debtedness to Professor N. Bjerrum, whose many valuable suggestions have been of great importance to my work, and to Mr. E. A. Guggenheim for helpful criticism.

Summary

1. The kinetics of the ketonic decomposition of α,α-dimethylacetoacetic acid, $CH_3COC(CH_3)_2COOH \longrightarrow CH_3COCH(CH_3)_2 + CO_2$, have been studied. Experiments were made in hydrochloric acid, glycolate and acetate buffers.
2. The dissociation constant of α,α-dimethylacetoacetic acid has been calculated from the experimental results.
3. It has been shown that the decomposition is catalyzed by amines.
4. From the fact that α,α-dimethylacetoacetic acid is unstable it follows that the keto form of β-keto carboxylic acids is unstable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

EXTRACTION OF COMMERCIAL RARE-EARTH RESIDUES WITH A VIEW TO THE CONCENTRATION OF ILLINIUM

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Historical

In 1926[3] one of the writers, in conjunction with Professor B. S. Hopkins of the University of Illinois, was able to isolate, although in an impure state, sufficient of Element 61 to be able to identify it by means of x-ray analyses. Since, however, some 700 pounds of original material yielded a concentrate of but a few grams, it would seem to indicate that (a) the element is extremely rare and hence, in order to obtain quantities sufficiently great for purification, enormous amounts of the original material must be worked on, or (b) that while not rare, our method of concentration was inefficient and considerable of the element was lost at different stages of the treatment involved.

Assuming the latter possibility, one of the most likely sources of loss would be inefficiency in extraction of original residues; this possibility is discussed in this paper.

The element has not yet been obtained in a state of purity great enough to permit the mapping of its arc and absorption spectra, so it is impossible

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[1] Part of this paper was presented as a thesis for the M.A. degree at the University of British Columbia.

[2] National Research Fellow. Paper completed at the Sorbonne, Paris, as part of work under National Research Council Award.

[3] Harris with Hopkins, THIS JOURNAL, 48, 1585 (1926).

to make use of these in following the progress of concentration. Similarly, x-ray analyses are not sensitive when amounts of less than one part per thousand are present. Hence it was decided that the best method for attacking this problem would be from the standpoint of the quantitative determination of total rare-earth content of the original material, by analytical methods.

Introduction

The materials used in the investigation were (1) commercial double sulfates, having the same source as those used in the original concentration of illinium, and (2) commercial hydrated oxides, prepared by the Welsbach Company for the University of Illinois, and kindly loaned to us by Professor Hopkins.

However, although much work has been carried out regarding the extraction of the rare-earth minerals, and several methods have been devised for decomposing the double sulfates, it is probable that all of these methods are selective in their action and it does not appear that a single one of the methods has been studied from a quantitative view-point.

Analysis

Extremely careful analyses were made of the original materials, first by the method outlined by Hillebrand[4] and, second, by a modification of the above method which appeared to give results consistently concordant with the Hillebrand procedure.

The average of these analyses is: (1) double sulfates, 39.40 g. of rare earth as oxide per 100 g. of material; (2) hydrated oxides, 73.05 g. of rare earth as oxide per 100 g. of material.

Part I. Extraction of Double Sulfates

(a) **Wet Extraction of Small Amounts.**—Two-gram samples of the carefully dried material were moistened with water and then digested with 25 cc. of concd. nitric, hydrochloric and sulfuric acids, respectively, until the volume was reduced to about 5 cc. These were then taken up in 250 cc. of water and, after filtering, the residue was again treated with hot water, filtered and the filtrates combined. After correcting acidity to reduce solubility of the oxalates to a minimum,[5] the rare earths were precipitated as the oxalates, washed, dried and ignited to the oxides. The maximum and minimum of the results, which were never concordant, are as follows

Acid	Nitric	Hydrochloric	Sulfuric
Maximum yield as oxide, %	15.73	29.07	39.87
Minimum yield as oxide, %	11.26	25.35	34.35

These compared to actual content of 39.40% as oxide indicated that concentrated sulfuric acid is the most efficient of the acids. Although the maximum value is more than the theoretical, the majority of extractions were in the vicinity of 39.0%.

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[4] Hillebrand, U. S. Geological Survey Bulletin **700**.

[5] Sarver and Brinton, THIS JOURNAL, 49, 943 (1927); Neckers with Kremers, *ibid.*, **50,** 950 (1928).

Turning now to alkali extraction, the one recommended, as mentioned previously, is the use of a 50% solution of sodium hydroxide.

Accordingly, two-gram samples were digested for several hours with such a solution. The resulting mixture was taken up in 250 cc. of water and washed by decantation until alkali free; the residue was then digested with nitric acid to dissolve the hydroxides, diluted, filtered and the residue leached with hot water. The combined filtrates were subsequently treated with oxalic acid and the resulting oxalates ignited and weighed as the oxide. In all cases where there was evidence of a basic salt forming, the sample was rejected; maximum yield as oxide, 38.89%; minimum yield as oxide, 37.98%. Thus it may be seen that the alkali extraction gives more consistent results than does the extraction with acids.

(b) **Fusion of Small Amounts.**—The fluxes chosen were sodium hydroxide and sodium carbonate and the acids used as extractants of the melt were dilute and concentrated hydrochloric, nitric and sulfuric acids.

As in the previous cases, samples of two grams each were used and fused with excess of the flux. After lixiviating with water, the mass was extracted with acid of varying concentration. In the case of the dilute acids the results were never concordant; this no doubt was due to the tendency of the cerium to become basic. The best results were obtained by fuming the melt with concentrated sulfuric acid, and then extracting several times with hot water.

Flux	Sodium hydroxide	Sodium carbonate
Extractant	Concd. sulfuric acid	Concd. sulfuric acid
Rare earth as oxide, %	Av. 39.06	Av. 39.32
Total rare-earth content, 39.40		

In the foregoing determinations, then, it would appear as though extraction by means of sulfuric acid, sodium hydroxide or fusion with sodium hydroxide or sodium carbonate would eliminate possibility of loss of illinium during the initial extractions.

Since, however, the rare-earth worker is usually interested in larger amounts, it was deemed advisable to investigate the efficiency of these reagents on larger amounts of original material, up to 3000 g.

(a) **Wet Extractions of Larger Amounts.** (1) **With Acids.**—These gave results too low and so inconsistent as to render their use valueless.

(2) **With 50% Sodium Hydroxide Solution.**—This method, while giving excellent results on small samples, for larger amounts of material gave a maximum yield of but 18.34% as oxide against the actual content of 39.4%.

(3) **Concentrated Sodium Hydroxide Solution.**—The method suggested by Professor Urbain and the one used in his laboratory for decomposition of sulfates is a digestion with a saturated solution of sodium hydroxide. Two digestions with this solution gave the following results for amounts in the vicinity of 300 grams: A. % as oxide, 38.88—98.68% efficient; B. % as oxide, 39.20—99.49% efficient.

(4) **Digestion with saturated Na_2CO_3 solution.**—A. % as oxide, 34.82—88.37% efficient; B. % as oxide, 35.30—89.59% efficient. Hence for wet extractions a concentrated solution of sodium hydroxide is extremely efficient.

(b) **Fusion with Sodium Carbonate.**—These fusions were carried out in fire-clay crucibles in a gas-fired muffle furnace. Amounts of the commercial double sulfates in the vicinity of one kilogram were mixed with excess of dry sodium carbonate and fused until the mass was thoroughly molten. The temperature was then maintained for about an hour, the furnace allowed to cool and the crucible removed. Great difficulty was experienced in removing the melt from the container—the crucible usually had to be broken. The mass was then extracted and treated as in the case of the small samples. The maximum yield obtained by this method was 37.26 g. of oxide per one hundred grams of original material.

Believing the discrepancy to be due to incomplete removal of the melt from the crucible, a method was devised which is outlined below and which we cannot recommend too highly for large-scale laboratory operations. In addition to being highly efficient, it has the advantage of being a practically continuous process.

TABLE I

RESULTS OBTAINED BY THIS PROCESS

Original residue, g.	872.00	1000.00	1500.00	2000.00	3000.00
Oxides, g.	324.8	392.73	587.40	774.00	1169.99
Oxide per 100 g., g.	37.75	39.27	39.16	38.70	39.00
Efficiency, %	95.81	99.66	99.39	98.22	99.00

In the first and fourth cases the results are low—no doubt due to the fact that in both instances new crucibles were used and hence some of the melt was retained as a glaze during pouring. The last two fusions were carried out as a continuous process to test its possibilities.

Conclusions

The following methods are recommended as being efficient in extracting the rare earths from double sulfate residues.

(1) **For Large Amounts.**—The dried double sulfates are thoroughly mixed with a large excess of dry commercial sodium carbonate. The mixture is then fired in a muffle until molten and the temperature maintained until reaction is complete. The crucibles are then removed and the molten contents poured into a vessel containing hot water; the still red-hot crucible is quickly recharged and returned to the muffle. The sudden cooling of the melt causes thorough disintegration. When the last pouring has been made the crucibles are cooled somewhat and the addition of dilute sulfuric acid to the container effectively loosens all adhering melt, which may then be added to the solution.

The mixture is allowed to settle and the residue washed thoroughly by decantation until alkali-free. It is then transferred to a large evaporating dish and evaporated to dryness.

The dry residue is now made up to a thin paste with concentrated sulfuric acid and evaporated until there is copious evolution of fumes, in order to convert the rare earths into the soluble acid sulfates. The resulting mass is extracted with water until the last extraction gives no test for the rare earths.

These extracts are combined, diluted and the rare-earth hydroxides precipitated with ammonia, washed thoroughly to remove any sulfate, taken up in as little nitric acid as possible, diluted and precipitated as the oxalates with subsequent ignition to the oxide.

(2) **For Smaller Amounts.**—For amounts below one kilogram the following method is perhaps more adaptable. Moisten the dried residues with as little water as possible and cover with a saturated solution of sodium hydroxide to a depth of at least one inch. Digest on a steam-bath, following by digestion on a hot-plate until the mass is thoroughly disintegrated and the rare earths converted to the bulky hydroxides. The mass is allowed to cool and any liquor is decanted. The hydroxides are then boiled with water until all alkali has been removed and extracted with dilute nitric acid, heating only sufficiently to aid the solution of the soluble portion. The undissolved residue is filtered off and extracted a second time. The filtrates containing the rare earths as nitrates are combined, precipitated by means of ammonia and after thorough washing treated as formerly.

Either of these methods will reduce to a minimum the possibility of loss of any rare earths and consequently illinium during the extraction of commercial double sulfates and will also yield a product of considerable purity.

Part II. Extraction of Commercial Hydrated Oxides

(a) **Acid Extraction.**—It is natural to assume that acid extractions of such residues would be the more efficient; consequently alkaline extractions were not used.

In the case of larger amounts, varying between 200 and 312 g., the maximum yields obtained from a great many extractions, covering both digestions with acid and addition of the material to the hot acid with constant stirring, were as follows

Extractant	Hydrochloric acid	Sulfuric acid	Nitric acid
Oxide per 100 g., g.	60.19	70.36	68.40

In all cases the tendency to become basic was very pronounced and had to be carefully guarded against. The best results are obtained by carefully moistening the original material with water, care being necessary as a great deal of heat is liberated. The material is then slaked with water and when concentrated nitric acid is slowly added complete solution takes place. The yield, however, is always low, but if a little hydrogen peroxide is added at this point the results are always concordant and much higher.

TABLE II

RESULTS BY THIS METHOD

Original material, g.	200	200
Oxides, g.	145.82	144.70
Wt. per 100 g., g.	72.91	72.36
Efficiency, %	99.80	99.04

Deep appreciation is hereby expressed to Professor Hopkins for the loan of material for the investigation; to the National Research Council and International Education Board for furnishing funds to allow a continuation of this work in Europe, and also to Professor Georges Urbain of the Sorbonne whose kindly advice and interest was a source of inspiration at all times.

Summary

1. As mentioned in the historical part of this paper, it was feared that there was a possibility of loss of illinium during original extraction of double sulfate residues. As the material used had been extracted with a 50% solution of sodium hydroxide, the foregoing experiments show that there is a possibility of loss of rare earths at this point.

2. A method has been outlined whereby using a sodium hydroxide solution, practically theoretical results—as compared with an accurate quantitative determination—have been obtained for amounts up to 300 g.

3. An equally efficient method for larger amounts, involving fusion with sodium carbonate, has been described.

4. The use of nitric acid and hydrogen peroxide is recommended for the extraction of commercial hydrated oxides. Hence, if the original material is extracted by any of the above methods, all of the rare earths, including illinium, should be found in the extract. All undissolved residues are, however, being investigated.

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DICHLORO-AMINE

BY ROBERT M. CHAPIN

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Available evidence for the existence of dichloro-amine, $NHCl_2$, including the most recent,[1] rests upon incidental observations made in the course of work on nitrogen trichloride. The conditions necessary for the formation of the substance remain undefined, while methods for its separation from the two other reaction products are lacking.

The nature of the product obtained through chlorination of an excess of ammonium ions is known to depend upon the reaction of the solution, acidity leading toward nitrogen trichloride and alkalinity toward monochloro-amine. It will be shown here that when the reaction is effected through rapid mixing of sufficiently cool and dilute buffered solutions, with ammonium ions always in excess, the nature of the product is governed solely by the concentration of hydrogen ions. In solutions more alkaline

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[1] W. A. Noyes, THIS JOURNAL, **42**, 2173 (1920).