was attached to a receiver, manometer and water pump.   Rubber stoppers were satis-
factorily used throughout, since they were not appreciably attacked by the hydrocarbon
at the temperature employed.   A water-bath, kept at 70–75°, was used to heat the
Claisen flask.   Since our experiments were designed to show the fate of all substances
used, the receiver was kept in an ice-bath to minimize losses from the distillate.   Were
concentration of the peroxide the only goal, this ice-bath could be omitted.   Usually,
two volumes of cymene were placed in the Claisen flask with one volume of either 30
or 60% hydrogen peroxide solution.   The distillation was stopped to analyze the various
fractions before all of the cymene had distilled.   These data also are collected in Table I.
    Similar vacuum distillation experiments were also conducted with xylene and with
tetralin.   Some experiments with cymene and with tetralin were carried out with an
oil pump, but no advantage was gained thereby.   The concentrated hydrogen peroxide
obtained when tetralin was used was always yellow in color.   The cause of the coloration
was not investigated.

Summary

If hydrogen peroxide solutions are vacuum distilled with p-cymene, a
peroxide of 88–91% strength may be obtained readily.   The yield of this
concentrated material which remains undistilled is 60–76% and most of the
remaining peroxide is to be found in the distillate.   Actual losses, therefore,
are negligible since a 91–98% recovery was always realized when the distilla-
tion temperature was kept below 57°.   The simplicity of the apparatus and
the rapidity of the concentration are also very desirable features.

Tetralin behaves like cymene in this respect, but it imparts a yellow color
to the concentrated peroxide.   Xylene also was studied but its high vapor
pressure, as compared to cymene, makes it undesirable for use at 25–30 mm.
pressure.   With distillation at atmospheric pressure the losses due to de-
composition of the peroxide into oxygen become quite appreciable.

EVANSTON, ILLINOIS

THE SENSITIVITY AND APPLICABILITY OF THE PICRIC ACID TEST FOR POTASSIUM

BY EARLE R. CALEY

The fact that an alcoholic solution of picric acid can be used as a reagent
for potassium has been frequently noted in the literature of analytical
chemistry.   There exist, however, no quantitative data regarding either
the sensitivity of this reagent toward the potassium ion or the allowable
concentrations of other ions that can be present without causing inter-
ference.   The present experiments were undertaken in order to determine
these points and to find the optimum conditions for this reaction.

Experimental Part

Preparation of the Reagent.—The reagent used in these experiments,
and the one found most suitable, was prepared by drying the moist picric

acid of reagent grade in an air oven at 70–80°, recrystallizing the dried product from benzene and, after allowing the drained crystals to stand exposed to the air until the adherent benzene had evaporated, dissolving the final product in 95% ethyl alcohol to form a solution saturated at room temperature. Recrystallization from benzene was found necessary with the particular grades available since alcoholic solutions made from the picric acid not so treated developed a slight turbidity, on being added to distilled water, due to the presence of impurities. Experiments were also made with reagents consisting of solutions of picric acid in absolute alcohol, dilute alcohol and various organic solvents, but these attempts led to no useful results.

Characteristics of the Reaction.—When a saturated alcoholic solution of picric acid is added to an aqueous solution of an alcohol-soluble potassium salt, preferably the chloride, a well-defined crystalline precipitate of anhydrous potassium picrate results. With concentrated solutions precipitation is almost instantaneous, while with dilute potassium solutions the crystals separate only after some minutes. The chief factors influencing the reaction, from an analytical view-point, were found to be the concentration of the potassium solution, the ratio of the volume of reagent to the volume of the test solution, the influence of the time of reaction and the effect of the presence of other substances.

The Effect of Volume of Reagent.—The ratio between the volume of the saturated alcoholic solution of picric acid and the volume of the test solution is of marked influence on the sensitivity of this reaction. In the experiments on this point varying volumes of reagent were added to fixed volumes of solutions containing varying concentrations of potassium chloride. Table I shows the results obtained when using 1.0 cc. of potassium chloride solution.

TABLE I

THE EFFECT OF VOLUME OF REAGENT (REACTION TIME, 30 MINUTES)

Potassium present, g.	Reagent volume				
	2.5 cc.	5 cc.	7.5 cc.	10 cc.	15 cc.
0.0006	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
.0007	No ppt.	No ppt.	Doubtful	No ppt.	No ppt.
.0008	No ppt.	No ppt.	Slight ppt.	Doubtful	No ppt.
.0009	No ppt.	Doubtful	Fair ppt.	Slight ppt.	No ppt.
.0010	Doubtful	Slight ppt.	Good ppt.	Fair ppt.	No ppt.

Similar results were obtained when using volumes of potassium chloride solution greater or less than 1.0 cc. In all cases the optimum results were obtained when the volume of reagent was from seven to eight times that of the test solution.

Effect of Time of Reaction.—Since the reaction between potassium ions and picric acid in alcoholic solution is not instantaneous with small concentrations of potassium, experiments were performed to determine

the effect of reaction time on the possibility of detecting small amounts of potassium. In these experiments 7.5 cc. of reagent was added to 1.0 cc. of potassium chloride solution and the effect observed after different elapsed times. The results appear in Table II.

TABLE II

THE EFFECT OF REACTION TIME IN THE PICRIC ACID TEST FOR POTASSIUM

Potassium present, g.	1 min.	5 min.	30 min.	24 hrs.
0.0006	No ppt.	No ppt.	No ppt.	No ppt.
.0007	No ppt.	Doubtful	Doubtful	Very slight ppt.
.0008	No ppt.	Very slight ppt.	Slight ppt.	Slight ppt.
.0009	No ppt.	Slight ppt.	Fair ppt.	Fair ppt.
.0010	No ppt.	Slight ppt.	Good ppt.	Good ppt.

It will be seen that, aside from the action during the first few minutes, a prolonged duration of the test affects but little the possibility of detecting potassium in concentrations that give no reaction in shorter periods.

Sensitivity of the Reaction.—From the various experiments it was concluded that, when the volume of reagent is from seven to eight times that of the test solution and a thirty-minute period is allowed before observing the results of the test, one part of potassium can be detected with certainty in twelve hundred and fifty parts of solution, i. e., the sensitivity of the reaction is 1:1250. This sensitivity can be further increased to 1:1650 by saturating the reagent with potassium picrate, but this procedure is not to be recommended.

Interfering Substances.—Owing to the nature of the reagent it is at once apparent that salts insoluble in strongly alcoholic solution cannot be present. In practice this restricts the application of the test to chloride solutions. The solutions tested should preferably be neutral. Strongly acid solutions reduce the sensitivity of the test. The following table shows the results of some of the experiments that were made to determine the specific action of the positive ions usually associated with potassium. In these experiments 1.0 cc. of solution containing varying concentrations of the metallic chlorides was treated with 7.5 cc. of reagent.

TABLE III

REACTIONS OF SODIUM, LITHIUM AND MAGNESIUM WITH PICRIC ACID REAGENT

Element	Concn., g./cc.	Reaction time, 5 min.	Reaction time, 30 min.
Na	0.0040	No ppt.	No ppt.
Na	.0050	Doubtful	Very slight ppt.
Na	.0075	Slight ppt.	Good ppt.
Na	.0100	Good ppt.	Good ppt.
Li	.1000	No ppt.	No ppt.
Mg	.1000	No ppt.	No ppt.

Ammonium, rubidium and cesium behave like potassium but, since the former is readily removed and the two latter are practically never met

with in weighable quantities, the interference from these elements is of no importance. The interference from sodium is more serious and prevents the use of the reagent for detecting potassium in the presence of sodium unless dealing with small residues of alkali chlorides. It should be mentioned, however, that the crystalline precipitates formed by potassium and sodium are quite different in appearance. The former yields short prisms and needles which, particularly when the amount of potassium is small, present an iridescent appearance in strong light while the latter forms long hair-like crystals which never present an iridescent appearance.

Conclusions

The interference of sodium in the above reaction restricts its use to a greater extent than has been generally supposed. Regardless of this limitation, however, it may be employed as a confirmatory test for potassium after the approximate separation of the two elements or for the examination of small residues of alkali chlorides. For these purposes it has certain advantages over the usual reagents for potassium. It is more sensitive than perchloric acid, chloroplatinic acid or tartaric acid and, while not as sensitive as sodium cobaltinitrite, it has the advantage of possessing much greater stability since solutions of picric acid in alcohol appear to keep indefinitely.

PRINCETON, NEW JERSEY

THE KINETICS, STATICS AND ENERGETICS OF THE THERMAL REACTION $CH_2I-CH_2I = CH_2=CH_2 + I_2$ IN CARBON TETRACHLORIDE SOLUTIONS

BY MILTON J. POLISSAR

Introduction

The object of this research was to determine the kinetics of the decomposition of ethylene iodide in carbon tetrachloride solutions. Since the number of reactions that proceed in a direct and simple manner is limited, it was of great interest to find that this one follows a fairly simple law through a large range of concentrations and temperatures.

The results are of further interest since it was possible, by assuming a simple mechanism of reaction, to give a complete interpretation not only of the so-called "energy of activation" but of the actual magnitude of the rate as well. The plausibility of the interpretation is enhanced by the fact that it can be applied successfully to two similar reactions previously studied by other investigators. One of the reactions referred to is the decomposition of ethylene iodide in alcoholic solutions, in the presence of