TABLE II

Temp., °C.	k(sec.$^{-1}$) × 10^6 in tetrahydronaphthalene	k(sec.$^{-1}$) × 10^6 in nitrobenzene
105	0.40	0.35
115	1.34	1.20
130	6.01	6.25
145	24.7	25.0

and for nitrobenzene

$$k = 8.68 \times 10^{12} e^{-33,500/RT}$$

The experimental error in the activation energy is estimated at ±0.4 kcal./mole and therefore the difference between the two activation energies is probably significant. Alder and Leffler[4] have shown that the decomposition of phenylazotriphenylmethane proceeds at roughly the same rate in a number of solvents, but that this is due to compensating effects of activation energies and A factors. They explained their results in terms of the desolvation of the azo compound before reaction. Only two inert solvents have been used in the present work, but it appears that a similar effect may be operative in the decomposition of triazobenzene.

With methyl methacrylate as solvent, the evolution of nitrogen was many times more rapid than with the other two solvents and it is concluded that the methyl methacrylate is taking a definite part in the reaction. Triazobenzene is known to react with compounds such as styrene to give diphenyltriazoline[5] and it is probable that a similar reaction occurs with methyl methacrylate, the triazoline then breaking down with the splitting off of nitrogen. This second reaction may also proceed through a diradical intermediate and, if so, the production of very small amounts of polymer would indicate that the diradicals are not efficient in initiating the production of long chain polymer. The uncertainties in the detailed nature of the reaction, however, make it unwise to attempt to reach any firm conclusion.

The author is grateful to Professor F. S. Dainton of the University of Leeds for suggesting the use of triazobenzene as a possible source of diradicals.

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The Fluoroplatinates. III. The Alkali Fluoroplatinates

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Of the alkali fluoroplatinates, the potassium, rubidium and cesium salts have been previously prepared. Schlesinger and Tapley[2] prepared the potassium salt by heating finely divided platinum with $3KF \cdot HF \cdot PbF_4$. The salt was found to be a yellow crystalline compound, sparingly soluble in water and having a characteristic absorption band in the ultraviolet region of the spectrum.

Sharpe[3] prepared potassium, rubidium and cesium fluoroplatinates by treatment of the chloroplatinates with bromine trifluoride. The crystal structures of these salts were determined.

The preparation of the lithium, sodium and ammonium fluoroplatinates has not been previously reported. This paper concerns the preparation and some of the properties of all the alkali fluoroplatinates.

Experimental

Reagents.—Lanthanum fluoroplatinate was prepared as previously reported.[4] All other reagents were C.P. grade.

Analyses.—The alkali content of the salts was determined by means of a Beckman flame spectrophotometer. For the ammonium salt, Nessler's solution was used. In all analyses, the samples were first dried at 100° under an atmospheric pressure of 625 mm.

Solubility.—The solubilities of the alkali fluoroplatinates were determined at 25 ± 0.5°. A Warburg apparatus was used. Agitation for 24 hours in polyethylene bottles was considered adequate for the establishment of equilibrium conditions. The solubilities were determined in grams per 100 ml. of solution.

Density.—The densities of the alkali salts were determined at 25 ± 0.5°. A 4.5-ml. pycnometer was used with toluene redistilled from sodium carbonate as the inert liquid.

Absorption Spectra.—The absorption spectrum study of these salts was performed with a model DU Beckman spectrophotometer using matched 1-cm. cells.

The Alkali Fluoroplatinates.—The potassium, rubidium and cesium fluoroplatinates were prepared by simple metathesis since they are sparingly soluble. In each case a saturated solution of the respective alkali nitrate was added to a 0.02 M lanthanum fluoroplatinate solution. The precipitates were centrifuged, washed and then purified by recrystallization from hot water.

Sodium fluoroplatinate was prepared by the titration of sodium hydroxide and lanthanum fluoroplatinate. The equation for the reaction is $6NaOH + La_2(PtF_6)_3 \rightarrow 3Na_2PtF_6 + 2La(OH)_3$. A 1 N sodium hydroxide solution was added slowly to the lanthanum fluoroplatinate solution. Lanthanum hydroxide precipitated immediately. The addition of the alkali was continued until the formation of any new precipitate could not be detected. The solution was centrifuged to pack the lanthanum hydroxide and then more alkali was added to the supernatant liquid until precipitation appeared complete. The solution was again centrifuged. Several drops of the supernatant liquid were placed in each of two holes of a black color reaction plate. To one of these a drop of sodium hydroxide was added and to the other a drop of lanthanum fluoroplatinate solution. If no precipitate was evident in either instance then the end-point was regarded as reached. The solution was filtered and it was evaporated nearly to dryness in a vacuum oven at 75° under a pressure of 625 mm. The concentrated solution was then placed in a water-bath at 5° until precipitation was complete. The salt was obtained by centrifugation, was then washed and purified by recrystallization from hot water.

By titration of ammonium hydroxide and lanthanum fluoroplatinate and following the procedure just described, ammonium fluoroplatinate was obtained.

Lithium fluoroplatinate was prepared in the same manner but its isolation free of hydrolytic products was not possible. The evaporation of the lithium solution produced no crystalline product until an almost completely anhydrous state was reached. Upon complete dehydration, well defined yellow crystals were present but were mixed with a white residue which was shown to be lithium fluoride. Measurement of the absorption spectrum of a solution made from the yellow crystals confirmed the indication that hydrolysis of the fluoroplatinate ion had occurred. The characteristic maxima of the fluoroplatinate ion at 275 and 318 mμ were absent. A new absorption curve with a maximum at 263 mμ was obtained. Further investigation of this hydrolysis reaction is being carried out.

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[1] Abstracted from a portion of the thesis submitted by Thomas E. Wheeler in partial fulfillment of the requirements for the degree of Master of Science.

[2] H. Schlesinger and M. Tapley, THIS JOURNAL, **46**, 276 (1924).

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Results and Discussion

Table I gives the results of the analyses performed on the alkali fluoroplatinates. Only the cations were determined since the presence of the anion was confirmed by its characteristic absorption spectrum.

TABLE I

ANALYTICAL DATA

Compound	Alkali, % Calcd.	Found
Na_2PtF_6	12.95	12.9
$(NH_4)_2PtF_6$	10.45	10.4
K_2PtF_6	20.18	20.2
Rb_2PtF_6	35.60	35.5
Cs_2PtF_6	46.23	46.2

The solubilities and densities of the compounds at 25 ± 0.5° are presented in Table II.

TABLE II

Compound	Solubility, g./100 ml. of soln.	Density
Na_2PtF_6	20.49	4.21
$(NH_4)_2PtF_6$	7.32	3.59
K_2PtF_6	0.750	4.83
Rb_2PtF_6	0.278	6.00
Cs_2PtF_6	0.484	5.39

The solubility of the ammonium salt is to be noted and contrasted with the appreciably smaller solubilities of the ammonium and potassium chloroplatinates. Cox and Sharpe[5] have mentioned the general tendency of the ammonium salts of fluoro complexes to be appreciably more soluble than the corresponding chloro complexes. This fact coupled with the smaller solubility of the potassium fluoroplatinate suggests that the gravimetric determination of potassium using fluoroplatinic acid as the precipitating reagent may be better than that with chloroplatinic acid.

Schlesinger and Tapley[2] reported that very dilute solutions of potassium fluoroplatinate obeyed Beer's law. This was confirmed by measuring the 275 mμ peak at various concentrations of potassium, rubidium and cesium fluoroplatinates. These solutions, however, are relatively dilute even when saturated. Therefore, the more concentrated solutions of the sodium and ammonium salts were used for a further study.

Ammonium fluoroplatinate solutions up to 0.05 *M* were measured and found to obey Beer's law within experimental error. However, the extinction coefficients of this salt differed slightly from those obtained for comparable concentrations of the potassium, rubidium and cesium salts. This may be attributed to the hydrolysis of the ammonium salt.

The results of the study with the sodium salt reveal a small but definite departure from Beer's law. When the concentration was plotted against optical density, a slight curve was obtained which did not pass through the origin.

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The System Na_2SO_4–Li_2SO_4–H_2O at 0°[1]

BY J. A. SKARULIS AND H. A. HORAN

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The determination of the 0° isotherm of the system Na_2SO_4–Li_2SO_4–H_2O was necessary in connection with a study of the system Na_2SO_4–Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°. Although Spielrein[2] reported, without presenting the supporting experimental data, a variety of double salts as stable solid phases ($Na_2SO_4 \cdot Li_2SO_4 \cdot 5.5H_2O$ at 0 to 16°; $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$, 16 to 24°; $Na_2SO_4 \cdot 4Li_2SO_4 \cdot 5H_2O$, 24 to 32°; $Na_2SO_4 \cdot Li_2SO_4 \cdot 3H_2O$, 32 to 100°), the only double salts found in the recent study of two isotherms by Cavalca and Nardelli[3] are $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ at 27° and both $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ and $Na_2SO_4 \cdot Li_2SO_4$ at 45.6°. The results presented here confirm the latter report in that the 0° isotherm is found to be similar, except for numerical relations, to that at 27°. The sole solid phases are $Na_2SO_4 \cdot 10H_2O$, $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ and $Li_2SO_4 \cdot H_2O$. It is likely therefore that the only stable double salt solid phases of the system are those reported by Cavalca and Nardelli, who also described their crystallographic characteristics.

Experimental Procedure

The anhydrous simple salts were employed in the preparation of mixtures of known composition. $Li_2SO_4 \cdot H_2O$, a J. T. Baker reagent product, was dehydrated without further purification. It was heated in platinum at 550–600° after a preliminary dehydration at 110°. Anhydrous Na_2SO_4, also a J. T. Baker reagent product, was similarly treated without the preliminary step. The sodium content of the dried Li_2SO_4 was estimated by flame photometry and corrections applied in the calculation of the compositions of the mixtures.

The apparatus and procedure was the same as that described in a previous paper by the present authors[4] dealing with another ternary system involving Li_2SO_4. All complexes were seeded with a small crystal of $Na_2SO_4 \cdot 10H_2O$. This was necessary to produce a solid phase in those mixtures which were relatively rich in Na_2SO_4. Changes were also observed in most of the mixtures where a solid phase was already present. The complexes were mixed 24 hours before seeding and at least 14 days before final analysis. Constancy of composition was used as a criterion of attainment of equilibrium.

The filtered saturated solutions were analyzed for combined sulfates and for lithium, the sodium being obtained by difference. A given sample was evaporated to dryness at 100° and the residue heated to constant weight at 180°. An ion-exchange chromatographic procedure,[5,6] with slight modifications, was then applied to the determination of the lithium in this residue. In the procedure, both sodium and lithium were adsorbed on Colloidal Dowex 50 resin, the

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