid–water layer. Reduction in both phases is catalysed by daylight, and in the ether phase is rapid in radiation of wave-lengths between 2536 and 4046 A. As absorption in aqueous and ethereal phases above 6000 A. is small, photochemical reduction would presumably be minimised by handling solutions in red or yellow light. Such precautions, however, were ignored in the present work.

Examination of a number of other commonly available solvents of low, or negligible solubility in water, showed that either the distribution ratios under the conditions used were less favourable than with ether or the solvents were more susceptible to oxidation by ceric cerium. Although equilibrium was, unavoidably, established incompletely in these extractions, it is usually believed that equilibrium is rapidly established in the system inorganic salt–water–organic solvent–acid or other complexing agent. If it is assumed that the extraction figures given approximate to equilibrium values, the order of extraction in homologous solvents may be compared with that given for the solubility in similar solvents of thorium nitrate tetrahydrate and uranyl nitrate hexahydrate (Templeton and Hall, *J. Phys. Coll. Chem.*, 1947, **51**, 1441; Rothchild, Templeton, and Hall, *ibid.*, 1948, **52**, 1006; Yaffe, *Canadian J. Res.*, 1949, **27**, *B*, 638). In general, for homologous compounds, the extractability of cerium parallels the solubility of thorium and uranyl nitrates in decreasing with increasing molecular weight of the solvent.

Recently, Warf [*J. Amer. Chem. Soc.*, 1949, **71**, 3257; A.E.C.D. (U.S.A.) No. 2524, 1949] proposed tri-*n*-butyl phosphate for extraction of ceric nitrate. Whereas ethyl ether extracts less than 0·3% of La_2O_3, from a 5N-nitric acid solution of lanthanum nitrate containing 65 g. of La_2O_3 per l., it was stated that butyl phosphate extracts from nitrate solutions 4—7% of La_2O_3 and up to 15% of Pr_2O_3. Ether is therefore to be preferred for separation of ceric cerium from other lanthanons, in spite of the greater stability claimed for butyl phosphate. Other disadvantages of butyl phosphate are the necessity for reduction of cerium before back-extraction into water, and the reported necessity for an additional treatment to overcome phosphate contamination of the products.

Nature of the Extracted Ceric Complex.—Negligible extraction of cerium from solutions of ceric nitrate, either weakly acid with nitric acid or 5N. with respect to ammonium nitrate, emphasises the important rôle of nitric acid in the extraction with ethyl ether and other solvents. The system differs, in fact, in a number of respects from the uranyl nitrate system which has been extensively studied in recent years.

Evidence that acidified ceric nitrate solutions contain an anionic complex has been briefly reviewed by Yost, Russell, and Garner ("The Rare-Earth Elements and their Compounds," John Wiley and Sons, N.Y., 1947, p. 61), and the existence of nitratocerate anions may be accepted therein at higher acid concentrations. According to Smith ("Cerate Oxidimetry," G. F. Smith Chemical Co., Columbus, Ohio, 1942) a 0·1M-solution of potassium hexanitratocerate in water has a pH of 1, suggesting hydrolysis according to the equation:

$$[Ce(NO_3)_6]^{--} + H_2O \rightleftarrows [Ce(OH)(NO_3)_5]^{--} + H^+ + NO_3^- \quad . \quad . \quad (i)$$

Hydrolysis of the ceric ion has been investigated by Sherrill, King, and Spooner (*J. Amer. Chem. Soc.*, 1943, **65**, 170) who postulated an equilibrium in perchlorate solution between the ions $Ce(OH)^{3+}$ and $Ce(OH)_2{}^{2+}$. Kraus, Holmberg, and Nelson (Amer. Chem. Soc., Abstract of 114th Meeting, 1948) concluded that cations $Ce(OH)_n{}^{(4-n)+}$ with $n = 1{\cdot}5$ at pH 2·3 were present in perchlorate solutions of ammonium hexanitratocerate. Since ion-migration experiments indicate the existence of anionic complexes only at high nitric acid concentrations, it may be supposed that cations of the type $Ce(OH)_n(NO_3)_m{}^{(4-n-m)+}$ or $Ce(NO_3)_m{}^{(4-m)+}$ are first formed at low or intermediate acidities in nitrate solutions of ceric cerium and that conversion of these ions into anionic complexes takes place at higher acidities, corresponding to an increase in $n + m$. The nitrate groups presumably occupy positions in the co-ordination sphere of cerium which in the partly hydrolysed ion were occupied by (H_2O) or (OH) groups. Similar types of complex ions have been noted recently for other quadrivalent ions. For instance, Connick and McVey (*J. Amer. Chem. Soc.*, 1949, **71**, 3182) attribute to n a value of between 0 and 1 for the zirconium ion $Zr(OH)_n{}^{(4-n)+}$ in 2M-perchloric acid. At this acidity in nitrate solution the ion $Zr(NO_3)^{3+}$ was postulated. An ion $Th(NO_3)^{3+}$ has been identified for thorium in nitric acid–perchloric acid media by Day and Stoughton (A.E.C.D. 2756, 1949). At acidities below

4·6M., Hindman ("The Transuranic Elements," Ed. by Seaborg, Katz, and Manning, Part I, p. 388) identified the ion $Pu(NO_3)^{3+}$ as the principal complex ion of plutonium(IV) in nitrate solutions; at higher acidities the ion $Pu(NO_3)_6^{2-}$ was present.

Extraction of ceric cerium is therefore possible through reversal of changes such as that represented in equation (i), resulting in the formation of a nitratoceric acid which is soluble in organic solvents containing nitric acid. Partly hydrolysed complex anions, such as $[Ce(OH)(NO_3)_5]^{1-}$, presumably fail to pass into the solvent because of the greater affinity of the hydroxyl group for the aqueous phase. More extensive hydrolysis may be presumed to result in the formation of ions such as $[Ce(OH)(H_2O)_5]^{3+}$ or $[Ce(OH)_2(H_2O)_4]^{2+}$.

The discussion has so far assumed a value of 6 for the co-ordination number of cerium. Although this is a likely value for cerium in crystalline ammonium hexanitratocerate and analogous salts, more definite evidence for the value in solution was obtained by calculating the difference between the quantity of nitric acid extracted by ether under similar conditions from a given volume of nitric acid solution both in the presence and in the absence of ammonium hexanitratocerate :

Initial acidity, N.	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
Mols. of HNO_3 extracted per mol. of CeO_2 at initial concentration of 39 g. of CeO_2 per l.	27	16	2·7	2·2	1·6	1·6	1·4	1·4	1·0

Chiefly because the amount of nitric acid co-extracted with the cerium complex was small, results of high accuracy were not obtained. However, within the range of initial acidities 4—9N., each molecule of ceric nitrate appears to co-extract between one and two molecules of nitric acid; $H_2[Ce(NO_3)_6]$ may therefore be present, though not as the sole complex. The aquo-complex $H[Ce(NO_3)_5(H_2O)]$ may also be present, since experiment shows that additional water, some of which may be constitutional, is brought into the ether phase by solution of the cerium complex. At acidities below 3·0N., it is assumed that ceric nitrate in the aqueous phase exerts a strong " salting-out " effect on extraction of nitric acid.

The absorption spectrum of solutions containing ceric cerium shows only the well-defined edge of a broad absorption band. The band edge shifts according to the acidity and cerium concentration from approximately 300 mμ. at low concentrations, where it overlaps an absorption band of the nitrate ion, to beyond 550 mμ. at higher concentrations. Although limited information is available from the spectrum, the absence of further shift in the absorption band above an acidity of approximately 5—7N. for the cerate concentrations given suggests that a stable complex has been produced which is not changed by further addition of acid.

The effect of " salting-out " reagents on extraction of cerium is presumed not to alter conclusions already drawn as to the nature of the extracted complex. Although no comprehensive investigation of the influence of such reagents was made, it was shown that extraction of ceric cerium into ethyl ether from a 5N-nitric acid solution of ammonium hexanitratocerate containing 39·2 g. of CeO_2 per l. was only slightly affected by additions of ammonium nitrate or " didymium " nitrate up to concentrations of 1·4 and 0·5M., respectively. By doubling the cerium concentration in 5N-nitric acid it was shown, however, that 0·76M-" didymium " nitrate caused a significant increase in the quantity of extractable cerium. High concentrations of ammonium nitrate produced a similar effect but eventually caused the separation of solid ammonium hexanitratocerate.

The Rôle of the Solvent in Extraction of Nitric Acid and the Ceric Complex.—Under the conditions used nitric acid takes with it into the solvent phase 0·4 mol. of water from a solution initially 5N. with respect to nitric acid, the resulting electrically conducting solution presumably containing nitrate ion and the oxonium ions H_3O^+ and Et_2OH^+.

Table III shows the variation in extractability of nitric acid for some ethers and ketones. With the *n*-alkyl compounds the efficiency of extraction at acidities up to 7N. lies in the order: Et > Pr > Bu > Am, resembling that found by Gordy and Stanford (*J. Chem. Physics*, 1940, **8**, 140) for the proton affinity of a number of ethers. Virtually no extraction was obtained in solvents such as chloroform, benzene, carbon tetrachloride, or light petroleum, which contain no donor oxygen atoms. There is some evidence, then, that the proton affinity of ethers and ketones is a factor influencing their extractive ability for nitric acid, oxonium-type compounds being formed in each instance. If this premise be accepted, a useful correlation between extractive power and the structure of the solvent may be derived in terms of current electronic theories of organic reactions. For example, solvents such as anisole which contain groupings which withdraw electrons from the donor oxygen atom have low extractive power for nitric acid. Conversely, others such as acetophenone or mesityl oxide, where the electron displacement is presumably towards the donor oxygen, have a relatively high extractive power. The donor properties of the oxygen atom appear to be strongly influenced by steric effects.

Extraction of the cerium complex with alkyl ethers is seen from Tables I and III to decrease more rapidly than that of nitric acid as the number of carbon atoms in the ether molecule is increased. In general, only those solvents which extract a substantial portion of nitric acid cause notable extraction of cerium. In all cases considerable excess of nitric acid over that associated with ceric nitrate in the cerium complex is present, suggesting ready decomposition of the complex in the absence of excess of acid. In this respect, the behaviour of the complex in ether appears to be essentially the same as in water. The organic layer may contain ethoxonium or other organic oxonium cations in addition to the ions present in water. Alternatively, some form of hydrogen bonding between the solvent oxygen and the cerate group may be involved.

In so far as the proton affinity of the solvent influences the extractability of nitric acid, high acid extraction and high cerium extraction are best obtained in solvents with sterically unhindered ether and ketonic groupings which are not subject to deactivation by other groups in the molecule. In order to be suitable, a solvent should be sparingly soluble in water and reasonably resistant to oxidation by ceric cerium. The choice of solvents is thus even more restricted with cerium than with other elements. For this reason ethyl ether, which fulfils the requirements better than other solvents investigated, was the only solvent used for separation of cerium from tervalent lanthanons, but there is no reason to suppose that a more suitable solvent could not be found. Alternatively, the value of ether might be noticeably enhanced by a more extended study of the effect of " salting-out " reagents on extraction of cerium.

EXPERIMENTAL.

Extraction of Cerium from Ammonium Hexanitratocerate with Ethyl Ether.—5 G. of the pure dry salt, dissolved in 40 ml. of nitric acid of various concentrations (initial CeO_2 concentration, 39 g./l.) were shaken at 20° with 40 ml. of peroxide-free " AnalaR " ether.[†] After 3 mins., the layers were separated and the ether extract was shaken with an equal volume of water. The layers were separated and the procedure repeated until the aqueous layer was neutral to litmus paper. Ether was expelled from the combined water layers by bubbling air through the solutions at 50°, and ceric cerium was reduced by dropwise addition of pure hydrogen peroxide. Satisfactory material balances were obtained by precipitating the cerium from each phase as oxalate, before ignition, and by titrating the free acid from each phase with standard sodium hydroxide. Bromophenol-blue was used as indicator. Results of duplicate extractions agreed to within $\pm 1\%$. In calculating the results allowance was made for acid liberated by the action of hydrogen peroxide on the ceric salt :

Initial acidity	0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
Extraction of CeO_2, %	nil	1·1	4·5	39	69	88	93	93	94	94
Extraction of HNO_3, %	—	15	23	31	36	40	44	45	49	53

At a constant initial acidity of 5·0N., the extraction varied with initial cerium concentration as follows

Concentration of CeO_2, g./l.	8·0	39	78
Extraction, %	88	88	76

Effect of " Salting-out" Reagents on Extraction of Cerium.—Conditions were the same as those used previously, the initial concentration of nitric acid being 5N. " Didymium " nitrate ($Nd_2O_3 : Pr_2O_3 =$ approx. 3·5 : 1) was analysed for total lanthanon oxide. Negligible amounts of neodymium or praseodymium entered the ether phase :

" Di_2O_3," g. per 40 ml. acid	0·93	1·86 [*]	2·79
Extraction of CeO_2, %	87	89	91
Extraction of HNO_3, %	42	44	45

[*] " Di_2O_3 "/CeO_2 as in monazite.

The effect of high " didymium " nitrate concentration on extraction of cerium was investigated by mixing 10 g. of ammonium hexanitratocerate, 40 ml. of 5N-nitric acid, and 12·5 g. of the nitrate (4·8 g. of " Di_2O_3 "). Extractions obtained were : CeO_2, 85; HNO_3, 52%. In the absence of " didymium " nitrate corresponding extractions were : CeO_2, 76; HNO_3, 50%. When ammonium nitrate was substituted for " didymium " nitrate the following results were obtained :

NH_4NO_3, g. per 40 ml. acid [*]	1·48	2·96	4·44
Extraction of CeO_2, %	88	87	86
Extraction of HNO_3, %	41	42	42

[*] Exclusive of NH_4NO_3 present in ceric salt.

[†] Commercial grades of solvent caused partial dissolution of the dry salt and reduction to cerous compounds. Pure dry ether neither reduced nor dissolved ammonium hexanitratocerate.

The effect of high ammonium nitrate concentration was investigated by mixing 10 g. of ammonium hexanitratocerate, 40 ml. of 5N-acid, and just sufficient ammonium nitrate (38 g.) to prevent precipitation of the cerium salt. An aliquot of this solution was extracted as before. Initial concentrations were: CeO_2, 29 g./l.; HNO_3, 3·95N. The extractions obtained were: CeO_2, 80; HNO_3, 55%.

Extraction of Nitric Acid with Ethyl Ether.—When pure nitric acid solutions of different concentrations were extracted under the same conditions as used for extraction of cerium, the following results were obtained:

Initial acidity, N.	1·0	2·0	3·5	5·0	6·0	7·0	8·0	9·0	10·0
Extraction, %	7·0	13	25	35	41	46	48	52	55

When the aqueous layers from the first extraction were re-extracted for 3 mins. with 40 ml. of fresh ether, the total (two-stage) extraction of acid was as follows:

Initial acidity, N.	5·0	6·0
Total acid recovery, %	54	57

Effect of "Salting-out" Reagents on Extraction of Nitric Acid.—By procedures already described, the following results were obtained with pure nitric acid containing 4·7 g. of "didymium" nitrate (1·86 g. of "Di_2O_3") per 40 ml. of acid. Shaking time was 3 mins. and only one extraction was given:

Initial acidity, N.	2·0	3·5	6·0	8·0
Extraction, %	17	27·5	43	50

With 1·35 g. of ammonium nitrate per 40 ml. of acid, the results were:

Initial acidity, N.	2·0	4·0	6·0	8·0
Extraction, %	14	28	40	61

Reduction of Ceric Complex in Aqueous and Solvent Phases.—An ether extract and a residual aqueous layer obtained by shaking equal volumes of peroxide-free ether and a 5N-nitric acid solution containing 39 g. of CeO_2 per l. were examined. The initial concentrations were: ether layer, 27 g. of CeO_2 per l., 3·3N-HNO_3; aqueous layer, 4·4 g. of CeO_2 per l., 2·4N-HNO_3. Aliquots from each layer were withdrawn at intervals and shaken with 100 ml. of 3% sulphuric acid before titration with standard ferrous ammonium sulphate solution. After 3 hrs. at 20° in diffused daylight no reduction of cerium could be detected in the ethereal layer. Less than 1% of the cerium was reduced in the aqueous layer. On warming the aqueous layer to 60° to expel ether, reduction of cerium occurred. Poorly reproducible analytical results were obtained but the figures suggested that approximately half of the cerium present was reduced after 1 hr. Mainly because of the lower acid concentration, cerium in the solution obtained by back-extracting from the ethereal layer into water was reduced to the extent of only 10—20% after 1 hr. at 60°. If the ether contained much peroxide, reduction in the aqueous layer was rapid at 20° and almost immediate at 60°. Reduction in the ethereal layer, however, was usually less than 3% after 1 hr. at 20°. Irrespective of the presence of peroxides, reduction in both phases was catalysed by sunlight, and was rapid in ultra-violet light of wave-lengths between 2536 and 4046 A. As with ethyl ether, reduction of cerium in the solvent phase of tetrahydropyran at 20° was negligible in diffused daylight; reduction in the aqueous layer, however, was almost immediate at 20°.

Separation of Ceric Cerium from Tervalent Lanthanons.—Mixed nitrates, containing ceric nitrate, were conveniently prepared by dissolving finely divided hydroxides in 66% nitric acid to give a 6N-nitric acid solution containing approximately 107 g. of CeO_2 per l. After 3 mins.' shaking with an equal volume of ether and separation, 93% of the cerium and 76% of the free acid entered the solvent phase. Re-acidification of the aqueous layer to restore the acidity from 2·4 to 6·0N., followed by a second extraction, caused 99% of the total cerium and 84% of the total nitric acid to enter the ether layer.

The lanthanon hydroxides for the above preparation were prepared by boiling the mixed double sulphates with sodium hydroxide and drying the filtered product in an oven at 120° until 99% or more of the cerium was converted into the ceric state. To prevent formation of emulsions, preparations contaminated with finely divided silica were avoided. Thorium was removed beforehand as it is partly extracted with cerium.

The ethereal extracts were conveniently purified by shaking with fresh 6N-nitric acid, impurities present then entering the aqueous phase. Some loss of cerium necessarily resulted from this procedure.

Extraction of Tervalent Lanthanons.—Cerous nitrate and lanthanum nitrate solutions containing 65 g. of oxides per l. severally were extracted once with an equal volume of ether at 20°. At a nitric acid concentration of 5N., the extraction of lanthanon oxides was less than 0·3%.

Spectrophotometric Examinations.—The neodymium and praseodymium contents of the extracted cerium were determined photometrically (Wylie, *J. Soc. Chem. Ind.*, 1950, **69**, 143), a Beckman quartz-prism spectrophotometer being used. After a single extraction the lanthanon contents (in terms of oxides) ranged from: Nd_2O_3, 0·25—0·87%; Pr_2O_3, 0·13—0·30%. After purification as described, bands due to neodymium and praseodymium could not be detected in 4-cm. thicknesses of solutions containing 100 g. of CeO_2 per l. Transmittance curves for various solutions containing ceric cerium and nitric acid were obtained on the same instrument, 1-cm. quartz cells being used. Nitric acid solutions in ether were made by extracting aqueous nitric acid solutions of appropriate concentration.

Four series of ceric solutions were examined in which separately (*a*) the cerate salt concentration in water was increased from 0·019 to 19·5 g./l.; (*b*) the nitric acid concentration was increased at constant ammonium nitratocerate concentrations of 0·1 and 4·1 g. per 100 ml. of solution; (*c*) the cerate salt concentration in 5N-nitric acid was increased over a similar range; (*d*) an extract was prepared by shaking

5N-acid solutions of the cerate with ether. Concentrations in the ethereal layer in (*d*) were CeO_2, 32 g./l., nitric acid, 1·7N., and in the aqueous layer, CeO_2, 4·5 g./l., nitric acid, 3·2N. Increasing cerate concentrations in water (*a*) or nitric acid (*c*) caused a progressive shift of the band edge towards longer wave-lengths. Addition of nitric acid at constant cerate concentration (*b*) caused the band edge to move to longer wave-lengths as the acidity increased; no further shift of the band edge, however, occurred in the more dilute cerate solution above an acidity of 5N. With the more concentrated cerate solution no further shift occurred above an acidity of 7N. In case (*d*), the presence of ether caused the band edge to shift to wave-lengths longer than observed with equal concentrations of cerium in aqueous ether-free nitric acid of the same acidity.

Determination of Water co-extracted with Cerium Complex.—Water in ethereal extracts was determined by Zerewitinoff's method, using methylmagnesium iodide reagent dissolved in redistilled anisole. Benzoic acid was used to calibrate the apparatus. Measurements at 20° were made of the volume of methane evolved from: (*a*) the ethereal cerium extract obtained from 40 ml. of a 5N-nitric acid solution which contained in addition 5 g. of ammonium hexanitratocerate; (*b*) the ethereal extract obtained from 40 ml. of 5N-nitric acid alone. The shaking time in all experiments was 3 mins., 5 mins., being allowed for separation of the phases. After separation, the ether layers were centrifuged to remove microscopic droplets of aqueous phase.

Since the Grignard reagent gave poorly reproducible results in the absence of free acid, the quantity of water dissolved by ether alone under the conditions outlined was measured by titration with the Karl Fischer reagent, which was standardised by direct titration of water weighed from a micropycnometer, the end-point being detected potentiometrically. The reagent was found to reduce nitric acid present in ethereal extracts. The water contents of the ethereal layers were: (*a*) 1·1 g. per 44 ml.; (*b*) 0·83 g. per 39 ml. The molecular ratio CeO_2 : total HNO_3 : total H_2O in (*a*) was 1 : 10·2 : 7·4; in (*b*) the ratio HNO_3 : total H_2O was 10 : 6·1. The molecular ratio of CeO_2 carried into ether layer to H_2O carried into the ether by the cerium complex only was 1 : 1·80. The solubility of water in ether under the conditions given was 0·72 g./100 ml. or 1·0 g./100 g. of solution.

Extraction of Ceric Cerium with Other Solvents.—3N-, 5N-, and 7N-Nitric acid solutions of ammonium hexanitratocerate containing 39·2 g. of CeO_2 per l. were vigorously shaken for 3 mins. at 20° with various solvents to determine the extraction of cerium. Reagent-grade solvents were purified by distillation.

TABLE I.

Extraction (%) of ceric cerium and nitric acid by various ethers.

	3·1N-HNO_3.		5·0N-HNO_3.		7·0N-HNO_3.	
Ether.	CeO_2.	HNO_3.	CeO_2.	HNO_3.	CeO_2.	HNO_3.
n-Ethyl	39	31	88	40	93	45
n-Propyl	*	*	25	*	*	*
n-Butyl	*	*	<1	13	2	21
n-Amyl	<1	4·1	<1	9	<1	15·6
*iso*Propyl	1	19	19	31	51	39
Dibenzyl †	<1	4·0	1	5·0	1·4	11

* Signifies not determined.

† Some uncertainty as to the significance of very low extractions was caused by the slow rate of settling of minute droplets of aqueous solution from the solvent layer of this substance.

Only ethers free from peroxides were employed. Peroxidised samples were first shaken with acid ferrous sulphate, separated, and dried (K_2CO_3) before distillation. Results for ethers are given in Table I, those for ethyl ether being included for comparison.

Anisole and phenetole, which did not appear to extract cerium, formed dark oxidation products. Tetrahydromethylfuran caused rapid reduction to cerous compounds even in 1N-acid. Although tetrahydropyran and di-2-butoxyethyl ether gave high extractions of cerium, variable results were obtained owing to very rapid reduction of cerium remaining in the aqueous phase. Tetrahydropyran (dried over sodium) was the only ether which dissolved solid cerate or extracted cerium from unacidified solutions. Pale yellow solutions formed in each instance. Results for some ketones are given in Table II. Slowly separating emulsions formed with the last four solvents, particularly during back-extraction of cerium into water. Only the water layer was analysed in such cases. Di*iso*propyl ketone, amyl methyl ketone, hexyl methyl ketone, *cyclo*hexanone, and mesityl oxide caused immediate reduction to cerous compounds. Diethyl ketone, methyl propyl ketone and *iso*butyl methyl ketone all extracted

TABLE II.

Extraction (%) of ceric cerium and nitric acid by various ketones.

	3·0N-HNO_3.		5·0N-HNO_3.		7·0N-HNO_3.	
Ketone.	CeO_2.	HNO_3.	CeO_2.	HNO_3.	CeO_2.	HNO_3.
tert.-Butyl methyl	—	—	73	34	—	—
Benzyl methyl	—	—	<2 *	—	—	—
Dibenzyl	<1 *	<1 *	<2 *	7·0	6·5	19
Acetophenone	60	22	71	28	71	34
Propiophenone	—	—	41	23	—	—

* See second footnote, Table I.

cerium, but rapid reduction in the aqueous phases, and slower reduction in the solvent phases, prevented useful results from being obtained. Of these three ketones, the last was the most stable. Only acetone, methyl propyl ketone, *iso*butyl methyl, and *tert.*-butyl methyl ketones dissolved dry ammonium hexanitratocerate.

Aliphatic alcohols dissolved ammonium hexanitratocerate freely, higher alcohols causing extraction of cerium from 0·2M-aqueous solutions of the salt. Visual observation showed the intensity of the red-brown colour of cerate–alcohol extracts to decrease with increasing molecular weight of the alcohol. Rapid reduction of cerium in 5N-acid occurred with commercial hexyl and octyl alcohols and with *cyclo*hexanol. With *n*-amyl alcohol, extractions from 5N-nitric acid solutions containing 39·2 g. of CeO_2 per l. were: CeO_2, 13%; HNO_3, 44%. In the absence of acid, extraction of CeO_2 was 12%, but instability of the solvent influenced the results obtained.

TABLE III.

Extraction of nitric acid in various solvents.

	Extraction, %.*		
Solvent.	3N.	5N.	7N.
Diethyl ether	21	36	47
Di-*n*-propyl ether	—	15	—
Di*iso*propyl ether	14	26	36
Di-*n*-butyl ether	3·6	11	19
Di-*n*-amyl ether	2·5	7·1	14
2 : 2′-Dichlorodiethyl ether	1·9	4·2	9·8
Tetrahydropyran	39	51	62
Di-2-butoxyethyl ether	29	39	45
Anisole	—	<2	10
Phenetole	—	<1	2·6
Dibenzyl ether	—	5·3	—
Methyl *n*-propyl ketone	31	39	50
*iso*Butyl methyl ketone	25	33	39
tert.-Butyl methyl ketone	22	28	38
n-Amyl methyl ketone	20	28	35
n-Hexyl methyl ketone	17	25	30
Methyl *n*-nonyl ketone	10	16	21
Diethyl ketone	24	34	41
Di*iso*propyl ketone	17	25	30
Acetophenone	18	28	35
Propiophenone	—	15	—
Mesityl oxide	34	42	51
Dibenzyl ketone	—	7·0	—
Benzyl methyl ketone	—	23	—

* With 1N-nitric acid extractions with tetrahydromethylfuran and 2 : 5-dimethyldioxan were 24% and 4%, respectively.

Extraction of Nitric Acid with Organic Solvents.—5N-Nitric acid was shaken for 5 mins. at 21° with various solvents to ascertain the extent of nitric acid extraction in the absence of cerium. *cyclo*Hexanone, 2 : 5-dimethyldioxan, and tetrahydromethylfuran gave single-phase solutions. Results with other solvents are shown in Table III.

This investigation was carried out as part of the research programme of the Division of Industrial Chemistry of the Commonwealth Scientific and Industrial Research Organisation. The author thanks Miss J. V. Mather for assistance with analytical work and Mr. I. Brown for a loan of apparatus and Karl Fischer reagents.

MELBOURNE, AUSTRALIA.

[*Received, December* 30*th*, 1950.]