The isotope shift observed in going from the molecule containing only B^{10} to that containing only B^{11} was 101 ± 10 cm.$^{-1}$. Assuming a bipyramidal model (of symmetry D_{3h}), the isotope ratio for the A''_2 frequency and for the E' frequency involving predominantly the boron atom motions is calculated to be 1.045, or a shift of 91 cm.$^{-1}$. The agreement is reasonable, and in particular much better than with any less condensed structure which might be proposed for B_2O_3. For example, models such as linear or bent O=B—O—B=O predict isotope shifts of 25 cm.$^{-1}$ or less.

A D_{3h} model predicts three infrared active fundamental frequencies, of which the observed band, at 2013 cm.$^{-1}$ is presumed to be of symmetry E' and to involve primarily the B atoms. The other fundamentals will probably occur at considerably lower frequencies. It is estimated that under the conditions used in this study, an emission band *with the same absolute absorption intensity as the band at 2013 cm.*$^{-1}$ would not be detected if it occurred below 1000 cm.$^{-1}$ because of the frequency-cubed factor in the emission intensity. This may explain the absence of other bands, and indicates a need for absorption measurements.

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[CONTRIBUTION NO. 460 FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

The Separation of Lithium from Alkali Metal Ions[1,2]

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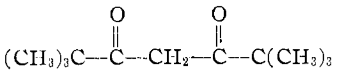
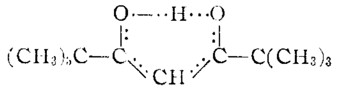
It has been found that dipivaloylmethane, DPM, binds lithium ions selectively and firmly under alkaline conditions. By use of an ether solution of the reagent as an extractant, it is possible to determine lithium in the presence of the other alkali metals. A small correction is necessary if large amounts of sodium are present.

Despite the increasing use of organic chelating agents in the separation and determination of metal ions, no reagents have heretofore been found which permit the separation of lithium from other metals except by tedious procedures which involve the stepwise removal of other ions from lithium. We have found that a new chelating agent, dipivaloylmethane, DPM (I), is applicable to the separation of lithium from sodium and potassium.



$$(CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C(CH_3)_3$$

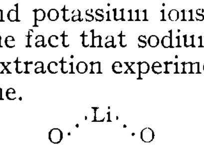
I



(1)

II

This compound, which is found to exist almost entirely in the form of the symmetrical enolic modification II in the pure liquid and in organic solvents, binds lithium firmly in the form of a lithium chelate which is soluble in ether and other organic solvents but is sparingly soluble in water. It is very probable that the chelate has structure III and that the specificity for the lithium ion is due to the small radius of that ion (0.60 Å.)[3] as compared with the sodium and potassium ions. In keeping with this view is the fact that sodium gives a minor interference in extraction experiments whereas potassium gives none.



III

We have found that ether is the best of the common organic solvents for use in extraction procedures. As is indicated by the data presented in the Experimental section, it is possible to extract substantially all of the lithium from alkaline aqueous solutions under conditions which lead to the removal of only minor amounts of sodium. Because only limited amounts of DPM were available at the outset of these studies, a large number of orienting experiments were carried out (and are reported) under conditions which were recognized not to be ideal for quantitative procedures.

Experimental

Dipivaloylmethane.—The compound was prepared by the method of Hauser and Adams.[4] It forms a white, gelatinous precipitate when shaken with lithium hydroxide solutions. The chelate is readily soluble in ether at room temperature and only slightly soluble in water. DPM dissolved in benzene, petroleum ether, butyl ether, carbon tetrachloride and chloroform would not extract the lithium chelate from alkaline solutions.

The diketone, a colorless oil which boils at 94.0–94.5° at 20 mm., has an absorption maximum at 275 mμ, which is attributed to the cyclic enol form. The molecular extinction coefficients at the maximum in three solvents are as follows: acetonitrile, 1.09×10^4; isoöctane, 1.27×10^4; water, 0.19×10^4; 0.1 *N* NaOH, 1.60×10^4 (max. = 294 mμ).

Acidity Constant of DPM.—The pK_a in water was determined spectrophotometrically at 25.0° and calculated[5] from the data in Table I.

Extraction Experiments.—An ether solution of DPM was shaken with aqueous solutions of metal ion. The amount of metal chelate in the ether was determined either by non-aqueous titration or by hydrolyzing an aliquot of the ether with neutral water and titrating the water–ether mixture as metal hydroxide. For the non-aqueous titrations an ali-

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) Abstracted from the doctoral dissertation of Gerald A. Guter. Presented at the National Meeting of the American Chemical Society, September, 1954.

(3) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, 2nd Ed., p. 346.

(4) C. R. Hauser and J. T. Adams, THIS JOURNAL, **66**, 1220 (1944).

(5) The absorbance of the solution containing no OH^- was used to calculate the extinction coefficient, ϵ, of the diketone at 295 mμ. The extinction coefficient, ϵ^8, of the anion was estimated from a plot of log I_0/I *vs.* OH^- concentration as being 1.58×10^4 at 295 mμ. The data were then used to solve the two equations

$$\log(I_0/I)_{295\ m\mu} = \epsilon[AH] + \epsilon'[A^-]$$
$$1 \times 10^{-4} = [AH] + [A]$$

TABLE I

ABSORBANCE OF AQUEOUS ALKALINE SOLUTIONS[a]

log I_0/I at 295 mμ	$[OH^-] \times 1^{04}$, M	pK_a
0.113	0.000	11.85
.242	5.95	11.76
.418	11.87	11.77
.534	17.83	11.74
.655	23.79	11.74
.738	28.57	11.81
1.051	59.80	11.75
	Av.	11.77

[a] Total [DPM] + [anion] = 1×10^{-4} M; ionic strength maintained at 0.01 M by addition of tetramethylammonium bromide. Absorbances were read on a Beckman DU spectrophotometer using 1-cm. cells.

quot of the ether layer was mixed with an equal volume of glacial acetic acid and titrated with perchloric acid in dioxane. The titrant was standardized with potassium acid phthalate dissolved in acetic acid. Methyl violet was used as an indicator but good end-points were not obtained at high chelate concentrations. For the aqueous titrations, an aliquot of the ether layer was shaken with an equal volume of water and the mixture was titrated with standard hydrochloric acid. Thymol blue was used as the indicator with the change from green to yellow being taken as the end-point. A micro-buret calibrated to 0.01 ml. was used in all titrations. Some of the significant experiments are summarized in Table II.

TABLE II

EXTRACTION OF SOLUTIONS OF ALKALI METAL IONS WITH DPM IN ETHER

Initial concn. in water*		Initial concn. of DPM in ether	Vol. ether layer / Vol. water layer	% Li^+ and/or Na^+ extracted[a]
Na^+	Li^+			
0.5		0.1	1	0.18
	0.5	.1	1	17.30
	1.0	.2	50	83.3
	1.0	.1	50	81.6
	0.5	.1	50	99.0
0.5	0.5	.1	50	53.2

[a] The concentration of KOH was 1.0 M in all solutions.

Procedure for the Determination of Lithium in the Presence of Potassium and Sodium.—One ml. of a solution 0.500 N in Li^+, 0.5 N in Na^+ and 1.0 N in KOH was shaken in a small separatory funnel for two minutes with 50.0 ml. of 0.1 N DPM in ether. A 25.0-ml. aliquot of the ether solution was mixed with an equal volume of water and titrated with 0.1000 N acid. A total of four such extractions was carried out on four one-ml. samples of the lithium solution; each time as much as possible of the aqueous layer was saved and the four of them were combined. Two one-ml. aliquots from the combined aqueous layers were treated separately with the reagent as above and the aqueous layers were again combined. A one-ml. aliquot from the last combined aqueous layers was again extracted to obtain a blank titer. Since only a small fraction of the Na^+ is extracted in each pass, the amount removed each time is essentially constant. The results are given in Table III.

TABLE III

DETERMINATION OF 0.50 N SOLUTIONS OF Li^+ ION CONTAINING 0.5 N Na^+ AND 1.0 N K^+

Vol. of 0.0928 N acid required for titers[a]		
First extraction	Second extraction	Found $[Li^+]$
2.859	0.262	0.492
2.846	.265	.488
2.875		.494
2.861		.492

[a] 0.239 ml. required for blank was subtracted from each figure in column one and from the average of the two second extractions. The average of the two second extractions was taken as the second extraction for each of the four samples.

Discussion

A systematic study[6] of sterically hindered β-diketones indicates that the enol form of DPM is stabilized by virtue of the fact that the enolic hydrogen functions as a shield between the two oxygen atoms. The same reasoning can account for the weaker acidity of DPM in water as compared to acetylacetone where the large steric requirements are absent. The pK_a value for acetylacetone[7] is given as 8.9. On the basis of this picture, it seemed that small positive ions which can fit into the cavity between the oxygens should similarly serve as shields. On the basis of this theory, we can also predict that other small ions will interfere with the use of DPM in lithium determinations and separations. We have not yet turned our attention to this problem, since there are ordinarily other easy methods available for separating most other metal ions from the alkali metal ions. We have, however, observed that chelates can be formed from Be^{+2}, Zr^{+4} and Hf^{+4}.

It is evident from our data that the use of DPM in the analytical determination of lithium will suffer interference from sodium. This can be compensated within reasonable limits by repeated extraction, since only a small fraction of the sodium will be extracted in any pass. Therefore, a sodium correction may be made by subtraction of the titer of a later pass after virtually all lithium has been removed. Our present method also suffers from the error inherent in the use of ether solutions in volumetric assays. It is to be anticipated that a better extraction solvent can be found.

AMES, IOWA

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(6) G. A. Guter and G. S. Hammond, unpublished.

(7) Schwarzenbach, Suter and Lutz, *Helv. Chim. Acta*, **23**, 1191 (1940).