

extracts for their power to inhibit the growth of S37 transplants and induced tumours in mice and rats, the following method has been devised to remove the compound.

The aqueous solution remaining after removal of the non-ketonic fraction, by repeated extraction with various solvents, is acidified to 0.5–1.0 *N* with hydrochloric or sulphuric acid, thereby decomposing the ketone-reagent 'T' hydrazones on standing or with gentle warming. To this aqueous solution is added approximately 2–3 times its volume of absolute methanol, followed by approximately 15–20 times its volume or more of ether. The minimum volume of methanol is added in order to ensure a one-phase system, and the maximum amount of ether without separation into two layers. Under these conditions, the Girard reagent 'T' is precipitated on standing and may be filtered off; any material remaining on the precipitate may be washed off by cold methanol, and filtered into a good volume of ether, when the small quantity of reagent 'T' dissolved by the methanol is precipitated, while the ketonic bodies present in small concentration are sufficiently soluble in the large volume of the methanol/ether mixture.

The total ether/methanol/water solution may then be concentrated under reduced pressure to a suitable residue, when the process may be repeated if necessary until most, if not all, of the Girard reagent 'T' is removed.

This separation has been found to be very useful in dealing with the small quantities of total solids from urinary and adrenal extracts, particularly as a comparatively large amount of reagent 'T' is recommended for a good separation of the ketonic bodies. By this method, for example, these extremely water-soluble ketonic fractions, extractable by ether with very great difficulty, can be bio-assayed without interference from the separating reagent, and it is hoped that it may be equally of value to workers of other fields who use this very convenient fractionation.

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¹ Girard and Sandulesco, *Helv. Chem. Acta*, **19**, 1095 (1936).

Possible *f*-Shell Covalency in the Actinide Elements

UNDER the above title, Glueckauf and McKay¹ have presented a discussion, based in part on data of Katzin and Sullivan², in which they suggest that the co-ordination of nitrate groups, and the extraction of uranyl, neptunyl and plutonyl nitrates into organic solvents, are phenomena different in kind from those found with elements lower in the periodic table, and are therefore indicative of possible *f*-shell covalency. I believe that the co-ordination of nitrate by uranyl ion is neither unique nor different in kind from that found lower in the Periodic Table, and in particular with a transition element such as cobalt.

Katzin and Gebert³ have shown that cobaltous nitrate, dissolved in an organic solvent such as acetone or tertiary butyl alcohol, is undissociated, and probably conforms to the formula $\text{Co}(\text{NO}_3)_2 \cdot 4X$, where *X* represents a solvent group. Furthermore,

the presence of nitrate ion in the solution results in formation of a trinitrato-cobalt (II) complex. Ternary phase studies, similar to those by Katzin and Sullivan² on the uranyl nitrate–water–solvent system, have been made on the systems cobalt nitrate–water–acetone and cobalt nitrate–water–tertiary butyl alcohol by Katzin and Ferraro⁴. These have demonstrated that the behaviour of cobalt nitrate in these systems is essentially like that found for uranyl nitrate. Spectrophotometric data on the changes induced in the light absorption of the nitrate group by various metal ions in tertiary butyl alcohol solution⁵ show that manganous, cobaltous, nickelous and cupric nitrates exhibit striking and characteristic modifications of the nitrate group absorption, which can be traced to formation of the undissociated salt. In addition, further investigation of cupric nitrate⁶ shows formation of trinitrato complex in acetone solution. Although the effects on the spectrum were not as marked as for the salts with incomplete *d*-shells, lithium, magnesium, calcium, aluminum, zinc, cadmium and thorium nitrates, as well as nitric acid, in tertiary butyl alcohol solution, showed modifications of the nitrate ion absorption from that in water⁵. Von Halban⁷ and co-workers have studied the nitric acid case in detail, showing the change to be due to formation of undissociated unhydrated HNO_3 , and there seems justification for assuming that all the spectral alterations noted reflect formation of undissociated molecules. Even in aqueous solution, the alkaline earth nitrates give evidence of partial association⁸.

In summary, then, rather than perceiving unique properties, one is struck by the similarity of behaviour of uranyl nitrate and the simple divalent metal nitrates, in particular, those of the transition elements. Furthermore, there is no evidence in any of our data for true covalency; all the complexes formed are by all criteria of the 'ionic' type. The behaviour in organic solution, common to uranyl nitrate and nitrates of the divalent transition elements lower in the periodic table, has led me to a generalized picture of the solution processes of salts in electron-donor solvents, including water, which it is hoped to present in detail at another time.

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¹ Glueckauf, E., and McKay, H. A. C., *Nature*, **165**, 594 (1950).

² Katzin, L. I., and Sullivan, J. C., Atomic Energy Commission Document No. 2537; *J. Phys. Coll. Chem.* (in the press).

³ Katzin, L. I., and Gebert, E., *J. Amer. Chem. Soc.* (in the press).

⁴ Katzin, L. I., and Ferraro, J. R., *J. Amer. Chem. Soc.* (in the press).

⁵ Katzin, L. I., *J. Chem. Physics*, **18**, 789 (1950).

⁶ Katzin, L. I., and Gebert, E. (unpublished work).

⁷ von Halban, H., "Contrib. étude structure mol.", Vol. commém. Victor Henri, 239 (1947/48).

⁸ Robinson, R. A., Wilson, J. M., and Ayling, H. S., *J. Amer. Chem. Soc.*, **64**, 1469 (1942). Harned, H. S., and Owen, B. B., "Physical Chemistry of Electrolytic Solutions", 423 (Reinhold Pub. Co., New York, 1943). Hagemann, F. (personal communication re radium nitrate).

DR. KATZIN bases his argument chiefly on certain similarities in the behaviour of uranyl nitrate and the divalent transition metal nitrates in acetone and tertiary butyl alcohol. In ethers, however, the differences in solubility are extraordinarily large, and this forms one of our main pieces of evidence. It implies that the free energy of transference from water to ether is some 10 k.cal./mol. greater for uranyl than for, say, cobalt nitrate.